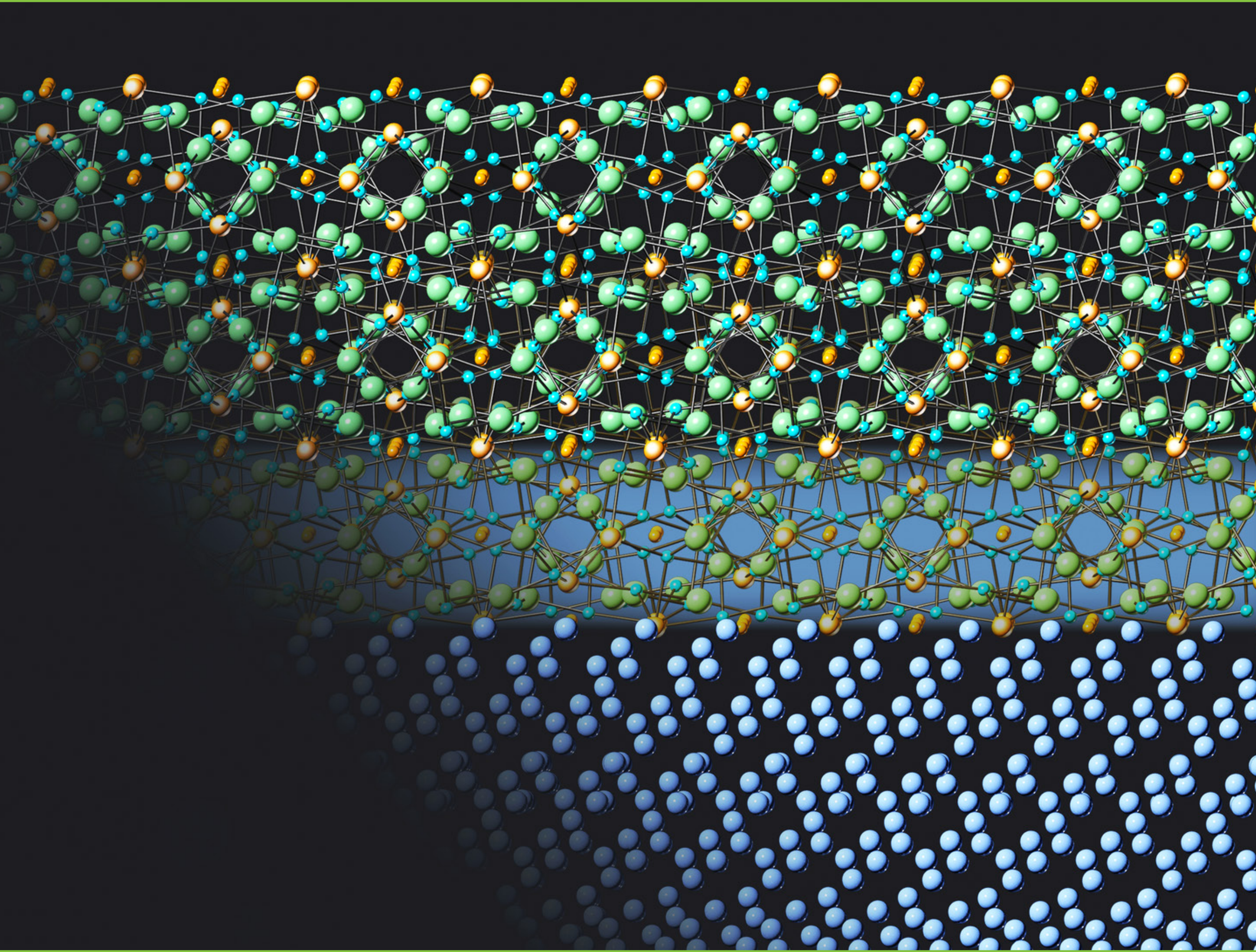
Basic Research Needs for

Next Generation Electrical Energy Storage



Report of the Basic Research Needs Workshop on

Next Generation Electrical Energy Storage

March 27 – 29, 2017

The cover image is a schematic representation of a lithium metal anode (bottom) and solid electrolyte (top) at the atomic scale. Scanning transmission electron microscopy revealed both the structure and chemistry of the interface region ($Li_{7-3x}Al_xLa_3Zr_2O_{12}$) between the anode and electrolyte—a key discovery if this promising next generation battery electrolyte (Ma, C.; Cheng, Y.; Yin, K.; Luo, J.; Sharafi, A.; Sakamoto, J.; Chi, M., *Nano Letters*, **2016**, 16, 7030-7036, DOI: 10.1021/acs.nanolett.6b03223) is ever to become a commercial reality. Image courtesy of Oak Ridge National Laboratory.

Basic Research Needs for
Next Generation Electrical Energy Storage

REPORT OF THE OFFICE OF BASIC ENERGY SCIENCES WORKSHOP ON ENERGY STORAGE

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Structure, Interphases, and Charge Transfer at Electrochemical Interfaces
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In Pursuit of Long Lifetime and Reliability: Time-Dependent Phenomena at Electrodes and Electrolytes
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Solid-State and Semi-Solid Electrochemical Energy Storage
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Jeff Sakamoto (3), University of Michigan

Cross-cutting Themes
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Mike Toney (2), SLAC National Accelerator Laboratory

PRIORITY RESEARCH DIRECTION (PRD):
PRD 1 – Tune Functionality of Materials and Chemistries to Enable Holistic Design for Energy Storage
PRD 2 – Link Complex Electronic, Electrochemical, and Physical Phenomena across Time and Space
PRD 3 – Control and Exploit the Complex Interphase Region Formed at Dynamic Interfaces
PRD 4 – Revolutionize Energy Storage Performance through Innovative Assemblies of Matter
PRD 5 – Promote Self Healing and Eliminate Detrimental Chemistries to Extend Lifetime and Improve Safety

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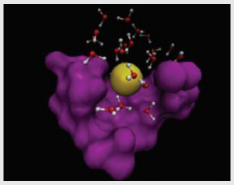
Executive Summary

The last decade has opened rich new horizons in electrical energy storage, with compelling impacts on society. Personal electronics have transformed from a novelty to a necessity. New options for transportation are burgeoning. In energy storage science, emerging new approaches are illuminating the inner workings of energy storage at the atomic and molecular scales with extensions to the meso and macro levels. The stage is set — with ripe new directions for basic energy storage science and promising new opportunities for energy storage for the electricity grid, transportation, the internet of things, and national defense. Next generation electrical energy storage could be as transformational for energy applications as lithium-ion batteries were for personal electronics.

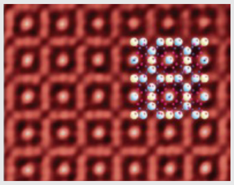
This report examines the opportunities in basic energy storage science that will bring this vision for the future to fruition. Sea changes are in the offing, moving from intuitive speculation to confirmed scientific knowledge, from trial-and-error serendipity to science-based design, and from qualitative models to quantitative predictions. To navigate towards these changes, Priority Research Directions (PRDs) were formulated by 175 leading scientists and engineers during a Basic Research Needs Workshop on Next Generation Electrical Energy Storage held in Gaithersburg, Maryland, on March 27-29, 2017. This diverse community included experts in theory, simulation, characterization, electrochemistry, and synthesis of electrochemically active materials and chemistries. They uncovered a rich horizon of compelling directions that promise to link diverse electrochemical phenomena (such as solvation, mobility, reactivity, and degradation) in a single interactive framework.

The PRDs focus on development of the scientific basis for new, transformational electrochemical energy storage concepts. Implementing these research opportunities will usher in a new era of deep understanding of basic energy storage science and enable predictive design of materials, architectures, and systems. These are the building blocks not only for rapid advances in energy storage science, but also for new storage technologies that will meet the needs of the future with high performance, longer lifetimes, and reliable, safe operation.

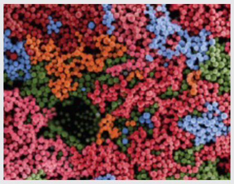
UNDERSTANDING HOW BATTERIES WORK



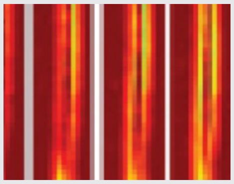
Computer modeling of ion movement in a membrane



Combined imaging techniques track chemical changes



Atomic structure of a solid electrolyte



Neutron imaging of batteries in operation

Electrochemical energy storage devices such as batteries store and release electricity on demand. As negatively charged electrons move out of the battery, positively charged ions must move inside the battery through multiple chemical and material interfaces. Critical battery components in this process include electrodes, electrolytes, and separation membranes. Powerful new computational, imaging, and characterization tools are enabling scientists to understand this complex coupling of electronic and ionic transport at an unprecedented level of detail across multiple length and time scales. Integration of this new knowledge will enable the scientific design of innovative, complex materials and architectures for next generation energy storage.

Images courtesy of Pacific Northwest National Laboratory (left) and Oak Ridge National Laboratory (right).

Electrical Energy Storage — Revolutionizing how we store and use electricity

PRIORITY RESEARCH DIRECTIONS

☐ **Tune functionality of materials and chemistries to enable holistic design for energy storage**

Key questions: *How can we understand the functionality of materials sufficiently to anticipate their behavior in electrochemical configurations? How can these insights inform the design of chemistries, materials, and structures for future energy storage?*

Advances in synthesis, characterization, and computation will open new doors to control, balance, and integrate novel materials and chemistries, enabling innovative designs for electrochemical energy storage.

☐ **Link complex electronic, electrochemical, and physical phenomena across time and space**

Key questions: *What modeling frameworks can express the spatiotemporal evolution of material-chemical systems across varying spatial and temporal scales? How can models inform experimental strategies to provide insight on electrochemical phenomena?*

Electrochemistry involves dynamic phenomena that vary during charging and discharging and are heterogeneous over space and time. Understanding the temporal evolution of spatially distributed properties in electrochemical systems will advance next generation energy storage.

☐ **Control and exploit the complex interphase region formed at dynamic interfaces**

Key questions: *Can we characterize the chemical and material reactions and behaviors that comprise dynamic interfaces? How can interfaces be designed and synthesized to enhance storage performance and/or mitigate degradation?*

As batteries charge and discharge, ions are transferred across multiple phase boundaries. During this process, interfaces between electrodes and electrolytes and at membranes undergo significant changes as a result of spontaneous chemical and imposed electrochemical reactions, often leading to degradation. Scientific insights that guide design of interfaces, and associated interphases, can improve battery performance and extend lifetimes.

☐ **Revolutionize energy storage performance through innovative assemblies of matter**

Key questions: *What strategies can we use to exploit high-capacity electrode materials and higher voltage electrolyte chemistries while ensuring reliable cycling? What approaches are needed to perform design, characterization, and simulation at the mesoscale?*

A major opportunity for innovation lies in understanding how to design and assemble nanoscale materials and structures into mesoscale architectures. New approaches are crucial to effectively manage the mesoscale effects of complex pathways in electrochemical systems.

☐ **Promote self-healing and eliminate detrimental chemistries to extend lifetime and improve safety**

Key questions: *What drives the key degradation and failure mechanisms? How can these, and possible mitigation strategies, be revealed through modeling and characterization of representative and model systems?*

The heart of electrochemical energy storage — ion transport through materials and across interfaces — presents an exceptional challenge to chemical and mechanical stability, as well as safety. Transformational science can uncover degradation mechanisms and discover pathways to mitigate them.

1 Introduction

"A ten-times increase in the weight-oriented density of batteries would enable so many moonshots, if we can find a great idea. We just haven't found one yet."
Astro Teller, Google X

Advances in how we store electrical energy have the potential to transform nearly every aspect of society, from transportation to communication to electricity delivery and domestic security. Next generation energy storage systems will support the energy requirements for advanced technologies and strengthen critical infrastructure. This vision for the future can only be achieved through a new generation of low cost, high performance, reliable, and safe batteries and related methods for energy storage.

This overarching impact on the nation's infrastructure and society is also felt in our daily lives — not just the batteries in laptops and smartphones, but those in vehicles, home security systems, personal health devices, and a wide range of commercial products. Many would say that today's batteries are not good enough — they do not last long enough, take too long to recharge, and can be unsafe. At the heart of these shortcomings lies our incomplete understanding of battery function and failure, and how batteries can be redesigned for transformative improvement.

Batteries and related devices rely on *electrochemical* energy storage. Unlike digital electronics that depend on control of electrons moving through circuits, batteries require controlled migration of electrons, atoms, ions, and/or molecules through demanding, dynamic chemical environments. This migration can dramatically change the chemistry and structure of the battery materials and limit their performance over time. Achieving greater efficiency, reliability, and resiliency in energy storage technologies requires a new level of understanding and control of the dynamics that govern electrochemical phenomena.

Science is poised to meet these challenges. Real-time nano- and meso-scale characterization of operating batteries will elucidate fundamental mechanisms of function and failure. Predictive computational simulations will move beyond discovery of new materials and chemistries to unlock innovative system-level capabilities. Further, holistic approaches to synthesis of materials, structures, and architectures will deliver new levels of electrochemical performance. The integration of this knowledge promises a revolution in processes, architectures, and designs for next generation electrochemical energy storage.

This future requires continued growth in research capabilities, with this evolution informed by profound advances in understanding of electrochemical behavior and how to control it. These include design, computation, synthesis, and characterization — and their deliberate coordination — to empower the community to move rapidly from qualitative speculation to predictive simulation, from serendipitous trial and error to rational design, and from compartmentalized knowledge to integrated understanding.

The PRDs outlined in this report, and summarized at the end of this chapter, lay the groundwork for a new era of basic energy storage science based on incisive *in situ* and *operando* experiments (see sidebar), comprehensive computational models of battery function and failure, and new multifunctional materials, architectures, and assemblies. These scientific directions build on rich opportunities in the synthesis of complex materials and architectures with designed functionality, characterization of materials as they perform and chemistries as they evolve, and predictive simulation to discover new materials and functionalities on the computer before they are made and tested in the laboratory. This is a new trajectory for electrochemical science, linking materials, chemistry, and functionality across multiple time and length scales to create new horizons of efficiency, performance, and cost.

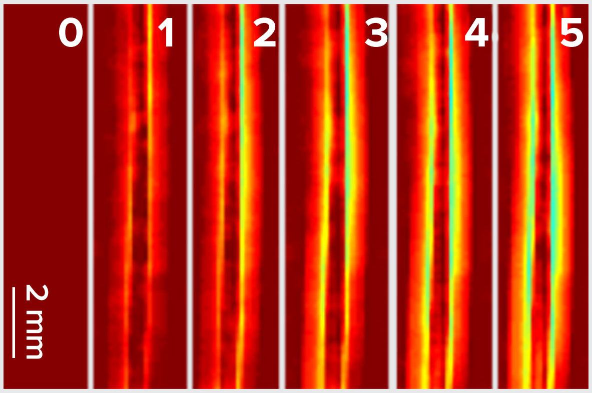
Basic energy storage science is poised for these transformational advances — the convergence of knowledge, techniques, and ideas outlined in this report provides unprecedented opportunities for next generation energy storage through an exciting, vibrant, and powerful scientific agenda.

This Report: DOE Basic Energy Sciences (BES) sponsored an initial workshop in 2007 to identify and describe Basic Research Needs in Electrical Energy Storage. Much has changed since then: the techniques and perspectives of research in the field; the materials, chemistries, and architectures of electrical energy storage embodiments; and public appreciation for its critical role. This report builds on these trends to elucidate basic research needs as envisioned for the next 5-10 years and was informed by a BES workshop held on March 27 – 29, 2017. Prior to the workshop, a "factual status document" was compiled that summarizes the current status of electrochemical energy storage technologies for both transportation and use on the electrical grid, as well as a brief discussion of the current state of scientific understanding of electrochemical phenomena. This factual document can be accessed at *http://science.energy.gov/bes/community-resources/reports*.

Leaders in the field invited to participate in the workshop were divided into six panels, with panel topics chosen as key research challenges for the next 5-10 years: *Pathways to Simultaneous High Energy and Power; Structure, Interphases, and Charge Transfer at Electrochemical Interfaces; In Pursuit of Long Lifetime and Reliability: Time-Dependent Phenomena at Electrodes and Electrolytes; Discovery, Synthesis, and Design Strategies for Materials, Structures, and Architectures; Solid-State and Semi-Solid Electrochemical Energy Storage;* and *Crosscutting Themes*. The deliberations from these panels are documented in Chapter 3. The primary workshop goal was the identification of a short list of PRDs, which are summarized below and described in depth in Chapter 2.

SEEING AND MEASURING ELECTROCHEMISTRY IN ACTION

Over the past decade, three modalities of research have become prominent in research on electrochemical reactions — *ex situ*, *in situ*, and *operando*. These approaches each have advantages and disadvantages. The long standing experimental approach is *ex situ* — characterization of materials removed from an electrochemical system following various lengths of operation. *Ex situ* assessments typically allow the full power and resolution of the characterization technique to be used, but are constrained to static measurements and by possible reaction or contamination during transfer. *In situ* refers to measurements that do not require removing the material from the system — allowing assessment in environmental conditions (for example, in an electrolyte). *In situ* measurements have greatly improved over the past decade with advances in both instrument resolution and engineering of the cell configurations that facilitate control of the chemical environment.



Neutrons can penetrate the layers that comprise a battery, making them an ideal characterization tool to learn about the evolution of battery chemistry and structure during operation. Above, the migration of lithium in the battery electrodes (the bright yellow-green regions) is shown during discharge of an operational battery (pouch cell).

More recently, *operando* configurations and methodologies have enabled materials studies *as electrochemical systems are operating*, conveying real-time characterization on a microstructural or even nanostructural level. This approach takes characterization to the next level — allowing analysis of materials and chemical evolution inside an operating battery (commercial or model system). The deep penetration of neutrons and hard X-rays in a material makes them particularly effective for investigations of 3D battery structures. Experimental designs that match battery configuration to the probing and analysis technique are essential. Several have been developed and refined, with commercial cells becoming available, and designs for electron microscopy and soft X-ray spectroscopy are on the horizon to address solid-state electrolytes.

Image courtesy of Oak Ridge National Laboratory.

THE PRIORITY RESEARCH DIRECTIONS

□ PRD 1 – Tune functionality of materials and chemistries to enable holistic design for energy storage

Batteries provide high energy density (small amounts of energy for a long time), and capacitors provide high power (a lot of energy for a short time). The inability to successfully blend both features into one electrochemical energy storage system is one example where innovative research approaches need to focus on both the multi-functionality of components and holistic design of the system. Recent advances in synthesis, characterization, and computation provide the tools needed to carry out this strategy.

Full realization of this vision depends on understanding functionality at a fundamental level and implementing the gained insights for effective design. Tuning the functionality of materials and chemistries will address an array of challenges: for example, design of electrode materials with ion and electrical conductivity, multifunctional separators that allow variable ion conductivity or control formation of solid-electrolyte interfaces, and enhanced binders that provide both electronic conductivity and mechanical stability. Advancement of experimentally validated computational models could guide materials selection and predict the feasibility of the needed synthetic pathways.

As a means of meeting these scientific challenges, this PRD focuses on identifying charge storage and transport mechanisms, understanding the nature of ion solvation, and illuminating the interaction of electrode materials with electrolytes through three research thrusts. First, to achieve simultaneous high power and high energy, materials behavior must be understood under varying rates and states of charge. Equally critical will be development of design methodologies that achieve a suitable trade-off between high proportional loading of active storage material (for high energy) and 3D geometric distribution of component materials (for high power). Second is the need for multifunctional solid electrolytes that enable safe solid-state batteries. Research must focus on gaining insight into ion diffusivity and improved mechanical properties, as well as the development of novel approaches to make the materials. Third, new battery chemistries based on environmentally benign, safe, and abundant materials must be identified. Establishing the scientific foundations to enable next generation aqueous batteries as well as novel hybrid aqueous/non-aqueous configurations featuring solid electrolytes is required to achieve this goal.

□ PRD 2 – Link complex electronic, electrochemical, and physical phenomena across time and space

A truly comprehensive understanding of the complexities at the heart of battery electrochemistry requires "connecting the dots" among the multiple phenomena that occur across many length and time scales in an unprecedented way. There are two fundamental challenges: (1) creating and seamlessly linking next generation modeling and characterization techniques with higher resolution, greater accuracy, and wider application and (2) integrating these multimodal tools in a tight feedback loop between experiment and theory.

The rise of coherent X-ray beams from synchrotrons and free electron lasers enables new horizons of 3D imaging with sub-nanometer resolution and the discovery of dynamic phenomena by using photon correlation spectroscopy with ultrafast time resolution. The penetrating power of neutron scattering enables innovative imaging of operating batteries. Together, such tools promise new experimental advances for understanding buried interfaces and the diffusion and transport across them. Comparable advances in theory, modeling, and simulation are needed to address the multiple length scales from atomic to mesoscale to macroscale and time scales from sub-seconds to years and to link chemical, physical, and mechanical phenomena.

Seamless merging of multimodal simulations and experiments is essential to bridge disparate phenomena across length and time scales. Simulations are envisioned that can guide experiments and directly predict their outcomes. Feedback loops between simulation and experiment can improve predictive power and guide the next experiments. Simulations can also fill the observation gaps between experiments and can be used to design new experiments a step beyond what is now feasible. In summary, modeling and predicting the temporal evolution of spatially distributed properties will advance next generation energy storage.

□ PRD 3 – Control and exploit the complex interphase region formed at dynamic interfaces

Electrochemical energy storage systems incorporate multiple components (electrodes, electrolyte, current collectors, and others), producing a multiplicity of interfaces between and within the components. These boundaries evolve dynamically over time as chemical and electrochemical reactions alter the materials, new interphase regions grow, and new interfaces are created. In some cases, the resulting interphases perform beneficial functions, but they can also lead to inefficiencies, degradation, and system failure.

Given that the evolution of electrochemical interphases is critical to the energy storage function, managing interphase creation and evolution presents a significant opportunity to improve energy storage performance and mitigate degradation through the design, synthesis, and intentional incorporation of judiciously selected material interphases into system architectures. To accomplish this, new levels of understanding are needed about the complex processes that control interface formation and evolution — captured in models that can predict the consequences of specific designs and achieved through synthesis that produces the desired structures.

Two overarching research thrusts are crucial to realize this vision. First, the complexity of reactive interfaces must be unraveled through experiment and theory. Particular value can be gained from experiments emphasizing spectroscopy and imaging of operating systems to capture the dynamics of interphase formation. X-ray and neutron techniques can have a notable impact as these can penetrate full working cells. Theoretical approaches are needed to treat spatial gradients and their dynamics, with validation of the predictions through relevant experiments. Second, insights so gained must be incorporated into modeling frameworks that enable design of interphases for their desired function. Importantly, the ability to predict and realize new interphase structures opens the door to creative design solutions, e.g., responsive or adaptive membrane separators.

□ PRD 4 – Revolutionize energy storage performance through innovative assemblies of matter

Today's batteries are based on 2D architectures — stacked layers of anode, electrolyte, and cathode that interact across short inter-layer distances and over large lateral dimensions. New 3D mesoscale architectures are critically needed to tailor performance to diverse applications, allowing the design of the "perfect" battery to match the user's needs. Among the promising concepts are interdigitated electrodes, where the anode and cathode occupy adjacent "fingers" of the same layer. Nanowire batteries take this interdigitated concept to three dimensions with alternating nanowires of anodes and cathodes interacting across short interwire distances. Fully 3D architectures of adjacent cells, each holding a nanoparticle interacting with neighboring nanoparticles across cell surfaces, are a dramatically new opportunity with significant design flexibility.

Flow battery architectures with liquid instead of solid electrodes offer a host of new, alternative design opportunities that have been only marginally explored. Aqueous and non-aqueous electrolytes each offer special appeal, namely, low cost and high operating voltage, respectively. Organic active materials open a rich design space, allowing stability, solubility, and activity to be separately targeted. New possibilities for membranes that only pass desired ions can be based on polymers, glasses, ceramics, or composites. Catalysts afford a rich opportunity to promote targeted energy storage reactions and reduce detrimental side reactions. Semi-flow batteries with one solid and one liquid electrode could allow matching solid and solution-based chemistries in another alternative approach.

□ PRD 5 – Promote self-healing and eliminate detrimental chemistries to extend lifetime and improve safety

The charge and discharge processes that are central to the operation of batteries make them susceptible to gradual degradation that shortens battery life and, on occasion, to catastrophic failure, which is a safety concern. The use of ions for charge storage requires electrode materials to accommodate significant changes such as the stress/strain from volume change, atomic reconfigurations from electrochemical reactions, and localized extremes in temperature, current, and stress. The result is a myriad of unwanted phenomena leading to multiple forms of degradation, including fracture, corrosion, and gas evolution.

Understanding and controlling degradation scenarios is a major opportunity for energy storage in the future. Discerning early stages to more clearly illuminate initiating mechanisms is a difficult experimental challenge confounded by the possible presence of multiple degradation initiators. In turn, these initiators may be intrinsic to the battery configuration, may be accelerated by stresses (e.g., thermal, mechanical, or chemical), or may be simply introduced as manufacturing variations and defects. Current mitigation strategies often result in diminished performance. Correspondingly, the most promising battery chemistries for high performance have been unusable because of accompanying degradation mechanisms. Strategies for both eliminating and mitigating degradation as well as enabling self-healing are needed.

Two ambitious research thrusts are proposed to substantially advance the scientific understanding of degradation. First, experiments on operating batteries are needed to quantify degradation and failure, particularly measurements that provide dynamic imaging of the degradation process. When simultaneous electrochemical and materials characterizations are incorporated, these *operando* experiments can elucidate the causal relationships responsible for degradation. Second, continuum models are required to describe and predict a spectrum of degradation and failure scenarios. The challenge is to model chemical, electrochemical, mechanical, and thermal phenomena dynamically across multiple length scales, translating an understanding at the nanoscale through its manifestations at the macroscale in battery components and cell design.

2 Priority Research Directions in Next Generation Electrical Energy Storage

The workshop discussion identified five Priority Research Directions (PRDs) that define the basic research needed to develop energy-relevant technologies based on next generation electrical energy storage. Each PRD is discussed in depth with the associated research thrusts in this chapter. As background, Chapter 3 of the report provides an in-depth assessment of the status of research in the field of electrical energy storage.

TABLE 1: LIST OF PRIORITY RESEARCH DIRECTIONS AND ASSOCIATED RESEARCH THRUSTS

1. **Tune functionality of materials and chemistries to enable holistic design for energy storage**
   How can we understand the functionality of materials sufficiently to anticipate their behavior in electrochemical configurations? How can these insights inform the design of chemistries, materials, and structures for future energy storage?
   - Thrust 1a: Achieve simultaneous high power and high energy
   - Thrust 1b: Develop multifunctional solid electrolytes that enable safe solid-state batteries
   - Thrust 1c: Identify new battery chemistries based on environmentally benign, safe, abundant materials
2. **Link complex electronic, electrochemical, and physical phenomena across time and space**
   What modeling frameworks can express the spatiotemporal evolution of material-chemical systems across varying spatial and temporal scales? How can models inform experimental strategies to provide insight on electrochemical phenomena?
   - Thrust 2a: Create state-of-the-art modeling techniques and characterization tools
   - Thrust 2b: Integrate computational and characterization tools
3. **Control and exploit the complex interphase region formed at dynamic interfaces**
   Can we characterize the chemical and material reactions and behaviors that comprise dynamic interfaces? How can interfaces be designed and synthesized to enhance storage performance and/or mitigate degradation?
   - Thrust 3a: Unravel interfacial complexity through *in situ* and *operando* characterization and theory
   - Thrust 3b: Design solid-electrolyte interphase (SEI) for function
4. **Revolutionize energy storage performance through innovative assemblies of matter**
   What strategies can we use to exploit high-capacity electrode materials and higher voltage electrolyte chemistries while ensuring reliable cycling? What approaches are needed to perform design, characterization, and simulation at the mesoscale?
   - Thrust 4a: Design and synthesize new mesoscale architectures
   - Thrust 4b: Develop new concepts for large-scale energy storage and conversion
5. **Promote self-healing and eliminate detrimental chemistries to extend lifetime and improve safety**
   What drives the key degradation and failure mechanisms? How can these, and possible mitigation strategies, be revealed through modeling and characterization of representative and model systems?
   - Thrust 5a: Conduct multi-modal *in situ* experiments to quantify degradation and failure
   - Thrust 5b: Develop multi-physics, multi-scale, predictive continuum models for degradation and failure

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2.1 PRD 1 — Tune Functionality of Materials and Chemistries to Enable Holistic Design for Energy Storage

Electrochemical energy storage presents untapped opportunities for exploiting multifunctional materials and components to meet the ever-increasing performance demands for full battery cells, including high energy density, high power, extended cycle stability, improved safety, and lower cost. Many examples of multifunctional materials and components are found in today's Li-ion batteries, such as electrodes comprised of particles, coatings, and binders that simultaneously conduct electrons and ions, implement electrochemical redox reactions, and remain stable for thousands of cycles. Multifunctionality and holistic design, however, can be exploited much more extensively to create not only higher performance, lower cost Li-ion batteries but also a diverse portfolio of "beyond Li-ion" batteries with a broader materials set, new multi-electron and conversion chemistries, and new architectures to implement them. This Priority Research Direction examines these new opportunities to exploit multifunctionality and holistic design to meet higher performance levels of energy density, power, cycle stability, safety, and cost. There are strong connections of this Priority Research Direction with PRD 4 for its treatment of higher level mesoscale architectures; to PRD 2 and PRD 3 for their emphasis on interface/interphase across space and time; and to PRD 5 for its explicit call for a science of electrochemical degradation and failure.

An expanded portfolio of design and synthesis approaches presents profound opportunities for innovation to embody multifunctionality through combined materials and component design – **exploiting new designs for structures, architectures, and assemblies that achieve improved performance metrics, and new functionalities not yet imagined for batteries.** Opportunities abound in the science of energy storage to create new foundations for technology. For example, could the conductive additives commonly added to the anode and cathode be removed? Could synthesis or nanostructuring bring benefits from more controlled and reproducible ion storage structures? Could separators between electrodes deliver chemicals to control solid-electrolyte interface or interphase (SEI) formation? Could a self-healing coating be interfaced to a material that expands during ion intercalation to prevent cracking and pulverization? Recent research shows promise for opportunities like this, with enhanced performance and expanded functionality ahead.

2.1.1 SCIENTIFIC CHALLENGES

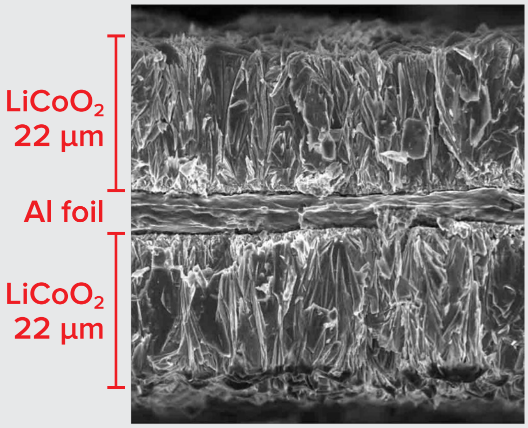
Ion- and Electron-Conducting Electrode Materials: Battery electrodes must clearly be redox active and mechanically stable, but they must also be arranged to transport electrons as well as ions to complete the redox reaction. Combined functionality for ions and electrons and mechanical stability during cycling present a design challenge on multiple length scales. Often, and commonly in today's batteries, some of these functions are primarily achieved by inclusion of electrochemically inactive components, such as carbon additives or polymeric binders, adding not only complexity but also electrochemically inactive mass and volume that limit performance. This condition inspires directions for design innovation providing either greater functionality of the redox-active material itself or structural arrangements that efficiently partner different materials to achieve similar benefit, so that the requisite high conductivity for ions and electrons at all stages of the electrochemical reaction is achieved along with stability in the presence of stress and strain created by ion transport and electrochemical reactions.

While the ultimate goal of an ion- and electron-conducting solid electrode remains quite challenging, there are current examples of materials in Li-ion batteries that can be cycled without requiring carbon additives for electronic conduction. For example, TiS_2 remains metallic through a reaction with Li, which enabled the original

ADDITIVE-FREE ELECTRODES

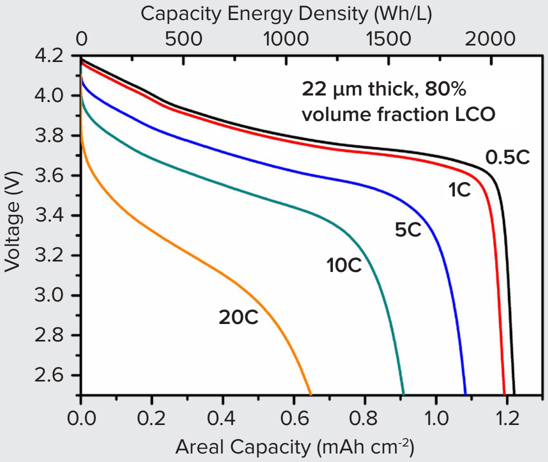
Conventional Electrode Limitations

A typical Li-ion battery electrode contains the active material in particle form embedded in a mixture of polymeric binder and conductive additives, and is formed by slurry casting a mixture of these materials on a conductive current collector followed by calendaring. Only the active material stores energy, so the inclusion of binder and conductive additives reduces the overall energy density, and the combination of slurry casting and calendaring results in a high tortuosity structure, lowering the power density.



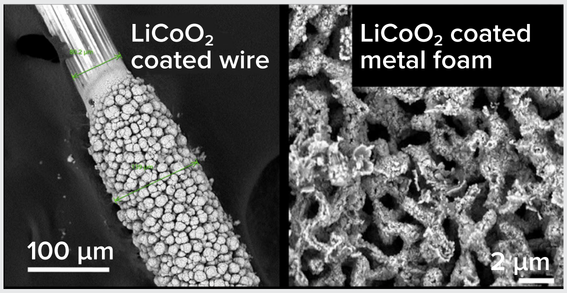
Additive-Free Electrodeposited Electrodes

Recently, it was discovered that high quality thick films of dense (80% dense and greater) phase-pure $LiCoO_2$, a common high energy density cathode material, could be directly electroplated onto a current collector (citation given below). Because $LiCoO_2$ has a high electrical conductivity, no conductive additive is needed, increasing the potential energy density relative to conventional composite electrode designs. The volume fraction of pores present in the electrode is determined by the electrodeposition process parameters, and the pores appear to run nearly vertical, lowering the tortuosity and providing an opportunity for high power.



Electrodeposition Enables Unique Form Factors

Conventional electrodes are slurry cast on solid and typically planar electrodes. Because electrodeposition is a conformal process, coating wires and 3D porous architectures is straightforward, offering opportunities to form electrodes with unique form factors and, for electrode materials which are not as electrically conductive as $LiCoO_2$, place the electrode materials in close contact to a current collector.



Images reproduced from H. Zhang et al., Electroplating lithium transition metal oxides, Science Advances, **2017**, 3, e1602427.

Exxon batteries to be free of conductive additives.[1] Lithium intercalation into $Li_4Ti_5O_{12}$ (and other Ti^{4+} oxides) induces the formation of mixed $Ti^{3+/4+}$ states while promoting ion diffusion.[2] As a result, electrodes of $Li_4Ti_5O_{12}$ at battery-relevant thicknesses have demonstrated low impedance and very high durability.[3] In addition, $LiCoO_2$ undergoes an insulator-to-metal transition upon Li deintercalation, a property that has been leveraged to fabricate remarkably functional electrodes that are free of both carbon and even binder.[1] (See sidebar on "Additive-Free Electrodes".) One research target would be to combine the high potential/capacity of $LiCoO_2$ with the cost and safety benefits of $Li_4Ti_5O_{12}$.

The quest for high performance electrodes has already led to complex material combinations, such as Ni-rich compositions of Ni, Mn, and Co oxides. When lithiated, this material is composed of five elements. Advanced chemical restructuring is only one of the major contributions that facilitate better ion and electrical access in batteries. For conventional composite electrodes made from particles without carbon additives, particle structure, size, and shape/size distribution may well be critical as particle-particle contacts control electron transport. Furthermore, phase transformations accompanying lithiation/delithiation (e.g., in conversion reaction materials) can induce anisotropic changes in grain morphology and corresponding issues involving mechanical strain at these contacts.[4,5] New developments in computational methods can be used to accelerate lowering the screening of all permutations available for multi-element materials. Screening materials at multiple facets of battery technology aids in the design strategy, accentuating the need for theoretical models that can rapidly screen through multi-parametric spaces involving composition, particle shape and size, and statistical distributions of properties.

In conjunction with improved computational methods, strategies for the synthesis of electrode particles need to be enhanced to enable well-controlled nanostructure designs that include multi-faceted components with the particular functionalities needed by the overall configuration.[6-10] Such an approach will deliver benefits at the research stage by enabling specific nanostructure designs to be realized experimentally, such that they will constitute effective platforms for characterization and scientific insight at the level of individual nanostructures or massive arrays realized in specific architectures.

Electrodes with Both Supercapacitance and Redox Capacities: Achieving the high energy density of batteries and the high power density and cycle life of pseudocapacitors simultaneously—in a single electrochemical energy storage device—is an exciting direction yet to be realized. It would have benefits across the application space for electrochemical storage since high power is an intrinsic requirement along with high energy density for fast charging, acceleration, and regenerative braking in electric vehicles, as well as for power leveling in grid or microgrid installations from variable demand or renewable sources.

It is an enticing question whether to approach this goal by increasing the power density of battery materials, increasing the energy density of supercapacitors, or pursuing some alternative, perhaps novel path. Kinetics plays a critical role in distinguishing between battery and pseudocapacitive materials. Measuring the functional dependence of peak current on sweep rate reveals mechanisms controlling the kinetics. When determined over a wide range of sweep rates, parabolic behavior, i.e., $\sim(\text{sweep rate})^{1/2}$, is characteristic of a redox reaction limited by semi-infinite diffusion, while linear behavior is indicative of a surface-controlled, capacitor-like process.[11] Most electrode materials (such as $LiFePO_4$) show parabolic behavior,[12] while only a few materials (such as Nb_2O_5) show linear response over a wide range of sweep rates, and are thus regarded as intrinsically pseudocapacitive.[13] However, at sufficiently small dimensions (<10-30 nm), traditional battery materials exhibit capacitor-like behavior (termed extrinsic pseudocapacitance) due to the short diffusion distances required to fully utilize very thin electrode materials at high power (Figure 2.1.1).[14,15] This opens the door to new domains of power-energy through nanostructured electrode designs with high surface area and short diffusion distances.

New Functionality from Electrochemical Storage Structures - Multifunctional Separators: The polymer separator in a battery currently plays a rather simple role: primarily, it allows the transport of ions between anode and cathode while preventing electrical contact between them. There are now early attempts to change this paradigm. Separators designed to shut down battery current when the temperature exceeds a certain value are commercially available,[16] and bifunctional separators containing layers designed to detect lithium dendrite formation have been reported.[17] The separator is at a unique physical position in a battery, sitting between the anode and cathode, and thus could concurrently improve the function of both electrodes. This leads to the question, how many properties might the separator concurrently provide? Could the separator serve as a source of chemicals that enhance SEI formation? What about allowing a variable ion conductivity to control charge and discharge rates? Such concepts have been proposed previously,[18-20] indicating that the separator could potentially be considered as a repository containing a large number of functional elements.

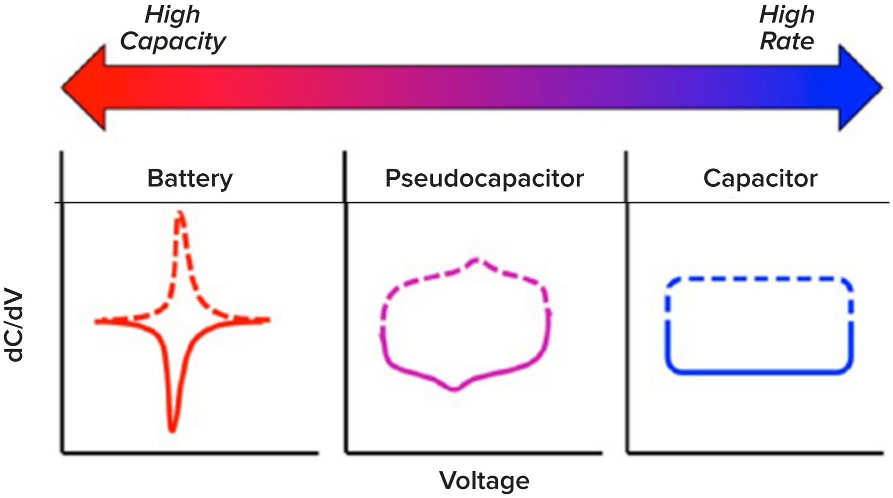


Figure 2.1.1. Idealized representation of differential capacity (dC/dV) profiles for three basic charge storage mechanisms. Reprinted with permission from Ref. 15. Copyright (2013) American Chemical Society.

New Functionality from Electrochemical Storage Structures - Multifunctional Binders: Fully unlocking the chemical versatility of polymers would be a potentially effective way to impart additional functionality to the binder in a battery electrode. In principle, this could reduce the number of battery components and simplify electrode fabrication, while potentially providing gains in energy density. As an example, electronically conductive binders could provide a means to eliminate the electronically conducting additive, typically carbon (Figure 2.1.2a). If combined with mechanical stability (Figure 2.1.2b), such enhanced binders could be a crucial component of electrodes involving active materials with large volume expansion, such as Si with Li (Figure 2.1.2c).[21,22] Mechanical stability could also be achieved indirectly with binders that are self-healing (Figure 2.1.2c).[23] Evidence exists that polymers with mixed conductivity could be used to eliminate both electronic additives and porosity.[24] Multi-functionality in polymers is likely limited only by the chemists' imagination, but guidance by high throughput computations based on screening critical descriptors[23] is likely to be a crucial component of discovery. Polymer chemists striving to achieve this goal will benefit from further advances in computational methods that accelerate the design of effective and efficient synthetic routes.[25]

New Functionality from Electrochemical Storage Structures - Multifunctional Electrode Particles: Almost all battery electrodes, Li-ion and other battery chemistries, are manufactured from a slurry containing particles of the electrochemically active material. The resulting porosity of the electrode thus provides a large contact area between the electrolyte and these particles, though the electrochemical instability of the resulting electrode-electrolyte interfaces creates a significant voltage limitation for operation.[26] Insulating products and/or electrode corrosion result, thereby increasing the resistance to charge transfer even to the point of passivating the electrode against the desired Li^+ insertion/deinsertion reactions.

A demonstrated strategy to avoid this outcome is to form a thin, preferably ion-permeable barrier between the two components that serves as a corrosion passivant.[27-29] Two general issues arise with this approach. First, this treatment is typically performed post-synthesis, i.e., on active material powder where particles are highly agglomerated. Buried interfaces are difficult to access and coat under these conditions, which creates a challenge to completely passivate the interfaces, especially considering that material shuffling during cycling can modify their exposure to the electrolyte with respect to the pristine state.[30] Atomic layer deposition holds promise in its ability to produce controlled conformal coatings, but further advances in chemical versatility while providing convincing evidence of homogeneity are still needed.[31,32] Second, ionically and/or electronically insulating coating phases may create high interfacial resistances, producing additional demands on the multifunctionality required. Core-shell or graded-composition structures could be the means to optimize the design of multifunctional particle architectures, e.g., where the core provides maximum storage capacity while the shell stabilizes electrode-electrolyte interfaces while enabling Li transport. Inspiration from biology, e.g., biomimicry, is one of the less explored avenues that may hold promise for guiding the design of smart and highly efficient architectures for energy storage components.[33]

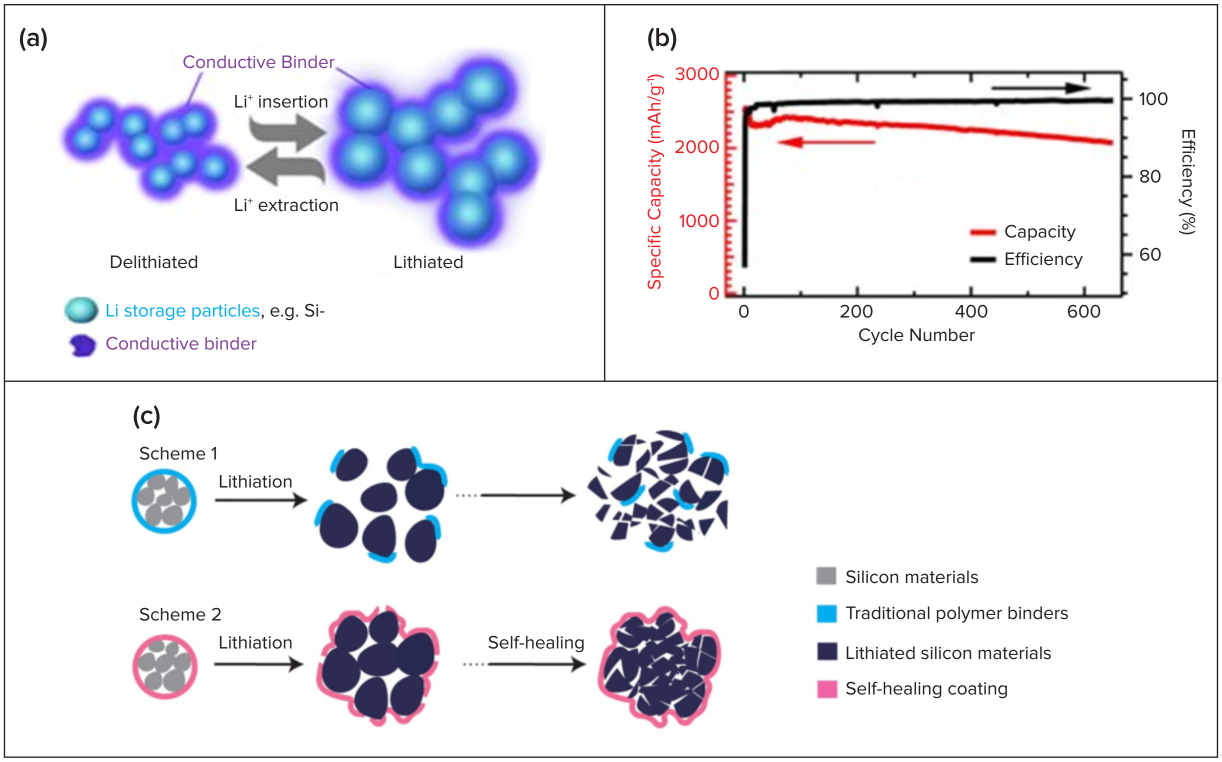


Figure 2.1.2. Design concepts for a multifunctional binder: (a) electronically conducting binder maintains electrical contact throughout the particle network; (b) proof of principle of stable cycling of a Si electrode containing an electronically conducting binder (from Ref. 22); and (c) design concept for a self-healing binder (from Ref. 23).

Core-shell and gradient architectures have already been demonstrated at both the nanocrystal[34] and the secondary particle level (Figure 2.1.3).[35] However, the library of compositions known in either case is still limited, especially in the case of nanocrystals, where methods of synthesis are still in their infancy. This poses a challenge, as the natural chemical complexity of electrode materials (with compositions of up to five or more elements) must now be balanced by tailored heterogeneity at short distances. Most importantly, the current selection of materials is mostly driven by empirical experience and still-incipient knowledge of the fundamental mechanisms of interfacial instability. As scientists improve this knowledge, design rules should be sought for multicomponent electrode particles with composition distributions aligned with multifunctional purposes, e.g., bulk for maximum storage capacity, surfaces for chemical passivation, and shape to preserve transport and mechanical robustness through smooth interfacial contacts.[36] These design rules will map a large parameter space, which should best be fed to machine-learning or genetic algorithms to accelerate the identification of suitable chemistry, as done for conventional coatings.[37]

Computational Science Guiding Materials Selection and Design: High throughput screening for specific material functionalities using theory and modeling approaches combined with machine learning techniques is attractive for battery materials. Models are automatically generated by algorithms based on data mining or machine learning, improving the probability of success in the field of new materials design. Examples of success of these approaches include rational design of self-assembling particles,[38] evaluation of molecular properties,[39] identification of nanostructures with specific electronic properties,[40] prediction of reaction outcomes for the crystallization of metal oxides,[41] and prediction of new crystalline compounds for photovoltaic applications.[42] For batteries, high-throughput density functional theory methods have been used in the design of cathode coatings.[37] Given predicted best candidates, a grand challenge for theory is to predict which materials can be synthesized and determine how to explore specific synthesis pathways by computational methods.

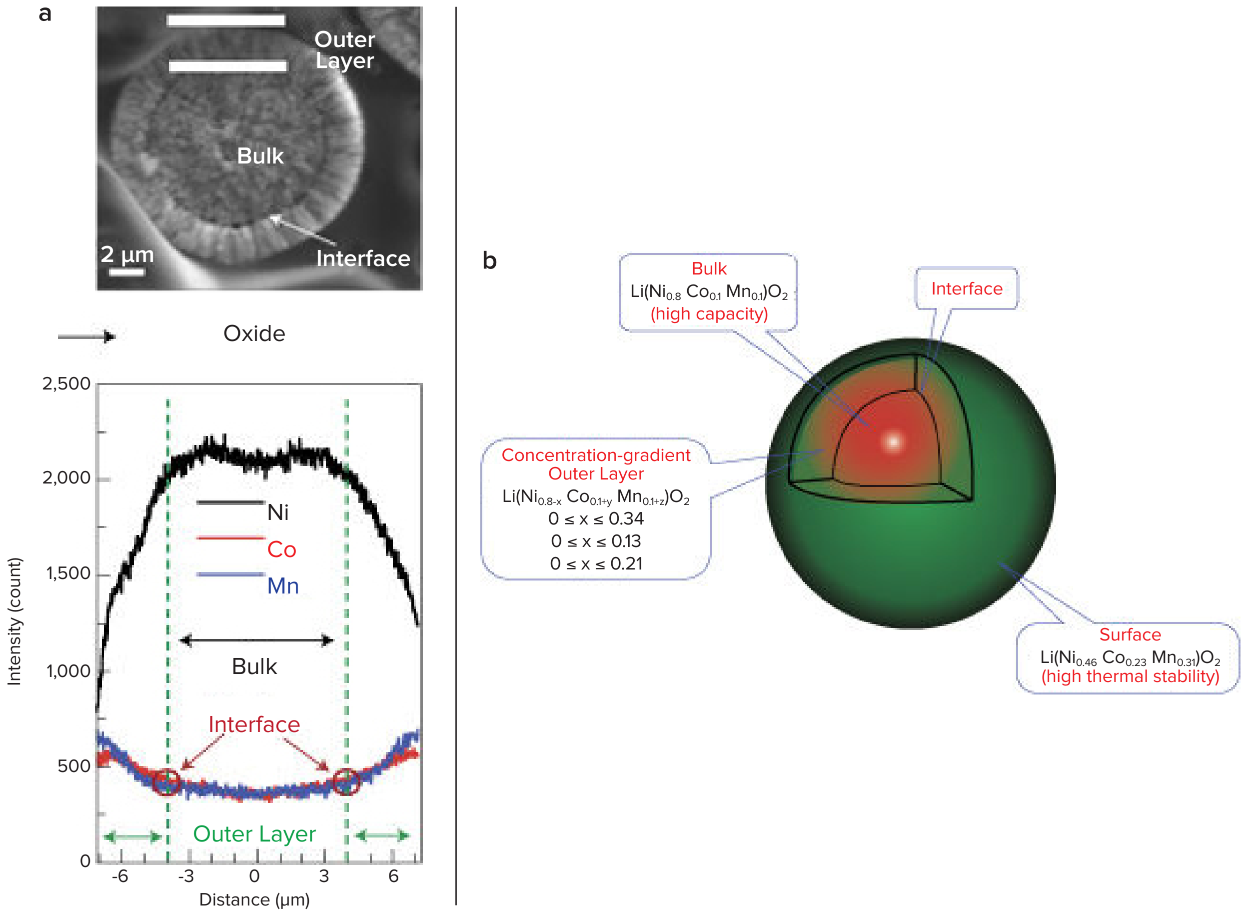


Figure 2.1.3. Scanning electron microscopy image and energy dispersive X-ray spectroscopy mapping of a secondary active material particle showing a concentration gradient from outside to inside. Schematic representation of the heterostructure. From Ref. 35.

2.1.2 RESEARCH THRUSTS

Thrust 1a: Achieve Simultaneous High Power and High Energy

While the nominal goal of energy storage is to hold energy, the function of energy storage devices is to capture, retain, and deliver energy from and to various components that supply and demand it. This threefold functionality places a primary focus on energy density, namely, how much energy can be stored per unit mass, volume, or area. On the other hand, the rate of capture or delivery of that energy is an issue of power per unit mass, volume, or area. The functionality of energy storage in an application specifies both the energy storage needed and the rate (power) at which it must be transferred to or from the storage device. Because both metrics for the storage function are important, comparing storage performance at both the fundamental (electrode-electrolyte combinations) and practical (full battery or cell) level is critical in the evaluation of new technologies.

Typically, there is an inverse relationship between energy and power, with batteries providing the former and capacitors the latter. At a system level, both high energy and high power are needed, spurring efforts to develop high energy capacitors and high power batteries. The critical scientific question is whether and how storage configurations might be designed to achieve both simultaneously, based on a sufficiently enhanced understanding of the behavior of the relevant materials and structures.

The inverse relationship between energy and power is often a consequence of slow ion diffusion in electrode materials: as faster charge or discharge is needed, ions cannot reach or escape from deeper locations in the electrode, so at higher powers less of the electrode material contributes to available energy; thus thinner active electrodes improve power capability at the expense of storage capacity and areal energy density. Ion flux can also be retarded by interphases that form at the electrode/electrolyte interface, posing a high impedance to ion transport. Transferring energy at high power also requires electron transport through the electrode materials—or through associated current collecting structures—to be fast enough to charge-neutralize the transported ion. In some cases, ion transport through the electrolyte can be the rate-limiting component, e.g., solid electrolyte materials where ionic conductivity is typically much lower than in liquid electrolytes (aqueous or organic). Power capability of an energy storage system can be limited by ion transport in electrodes and interphases, by ion transport in electrolyte, and by electron transport in active storage materials or current collectors.

In general, the scientific challenge to achieve simultaneous high power and high energy is formidable, requiring an understanding of materials behavior under varying states of charge (ion concentration) and rates. Also required is a design methodology to achieve a suitable tradeoff between high proportional loading of active storage material (for high energy) and 3D geometric distribution of component materials—active material, current collectors, and electrolyte (for high power). This tradeoff must be attained without incurring a performance penalty associated with formation of high impedance interphases or capacity degradation with charge/discharge cycling (especially at high power).

Design of 3D Storage Systems: As described above, pseudocapacitive behavior is strongly preferred for fast energy storage, capitalizing on both double-layer capacitance and faradaic capacitive contributions. While a few materials are known to show intrinsic pseudocapacitance—avoiding the rate limitations of slow ion diffusion—in general, the path to fast, pseudocapacitive behavior relies on realizing extrinsic pseudocapacitance through restricting the thickness of active ion storage materials. Achieving this requires large surface areas accessible to electrolyte and dense packing of the resulting electrode structures in order to reach high energy density. Such configurations favor 3D arrangements of materials to serve the purposes of ion transport and storage in active electrode materials, electron transport in electrode materials or distinct current collectors, and ion transport in electrolyte.[8,43,44] Important scientific goals include the identification of materials properties and their spatiodynamic changes during charge/discharge and the incorporation of this information into design methodologies and simulations of resulting power and energy, leading to design ground rules for simultaneous high power and high energy.

Synthesis of 3D Configurations: With 3D structures designed for simultaneous high energy and high power synthesizing such structures can become a significant challenge. The primary approach today uses thick film (sintered powder) technology to create electrodes made of particles of appropriate size, shape, orientation, and composition.[4] The particles will naturally display distributions of these parameters as well (e.g., standard deviation of particle size). As an alternative approach, thin film technology is already used for planar solid-state batteries[45] and could be employed to create nanostructured electrodes, achieving a tighter degree of control on the resulting structures in size, shape, orientation, and composition. Recently, combining both synthesis approaches has shown promise,[46] opening the door to a set of creative synthesis strategies.

Advances in Materials: Improved materials offer a pathway to simultaneous high energy and high power as well, particularly as replacement materials in electrode structures designed for high power. Systems that engage multiple charges, show exceptional ionic conductivity, or have high electronic conductivity are particularly notable opportunities.

Decoupling of Energy and Power: While the cases described above involve energy storage designs that inherently couple (or trade off) energy and power performance, flow batteries directly decouple energy and power. Energy is stored in redox species dissolved in liquids and stored in tanks, so that tank size and redox species concentrations are the primary determinants of energy stored. The redox species are pumped to the cell stack where they engage in electrochemical redox reactions on electrode surfaces, determining power. In this way, energy and power are fully decoupled, and the path to simultaneous high energy and high power is more direct. Redox flow batteries are promising for grid applications. An intriguing scientific question is whether similar concepts might find even broader applications and novel embodiments in portable energy storage for transportation or defense applications.

Thrust 1b: Develop Multifunctional Solid Electrolytes That Enable Safe Solid-State Batteries

Solid-state batteries are attractive because they can avoid the well-known safety issues associated with flammable organic electrolytes common in Li-ion batteries, while exploiting much the same electrode materials as already developed for Li-ion or other batteries. However, solid electrolytes are much less developed, and substantial research is needed to understand the materials, their critical properties (particularly ion diffusivity and mechanical properties), and the options available for their synthesis. Recent work has shown that the discovery and synthesis of solid materials with high ionic conductivity could enable advanced battery chemistries, e.g., use of a lithium metal anode for lithium-air and lithium-sulfur batteries.[47] Advances in solid electrolytes and their interfaces and integration in solid-state battery architectures represent the major challenges for energy storage.

Solid Electrolytes with High Ionic Conductivity: The use of solid electrolytes in conventional battery designs has historically been limited by the notoriously low ionic conductivities of the candidate solid materials. Solids with Li-ion conductivities sufficient for modern energy storage applications ($\sim 10^{-4}$ S/cm or greater at room temperature) have remained elusive. However, in recent years new solid electrolytes for batteries have been discovered, resulting in a handful of materials that achieve this conductivity threshold (Figure 2.1.4).[48] This removes one of the most stubborn barriers to solid electrolyte technology, although numerous challenges remain. Promising solid electrolyte candidates are few, and no one material from this limited list exhibits all the traits needed for a viable battery. Incomplete coupling between experiment and theory limits rational materials design; thus, the discovery of new materials is largely based on trial-and-error and serendipity. The role of structure (both local and long range), disorder, and defects inside phases and at interfaces is directly relevant but incompletely linked to ionic conductivity. Failure mechanisms in these materials are not well understood, largely due to their novelty and difficulties associated with characterizing buried interfaces. Consequently, solid electrolytes present a critical scientific challenge for the transformative change that solid-state batteries could mean.

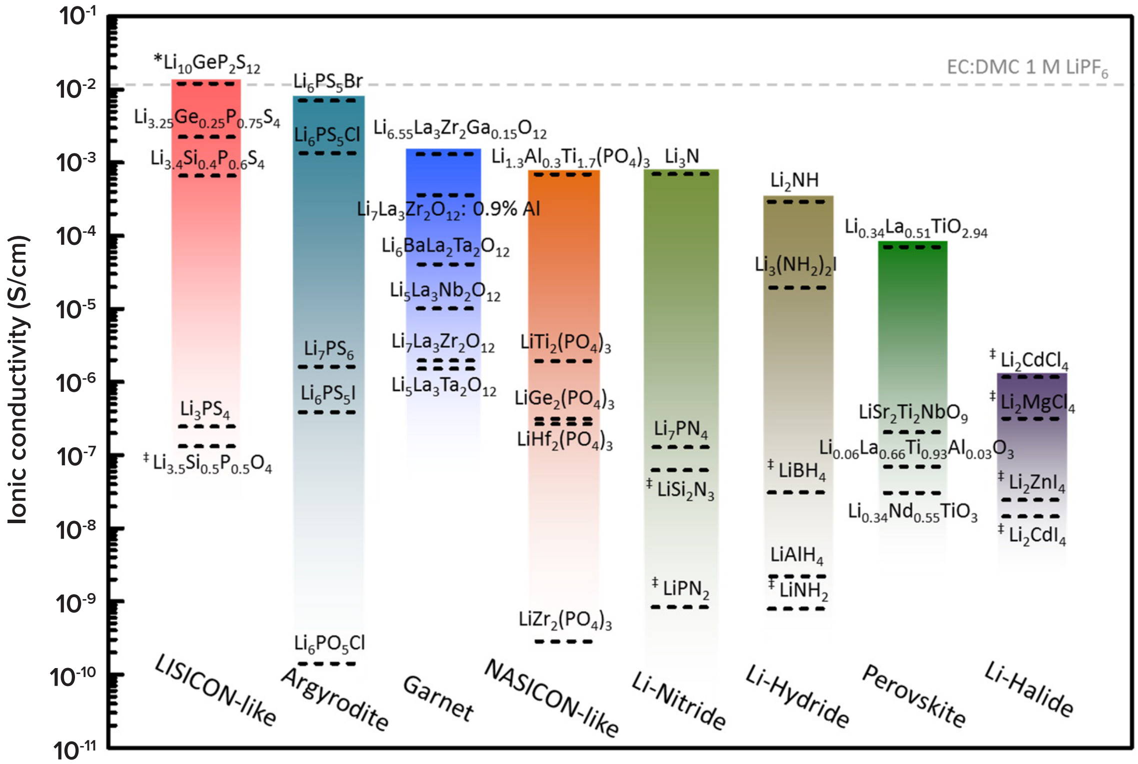


Figure 2.1.4. Total ionic conductivity and activation energies at room temperature for several prototype Li-ion conducting solid electrolytes. *$Li_{10}GeP_2S_{12}$ is considered LISICON-like due to its chemical and structural similarity to LISICON. ‡Compounds whose conductivity has been extrapolated from higher temperatures to room temperature. Reprinted with permission from Ref. 48. Copyright (2016) American Chemical Society.

An alternative to solid electrolytes with high ionic conductivity is very thin electrolyte layers.[49] Thin solid electrolytes have the potential to enable all-solid-state batteries where the solid electrolyte is not the limiting factor in ion transport. Recent work has demonstrated the synthesis by atomic layer deposition of solid electrolytes that are 40-100 nm thick in solid-state batteries.[49,50] This example of nanostructuring to increase conductance is analogous to nanostructuring to create extrinsic pseudocapacitance discussed above, in which sufficiently thin layers render ion diffusion times short enough not to be rate-limiting in battery performance.

Chemical and Electrochemical Stability at Solid Electrolyte-Electrode Interfaces: Interfacial reactions may trigger the formation of an interphase region between the solid electrolyte and the electrode surface due to electrolyte decomposition,[51-53] which may lead to high interfacial resistances and a decrease in the performance of the solid-state battery.[54] Besides generating new material components at the interface, the reactions at the electrode surface are typically accompanied by significant structural reorganization. It is crucial to monitor how these structural and chemical aspects change—and their effect on ionic transport and electrochemical performance—during interface formation and subsequent battery operation.

Products formed at the solid electrolyte-electrode interface may impede ion exchange and/or facilitate unwanted electronic transport in the electrolyte. Similarly, insufficient electrochemical stability can result in the injection of electronic carriers (electrons or holes) into the electrolyte beyond the space-charge region, potentially resulting in short-circuiting. A major challenge is to develop solid electrolytes that are "thermodynamically immune" to these failure modes (i.e., intrinsically stable) or can be stabilized kinetically through the application of coatings or by the *in situ* formation of desired interphases.

These issues are not exclusive to the Li metal anode, but more generally affect solid electrolyte interfaces with both electrodes, independent of specific electrode materials. Smooth interfacial contacts are needed as well. Besides controlling interfacial resistances, the correct assessment of ionic conductivities is a must in these systems. This aspect is particularly challenging due to restructuring of the solid phases and the defective nature of most solids and interphases. Thus, high-throughput screening methods combined with first principles computations and *in situ* experimentation would be of great utility to select and/or discover materials that exhibit all the required functionalities and architectures.

Dendrite-Free, Efficient Plating and Stripping at the Negative Electrode: The conventional wisdom in the battery community is that the high stiffness of a solid electrolyte (compared to a liquid) will suppress dendrite formation during plating (charging), enabling the use of high-capacity metal anodes. However, the solid electrolytes known today are not sufficiently robust to prevent dendrite formation: Li metal can penetrate highly dense solid electrolytes along the grain boundary network, calling into question the notion that a solid's elastic response alone (i.e., high stiffness) is sufficient to suppress dendrites.[55] Even if dendrites can be mitigated, reactivity at the interface with the Li metal during interface formation and subsequent battery operation remains a significant issue.[50] Consequently, understanding the impact of microstructural evolution on the performance of solid electrolytes is an important step in advancing this technology.

Thrust 1c: Identify New Battery Chemistries Based on Environmentally Benign, Safe, Abundant Materials

Today's batteries rely on some materials that are rather rare, costly, and toxic and/or environmentally damaging, and although these metrics are interrelated, the primary driver is often simply cost. A significant set of electrode materials and battery chemistries has been explored to date, including versions of mainline Li-ion anode/cathode combinations (graphite/oxide, silicon/oxide) and also candidates for a higher-performance beyond-Li-ion generation (e.g., lithium/sulfur, lithium/nickel-metal-cobalt oxide). In the latter cases, the accumulated knowledge base is already significant, though profound science challenges remain. Nevertheless, expanding the scope of electrode materials and battery chemistries is attractive to achieve benefits from greater environmental compatibility and earth abundance as well as lower toxicity and cost. As such, there is a significant and continued need for abundant, inexpensive, durable, environmentally benign, and manufacturable battery chemistries.[56] Such alternatives could conceivably provide new pathways to higher energy density and power capabilities.

Charge Storage and Transport Mechanisms: A major challenge in adopting new electrochemical materials is to understand charge storage and transport mechanisms in the materials themselves and in cell configurations in which they would be used. Using abundant, low cost elements is particularly attractive to enable large-scale energy storage.[57-59] For example, since their invention in 1940, alkaline Zn/MnO_2 batteries have become the dominant primary battery system available, with an annual market value of $10 billion.[60] Reversible aqueous Zn-ion batteries are currently sought because of the low cost of the materials and components, but such systems illustrate the challenges: complex, multivalent reactions of electrode materials; limited reversibility of manganese dioxide (MnO_2)[61-63] and prussian blue analogue materials[64,65] as cathodes for Zn-ion storage; an array of polymorphic forms (α-MnO_2,[63] mesoporous γ-MnO_2,[64] δ-MnO_2 nanoflakes,[66] and todorokite-type MnO_2[67]); structural transformations upon Zn-ion intercalation; complex chemical conversion[62]; and the complex role of water in facilitating Zn-ion transport in the electrode materials (Figure 2.1.5).[68-70]

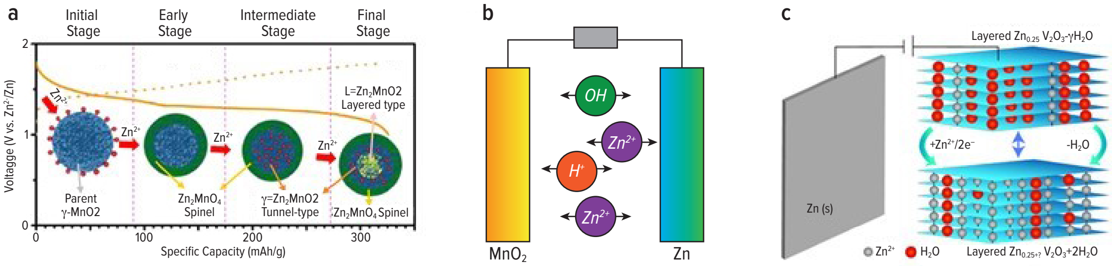


Figure 2.1.5. Schematic illustrations of different mechanisms for Zn ion storage. (a) Zn-ion intercalation in a γ-MnO_2 cathode (from Ref. 68). (b) Chemical conversion reaction for reversible Zn-ion storage. (c) Water molecule-assisted Zn-ion interaction in $Zn_{0.25}V_2O_5$. Reprinted with permission from Ref. 61. Copyright (2015) American Chemical Society.

The example of Zn-based systems illustrates the complexity encountered in alternative materials and battery chemistries. In aqueous systems, in particular, the interaction of the electrode materials with water, as well as the solvation of the cations, must be carefully studied to identify and overcome barriers to achieve high capacity and fast charge transport.[62]

Aqueous Battery Systems: Aqueous electrolytes are particularly attractive due to their low cost, safety, and abundance, but they suffer from a relatively small usable voltage window of ~1.7 V. Above this voltage, water decomposition and gas evolution occur at the electrodes, leading to coulombic losses. Aqueous systems are particularly desirable if they could be redesigned to enable higher voltage operation, and indeed recent findings demonstrate that voltage windows approaching or even exceeding 2 V are possible between electrode pairs immersed in an aqueous electrolyte.[71,72] These results suggest a promising route to high-performance energy storage systems that can be produced at scale. Attaining this goal may well depend on fundamental research on novel high-solubility aqueous salts, electrode structures for cultivating favorable pH environments, the fundamentals of electrochemical stability in aqueous electrolytes, and ionic transport in electrolytes with different degrees of solvated species, effects that are largely undocumented and poorly understood.

Diverse Chemistries with New Architectures: Mediator-ion solid electrolytes[73-75] provide the basis for an architecture that enables novel combinations of aqueous and non-aqueous chemistries and the use of abundant and environmentally benign elements like iron, zinc, oxygen, sulfur, etc., in aqueous media. While conventional polymeric porous separators are inadequate to prevent dendrite penetration or chemical crossover between the positive and negative electrodes, a solid electrolyte permeable to divalent ions like Zn^{2+} and Fe^{2+} would be attractive, but it is exceedingly difficult to realize, considering the challenges already observed when using solid electrolytes to transport even lighter monovalent ions like Li^+ and Na^+. This problem could be overcome by adopting new strategies, such as the concept of a mediator-ion solid electrolyte as depicted in Figure 2.1.6.

With solid electrolytes that act as ion mediators and also prevent chemical crossover, it may be possible to achieve low-cost, safe, aqueous battery systems, including a metallic Zn or Fe anode, an aqueous electrolyte, a lithium-ion or a sodium-ion solid electrolyte, and a variety of redox systems (oxygen, sulfur, bromine, permanganate, ferrocyanide, quinones, etc.). Importantly, a solid electrolyte separator with liquid anolytes and catholytes eliminates the commonly encountered problems of huge charge-transfer resistance between solid electrolytes and solid electrodes (as in all-solid-state batteries). The strategy also offers the flexibility to use, for example, an alkaline medium at one electrode and acidic medium at the other electrode, or a non-aqueous medium at one electrode and aqueous medium at the other electrode (Figure 2.1.6), in contrast to conventional battery systems (e.g., in Li-ion batteries, transition-metal ions can crossover from cathode to anode).

Such hybrid battery configurations, featuring solid electrolytes as ion mediators, are in their infancy in exploiting new architectures to enable diverse chemistries, but research opportunities are plentiful, including issues such as design and development of mediator-ion solid electrolytes for Li or Na ion transport while allowing different electrolytes on either side; solid electrolyte surface protection with ion-transporting surface coatings or compositions, which may also drop voltages at the liquid electrolyte interface; compatible catholyte/anolyte systems for a given mediator-ion solid electrolyte; and long-term stability, kinetics, and reaction mechanism.

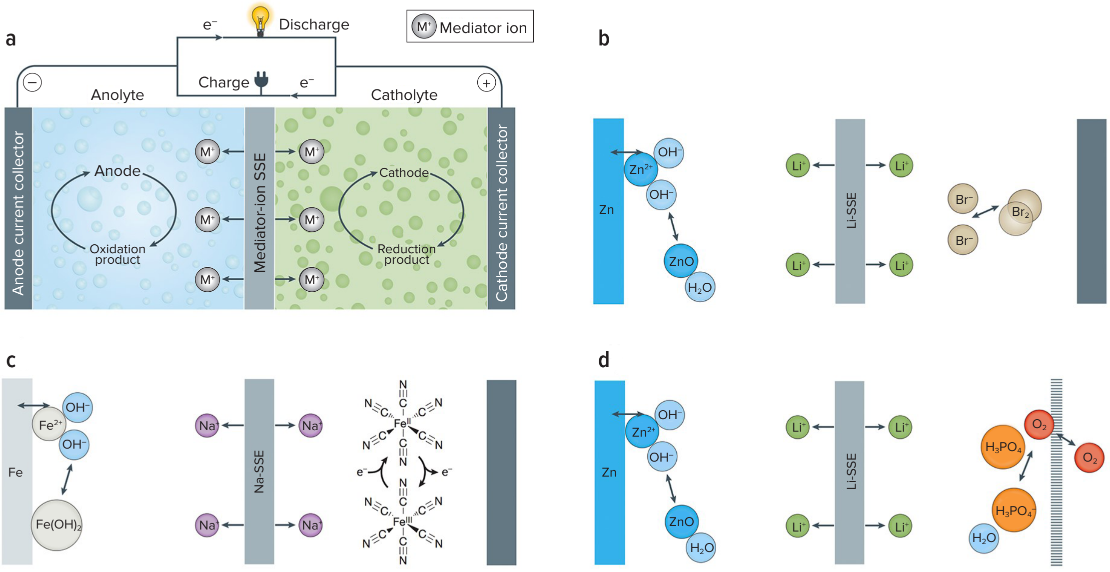


Figure 2.1.6. Aqueous batteries with mediator-ion solid electrolytes. Schematic diagram of an aqueous electrochemical energy storage system enabled with a mediator-ion solid electrolyte (panel a). The solid electrolyte prevents mixing of the anolyte and catholyte. The redox reactions at the anode and cathode are sustained by the shuttling of the mediator ion through the solid electrolyte. Also shown are schematics of aqueous electrochemical energy storage systems enabled with either a lithium-ion or a sodium-ion solid electrolyte: Zn(LiOH) || Li solid electrolyte || Br_2(LiBr) (panel b), Fe(NaOH) || Na solid electrolyte || $K_3Fe(CN)_6$(NaOH) (panel c) and Zn(LiOH) || Li solid electrolyte || air (H_3PO_4/LiH_2PO_4) (panel d). SSE = solid-state electrolyte. From Ref. 73.

Advanced Lead-Acid Batteries: Lead acid batteries, long the dominant energy storage technology, have low cost, the highest cell voltage among all aqueous electrolyte systems, the ability to operate over a wide range of temperatures, an energy efficiency over 80%, low self-discharge, and a high recycling rate. While excellent in fast discharge applications such as vehicle starting and uninterrupted power, lead-acid batteries perform much more sluggishly in fast charge applications, such as regenerative braking in vehicles and partial state-of-charge applications like time-shifting generation and load on the grid. The origin of their sluggish charging rate and limited lifetime when partially charged is the growth of large insulating single crystals of the discharge product $PbSO_4$ at the anode, which cannot be easily reversed on charging to Pb and H_2SO_4.[76] Formed as an amorphous gel, $PbSO_4$ converts to small crystallites that coalesce spontaneously and grow continuously to large size with proportionately smaller surface area. The charging reaction from $PbSO_4$ to Pb and H_2SO_4 occurs in solution, requiring the large crystals to first dissolve before they can chemically react. The disparity in charging and discharging rates is significant, as much as a factor of 30.[77] Beyond preventing fast charge, formation of large crystals of $PbSO_4$ removes Pb in the interior from the charge-discharge process, causing capacity fade and short lifetimes.

New approaches for increasing charging rate and extending lifetime in lead-acid batteries include nanostructuring of components. Graphene and carbon nanotubes, for example, can be incorporated into the anode to provide a nanoscale substrate with high electronic conductivity, an ordered structure, and high chemical stability.[78] Also, $PbSO_4$ may precipitate from solution onto this large-area, highly conducting substrate, preventing agglomeration into crystals and allowing the charging reaction to proceed on the substrate instead of in solution. Such novel solutions could enable a new generation of faster-charging, longer-lifetime lead-acid batteries.

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2.2 PRD 2 — Link Complex Electronic, Electrochemical, and Physical Phenomena Across Time and Space

Over the past decade, much progress has been made in developing and using particle- and photon-based spectroscopy, scattering and imaging techniques, and new modeling frameworks for understanding and predicting mechanisms involved in electrochemical energy storage.[1-3] These advances have been achieved largely on a phenomenon-by-phenomenon basis, with each experiment or simulation directed to a particular piece of the electrochemical puzzle, such as lithiation mechanisms, SEI composition, or capacity fade. Connecting the diverse phenomena contributing to battery and electrochemical capacitor operation and failure remains a rich and productive challenge. Understanding coupled phenomena spanning electronic, chemical, structural, and mechanical behavior on the spatial and temporal scales over which they occur is central to moving electrochemical storage from serendipity and trial and error to predictive design. A holistic understanding of electrochemical energy storage devices and deeper insight into the coupling of redox processes, kinetics, reversibility, and degradation phenomena are needed to bring energy storage to the next level. This critical advancement requires the development of more sensitive and accurate multidimensional tools for *in situ* and *operando* observation of operating electrochemical systems, new simulation and modeling tools to describe and predict electrochemical outcomes, and greater integration of characterization and modeling.

Modeling tools spanning first-principles atomistic to phenomenological mesoscale and continuum levels play increasingly important roles in energy storage research. Density functional theory has significantly advanced the frontier of energy storage materials, both in understanding energy storage phenomena and in predicting new materials by means of high throughput computation. Meanwhile, significant achievements have been made over the past ten years in developing new modeling frameworks to account for the coupling of electrochemical, structural, and mechanical phenomena. The models have been validated by newly developed *in situ* methods,[4] which have allowed these models to be applied for materials invention and optimization within both academia and industry. The new challenge is to link phenomena over a wide range of time and length scales in new models to achieve rational design of batteries *as a system*.

Spectroscopy, scattering, imaging, and electrochemical techniques have seen tremendous advances in the last decade and are the bedrock of energy storage research,[5] although at present these techniques are typically used individually. For example, spectro-microscopy has been used to track the reaction dynamics of $LiFePO_4$ electrodes by measuring the relative concentrations of Fe^{2+} and Fe^{3+}, with the conclusion that nanoscale spatial variations in rate and composition control the lithiation pathway.[6,7] While these techniques are fundamental when used individually, there are new horizons of insight attainable by coupling these techniques and the phenomena they probe. Simulation can be similarly coupled and advanced to directly predict measurable experimental outcomes: for example, spectroscopic signatures of reaction pathways, structural degradation on cycling, or SEI formation at interfaces. Overall, the challenge is to develop experiment, simulation, and theory to investigate these coupled phenomena of electrochemical energy storage systems over the full time and length scales on which they occur.

2.2.1 SCIENTIFIC CHALLENGES

This PRD focuses on understanding the interplay of electronic, chemical, structural, and mechanical phenomena that underlie the capacity, kinetics, reversibility, irreversibility, and ultimately degradation and failure of electrochemical energy storage systems. The ultimate goal is to understand the spatial and temporal evolution of operating electrochemical systems, allowing rational design of energy storage devices from atomic and molecular to mesoscopic and system levels. Approaches are needed to link experiments and simulations across spatial scales from atomic to particle level (100s of nanometers to microns) to the electrode level (millimeter-centimeter) and time scales from picoseconds to seconds to years. The challenge is to develop and apply methodologies and tools that can seamlessly link the spatial and temporal scales of coupled electronic, chemical, structural, and mechanical phenomena.

This large range of spatial and time scales is illustrated in Figure 2.2.1 for Li-ion battery electrodes.[8-14] Similar spatial and temporal ranges apply for interphases (see PRD 4), supercapacitors, membranes, and electrolytes. At the smallest scale is atomic lithium hopping through the lattice by diffusion and entering or leaving the electrode by intercalation, alloying, or surface redox chemistry. Associated with these atomic motions are local, coupled, structural and electronic changes that directly impact the redox processes and storage capacity. As ions continue to enter the electrode, its volume expands and often there is a phase transition, especially for alloying or conversion electrodes such as Li alloying with Si to form $Li_{15}Si_4$-like phases or Li reducing FeO to form Li_2O and Fe^0. As the volume change propagates throughout the electrode, stress builds up in ~100-nm size particles through chemo-mechanical coupling and mechanical incompatibilities,[15] which can cause particle cracking. Alternatively, mechanical constraints can limit volume expansion, which can close internal pores and limit ion transport. If the particle state of charge is spatially heterogeneous, differential expansion can build up within and between particles and become another source of cracking. Such mechanical failure can cause fragments to disconnect from the conduction pathway to the current collector, and SEI formation on the fractured surface can consume Li, leading to degradation in capacity. These detrimental effects accumulate during cycling and can cause catastrophic failure, with implications for battery safety.

Capturing the Coupling of Electronic, Structural, Chemical, and Mechanical Phenomena over a Wide Range of Space and Time: This is especially important for rare events in space and time that trigger coupled phenomena that grow uncontrollably and ultimately lead to catastrophic failure. By their nature rare events are infrequent and usually irreversible, but the inhomogeneous structures and coupled phenomena of energy storage devices can promote the occurrence of rare events. While the consequences of the event can span nanoseconds to days and can be local or extended, the event itself initiates at a small length and short time scale. At present, the occurrence of rare events cannot be predicted, nor can the sequence of coupled electronic, structural, chemical, and mechanical events that they may trigger leading to macroscopic failure. An example is dendrite nucleation (see Figure 2.2.2),[16] which initiates locally in nanoseconds at a nucleation site of nanometer dimensions, but grows to micrometer size during cycling and eventually creates a short circuit between the anode and cathode, which often leads to thermal runaway.

Correlation and Analysis of Coupled Phenomena and Processes: This is a key challenge across all aspects of understanding and improving electrochemical energy storage. Many techniques and approaches are available to address a limited range of individual phenomena at specific space and time scales, such as the change in microstructure of electrodes on lithiation.[2,17,18] By linking the necessary length and time scales across diverse phenomena into a global, 3D representation of an electrochemical energy storage device, one could selectively zoom in or out of spatial regions of interest (e.g., a primary particle or the surface region of a particle) over a desired time scale and select the properties to display (e.g., elastic modulus or local state of charge). Understanding the interaction of coupled phenomena is critical for many energy storage processes, including interfacial evolution, electron and ion transport, charge transfer at interfaces, and degradation with charge-discharge cycling.

Interface Evolution: This includes SEI formation and evolution, general passivation, and interface (surface) segregation. The length scales relevant for this phenomenon are nanometers to micrometers and the time scales are nanoseconds to years, as the interface continually evolves. For example, while the initial SEI formation is a one-time event occurring over milliseconds to hours, the SEI evolution is a continuous process effectively spanning the lifetime of the battery. For interphases, traditional electrochemical modeling solves coupled diffusion equations with predefined boundaries and boundary conditions. As materials change their size, interphases form and grow over time, and it is important to model and track the moving boundaries to describe the interface evolution. Approaches such as the phase-field method, which has been successfully applied to modeling temporal and spatial microstructure evolution in materials undergoing phase transformation, deformation, and particle coarsening, could be extended to include electrochemical processes.

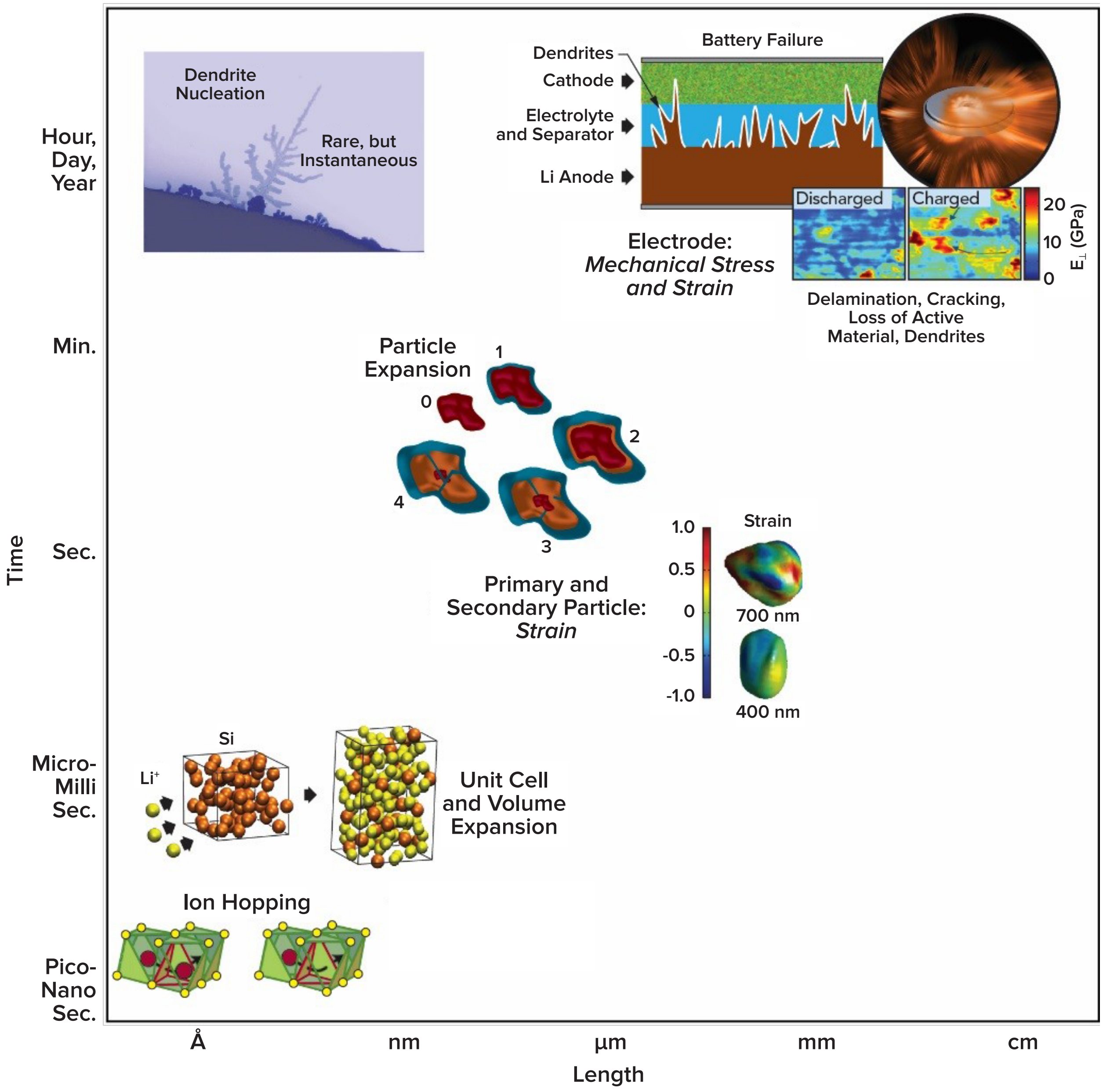


Figure 2.2.1. Plot of approximate time and length scales for phenomena occurring in the electrochemical energy storage materials during charging and discharging using Li-ion batteries as the example. The insertion and removal of Li ions in the electrode (lower left showing Li diffusion and alloying) cause volume changes and defect formation in particles (middle images of expansion and spatially resolved strain), which induce stress and strain on larger length scales, leading to degradation and, possibly, battery failure (upper right images showing local elastic modulus and dendrites). The upper left corner indicates rare events that might occur over short time periods and infrequently in the space of a few cubic nanometers, but are a root cause for an effect that evolves over days to seriously impact the entire battery. Images in figure drawn from Refs. 8-10, 12.

Electron and Ion Transport: This is critical to the operation of a battery, whether driven by diffusion, migration, or convection. The length scales of interest span from the Ångstroms associated with ion hops to the full cell dimensions of millimeters to centimeters, and the time scale ranges from picoseconds to hours, largely determined by diffusivities. While much progress has been made in understanding phenomena at slower time scales of seconds and longer, there is a critical challenge, especially with experiments, to understand faster dynamics associated, for example, with ion motion (hopping) or transport across interphase regions. Electrochemical impedance spectroscopy can reveal dominant transport processes both in electrodes and at interfaces. Specific phenomena appear at different frequencies, and the resulting spectrum can be fit by equivalent circuit models to elucidate the magnitude and source of these processes, including, for example, mixed conductivity and surface resistance. However, there is often ambiguity in interpretation. The challenge is to more directly relate transport properties derived from impedance spectroscopy to global and local physical and electronic structures and mechanical properties. Nuclear magnetic resonance is a sensitive local probe of bulk atomic environments[19] that can be used for *in situ* characterization of electrodes and, importantly, electrolytes, but is infrequently used. Advanced scanning probe microscopy techniques have provided insight into ion dynamics,[20-22] but often the information obtained is qualitative. In addition, understanding how these ion dynamics couple into other phenomena, such as physical and electronic structure, remains a serious scientific challenge.

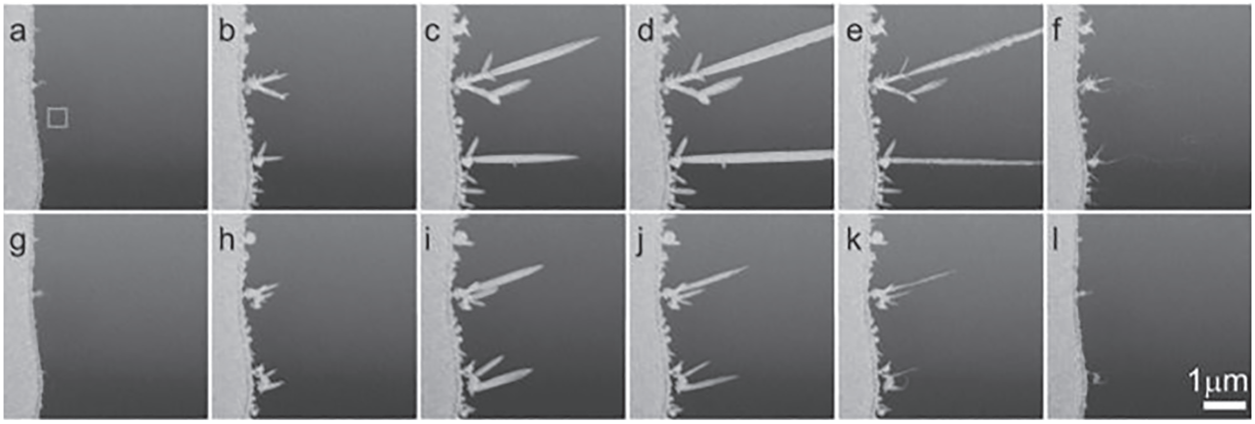


Figure 2.2.2: Repeated growth and collapse of lead dendrites from an aqueous solution, as observed with real-time electron microscopy. The rows of frames a–f and g–l are taken from consecutive cycles. Certain nucleation sites consistently nucleate larger dendrites. From Ref. 16.

Development of a Continuum Modeling Framework: Such a modeling framework is needed to efficiently describe the complex morphological evolution during coupled processes such as ion/electron transport, electrode reactions, and mechanical deformation and fracture. When coordinated with new observations, this framework may help to deconvolute these mechanisms and identify the rate-limiting steps. While density functional theory (DFT) simulations have provided valuable insight into the ion lattice site hopping at the Ångstrom and picosecond scales and its dependence on the interaction of ionic orbitals and lattice symmetry, these conclusions are largely untested experimentally. It is a significant challenge to test and refine these models and to improve our predictive ability for materials design of electrodes with inherently high ionic diffusivities.

Charge Transfer Reactions at the Electrode/Electrolyte Interface: These reactions are central to energy storage operation and electrochemistry. Often, an electron and ion will react before they can be stored in the electrode, resulting in lost energy. One challenge is how to accurately predict charge transfer reaction kinetics at realistic interfaces by means of DFT-based calculations to build the bridge with the continuum level Butler-Volmer equation. For simple systems with dilute electrolytes and conductive surfaces, Marcus theory provides a quantum mechanical basis for the Butler-Volmer equation and a means to estimate its parameters. However, as ion concentration increases and the electrode interface is covered by a nanometer-thick insulating SEI layer, the complexity at the interface requires high levels of quantum simulation that span larger length scales. This requires correspondingly increased computational power and the development of new computational methods. Developing these new methods will help to address many key questions raised in PRD 4 that are essential in energy storage, such as elucidation of the atomic structure of the electric double layer on interphase film-covered electrodes, the interphase potential drops, and their effect on charge transport and degradation.

Mechanical Changes That Accompany Structural and Chemical Changes in Electrodes: These have an important impact on battery performance and occur from the sub-nanometer to centimeter scales over microseconds to days. For example, in some materials[23] there is a strong connection between ion concentration and electrode mechanical properties that affect battery performance. This electrochemical-mechanical coupling follows from the influence of the crystal lattice and chemical bonding on the electrode volume and elastic modulus.[15] As shown recently, contact resonance scanning probe microscopy can image the ion insertion pathways through changes in Young's modulus,[8] and electrochemical-acoustic time-of-flight analysis has been used to study changes in the elasticity of cells.[24] While investigation of the electrochemical-mechanical coupling remains a challenge, the advent of new tools that probe the elastic modulus changes from the particle to pack level at high speed (~1 ms) offer promise. Yet, it remains a challenge to link these mechanical changes to even smaller length scales and to structural and chemical changes.

Bridging Length Scales and Phenomena Probed with Different Experimental Techniques and Modeling Methods: The challenge is to devise methods to bridge different experimental techniques and length scales to give a holistic view of batteries. Ideally, one experimental technique would be able to fully characterize all phenomena and provide a knob to allow a user to zoom in and out at will. Such a capability would allow the user to determine how strongly different phenomena are coupled, and what is the nature of this coupling in space and time. However, no such technique will ever exist, as there are fundamental limits to space, time, and energy resolution of every experimental technique. Therefore, systematic methods to link different information outputs from experiment and theory are required,[25] as well as ways to link different experimental methods through the use of common sample designs.[26]

While continuum-level modeling can bridge spatial scales, the method's accuracy depends on the accuracy of the input parameters (e.g., free energy landscape, diffusion coefficients, and reaction rates). Instead of obtaining these parameters by fitting limited experimental data, it is better to directly measure them in experiments or predict them in DFT-based simulations. Significant challenges for bridging models include how to provide parameters for continuum models, how to predict directly measurable results that allow validation of predictions, and how to pass essential information between simulation and experiment. Although continuum-level modeling can describe coupled electrochemical-mechanical phenomena, the theory may break down at the nanometer scale, creating a further challenge for bridging scales.

2.2.2 RESEARCH THRUSTS

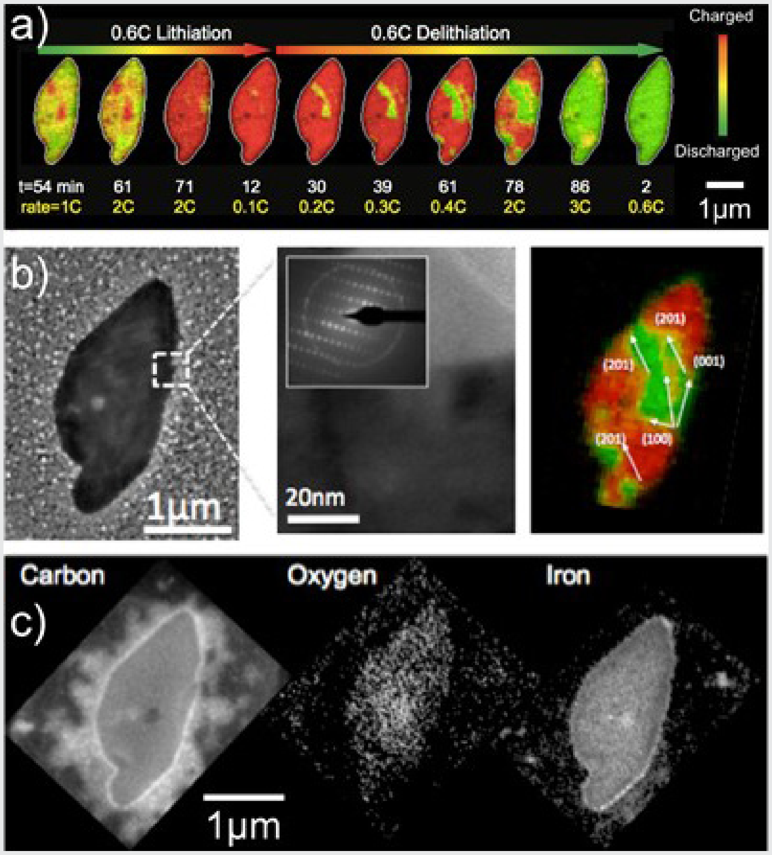
The challenges of understanding the coupled electrochemical-mechanical phenomena that govern electrochemical energy storage require new observational and computational tools and methodologies that span disparate phenomena, along with length and time scales. There are two fundamental needs. The first is creating next generation modeling techniques and characterization tools with higher resolution, greater accuracy, and wider application to diverse length and time scales. The second is integrating these new computational and characterization tools in a coordinated, synergistic approach to capture and analyze the coupled electrochemical-mechanical phenomena that enable electrochemical energy storage.

Thrust 2a: Create State-of-the-Art Modeling Techniques and Characterization Tools

Current techniques need to be leveraged to their full potential and upgraded to push their spatial and temporal limits and their sensitivity and accuracy for *ex situ* and *in situ/operando* characterization. Equally important, new multimodal and complementary techniques are needed to simultaneously or serially measure coupled phenomena. This is especially critical when observing rare events in real time, which may not be easily reproducible, and yet may trigger chains of consequential follow-up events that significantly affect battery performance.

Coordination of multiple measurement techniques is needed to characterize a specific region or phenomenon in a multimodal fashion. For example, the combination of X-ray spectroscopy and diffraction provides complementary chemical and structural information. Where simultaneous characterization on the same sample is not possible, sophisticated and robust methodologies are needed to allow multimodal characterization across different instruments that are physically separated, in different buildings or different geographical regions. A heroic example is shown in the sidebar ("Connecting Time and Length Scales with Properties") on connecting dynamics and outcomes of lithiation by scanning transmission X-ray microscopy, transmission electron microscopy, and scanning Auger microscopy. Such developments with different techniques at different length and time scales reveal the fundamental connections among electrochemical-mechanical phenomena. This methodology requires a robust means of tracking a specific region of interest when probe sizes vary dramatically; the geometry of the probe, sample, and detector may be different; and collected data may be a combination of real and reciprocal space and time, as well as frequency and energy domains.[6,26,27]

CONNECTING TIME AND LENGTH SCALES WITH PROPERTIES



This image shows an example of connecting length scales (from nano- to micrometer) and properties (structural and chemical) on the same carbon-coated $LiFePO_4$ micron-sized particle. (a) *Operando* scanning transmission X-ray microscopy of an $LiFePO_4$ platelet-like particle showing lithiated (red) and delithiated (green) regions at different global states of charge. The $LiFePO_4$ particle is charged and discharged at 0.6C and shows considerable heterogeneity. Notice the "hotspot" heterogeneity near the particle center, visible as the red regions on the left images. This is an area that lithiates and delithiates first. The latter is visible as the yellow region that develops first on delithiation in the middle images. (b) Subsequently, the $LiFePO_4$ particle is transferred into a transmission electron microscope. This enables determination of the particle crystallite orientation (right image) through selected area electron diffraction (middle image), although due to beam damage it is not possible to obtain atomic resolution. (c) Scanning Auger microscopy of the $LiFePO_4$ particle, providing surface elemental composition with carbon, oxygen, and iron concentration maps. There is a correlation between the hotspot in (a) and the region with low carbon and high iron surface concentration. This suggests a local thinning of the carbon coating resulting in a hotspot with locally faster lithiation kinetics.

Images from J. Lim et al., Origin and hysteresis of lithium compositional spatiodynamics within battery primary particles, Science, **2016**, 353, 566-571. *Also courtesy of J. Lim and W. Chueh, SLAC National Accelerator Laboratory.*

There also needs to be a focus on developing and leveraging new techniques with improved resolutions and sensitivities, which will allow probing phenomena at length and time scales that are currently inaccessible. For example, ptychography is an emerging coherent imaging technique that promises to allow *operando* microscopy with chemical sensitivity and tomography capabilities at resolutions (sub-nanometer for hard X-ray) better than what is currently available with state-of-the-art X-ray optics (Figure 2.2.3). The recent completion of the National Synchrotron Light Source II and the planned upgrade to the Advanced Photon Source with dramatically more coherent X-ray beams will further expand the capabilities of X-ray imaging techniques. Also, more sensitive and accurate experimental tools are required, such as those that can quantify changes corresponding to as small as 0.01% capacity loss, corresponding to a lifetime of about 10,000 cycles.

While modeling capabilities have improved, DFT and DFT-based *ab initio* molecular dynamics are practically limited to ~500 atoms. However, many properties or processes require a simulation size larger than the current DFT limitation. For example, the complete lithiation of a 2-nm-thick Si film will require ~10,000 atoms. Semi-classical force fields with inclusion of charge equilibration, such as the reactive force field (ReaxFF), can be parameterized from first principles based on actual dynamical charge output. This type of bridging could allow systems with >10,000 atoms to be efficiently simulated. However, force-field development is currently inefficient and limited to specific bulk cases. Systematic studies, data science, and automated fitting can expedite the development of accurate force fields. (See sidebar "Simulation of Charge Transfer Reaction at the Complex Interfaces in Li-Ion Batteries".)

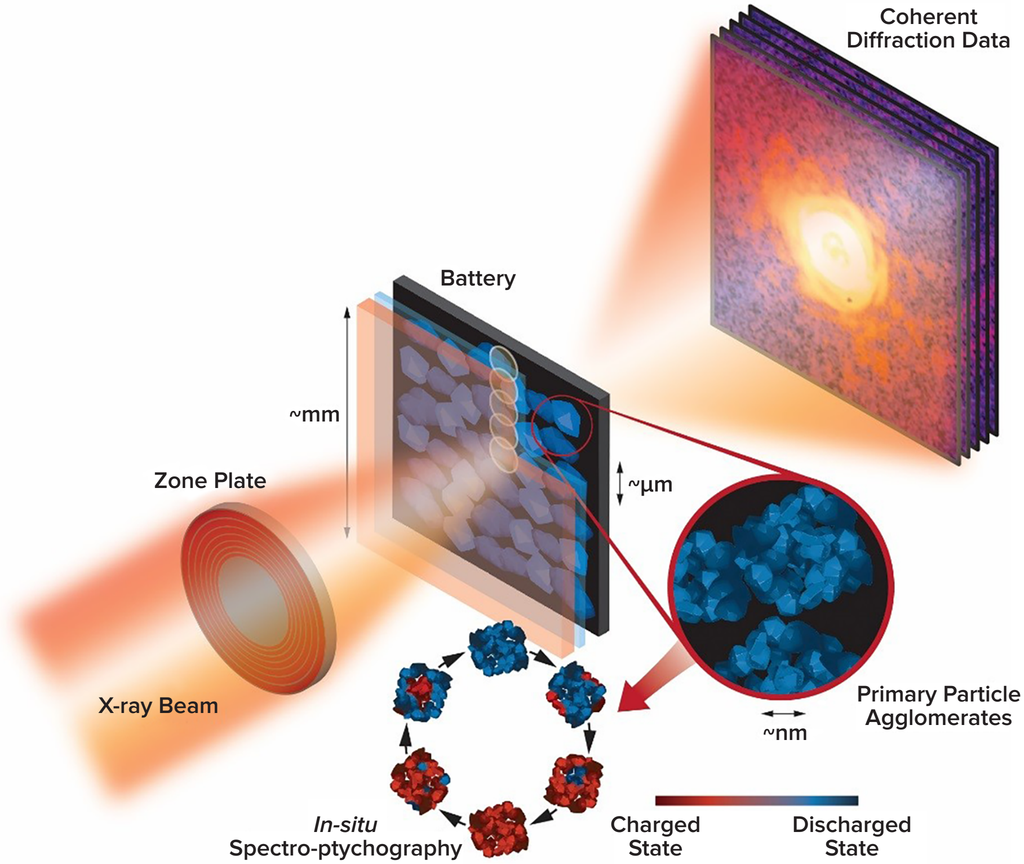
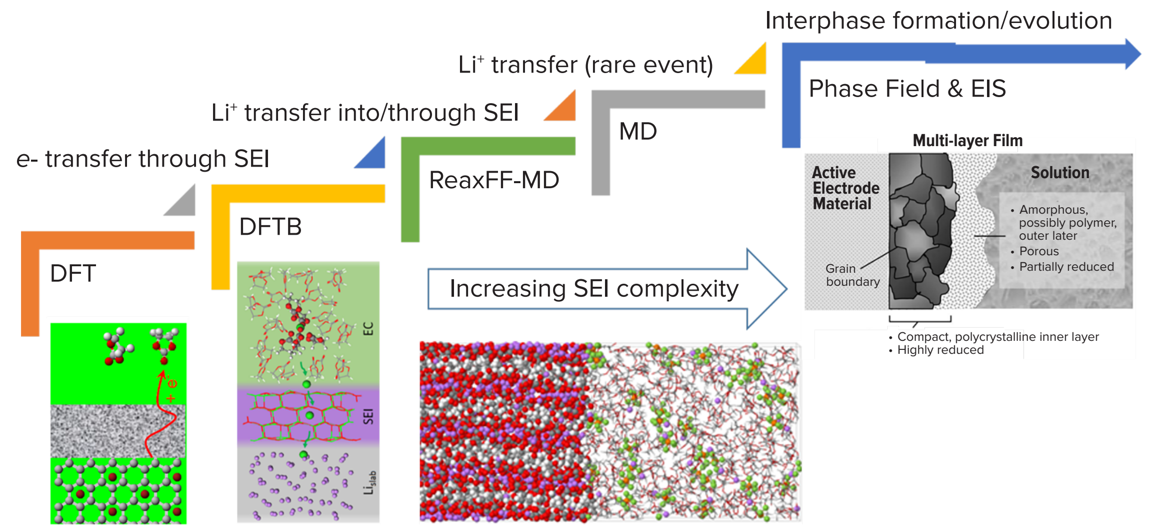


Figure 2.2.3. Schematic of ptychography setup. This is an emerging scanning coherent imaging technique with sub-nanometer resolution capability for hard X-rays. With the continued development of this technique, *operando* spectro-microscopy and tomography with both absorption and phase contrast will allow direct visualization of the state of charge of individual primary particles within larger agglomerates. *Adapted from A.M. Wise et al., Development of a soft X-ray ptychography beamline at SSRL and its application in the study of energy storage materials, SPIE Optical Engineering + Applications: X-Ray Nanoimaging — Instruments and Methods II*, 2015, *9592*, 95920B.

Semi-classical force fields are often suitable for simulation of chemical reactions, but are not reliable for charge transfer oxidation and reduction reactions across complex interfaces or for electrolytes. Such reactions require simultaneous modeling of strong coordination, complexation, polarization, weak charge transfer/hybridization, and multiple possible species, including ion pairs, oligomers, and varying solvation spheres with strong sensitivity to initial conditions. Additionally, modeling the dynamics of interfaces and electrolytes requires quantum mechanical accuracy on large length and time scales more suited to classical force field molecular dynamics.

Density functional tight binding can be an appropriate extension of conventional DFT because it allows accurate electronic structures to be computed and electrons and ions to be separated properly while merging the reliability of DFT with the simplicity and efficiency of the original tight binding ansatz.

SIMULATION OF CHARGE TRANSFER REACTION AT THE COMPLEX INTERFACES IN LI-ION BATTERIES



The ultimate goal of coupled simulation methods is to understand the structure-function relationship associated with charge transfer and interface evolution. This set of theory-based images shows examples of connecting length scales from Ångstrom to micron and properties including mechanical, structural, chemical, and charge and mass transfer. It highlights the importance of linking multiscale and multiphenomena modeling methods. From left to right, the panels depict electron tunneling through an atomic-layer-deposited oxide film to electrochemically reduced ethylene carbonate molecules, modeled by constrained DFT; DFT tight binding modeling of Li^+ transfer from a liquid electrolyte through an inorganic (Li_2CO_3) interphase layer into a Li metal anode; Li^+ transfer from liquid electrolyte into an organic (ethylene dicarbonate) interphase layer; and the structure of a multicomponent solid-electrolyte interphase. The complexity and heterogeneity of the models increase from left to right, along with the level of theory required. More accurate electronic structure methods are needed to deal with charge transfer and Li motion in inorganic solids (e.g., Li_2CO_3), while more coarse-grained methods such as force field-based molecular dynamics and phase field models are needed to depict liquid-state fluctuations and to identify hotspots at liquid-solid interfaces, mechanical deformations, and multi-component interphase morphologies. The coarse-grained methods, therefore, provide well-equilibrated starting interfacial configurations for accurate electronic structure calculations. In turn, electronic structure calculations provide parameterization for the coarse-grained simulations. The modeling results will help better interpret measurements such as electrochemical impedance spectroscopy.

Images from Li et al., Computational exploration of the Li-electrodelelectrolyte interface in the presence of a nanometer thick solid-electrolyte interphase layer, Acc. Chem. Res.*,* ***2016****,* 49 (10), 2363-2370; *K. Leung et al., Using atomic layer deposition to hinder solvent decomposition in lithium ion batteries: First-principles modeling and experimental studies,* J. Amer. Chem. Soc.*,* ***2011****,* 133 (37), 14741; *O. Borodin and D. Bedrov, Interfacial structure and dynamics of the lithium alkyl dicarbonate SEI components in contact with the lithium battery electrolyte,* J. Phys. Chem. C*,* ***2014****,* 118, 18362-18371; *J. Christensen and J. Newman, A mathematical model for the lithium-ion negative electrode solid electrolyte interphase,* J. Electrochem. Soc.*,* ***2004****,* 151, A1977-A1988.

The combination of DFT → density functional tight binding → ReaxFF naturally bridges the length scales from sub-nanometer to submicron but has not been widely used for electrochemical energy storage. With these size-bridging methods, parameters used in continuum modeling can be simulated, such as the activity coefficients in real electrolytes with large concentrations of salt. Beyond simulating the operation and degradation of materials for energy storage, these size and length-scale bridging strategies can also be used to simulate material synthesis processes.

Diffusion of electroactive ions through electrodes and across interphases is central to the function of energy storage devices and has an impact on storage capacity, lifetime, and especially, rate capability. New approaches to measuring, understanding, and predicting the faster dynamics associated, for example, with ion hopping in crystalline materials or transport across interphases are required. How do we microscopically probe and improve transport in electrodes and electrolytes? Can we develop new methods to see faster dynamics associated, for example, with ion motion in electrodes and transport across interfaces? It is important to couple this with physical, chemical, and electronic structure to better design materials for high specific power and engineered interphase layers.

New experimental techniques that provide insight into long-range diffusion and transport across interfaces are also needed. Nuclear magnetic resonance (NMR) of Li and other ions can explore the dynamics of Li-ion diffusion within electrodes and electrolytes;[28] however, it is difficult to measure the slower diffusion across interfaces and grain boundaries. Furthermore, NMR experiments are typically limited, with a few exceptions, to *ex situ* measurements of the bulk material and require the absence of paramagnetic species. When possible, *in situ* NMR experiments are exceedingly valuable in determining not only the diffusion behavior, but also the structure.[29] Combining molecular dynamics simulations with NMR of two isotopes of lithium (^{6}Li and ^{7}Li) can be used to probe diffusion pathways in electrodes.[30] Isotopic labeling, together with secondary ion mass spectrometry and DFT, has also provided insight into Li diffusion mechanisms through the interphase layers.[31,32] Can we use the easy isotopic labeling for Li (and other relevant ions) to better understand ion transport, especially through interphases? How do we more directly couple the observed transport directly to the physical, chemical, and electronic structure? Electrochemical impedance spectroscopy provides insight into dominant transport processes occurring in batteries in electrodes and at interfaces, but lacks structural and chemical specificity. Can we couple electrochemical impedance spectroscopy with probes other than current flow, such as X-ray and optical absorption spectroscopies or electron and X-ray microscopies, to reveal structural and chemical details? The use of simple model systems, as outlined in Thrust 2b, has significant potential to provide insight here.

For the shortest time and length scales, considerable progress has been made in the theory of lattice jumps underlying bulk diffusion, but few experiments can test these simulations. The sidebar “Ion Diffusion at Atomic Length and Picosecond Time Scales” illustrates one possible approach, using X-ray photon correlation spectroscopy, the X-ray analog of dynamical light scattering, with a free electron laser, to experimentally obtain the lattice distortion during an ion hopping with about 10 fs time resolution. Such approaches can provide badly needed data to test *ab initio* predictions of jump pathways (and the associated activation energies) and help to improve simulation-based design rules for electrodes with high specific power capacity. Similarly, studies using this method for liquids or polymer electrolytes can lend some insight into transport in these disordered systems.

Thrust 2b: Integrate Computational and Characterization Tools

Seamless merging of simulations and experiments is essential to the multi-modal approach to bridging disparate time and length scales. There needs to be more focus on simulation-experiment coupling where simulations guide the experiments and directly predict their outcome. The results of these experiments are then explicitly compared to the simulations and fed back into the next iteration of the simulations to update the models and improve their predictive power. Moreover, simulations should be used to link experiments carried out at different length and time scales to fill in the knowledge gaps between experimental windows and propose experiments a step beyond what is now feasible. For example, phase field simulations can link transport properties of a material such as the bulk diffusion rate to the local chemical dynamics visualized by, for example, *operando* microscopy (see sidebar “Connecting Time and Length Scales with Properties”).

A closer coupling of experimental measurements with computational models and theory can bridge the knowledge deficiencies at multiple different length and time scales arising from measurement limitations and compromises made on *in situ/operando* cell designs. For example, models may be used to determine if a rare event observed at one length scale can ultimately lead to cell failure at a much different length and time scale or if this event is benign. Currently, such predictive modeling on cell failure does not exist.

In general, stronger connections among experiments and simulations will accelerate progress in understanding the coupling of electrochemical-mechanical phenomena. Atomistic simulations should mimic testing conditions and predict directly measurable properties. Hence, constant-voltage DFT calculations are needed, because experimental measurements are made with electrodes at a constant potential, requiring referencing the Fermi level to an external potential. For electrochemical capacitor applications, this can be achieved with newly developed methods and boundary conditions that combine DFT and implicit solvent-like methods, such as the effective medium approach. When direct comparisons between atomistic simulations and experiments are not possible or are ambiguous, meaningful connections can still be made via continuum modeling, which can capture both the experimental time and length scales. For example, just comparing energy barriers may not be adequate to distinguish different diffusion mechanisms. However, a one-dimensional diffusion model that builds upon the mechanisms, mimics the testing conditions, and takes key input from DFT simulations can be constructed to predict measurable concentration profiles that can be compared to experiment.[32]

While there is a need for more complete measurements of the fundamental properties of electrodes, such as the Li wetting of materials and rate constants for various dynamic processes, new characterization tools and methodologies are needed for more fully linking electronic, chemical, structural, and mechanical phenomena. How do we accurately measure mechanical and electronic properties at the same spatial location on an electrode, for example, by developing a combined microscope for scanning probes (mechanical), scanning electrochemical probes (redox), and scanning X-ray probes (chemical, electronic)? Can we more accurately relate the electrochemistry (measured *in situ* in the characterization cell) to the structure and electronic properties of the electrode and its interface with the electrolyte? Can the electrode state of charge be quantitatively connected to the spatial distribution of Li, while directly addressing the question “Where does the Li go, and how does it interact with its local environment?”

Connecting experiments and simulations to understand complex, coupled phenomema can be facilitated by careful selection of the system to be studied. Simple model systems have significantly advanced our understanding of energy storage, as they reduce complexity and focus on a few variables and outcomes that often reveal mechanistic causes and relationships. Researchers have adopted model systems to understand energy storage mechanisms by using these idealized geometries to find and test specific hypotheses that otherwise may be lost in unrelated complexities. This approach is well expressed in the catalysis community where, for example, single crystals are used as model substrates rather than nanoparticles.[35] Models may involve *in situ* characterization using single crystals,[36,37] thin films,[38] or open cell geometries[39,40] for nanostructured electrodes to explore specific features and relationships.

One example is the coupled mechanical and transport properties of multi-component interphase layers that are generally too complex for modeling studies to capture. These interphases are strongly affected by the composition of the electrolyte, including uncontrolled impurities, the charging and discharging rates, voltage variation across the charging and discharging profile, and repeated cycling. Instead of trying to treat all of these variables, a simpler experimental model carried out with pure electrolytes with systematically controlled voltages and charging rates allows specific phenomena and their causes to be isolated and controlled. Such a model experimental system can be simulated, and when the simulation is refined by experimental validation and feedback, predictive capability outside the range of measured experience can often be achieved.

An example of coordinated experiment and simulation of a model SEI comes from the study of the lithiation of Si on a single-crystal surface in the presence of an electrolyte composed of ethylene carbonate and dimethyl carbonate solvent and LiPF$_6$ salt.[37] The surface and subsurface layers were examined with X-ray, neutron, and electron scattering, and the surface with atomic force microscopy (Figure 2.2.4). These *in situ* studies revealed not only a structure of sequential layers produced by the lithiation process, but also the evolution and breathing of the layers with charge and discharge cycling.

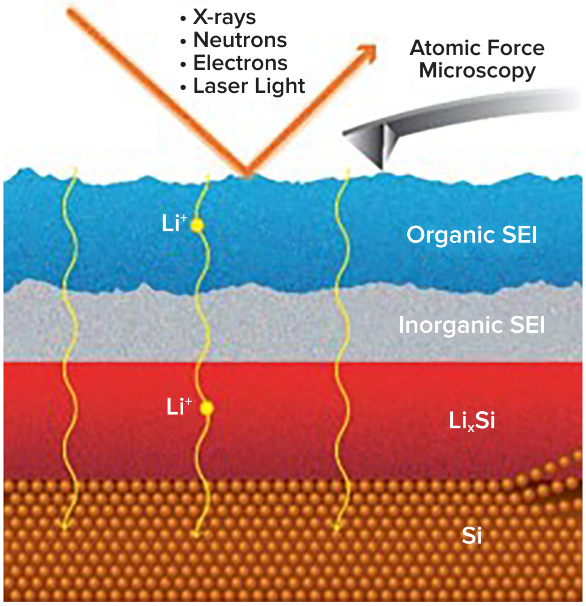
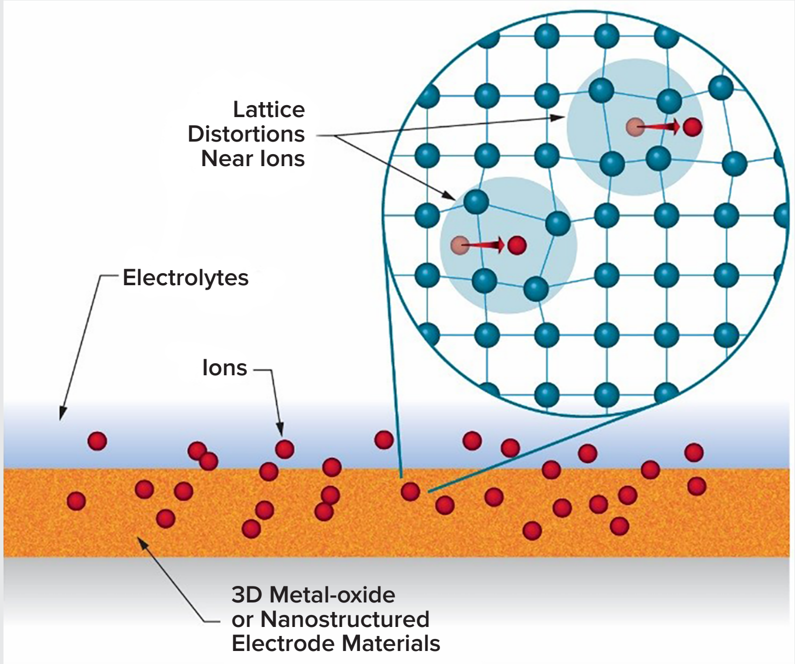


Figure 2.2.4. A model Si-SEI lithiation system composed of a single Si crystal substrate in ethylene carbonate-dimethyl carbonate solvent with LiPF$_6$ salt. Based on Refs. 7, 36, 37.

The control of experimental parameters and the relatively simple structure of this model system were amenable to simulation, and the combined results were consistent with a three-stage lithiation mechanism with a reaction-limited, layer-by-layer lithiation of the Si substrate.

ION DIFFUSION AT ATOMIC LENGTH AND PICOSECOND TIME SCALES: CONNECTING LENGTH SCALES



The diffusion dynamics of the ions (e.g., Li^+, Na^+, or multivalent ions) through the crystal lattice of an electrode have a tremendous impact on the energy storage capacity, material lifetime, and especially, rate capability. Often, slow diffusion is the limiting factor in charge and discharge rates in electrodes, and, therefore, inhibits faster charging of electric vehicles.

While first-principles calculations create a detailed picture of electroactive ions diffusing through a lattice,[6] little is known experimentally about the atomic-scale processes involved in ion diffusion. Time scales for individual ion hopping events between adjacent interstitial sites approach ~100 fs to ps. These "jumps" are associated with significant transient changes in the crystal strain field, which, in turn, can influence the dynamics of neighboring ions at high concentrations. Such statistical ultrafast local events ultimately link to longer range dynamics spanning many orders of magnitude in time, because these slower coupled diffusional motions occur as a result of many local hops. Our ability to characterize such phenomena over the length and time scales required for comparison with theory has been limited by available experimental tools, and this has restricted our ability to develop validated design guidelines to improve ion diffusion in functional materials.

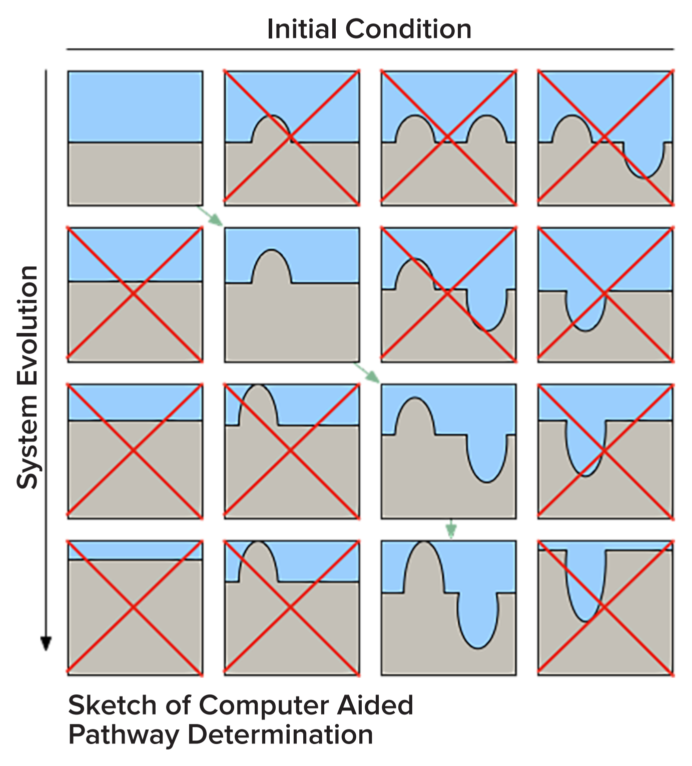
The capabilities of free electron X-ray lasers will enable much more detailed insight into ion and atom migration in complex materials under operating conditions. Dynamic scattering with coherent X-rays (X-ray photon correlation spectroscopy) has already been shown to be a powerful probe of atomic diffusion,[33] but is limited to relatively slow timescales (>milliseconds) by present X-ray sources. Advanced high-flux X-ray photon correlation spectroscopy with high-repetition-rate free electron lasers[34] will enable *operando* studies of the local aspects of ion diffusion at high spatial resolution. Systematic studies will reveal how these processes depend on electrode nanostructure, crystal structure, diffusion direction, and ion concentration. Coherent X-ray scattering from the electrode material will directly probe transient distortions of the lattice and associated longer range strain fields that arise from stochastic ion hopping events. By using a megahertz repetition rate and split-delay-line X-ray photon correlation spectroscopy, times scales between picoseconds and milliseconds can be bridged. On the hopping time scale, <1 ps, this approach can determine the local distortion *during* the hop, which can be related to the energy barrier and speed of the hop, key features of simulations.

Image courtesy of Hans-Georg Steinruck, SLAC National Accelerator Laboratory.

Overall, direct comparison between simulation and experiment is often more accurate and straightforward in model systems, especially for interphases.[7,37,40,41] Working in tandem, the experimental model system and the simulation can add critical new features reflective of a real-world interface, such as a nanostructured and eventually nanoparticle surface, and additional components to the substrate and electrolyte. Such a step-by-step approach with strongly coupled modeling and experimental efforts can generate the knowledge needed to understand the complex coupling between transport and mechanical properties as well as the dynamics and evolution of interphases.

ARTIFICIAL INTELLIGENCE-ASSISTED HYPOTHESIS TESTING: MORE DATA, MORE PROBLEMS

Over the last decade, modern characterization tools have created a plethora of data. Currently, the time required to analyze data is often an order of magnitude longer than the time required to acquire the same data. For example, the data from a 48-hour synchrotron experiment may take at least a month to reduce and analyze into an actionable hypothesis.



Time-consuming data analysis can be streamlined with the help of artificial intelligence. Experiments are usually done either to check a specific hypothesis or to gather sufficient information about a material or phenomena to create a hypothesis that, with validation, may evolve into confirmed knowledge or a new physical law. Artificial intelligence can address both needs. The strength of artificial intelligence is finding and verifying correlations. Proposed hypotheses can be cast as expected correlations, such as that alloying graphite with Si increases lithiation capacity. Artificial intelligence can be used to look for evidence of this correlation in the data, quantify it, and capture it as a plot. Once the required artificial intelligence techniques are created, the time to find a correlation in 48 hours of synchrotron data is much less than the month required to analyze the data by hand.

If experiments are done to gather information in search of a hypothesis, artificial intelligence is even more powerful. Artificial intelligence can search for correlations in a data set even if the form of the correlation is not specified in advance. Such unsupervised learning from a large data set can find correlations that were not known or anticipated, revealing new knowledge without a starting hypothesis. A set of reaction pathways from reactants to products through intermediate states is one compelling example. The correlations revealed are, of course, simply statistical and come without the benefit of an underlying mechanism or physical law to motivate them. Nevertheless, these statistical correlations reveal unexpected trends than may lead to new mechanistic understanding when considered in the larger context of known, coupled electro-chemical-mechanical behavior.

The diagram above shows a particular pathway from a single peak initial state on the top row to a single peak-single valley final state on the bottom row. The computer can "connect the dots," eliminating unrelated states from consideration, and finding not only the pathway but also the speed and quantitative degree of development along the pathway.

When science can be expressed in correlations, artificial intelligence can dramatically streamline analysis.

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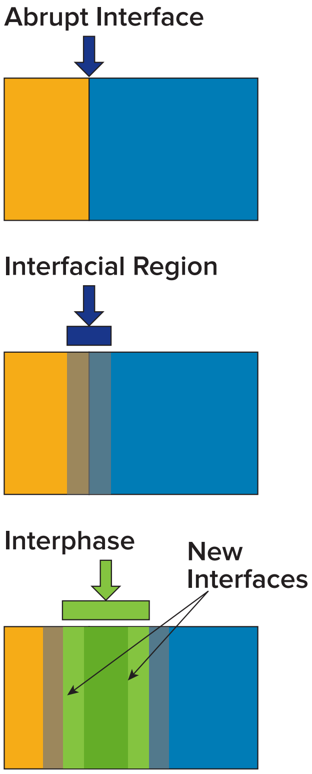
2.3 PRD 3 — Control and Exploit the Complex Interphase Region Formed at Dynamic Interfaces

Electrical energy storage (EES) systems are built from multiple components – electrodes, electrolyte, separator, binder, current collectors, and additives – and their performance depends on how charges transport across or accumulate at interfaces between components. Furthermore, these materials boundaries are dynamic, moving in space, changing their composition in time, and undergoing chemical/electrochemical reactions to define entirely new *interphases,* which themselves become active components of the system. These interphases typically deliver mixed outcomes, including benefits, sources of inefficiency, and pathways for cell degradation and failure. An attractive alternative is to design, synthesize, and intentionally incorporate material interphases into EES systems to achieve beneficial functionality, including mitigation of degradation scenarios. This requires new levels of understanding and predictive capability for the complex processes that control interphase formation and evolution in electrochemical storage structures, posing crucial priorities for future research.

Interfaces play a key role in determining electrochemical function in devices whose working principle is based on the separation of electronic and ionic current: electronic current flows from the electrodes through an external circuit to perform useful work while ionic current flows through the electrolyte. This process is mediated by the interaction of two oppositely charged current carriers at the boundaries between electrodes and electrolyte. These interfaces can be idealized as sharp and two-dimensional but may actually have a more complex structure (Figure 2.3.1).[1] In practice, many electrodes are themselves composite mesoscale materials consisting of active material, binder, and conductor, and as such, are rich with opportunities for understanding and designing interfaces. More precisely, even at ideal junctions between flat surfaces, the deviation from bulk properties extends over a region with a finite (nanoscale) thickness, with its own emergent properties – an *interfacial region* (see sidebar "Interfaces and Interphases"). This region can evolve over time, driven by mechanical, chemical, or voltage-dependent processes to define an entirely different, perhaps irreversible, *interphase*, with quite distinct properties. In some cases, these properties can be beneficial to the energy storage function, as in the protective function served by the SEI of Li-ion batteries. In other cases, and sometimes for the SEI, this interface may be detrimental, introducing excess resistance and inviting degradation phenomena through instabilities in the SEI. A thin porous membrane/



Interfaces and Interphases — The interface between two distinct materials is usually conceptualized as atomically abrupt, for example, between the electrode and electrolyte. However, the presence of the interface can alter properties, composition, stress, etc., over a more extended region from the interface, defining an *interfacial region*. Transport and/or reaction of matter at the interface may generate an *interphase* sufficiently thick to exhibit its own properties and to define new interfaces. Interphases may evolve according to the function of the original materials interface, driven by electric fields, concentration gradients, charge and mass transfer, and transport.

While interphases can be beneficial, their evolution can be unpredictable, producing features that can lead to degradation: a central example is formation of a solid-electrolyte interphase (SEI) by electrolyte decomposition, which protects reactive electrodes but is subject to cracking and uncontrolled regrowth. Impactful research opportunity lies in designing materials in configurations that incorporate or evolve beneficial interphases without such instabilities.

separator inserted between electrodes in EES systems to prevent direct electrical contact also introduces additional interfaces, which present both challenges and opportunities in modulating function.

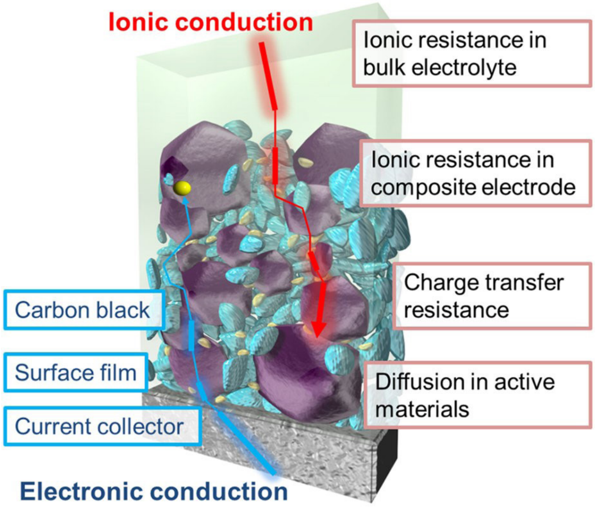


Figure 2.3.1. Schematic of a multicomponent electrode interfacing with both the electrolyte (top) and current collector (bottom), presenting a multiplicity of internal interfaces, each with the possibility of evolving an interphase during the energy storage function. From Ref. 1.

The hypothesis that frames this Priority Research Direction is that explicit design of interfaces and interphases for function will enable better energy storage devices, whether these devices use conventional liquid or solid electrolytes. From detailed knowledge of the composition and properties of electrochemical interfaces and interphases in both exceptional and poorly functioning cells, we foresee an emergence in expertise in design and synthesis of optimal interfaces/interphases for a desired energy storage device/context. Several questions then emerge: What can we learn from model systems or from aspects of working cells to guide development of interphases that allow explicit control of reactivity and electrochemical function? Which interfacial phenomena are key to achieving a desired energy storage function? How do we build adaptive interphases to respond to cues in closed systems to achieve high efficiency and extended lifetime? Furthermore, how would one learn about and curate knowledge of useful, ideally exceptional examples of functional interphases from research on best-in-class type electrochemical systems? How would one transform that knowledge into rational design principles for tailoring interfacial composition, morphology, stability, strength, etc., required for achieving electrochemical function? These questions define Priority Research Directions for future research on next generation electrical energy storage solutions. The goal is to enable new approaches that provide mechanistic insight into how interfacial function is determined and, from this, to rationally design and realize interphases as integral components that substantially improve the performance and robustness of electrochemical cells.

2.3.1 SCIENTIFIC CHALLENGES

During the initial lithiation cycles of a Li-ion battery, an SEI forms on the anode surface due to the electrochemical instability of the electrolyte to lithiated anodes. The SEI allows Li-ion conduction but is electrically insulating, inhibiting further reduction of the electrolyte. SEI formation is one of the most important and fundamental reactions in Li-ion batteries and is critical to achieving reversible cycling performance. The SEI in these batteries has been under investigation for over 30 years, and a general understanding of the primary components has emerged from characterization studies.[2-5] However, while the SEI is now understood to be a mixture of known insoluble lithium salts and Li-conductive organic polymers, very little is known about how the morphology and nanoscale structure of the materials influence properties and function. Even less is known about how basic variables such as current density, temperature, salt concentration, or mechanical properties of an electrolyte influence SEI structure and morphology. How the SEI structure and physical properties change in response to volume change at metallic electrodes (e.g., Si, Sn, Li, and Na) and why these changes compromise electrochemical stability of some liquids, but not others, are additional open questions.

Widening the Electrochemical Stability Window of Liquid Electrolytes: Recent findings on concentrated liquid electrolytes show that compared to conventional electrolytes (salt concentration in the range of 1-1.5 M), interfaces formed in both aqueous[5] and non-aqueous electrolytes[6,7] display a host of unusual properties, including measurably expanded voltage stability windows. The appearance of such electrolytes has significantly changed what one can expect from a typical liquid-electrolyte electrochemical cell and is considered a breakthrough in the field. In one study, the electrochemical stability window of conventional aqueous electrolytes was shown to be expanded from less than 1.50 V to more than 3.0 V simply by increasing lithium salt concentration to > 20 M. This increase was found to coincide with an entirely new Li^+-solvation sheath structure and unusual interphase electrochemistry (Figure 2.3.2a).[5] Enclosed in the expanded stability window are most cathode materials that would have been otherwise impossible for aqueous cell applications (Figure 2.3.2b), and high energy densities have been achieved.[8] Similar observations have been reported in electrolytes with lower salt concentration containing nanoparticle additives functionalized with ionic liquids and ion-conducting oligomers.[9,10] In the latter case, the enhanced stability has been correlated with the appearance of a nanoparticle-rich adsorbed layer on the electrode, implying that a particle-rich SEI that limits contact between liquid electrolyte solvent and the electrode can be a source of enhanced stability.

Developing a better understanding of the interphase formation mechanisms, ion and mass transport processes, and their relationship to SEI composition, structure, and function in such electrolytes is a priority for rational development of superior SEI for aqueous electrolytes; anodes, including graphite, silicon, lithium, sodium, and other reactive metals; and conversion cathodes, including transition metal fluorides, sulfur, oxygen, and carbon dioxide. The SEI formed from saturated solutions of poorly soluble LiF salt in carbonate solvents has also been reported to exhibit enhanced chemical and electrochemical stability in Li metal cells. Likewise, electrolytes based on non-aqueous liquids (4 M lithium bis(fluorosulfonyl)imide in 1,2-dimethoxyethane) have been reported to form an SEI with enhanced chemical stability in contact with a metallic Li anode.[7]

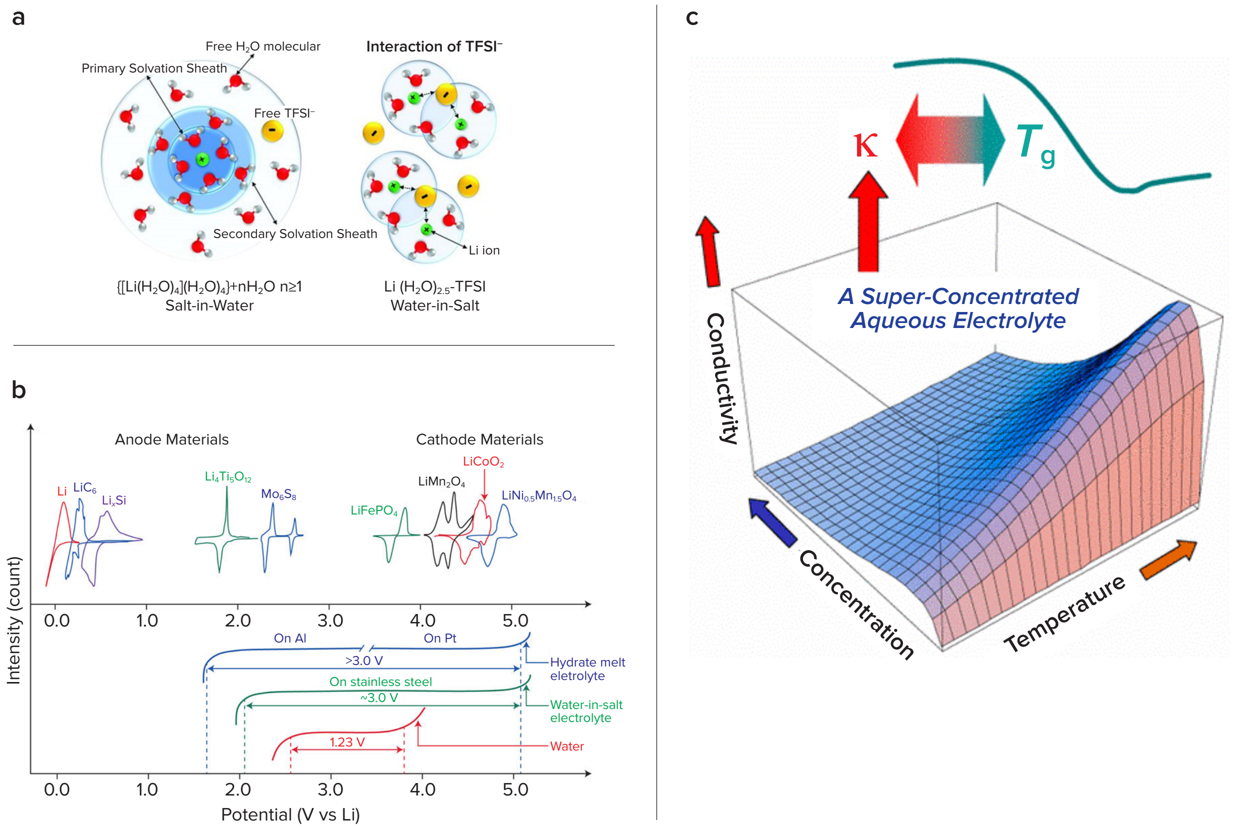


Figure 2.3.2. (a) Dependence of Li⁺-solvation structure on salt concentration, (b) expanded electrochemical stability windows of aqueous electrolytes and their comparison with most Li-ion battery chemistries on potential scale, and (c) dependencies of ion transport in aqueous electrolytes on temperature and salt concentration. From Refs. 5, 8, and 11.

Basic research that leverages the full suite of experimental and theoretical methodologies is needed to advance fundamental understanding of the source of enhanced stability. Specific goals of such work may include: (1) advancing the state of knowledge of the electric potential distribution and its effect on ordering of ionic and particulate components in liquid electrolytes near electrified interfaces; (2) understanding the interplay among ion aggregation, ion/ion pair/solvent network, viscosity, and diffusivity of the complex electrolyte media and determining how these factors mediate the formation and structure/chemical composition of the new SEIs in salty electrolytes; (3) elucidating mechanisms of solvent and Li⁺ transport through the SEI and the origins of its stability against chemical and electrochemical aging (dissolution, degradation, and decomposition at extremely high and low voltage or temperatures, etc.); and (4) identifying the source of the expanded stability window to facilitate rational design for achieving stable 4-V aqueous and 5-V non-aqueous electrolyte systems, with emphasis placed on the anode side.

Structuring of Ions at Interfaces and Electrical Double Layer: While interfacial fluid structure and transport of aqueous-based electrolytes at low (micromolar) and moderate (millimolar to molar) salt concentrations are mature areas of inquiry, the analogous features for aqueous electrolytes containing very high concentrations (e.g., 10-20 M) of dissolved salts and for non-aqueous electrolytes, including room-temperature ionic liquids and hybrid electrolytes containing nanoparticulate additives, are poorly understood. An emerging theme from recent experiments is that these materials exhibit complex structure and unusual interfacial transport behavior with a rich variety of features on different length scales. This includes the presence of dislocation-type defects in liquid crystal-like arrangement of ions at solid interfaces, lateral ordering on the electrode surface on the molecular scale, and the presence of large-scale structural domains composed of particles or molecules as seen in Figure 2.3.3. There is evidence that the presence of such structures at a liquid electrolyte/solid interface can increase the electrochemical stability of the liquid by more than 1 V.[12]

The evolution of these interfaces under a bias voltage has not been explored, and the effect on ionic transport across the structured electrical double layer (EDL) is entirely unknown. Similar experimental observations with high lateral resolution for organic electrolytes are entirely missing. However, molecular dynamics simulations[13] and neutron scattering experiments[14] suggest rich interfacial physical phenomena in such systems. Further, the structural details of the EDL are not captured by theoretical simulations, despite their importance to explain unusual charging dynamics, as observed with scattering techniques,[15,16] and the enhanced electrochemical stability of aqueous electrolyte with high salt concentration.[5] Likewise, understanding is lacking of the EDL structures across multiple length scales involving local surface charges and chemistry, their evolution with bias, and their correlation to energy storage properties. Of special interest is the role played by field-induced structuring of ions in electrolytes on interphase formation processes and morphology. A potential added benefit for understanding the EDL in confined spaces is that such knowledge will allow a deeper understanding of the processes by which multivalent ions are transported in electrochemical membranes and at electrodes.

Electrode/Solid-Electrolyte Interfaces: Replacing liquid electrolytes with solid electrolytes could revolutionize battery technology. Long-standing challenges related to poor room-temperature ionic conductivity of solid-state electrolytes, higher overhead costs associated with high temperature operation of electrochemical cells, and environmental sensitivity of promising solid electrolytes have limited progress in this area. While there have been recent advances in solid ion conductors exhibiting conductivities comparable to liquid electrolytes, little is known about their integration with solid electrodes and into solid-state batteries. What are the design rules? How are solid-solid interfaces formed? How does charge transport and charge transfer occur at these interfaces? What mechanical stresses arise during fabrication and during cycling? How does the material respond to these stresses and influence reaction rates at the electrodes? These are examples of aspects that must be considered to realize the potential of all-solid-state batteries. These questions relate to solid electrolyte interfaces at the anode and cathode. Phase or grain boundaries within the solid electrolyte or the electrodes provide additional interfaces, which may evolve during cycling as changes in crystal phases or grain boundaries or the formation of a crystalline/amorphous interface. Research on these interfaces is needed to understand, quantify, and control reaction kinetics during metal plating both at the current collector and within a solid electrolyte due to defects. To date, there is a good predictive foundation for reactions at a crystalline interface, but these models break down with glasses and meta-stable materials that can cycle thousands of times with Li anodes in micro-batteries.[17]

Among all solid-state electrochemical cells, batteries based on Li, Na, and Si anodes are considered most promising because they enable battery designs that offer large improvements in specific energies on a volume or mass basis. Solid-state thin film batteries provide a mechanism to prepare materials with well-defined and stable interfaces. Recent work on a 5-V solid-state battery (Li/$LiMn_{1.5}Ni_{0.5}O_4$) revealed that, with the formation of the right interface structure, these batteries can operate for over 10,000 cycles with greater than 90% capacity retention (Figure 2.3.4).[17] This result demonstrates that it is possible to cycle Li metal and an advanced high-energy cathode. Detailed knowledge of the interfaces between the Li metal, a lithium phosphorus oxynitride (LiPON) solid electrolyte, and $LiMn_{1.5}Ni_{0.5}O_4$ cathode will provide a pathway to prepare suitable interfaces on new solid electrolytes that may be compatible with Li metal and other cathode chemistries. This understanding could be leveraged to direct the formation of suitable bonding motifs and configurations to enable low impedance interfaces. If further developed, these techniques could also be utilized to understand the structure and morphology for the solid-liquid interface in non-aqueous as well as aqueous electrolytes.

Design strategies to enable fast ion transport at metal/solid-electrolyte interfaces is a requirement for solid state batteries, and such strategies must also directly address the substantial influences of volume change, dendrite formation, and metal reactivity. Solid inorganic, polymeric, or ceramic/polymeric composite electrolytes offer synergistic properties, including a high mechanical modulus that can provide a foundation upon which to design electrolytes that overcome these challenges. An additional requirement for stable cell performance is that the interface must be a good ionic conductor and must be mechanically and chemically resilient to changes at the metal electrode during battery operation.

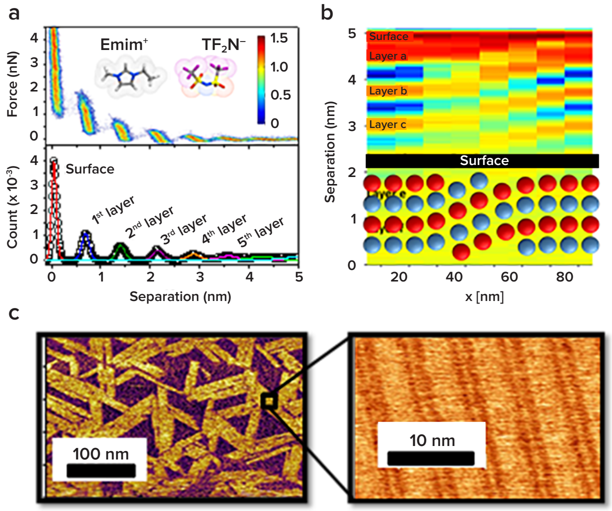


Figure 2.3.3. Scanning probe microscopy of the structure of the electric double layer of the room-temperature ionic liquid represented as [Emim$^+$] [Tf$_2$N$^-$] on graphite. Vertical to the electrode surface, force-distance curves reveal the position of individual ion layers (a) which can be mapped revealing set edges as structural defects (b). Imaging of the first ion layer parallel to the electrode surface reveals big domains with layered structural details (c). Courtesy of Nina Balke, Oak Ridge National Laboratory.

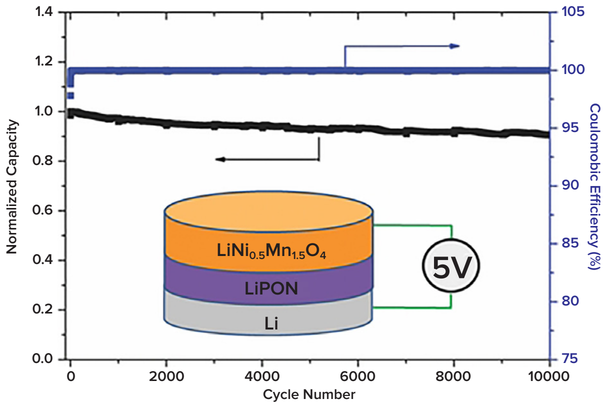


Figure 2.3.4. Capacity as function of cycle life for Li/LiMn$_{1.5}$Ni$_{0.5}$O$_4$ cell with LiPON electrolyte. Reliable cell performance can be obtained with the formation of the right electrode interface. From Ref. 17.

There are several hypotheses and a small number of theoretical analyses that analyze ion transport and mechanics of the interface; however, none of the predictions has been rigorously validated by experiment. Likewise, several experimental studies allow one to precisely determine how physical and chemical properties of the interface influence battery operation at currents approaching the diffusion-limited value for the electrolyte and interface. It is therefore unclear what sets the maximum current density of the interface reported in experimental studies and what steps might be taken to rationally design the interface to enable high-rate all-solid-state batteries. Currently, it is believed that Li penetrates grain boundaries in polycrystalline solid electrolytes above a few tenths of a mA/cm^2 (Figure 2.3.5).[18] Why this occurs is currently not understood. As elusive is an understanding of all of the factors that contribute to an observed resistance to dendrite formation at significantly higher current densities for solid electrolytes composed of cross-linked polymers and for conventional liquid electrolytes infused in the pores of nanoporous solid membranes.[19,20] Understanding the underlying mechanisms that govern stability of the metal/solid-electrolyte interface and the solid electrolyte is, therefore, a priority for future research.

Electrochemical solid-semisolid interfaces, such as electrode-polymer (and gel) electrolyte systems, bridge the behaviors found at solid-liquid and solid-solid interfaces, with gel polymer and solid polymer electrolytes resembling the liquid and solid electrolyte systems, respectively. Polymer-electrolyte-based supercapacitors have demonstrated similar capacitive performance equal to their liquid counterparts.[21] However, being a functional “glue” to put all the components together, electrode-polymer electrolyte interfaces can be the “weakest link” as they suffer the most stress during energy storage applications. Understanding these semi-solid interface phenomena not only can enable the applications of polymer electrolytes in many solid energy storage devices but also can facilitate the understanding of solid-solid interfaces.

Measuring Electric Potential Distribution across Electrode/Solid-Electrolyte Interfaces: High impedance interfaces are widely believed to represent a major challenge to integrating solid electrolytes with high Li-ion conductivity into practical batteries.[22] However, the mechanisms leading to high interfacial impedance remain unclear, in part, because these systems are physically complex, consisting of a variety of electrified materials undergoing electrochemical reactions; and those reactions occur in very narrow interface regions, typically few to hundreds of nanometers. Techniques that can visualize the electric potential distribution with nanometer resolution and correlate it to local microstructure and composition are, therefore, needed to identify sources of high impedance in electrode/solid-electrolyte interfaces and to help validate theoretical models.

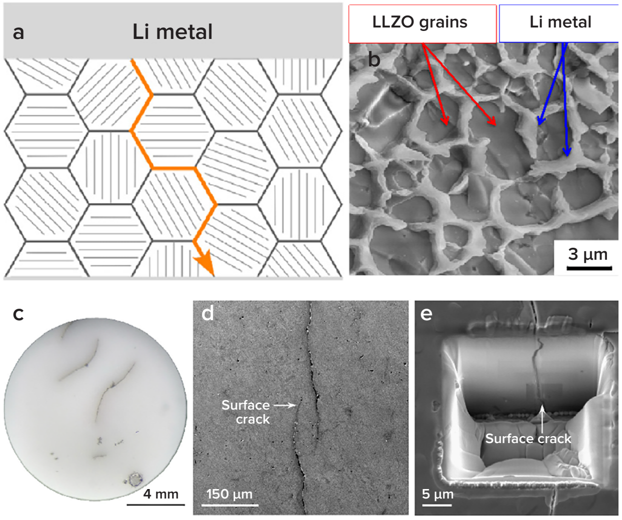


Figure 2.3.5. Lithium metal plating through polycrystalline solid electrolyte of $Li_7La_3Zr_2O_{12}$ (LLZO). Plating at relatively high current densities results in Li penetration in grain boundaries (a,b). Macroscopic cracks are a byproduct of Li metal penetration (c-e). From Ref. 18.

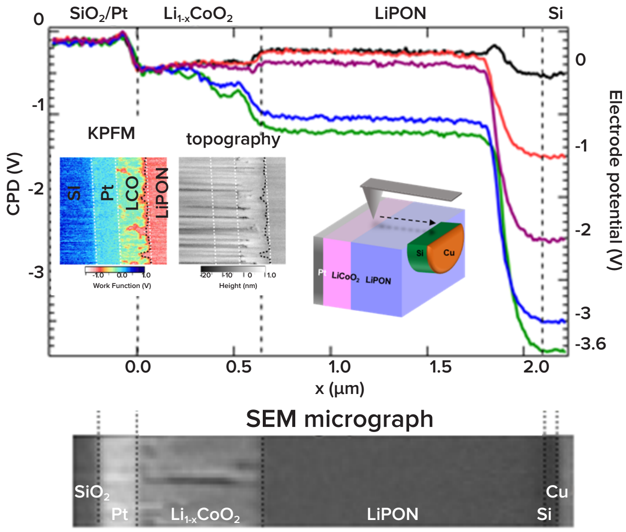


Figure 2.3.6. Potential line scans (top) measured using Kelvin probe force microscopy on a thin-film Li-ion battery cross section (bottom). Insets (from left to right) show potential map at $LiCoO_2$/LiPON interface (at 3-V open circuit potential), corresponding topography, and schematic of battery. Courtesy of E. J. Fuller and A. A. Talin, Sandia National Laboratories.

Electron holography is a well-established transmission electron microscopy method to measure potential distribution in electronic (semiconductor) devices with nanometer resolution.[23] However, application of electron holography to solid-state ionic interfaces is challenging due to several effects, including electron diffraction from polycrystalline regions; secondary electric field leakage, which interferes with the phase signal arising from the space-charge regions in the electrolyte; and damage and charging of the electrolyte by the electron beam and artifacts and damage produced during specimen preparation.[24] Few electrode/solid-electrolyte interfaces have, in fact, been studied by electron holography, and some of the results remain controversial, such as the ~1-µm scale space-charge region observed for a $LiCoO_2/Li_{1+x+y}Al_yTi_{2-y}Si_xP_{3-x}O_{12}$ interface.[25]

X-ray photoemission spectroscopy using either Al K-alpha or synchrotron radiation is another technique that was recently used to characterize the electric potential at an $LiCoO_2/Li_{2.9}PO_{3.3}N_{0.46}$ (LiPON) interface.[26] The advantage of this technique is that it does not require thinning of the specimen, but it is limited to very thin overlayers, which are difficult to implement with *in situ* biasing or electrochemical cycling of the specimen, and further limited by poor lateral resolution. These disadvantages can, in principle, be overcome by advances in synchrotron technology generating harder and smaller diameter X-ray beams.

Finally, Kelvin probe force microscopy (KPFM), a scanning probe technique that measures the contact potential difference between an oscillating conducting atomic force microscopy tip and the specimen surface, has also recently emerged as a technique for imaging the potential variation across electrified battery interfaces.[27] Figure 2.3.6 shows line scans extracted from KPFM potential maps of a cross section from a $LiCoO_2$/LiPON/Si thin film battery collected at -1 V, -2 V, and -3 V open circuit potential and at -3.6 V with a charging current of 4.4 µA.[28] Understanding how these measurements relate to inner potential variation and their impact on battery performance will require advances in both experimental procedures (inclusion of reference electrodes) and theoretical treatment such as multiscale models based on density functional theory, which could predict interfacial impedance and potential distribution.

Characterization of Functional Interfaces: The current status of interfacial analysis, in general, can be summarized as one driven by a mechanistic hypothesis – predominantly lacking visual insights into interfacial phenomenon. This status is in contrast to the ideal case, where one could visually identify components of the interface while integrating corroborating analytical characterization of the same. Simplified experiments with individual *in situ* tools could help bridge the existing knowledge gap (see, for example, Figure 2.3.7).[29-31]

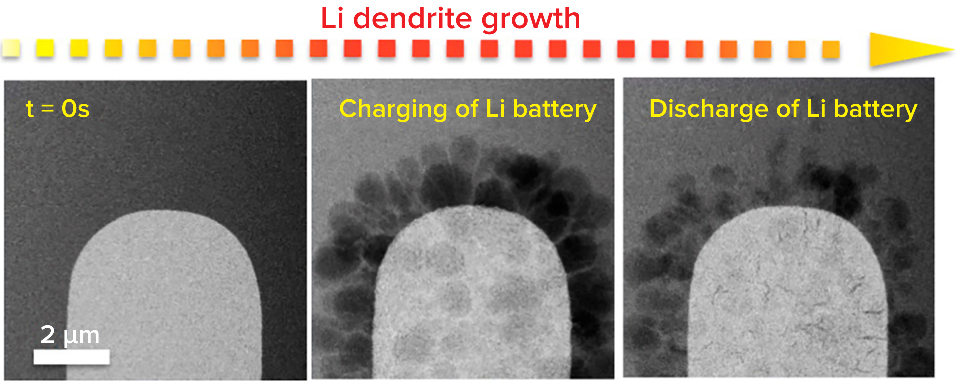


Figure 2.3.7. Example of high-angle annular dark-field imaging during Li dendrite growth. From Ref. 31.

To advance current understanding of composition, evolution, transport processes, and reactivity at electrochemical interfaces, empirical approaches are required that simultaneously enable visual observation and identification of interfacial phenomena. Significant relevant advances have been made in electron microscopy and X-ray spectroscopy. Multiple studies have appeared recently that combine theoretical simulations with fundamental *ex situ* and *in situ* characterization techniques. Figures 2.3.8, for example, combines X-ray spectroscopy and electron microscopy in a multi-modal effort for *operando* nanoscale characterization in batteries.[32] These studies provide a tantalizing glimpse of functional heterogeneity within a microscopic cathode particle, highlighting the importance of buried interfaces with respect to composition, structure, and depth of charge or discharge. Spatial resolution and data collection rates are still limiting factors that restrict how these processes might be manipulated/regulated to enhance capacity, ionic conductivity, or mechanical stability. Complementary information from electron energy loss spectroscopy, for example, may soon become possible using direct electron detectors,[33] while increased coherence in synchrotron light sources enabled by upgrades of the Advanced Light Source is expected to provide improved spatial resolution for scanning transmission X-ray microscopy by exploiting ptychography[34] or coherent diffractive imaging.[35]

Current knowledge of the heterogeneous ionic interfaces extant in operational electrochemical cells is even more limited, largely because of the complexity of the interfacial structure and chemistry in such systems. Not only can chemical inter-diffusion, lattice strain, defects, and chemical reactions occur, but space charge effects near the electrodes also complicate detailed analysis. As these phenomena are correlated, all associated microscopic factors (i.e., lattice, electrons, and ions) must be simultaneously considered when studying the effects of spatial, temporal, and space charge. New characterization techniques, which could analyze all these factors simultaneously under relevant and simulated operating environments, are an aspirational goal. Few studies have probed interfacial mechanical properties *in situ* in the context of ionic transport. For solid-liquid interfaces, a proof of concept was provided by using contact resonance scanning probe microscopy to image the ion insertion pathways through changes in Young's modulus when Li^+ ions are electrochemically driven into layered Ti_3C_2 (a member of the 2D-layered transition metal carbide family known as MXenes), as shown in Figure 2.3.9. This study provides evidence that the ionic transport across the interface is heterogeneous, resulting in strongly heterogeneous mechanical properties and stresses.

Addressing these scientific challenges would provide the community with access to a live visual record of interfacial behaviors, such as SEI formation from infancy through its development, SEI aging and failure processes, and the nucleation and growth processes important in deposition at metal electrodes. Comparative studies between various metal anodes in terms of propensity to form dendrites and its effect on the physical and mechanical properties of the interface and interphase (porosity, crystallinity, and thickness) would also become possible. Availability of such live records would aid the development of theory, electrode designs, and artificial interface synthesis able to bypass the current trial-and-error paradigm for evolving electrode and electrolyte designs for enhancing cell lifetime.

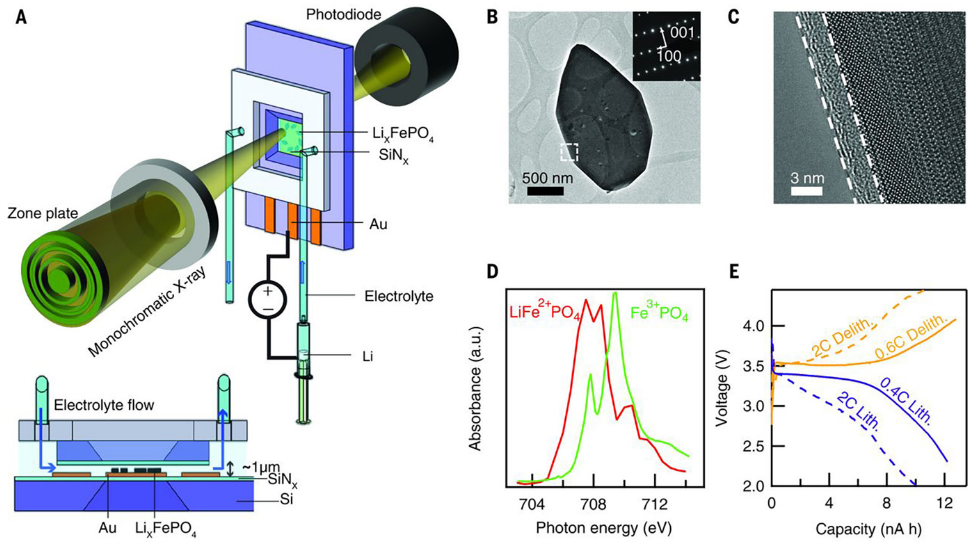


Figure 2.3.8. Examples of X-ray spectroscopy and electron microscopy in multi-modal effort for *operando* nanoscale characterization. From Ref. 32.

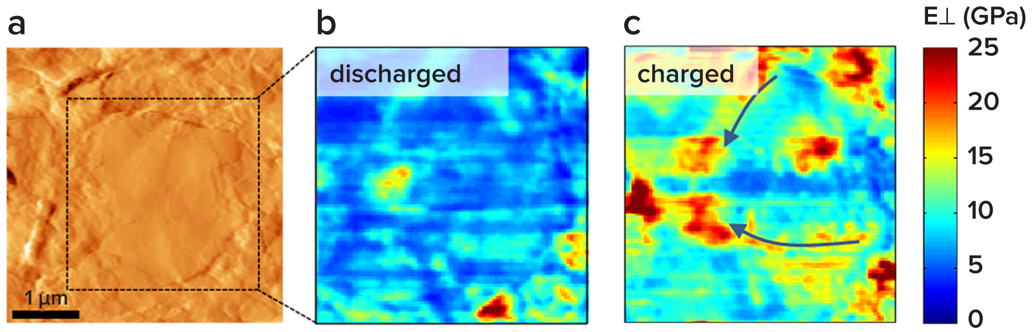
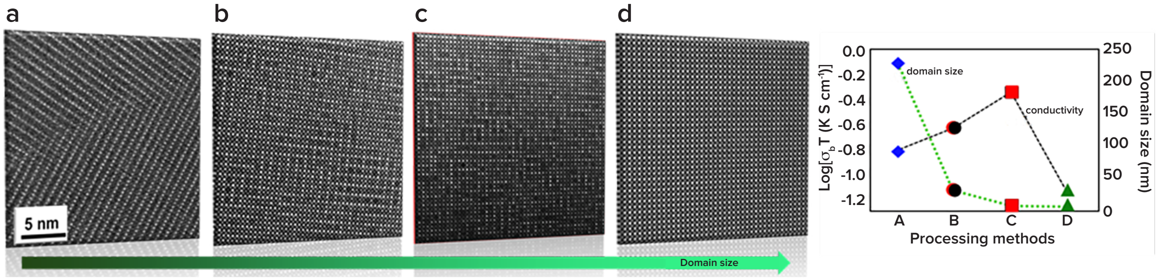


Figure 2.3.9. (a) Surface of 2D Ti_3C_2 electrode. Elastic modulus images of a few-layer MXene particle at discharged (b) and intercalated (c) states captured with scanning probe microscopy *in situ* under electrochemical control. From Ref. 36.

The interaction between chemistry, structure, morphology, and mechanics and its effects on ionic transport across the interface is very complex and cannot be investigated simultaneously under operating conditions with current techniques. The major deficiency of these methods is that they are either limited to *ex situ* analysis or can address only one aspect of the interface properties. The mechanics at the interface, particularly at high-capacity metal anodes, which undergo large volume change during charge and discharge, play a dominant role in lifetime and are strongly connected to electrolyte stability and ionic transport. Mechanical stresses occur during synthesis, especially at solid/solid interfaces. In addition, material volume and stiffness can change during intercalation or conversion processes. In turn, ionic transport will be influenced by the mechanical stresses surrounding the ion. Therefore, changes in mechanical properties are critical to the performance and lifetime of energy storage devices. An example of this sort of multi-scale coupling can be taken from *ex situ* studies of structure-ion-transport coupling in $Li_{3x}La_{2/3-x}TiO_3$ (Figure 2.3.10). It is therefore apparent that structural features that span multi-length scales (i.e., not limited to the unit cell level) deserve to be explored.

Buried Interfaces and Unknown Charge Pathways: Common to any interface is the perturbation the two media present to each other as mutual interactions, resulting in structural or other changes that extend into each medium. A dramatic manifestation of these behaviors is observed in two forms at solid-liquid interfaces as interfacial solvation layers (similar to the solvation shell that forms around dissolved ions in solutions) and as the electrical double layer structure associated with the screening of the electrostatic fields from the electrode. This is observed as the specific adsorption of ions (e.g., as a Stern layer) as well as the formation of a diffuse ion profile (e.g., in the simplest case, as described by the Gouy-Chapman model). A few of these complex processes at the solid-liquid interface are schematically depicted in Figure 2.3.11. In energy storage materials that utilize aprotic solvents and complex salts, there is large uncertainty as to the ordering and solvation of the electrolyte components and understanding of how these change as a function of temperature, state of charge, and time. Deviations from this simple behavior leads to phenomena such as over-charging (e.g., for multivalent ions at interfaces with a high surface charge) that is reflected in thermodynamic properties relevant to capacitive energy storage.

Beyond interfacial reactivity, significant challenges exist to design robust high-energy-density electrode interfaces for conversion or alloying materials such as Sn, Si, and P anodes. The challenge of these materials is the constant rearrangement of the heavy electrode atoms and light alkali atoms, resulting in the formation of amorphous and crystalline phases with different diffusivities and performances. Developing an understanding of the migration of atoms at the interface of the crystalline to amorphous transitions will enable doping or structural solutions to overcome rate limitations and ensure long cycle life. Similar examples are available for cathode compounds such as conversion cathodes (FeF_3, CuF_2, etc.) which undergo multiple electron redox processes. At present, understanding can be obtained for static interfaces at well-defined conditions. Looking forward, anticipated advances in both experimental and computational approaches will reveal the structural basis for understanding the dynamic evolution of these interfaces for fast and slow processes. Eventually, such studies, when extended to observing kinetic evolution as a function of temperature, will reveal the free energy landscape of ion-interface interactions that will inform conceptual understanding of the complex ion transport processes.



1350°C quench + 800°C annealing (12h)

1100°C quench + 800°C annealing (1h)

135°C quench

1450°C quench

Figure 2.3.10. TEM of $Li_{3x}La_{2/3-x}TiO_3$ under different synthesis conditions to tune structural domains and the corresponding ionic conductivity measured macroscopically. Courtesy of Miaofang Chi, Oak Ridge National Laboratory.

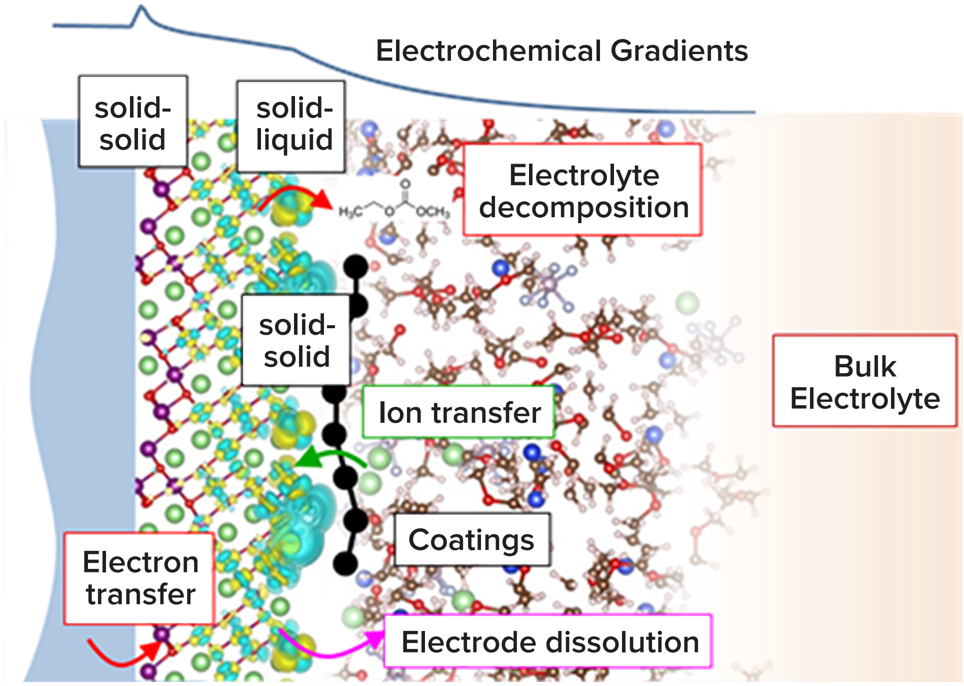


Figure 2.3.11. Schematic charged electrode-electrolyte interface under potential control with electrochemical gradients (top), from the current collector (grey on left), electrode, interfacial modification, and liquid electrolyte. The functionality of the interface is reflected in charge and ion transfer, and the modification of the reactivity of the active material by the interfacial modifications (e.g., coatings). Image courtesy of Paul Fenter, Argonne National Laboratory.

There is a pressing need to develop new methodologies to elucidate the complexity of the formed interphases. Labeling approaches can be applied to track chemical species throughout the reaction pathway and thereby to elucidate their role in the development of the final interphase product. For example, direct observation of solid-phase electrolyte products resulting from decomposition of acetonitrile on activated carbon has been investigated by ^{13}C, ^{1}H, and ^{15}N solid-state nuclear magnetic resonance. Such approaches can be used to understand true interphase development.

Realizing Simple but Representative SEIs: An important barrier to complete molecular-level understanding of interfacial transport and chemistry in energy storage systems arises from the difficulty in validation of theoretical predictions using well-characterized experiments performed on relevant model systems. An analogous impasse to progress in understanding surface reactivity of molecular agents was removed with the introduction of ultra-high vacuum surface science, which provided a fundamental experimental framework able to validate theoretical predictions for quantities such as heats of adsorption, rates of reactions, and mechanisms of surface reactions.[37-41] This approach is, in principle, applicable to condensed matter and at electrified interfaces, but requires well-characterized systems of sufficient complexity. The systems must not only be designed to advance fundamental understanding of chemical physics at interfaces, but must ultimately be robust enough to couple with intrusive experiments able to mimic conditions used in theoretical work for accurately describing interfacial complexity.

A recent example of such an experiment was achieved through the synthesis of well-defined planar electrodes for detailed desolvation studies of sodium ions, which showed a six-fold variation in desolvation energy depending on the anion donor number.[42] Expanding these types of studies while identifying the interface structure and introducing additional functionality from binders or porosity will develop a foundation to support theoretical model development and the prediction of optimized artificial SEI layers needed to focus experimental developments.

How to Understand and Build Ideal Electrochemical Interfaces: An interphase is an enabling aspect of the entire Li-ion state-of-the-art battery and also offers a pathway to next generation materials. In many cases an effective interphase, whether it is synthesized by *in situ* or *ex situ* chemistry, should be electronically insulating, have high ionic conductivities, exhibit self-passivating growth, and be stable against dissolution.[43] As a result, electrolyte components operating outside their potential window of stability are stabilized.

Artificial interphases can be created by coating electrodes with very thin (1-50 nm, typically 1-3 nm), insulating polymer[44,45] or ceramic coatings,[9,10,46-49] which mimic the effects of spontaneously formed interphases and may be deposited by techniques ranging from solution casting to atomic layer deposition. There is currently little understanding of the chemistry or mechanisms by which these coatings work, whether they are robust enough to protect the interface during extended cycling of metals at high current density, and how they fail. As a consequence, few insights are possible into optimal designs for coatings with specific functionality, mechanics, and lifetimes. New characterization tools are required to enable progress. When coupled with detailed mechanistic studies of electrolyte decomposition pathways, supported with theoretical and computational analyses of adsorption and reaction mechanisms, this research would fundamentally alter the current Edisonian trial-and-error approach to coating development.

The free-energy landscape for migrating charges has its origins at the atomic- to nano-scale for charge transfer and at meso- to macro-length scales for charge transport. In a typical device architecture, these interfaces are buried and, therefore, difficult to study. To highlight the key roles played by interfaces, consider ion-transport selectivity in a membrane for a flow battery, which occurs at a membrane-electrolyte interface; in this case, eliminating crossover is key to preventing internal shuttling and deleterious cross-annihilation of constituent active materials that are dissolved in the electrolyte.[50-54] Similarly, consider electron transfer across metal anode-electrolyte or cathode-electrolyte interfaces, which degrades the electrolyte and ultimately yields new interphases;[55-58] if left uncontrolled, their continued growth increases cell impedance, and active materials are increasingly underutilized in the cell for a given operating voltage range.[59,60]

While still nascent, our emerging knowledge of these interphases and the interfacial processes generating them points to an emerging materials challenge: new materials, characterization tools, and theoretical frameworks are needed to enable interphases to be designed rationally for function, whether that function is chemical, physical, or mechanical. If successful, these functions can be responsive to or modulated by local cues in the device, e.g., spikes in electric fields, harsh thermal gradients, or extreme heterogeneities in ionic or electronic current. In this way, the implementation of responsive and reconfigurable interphases may make available new behaviors within the device that are adaptive or even self-rectifying with the intent of minimizing energetic losses or chemical degradation over time.

A coordinated future direction focused on molecularly tailored interfaces with active or adaptive transport behaviors represents an important departure from the majority of today's state-of-the-art strategies, which are decidedly passive.[61] Discovery of new chemistries with switchable functionality (e.g., metal-insulator, semiconductor-insulator, ion conductor-ionic insulator, thermal conductor-thermal insulator, redox-mediating, shape-changing, etc.) that gate the transport behavior of energy carriers (e.g., electrons, ions, phonons, mass, etc.) could be transformative with respect to carrier transport under specific conditions or upon application of an external stimulus, both locally and globally.[62]

Success hinges upon the ability to initiate or arrest the formation and growth of the interphase responsible for charge transfer under conditions relevant to use of the battery. To guide the design of such concepts, new predictive tools are needed to direct the choice of materials, with validation provided by interface-specific *operando* analytical techniques. Presently lacking is a reliable theoretical framework for modeling charge transfer at an atomically defined heteromaterial interface (e.g., liquid-solid, liquid-semi-solid, and solid-solid) at the nanoscale. Research of the future will need to appreciate, in turn, the value of incorporating bias in a theoretical framework, which will certainly alter the free-energy landscape for charge transfer and transport. The impact of a coordinated effort in understanding and controlling interphases (and their interfaces) will reveal new paths to significantly enhance cycle life, rate capability, and energy density, as these are among the properties in the cell that most critically depend on charge transfer across and charge transport along such interfaces. Furthermore, it has not been possible previously to direct the evolution of the interphase or interface in a component of the cell to something that sustains its useful functions indefinitely. Coordinated efforts between experimental, characterization, and modeling efforts stand to reveal the first links between molecular-level processes and bulk electrochemical phenomena.

2.3.2 RESEARCH THRUSTS

To address these fundamental challenges at electrochemical interfaces and interphases, two connected research themes emerging over the next decade are envisioned. Integrated experimental and theoretical strategies able to elucidate the complex processes that control electrochemistry and transport at interfaces in their full electrochemical context are a high priority. The second emerging theme seeks to harness knowledge of interphases from best-in-class EES systems, idealized EES systems that serve as model systems, and fully operational EES devices to design electrochemical interfaces and interphases with explicit properties required for performing a desired electrochemical function. Specific opportunities in each of these two themes are highlighted next.

Thrust 3a: Unravel Interfacial Complexity through *In Situ* and *Operando* Characterization and Theory

Unravelling the complexity of coupled processes that control the function of heterogeneous electrochemical interfaces demands new approaches that use combinations of tools for complementary insights. This goal is being pursued through theoretical approaches, the results of which are then verified by *in situ* probing of the solid-liquid interface through advanced microscopy and spectroscopy. The experimental methods cited below have shown great promise in recent years, and their research trajectory promises continuing development and applications that will propel the frontiers of energy storage science and possibly stimulate innovations not yet conceived. Using these approaches, major advances are envisioned that will provide a mechanistic understanding of the interfacial processes linking morphology and function in EES systems as well as the foundations for directed design of functional electrochemical interfaces.

Characterizing Interfacial Phenomena in Functional EES Contexts: At one end of the spectrum, there are opportunities for studies that take advantage of well-controlled model systems in which the functional aspects of the electrochemical cell are preserved. Such studies would enable detailed understanding of how interfaces of well-defined chemistry contribute to overall function. At another extreme, there are opportunities for approaches that enable intrusive *ex-situ, in-situ,* and *operando* interrogation of specific features of a heterogeneous interface to unravel structure-function relationships in both explicit and buried interfaces. Each of these approaches brings obvious drawbacks. *Operando* investigations, for example, require more intensive, longer-term commitment to instrument development and large-scale collaborative efforts between theory, computation, and experiment for success. Thus, a multifaceted approach is needed, and studies of the same model systems by multiple teams can be very beneficial.

Bridging Theory and Experiment to Understand Underlying Physical Phenomena: Equilibrium properties—such as the potential of mean force of an ion moving from a bulk phase (e.g., the electrolyte) through an interphase or interface to another bulk phase (e.g., the electrode)—directly impact the free-energy landscape of ion transport. To this end, methods must be further developed to allow for the accurate determination of concentration profiles in the vicinity of a solid-electrolyte interface. Grand canonical methods using classical force fields between a bulk reservoir of electrolyte and an interfacial region have been previously used.[63] The aforementioned methods may suffer from inaccurately representing the response of the electrolyte to a dielectric interface. Extension of grand canonical methods to couple accurate descriptions of electrostatics of the dielectric as described by quantum methods (e.g., quantum density functional theory) to reduced descriptions of the electrolyte solution by using classical liquid theories will be vital to advance understanding of the electrode-electrolyte interface down to the molecular level.

The deep understanding of equilibrium properties must also go hand in hand with the study of non-equilibrium properties necessary to understand phenomena at the device level.[64] The coupling of electronic structure methods with reduced theoretical frameworks will enable the connection of molecular detail to emergent phenomena. To model a true electrochemical system, it will be necessary to include a driving force such as bias potential.

Neither interfacial systems nor interphases present metrics that can be directly compared with new experiments. Therefore, leveraging models to understand distinguishing features of the interface will rely heavily on extending computational models to include simulation of spectroscopic or microscopic observables.[65]

***Operando* X-ray Methods:** In addition to the progress made with *operando* Raman spectroscopy, there has been much progress with analytical tools utilizing X-ray radiation. X-ray scattering (e.g., crystal truncation rod and X-ray reflectivity) probes the structure of interfaces, while X-ray spectroscopies such as X-ray photoelectron spectroscopy[66] and X-ray absorption spectroscopy[67] probe element-specific chemistries and electronic structures of surfaces and interfaces. The use and application of hard X-ray (> 8 keV) tools benefit from a number of favorable characteristics, including their ready penetration through matter (e.g., through millimeters to centimeters of material), their ability to resolve structures with angstrom-scale resolution (wavelengths that are comparable to atomic dimensions), and the development of high-brilliance synchrotron sources that provide opportunity for high dynamic range and real-time studies. The energy tunability of synchrotron sources enables element-specific probes that couple with the excitation of core electrons (e.g., X-ray absorption spectroscopy). The state of the art has demonstrated robust interfacial sensitivity, such as the formation of interfacial hydration layers, adsorbed species, and solid surface reconstructions, especially for well-defined (i.e., flat) interfaces. Soft and tender X-ray (< 2 keV and 2 keV to 8 keV, respectively) spectroscopies and microscopies have made significant advances in the last few years—bringing atomic concentration, chemical structure, and electronic structure insight, from traditional ultra-high-vacuum surface science, to functioning electrochemical interfaces (Figure 2.3.12).[67] With the emergence of X-ray transparent windows, differentially pumped analyzers, and tunable synchrotron X-ray facilities, solid/gas,[68,69] solid/liquid,[65,69,70-74] and solid/solid[75-77] interfaces are now at the forefront of characterization.

The anticipated availability of coherent hard X-ray sources will enable the extension of the molecular-scale understanding of model interfaces to obtain a robust understanding of materials having complex morphologies. Applied to crystalline grains within a binder, proof-of-principle studies have demonstrated the ability to image the structure changes, in particular, the evolution of lattice strain as a function of state of charge. These capabilities will become widely available with next generation synchrotron facilities (such as the planned upgrades of the Advanced Photon Source and Advanced Light Source, as well as the Linac Coherent Light Source). In addition to the chemical identity of species at the solid-liquid interface, mechanical stress can have a large impact on ion transport. To study these mechanical effects requires development of *in situ* microscopic techniques, including coherent diffraction imaging.

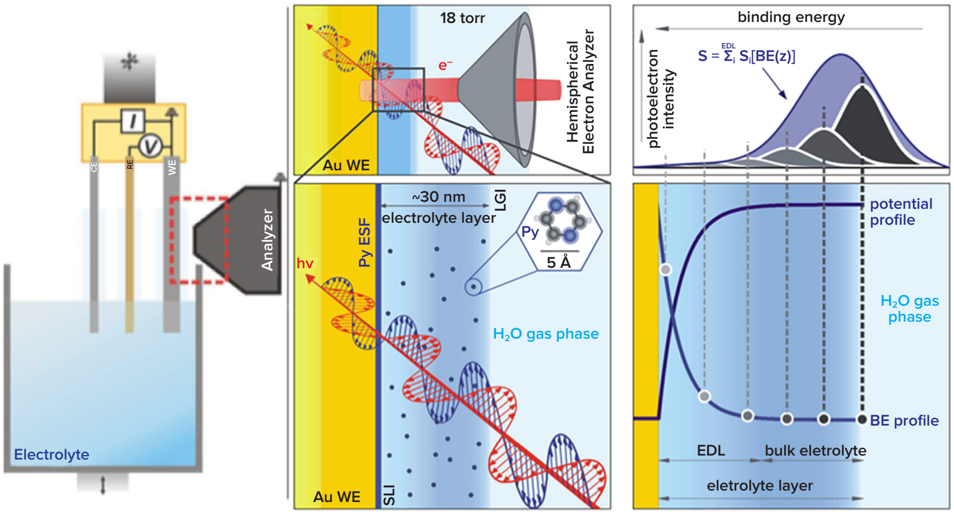


Figure 2.3.12. ***Operando*** **ambient-pressure X-ray photoelectron spectroscopy of the solid/liquid interface. (Left) The "dip & pull" method is used to form an electrochemically active solid/liquid interface that, when combined with tender X-rays, allows the probing of both the solid and liquid phases simultaneously to capture bulk-to-bulk properties, including interfacial phenomena. (Right) Ambient-pressure X-ray photoelectron spectroscopy is used to probe the electrochemical double layer under applied potentials. From Refs. 70 and 71.**

Operando **Neutron Depth Profiling:** Neutron probes have for the first time revealed the complex dynamic surface chemistry of the SEI layer and is providing insights into SEI formation and dynamics.[78-80] These studies are foundational in demonstrating the ability to study interfaces and interphases with chemical specificity and atomic resolution and afford an opportunity to study solid-solid, solid-liquid, polymer-liquid, and solid-polymer interactions both within the bulk and on the surface. Furthermore, with anticipated advances in data binning and processing, kinetic measurements of diffusion and reaction processes become possible.

A major challenge of designing and understanding electrode and solid-electrolyte materials is determining diffusion pathways. Recent neutron scattering results demonstrated the ability to directly measure intrinsic diffusion distances based on quasi-elastic neutron scattering.[14] In this work Li jump distances were determined to be between 2.4 and 6 Å depending on the phase of an amorphous Li-Si alloy produced. When combined with other diffraction methods such as pair distribution function analysis, it will now be possible to relate structural elements of a glass or crystalline material with the hopping path of a Li ion. This will enable the study of new materials in a way that had not been possible previously and will facilitate the design of new materials.

Thrust 3b: Design SEI for Function

The design of SEI for function requires two steps: first establishing design principles to determine the desired SEI and then designing and controlling synthesis and fabrication of the tailored SEI. Most interphases known today impede carrier transport, and do so broadly for electrons, ions, and mass. Needed are smarter interphases that instead facilitate transport of specific carriers that contribute favorably to the operation of the cell. For example, can we create well-defined structures that promote the de-solvation of ions at electrode-electrolyte or electrolyte-solid-ion conductor interfaces at near-zero overpotentials, which would, in turn, maximize energy efficiency and active material utilization? To secure our energy storage needs for the future, research is needed to identify, constitute, and direct the synthesis of new interphases—on active materials or on other components in the cell—that allow for active and ideally responsive control over how energy carriers move across heterogeneous interfaces. Only in this way will it be possible to intelligently direct matter and energy at the electronic, atomic, and molecular limits in electrochemical energy storage devices.

Establishing Design Principles: Ion transport through the SEI must be quantified to determine requirements for long-term interface stability against chemical and electrochemical aging (e.g., dissolution, degradation, and decomposition at extremely high and low voltage or temperatures). It is critical to determine mechanisms that enhance transport of selected ions by understanding the interplay among ion aggregation, ion/ion pair/solvent networks, and the viscosity and diffusivity of the complex electrolyte media in both conventional and highly concentrated electrolytes. The role of the interface and interphase continuum and the quantum chemical properties in enhancing stability must also be understood.

The separator in a conventional battery presents intriguing interfaces with electrolyte as well. It may further be desirable to conceptualize and advance interfaces or interphases that can switch between different states, chemical or physical, so as to block or facilitate the transport of specific energy carriers within a cell component on demand.[62] For example, can we create responsive membranes that adapt their transport selectivity for ions vs. dissolved active materials when the active materials are present at a specific state of charge? Doing so could dramatically improve the efficiency of energy storage devices, particularly those implementing flow or conversion electrodes. A remarkable example of redox-switchable ion selectivity by a responsive polymer membrane was recently reported. It bears resemblance to how the transport of ions across biological cell membranes is regulated by transmembrane proteins (Figure 2.3.13).[76] The ion-transporting character of transmembrane proteins is sensitive to the environment; any perturbations to that environment are typically met with an adaptive response. An analogous strategy was used to achieve adaptive ion transport in microporous polymer membranes while in a lithium–sulfur battery.[81] Along the polymer backbone were placed redox-active switches that were activated *in situ* by the battery's dissolved polysulfides as they entered the membrane's pores. This transformation had little influence on the membrane's ionic conductivity; however, the polysulfide-blocking ability of the membrane was enhanced. In turn, these membranes offered the cell improved capacity retention, energy efficiency, and cycle life by sequestering dissolved polysulfides in the cathode.

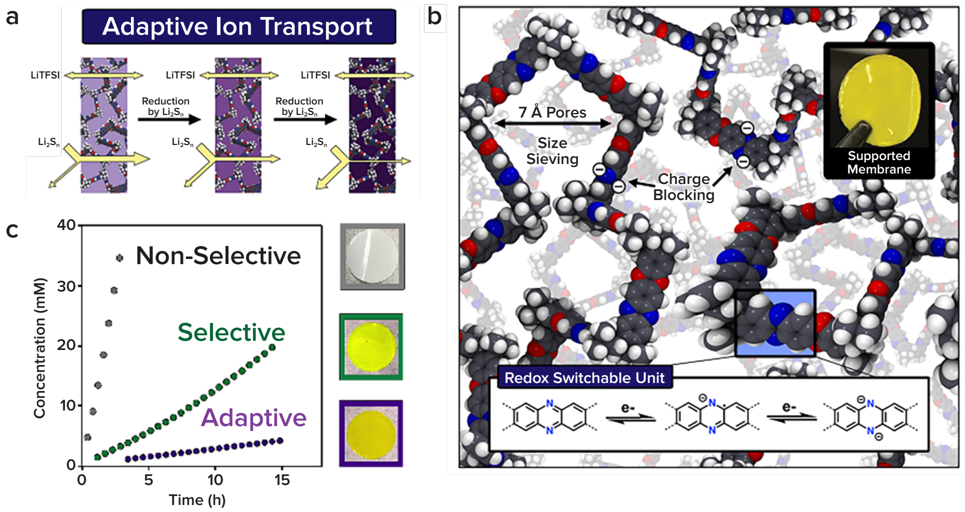


Figure 2.3.13. Example of redox-switchable ion selectivity by a responsive polymer membrane. (a,b) The ion-transport selectivity of membranes cast from polymers of intrinsic microporosity (top right inset) can be enhanced to the benefit of Li–S battery cycle life when redox-switchable phenazine-containing monomers are activated *in situ* (inset at bottom) by reducing polysulfides that are endogenous to the cell. (c) This leads to a feedback loop whereby progressive reduction of the membrane by polysulfides only further restricts their access to the membrane's pore voids, which slow the rate of polysulfide crossover in the cell relative to non-transformable size-selective membranes and conventional, non-selective Celgard separators. From Ref. 76.

Designing and Controlling Synthesis and Fabrication of the Tailored SEI: It may also be possible to intentionally reconfigure an interphase through its controlled dissolution-precipitation, interface reconstruction, amorphous-crystalline phase transformations, or transitions between rigid and elastic states. For example, can we create an ionically conductive and electronically insulating interphase on metal anodes that is capable of self-repair indefinitely after interphase-disrupting dendrite-forming events? Doing so would resolve a long-standing challenge associated with the continuous consumption of interphase-forming agents added to the electrolyte, which are depleted rapidly and thus have diminishing influence on anode stability. Furthermore, can we synthesize an elastic and ionically conductive interphase that can accommodate extreme volume changes during cycling and, in turn, rigidifies or becomes ionically insulating when a dendrite emerges at the electrode surface? Doing so would enable a dual-responsive mechanical blocking ability while also starving the dendrite of its constituent ions and thus stunting its growth. Our ability to control the spatiotemporal aspects of these reconfiguring events will likewise be critical to achieving a specific type of adaptive behavior in response to an excursion or perturbation in the system.

Self-repairing or self-rectifying interphases may be realized when coupled to metal anodes. They represent the most efficient use of mass and volume in an energy storage device as the penalty of a host material (e.g., graphite, Si, or Sn) is eliminated. Rather than rely on an intrinsic SEI for protection, methods for creating protective films through vapor and liquid-phase chemical modification of lithium prior to introduction to the cell have demonstrated improvement in cell performance[82,83] and lithium anode stability with cycling.[84-86] However, further gains could be made with flexible, mechanically adaptable interfaces. Preformed Li^+ cation transmissive membranes[87,88] as well as membranes formed *in situ* by jamming of nanoparticle salts[89] and their integration with Li anodes have been proposed, where select examples have demonstrated dimensional control of the anode with electrodeposition and dissolution. These and related approaches designed to overcome the underlying electroconvective instabilities, which are known to be the source of unstable, dendritic deposition, must also solve the underlying anode reactivity/coulombic efficiency problem before ultimate success can be achieved.

Management of the local volume change within a cell that employs a metal anode must also be addressed. Discharge of the anode produces local volume loss and threatens gaining the ability to maintain a coherent, low impedance interface with the artificial SEI membranes and films integrated with the anode. One solution to this problem is to design for volume change through an appropriately sized host scaffold, where the scaffold material mass and volume are minimal relative to the metal. It may be that heterostructuring of the reconfigurable interphases with the anode is the key to success to amplify threshold behavior around phase transitions so that the system evolves toward optimal ion-transporting properties even when operating conditions fluctuate, such as inhomogeneities in mechanical stress, ion current, or electric field. The interplay between electrons, ions, phonons, and chemical bonds in interphases could be used to create ion transduction behaviors that can be controllably damped, focused, and distributed, or made to be oscillatory as needed.

Surface structure, reaction products, potential profiles, and interfacial chemistry all contribute to the nature of the interface. Deliberate design of mechanistic aspects could enable active (rather than passive) control of chemical structure and composition at interfaces, which may facilitate new electrode development and the establishment of more resilient interfaces. Harnessing the powerful tools of synthetic chemistry to create designer interphases that offer explicit control of function will lead to significant progress in the design and synthesis of dynamic interfaces that are able to respond to electrical, chemical, or physical cues to self-repair or to trigger a change in interface structure and transport properties, resulting in increased safety and enhanced lifetime for EES systems.

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2.4 PRD 4 — Revolutionize Energy Storage Performance through Innovative Assemblies of Matter

Energy storage is central to many potentially groundbreaking applications in transportation, the electricity grid, national security, and communication. The performance and cost requirements for many of these game changing energy storage applications exceed the capability of today's batteries in energy density, power density, rate of discharge, or lifetime. Achieving the full potential of energy storage requires the discovery of new chemistries, materials, structures, and architectures that will enable tailoring battery performance and cost to specific functionalities and use cases. Next generation energy storage will be based on a diversity of chemistries and architectures that allow the battery to be designed for the application, instead of requiring the application to be designed for the battery. The targeted functionality of the system should be of foremost importance, with the chemistry, materials, and architectures of the battery selected to enable the targeted functionality. This paradigm will allow for the deliberate design of energy storage systems utilizing emerging concepts and materials.

Beyond new chemistries and materials, next generation batteries require discovery of new architectures. Tailoring the battery to the application requires combining diverse performance metrics in a single package, such as fast charging, high energy density, and long lifetime for transportation, or high capacity, long discharge, and low cost for the electricity grid. Novel architectures provide the enabling framework for simultaneously achieving diverse performance metrics. Three-dimensional architectures of small nanoparticles combine high energy density with high mobility for fast charging, for example, or cathode architectures integrating catalysts with reactants selectively promote targeted conversion reactions with low overpotential, high efficiency, and increased energy and power.

2.4.1 SCIENTIFIC CHALLENGES

The energy, power, and stability of electrochemical energy storage systems depend on factors and processes that are interlinked across multiple length scales. Such factors include the fundamental properties of active materials (ionic/electronic transport, specific capacity), the mesoscale arrangement, chemo-mechanical interactions between active materials, and the macroscale design and layout of the entire system. The active materials and their interfaces undergo dynamic phase transformations and volume changes during charge and discharge, which can alter local structures and influence ion/electron transport. The architecture of the system provides the framework that enables continuing functionality in the face of these dynamic changes. To meet the functional demands of a given application, the high-level architecture of an energy storage device plays as much a key role as the materials choices.

In today's systems, the multiscale structures of energy storage electrodes are mostly based on solid electrodes and liquid electrolytes. Liquid electrolyte-infiltrated films provide the ionic and electronic conductivity necessary for operation, but these electrode architectures have limited volumetric capacity and rate capability due to significant fractions of passive materials and long transport distances. Furthermore, the use of conventional slurry-coated electrode architectures for emerging high-capacity electrode materials, such as alloying anodes and conversion cathodes, often results in rapid capacity decay during cycling due to local loss of active material and unwanted side reactions, phase transformations, or irreversibility.[1,2] The current architectural paradigm is reaching its capability limits for advanced energy storage; there is a clear need for different architectures in the design of new energy storage systems.

There are a number of broad scientific challenges and opportunities associated with pursuing new design frameworks for battery systems, components, and materials. First, because energy storage systems will only make an impact if they can be manufactured effectively, the methods for creating such systems must be scalable. Therefore, the fundamental science underlying materials synthesis, processing, and especially the controlled assembly of nanoscale building blocks into mesoscale structures and higher order architectures[3] will be foundational for progress in this area. Additionally, it is necessary to attain a greater understanding of how chemo-mechanical interactions among active structures within an electrode influence overall electrochemical performance.[1,4] This is an open field in which emerging *in situ* and *operando* techniques can be used to uncover important fundamental aspects of electrochemical phenomena,[5] with scientific impacts expected in other areas of electrochemistry as well.

New ways of designing energy storage architectures across multiple length scales are required to move towards batteries that address the needs of the future. A critical approach to such multiscale design is to first consider the desired functions of an application and the battery characteristics needed to meet those needs. Modeling and simulation, particularly when connected hierarchically, presents a pathway to improved battery design by addressing the selection of active material, material properties, the electrode architecture, and the overall system layout. Knowledge of the properties and the dynamic transformation processes of the active material at the nanoscale would inform decisions regarding structure at larger length scales. It is expected that the specific design elements derived through this process would vary significantly for different battery use cases and active materials.

In this context, a set of critical scientific challenges regarding fundamental phenomena in battery systems is set out below. Can we understand and control complex reaction processes in highly abundant and environmentally benign materials? Can we understand dynamic charge transport and charge storage mechanisms in materials that exhibit multiple storage modalities for high energy and power? Can we understand and predict the stability and reversibility of molecular and/or flowable electrochemical materials for novel large-scale systems? Answering these questions will lead to improved understanding of various aspects of material and systems behavior, which will pave the way towards designing tailored components and architectures for future battery systems. These scientific challenges lead directly to two specific research thrusts to address these challenges: (1) design and synthesize new mesoscale architectures and (2) envision and demonstrate new concepts for large-scale energy storage and conversion.

2.4.2 RESEARCH THRUSTS

Thrust 4a: Design and Synthesize New Mesoscale Architectures

New mesoscale architectures and their constituent materials are intricately intertwined for energy storage. Architectures and their material building blocks cannot be separated from one another—the architecture enables emergent behavior of the materials, and the materials provide the nascent functionality brought to blossom by the architecture. Three key features of the architecture-materials nexus are elaborated below: novel architectures, guided synthesis, and smart design.

Novel Architectures: Today's battery designs are nearly all 2D layers of anode, electrolyte, and cathode that interact through short interlayer distances and over large lateral areas. There are radically different 3D designs that pack higher energy and power into smaller volumes, and that shorten the interaction distances. Architectures based on 2D interdigitation, which allow intralayer interactions between anode and cathode, have already begun to be explored. The interdigitation concept can be extended to three dimensions as arrays of nanowires comprising alternating anodes and cathodes interacting laterally over the length of the wires.[6] This novel architecture achieves high surface area, short conduction paths, and high energy and power density.

An alternative 3D architecture divides space into close-packed mesoscopic cells that interact with each other across common planar boundaries. The five platonic solids allow significant diversity of cell boundaries and architectural structure, from tetrahedral cells interacting with four adjacent neighbors, simple cubic cells with six adjacent neighbors, up to icosahedral cells interacting with 20 adjacent neighbors. These cell architectures can consist of a metal-organic-framework (MOF)-like or covalent-organic-framework (COF)-like superstructure that modulates the interactions between adjacent cells, and a cell interior that may contain active anode or cathode material.[7] The active material can be in the form of a nanoparticle whose size is chosen to maximize energy or power density, perhaps coated with inactive membrane-like materials to selectively pass the working ion but block unwanted side reactants. Such a 3D architecture can house anode-only or cathode-only nanoparticles, allowing access of liquid electrolyte to each cell to promote electrochemical reaction in all cells simultaneously. Alternatively, alternating cells may contain anode and cathode nanoparticles to achieve short interaction distances and high power. The architectural framework can contain catalysts to promote the targeted electrochemical reactions, or catalysts can co-occupy cells along with active materials. The design parameters of such cell-based architectures are nearly limitless; examples are just beginning to be explored.[8,9]

Guided Synthesis of Complex Materials: High-throughput DFT computation of hundreds or thousands of candidate materials has become a standard approach for identifying new materials.[10-13] This materials genome approach produces comprehensive libraries of comparative properties and reveals trends that otherwise may go unnoticed by human intuition. Once a material has been selected, the major challenge is synthesis of the targeted material. Synthesis of single-phase compounds typically identified by today's genomic approaches can require months of trial and error. Synthesis of composite materials comprising several compounds or phases that may be identified by tomorrow's genomic approaches will be even more challenging. The emerging area of guided synthesis seeks to replace laborious trial and error with predicted synthesis routes for targeted materials through modeling and simulation combined with *in situ* monitoring during synthesis to interrogate and refine the synthesis protocol.

The synthesis challenge is to identify which chemical reactions will produce the targeted compounds without interference by competing side reactions, and to produce not only the targeted bulk material but also its targeted morphology as a film, nanoparticle, foam, or other nanostructured format. The multiplicity of possible chemical reactions leading to the targeted material composition and the many possible competing morphologies make this a monumental challenge for traditional simulation by DFT. Guided synthesis uses machine learning as an alternative approach where correlations between synthesis conditions and synthesis outcomes predict synthesis routes without the need for first principles understanding of the synthesis mechanism.[14]

Traditional synthesis relies on researcher intuition about reagent properties and composition ratios that govern synthesis outcomes. Guided synthesis relies on machine learning to discover correlations among synthesis conditions and outcomes that may be sufficiently subtle or obscure to have escaped researcher notice. Extensive databases of attempted synthesis protocols for a class of materials are the training set, including failed experiments that are not normally reported in the literature. The guided synthesis approach, just beginning to be explored, has already achieved some notable successes.[14-16] Given sufficient development and experience, this approach has disruptive potential to significantly streamline and permanently alter the way we think about synthesis of targeted complex materials.

Defected and disordered phases are an outstanding example of materials that resist simulation by conventional techniques, often requiring extremely large supercells and prohibitive computational time to produce credible results. Defected and disordered materials such as alloys, foams, aerogels, glasses, and porous membranes are commonly used in batteries and electrochemical capacitors. There is a strong need to develop simulation tools that can describe these disordered materials and the synthesis routes that govern their properties. Machine learning to reveal correlations among defects, disorder, and properties is an attractive alternative to first principles supercell approaches.

Smart Design of Materials and Architectures: High-throughput DFT methods have also shown significant success in battery materials design.[10-13] Machine-learning and data-mining algorithms have recently emerged as viable next steps for rational materials design. Machine learning for materials discovery differs from machine learning for synthesis routes in that the material itself, not the synthesis route, is the target. The concept motivating the use of machine learning methods for materials discovery is the use of correlations between structure and functionality to predict materials and design rules for materials and architectures. Machine learning and data mining require access to large data sets of experimental, theoretical, and computational models that implicitly contain the correlations.[14] The information contained in the databases needs to be transformed into a set of attributes that can be recognized by a computer algorithm that analyzes the data for correlations between structure and the desired functionalities. The correlations found by machine learning algorithms can be deeper and unbiased by conventional wisdom than those generated by the chemical intuition and background knowledge of human researchers. Machine learning has been extensively used in the pharmaceutical industry for drug development but has hardly been applied to materials science. New methods and algorithms[17] are needed for an even more flexible framework that may automatically identify the structure-functionality correlations and the necessary attributes to achieve targeted functionalities. Machine learning will greatly accelerate the rational discovery of materials with multiple functional requirements, such as high energy density, fast charging, long lifetime, and safety. An example of a set of design rules generated by a computer algorithm trained on reaction data to predict reaction outcomes for the crystallization of templated vanadium selenites is shown in Figure 2.4.1.[14] The outcome of this model is a set of recommended reaction conditions for the crystallization of inorganic compounds. This example clearly illustrates how discovery of new materials can be systematically implemented based on existing databases of successful and failed experiments.

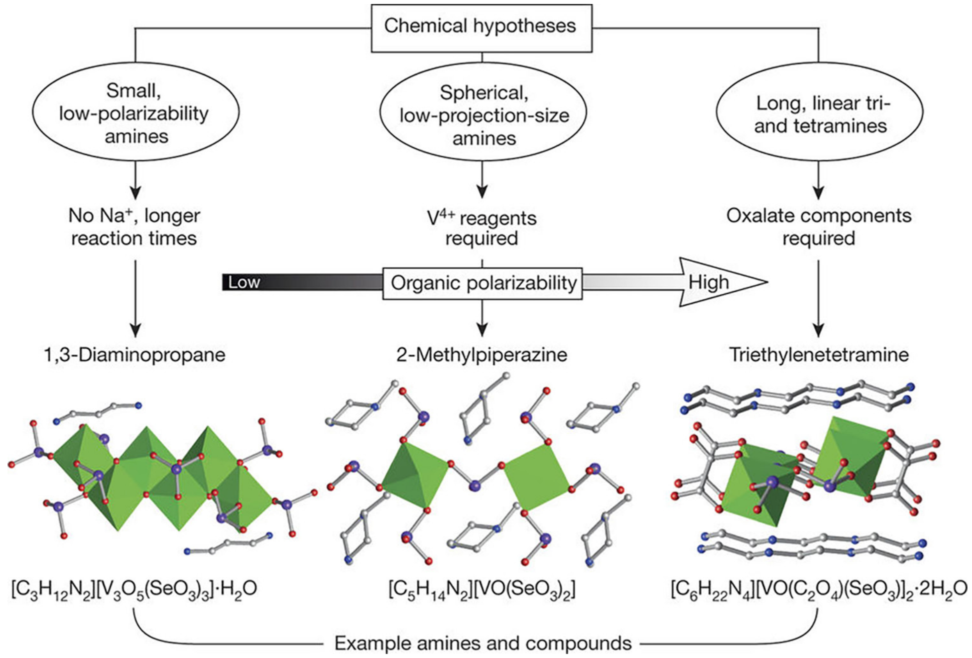


Figure 2.4.1. Graphical representation of the three hypotheses generated from the model, and representative structures for each hypothesis. From Ref. 14. Reproduced with permission of Nature Publishing Group.

At the mesoscale level,[18] there is a strong need to develop tools for predicting the design and function of mesostructured architectures for energy storage. These architectures include 3D electrode frameworks and interpenetrating phases (dense and porous) that can be assembled into 3D architectures. Genetic algorithms and evolutionary optimization have been applied to MOFs, surveying over a trillion candidate architectures and identifying design modifications with a predicted 400% increase in CO_2 absorption capacity over the parent MOF.[19] In contrast to MOFs, molecular crystal architectures arise from the balance of many weak interactions, rather than from the strong and predictable bonding patterns of MOFs and COFs. Small changes to the structure of individual molecules can cause profound changes in crystal packing and polymorphism in the crystals they form, making their structures and properties notoriously challenging to predict. *A priori* design of functional molecular crystals requires a predictive strategy that does not rely on intuitive bonding rules or topologies taken from apparently similar molecules. A new approach exploiting correlations between known single-molecule structures and their functional properties of the crystals they form promises to discover new molecular architectures with targeted functionalities by using only single-molecule structures as input. In a notable success, these energy-structure-function maps discovered new highly porous molecular solids with record low densities.[20] These new approaches to architecture discovery offer promising pathways to practical, scalable, safe, and cost-effective smart design of functional mesoscale architectures.[21-24]

The non-equilibrium charge-discharge cycles of batteries and electrochemical capacitors demand guidance of a higher order than mostly static structural applications. There are volume changes, along with mass transport and dynamic chemo-mechanical interactions, that require special attention and introduce many variables that must be tracked simultaneously. In such complex dynamic systems, *in situ* experimental interrogation to validate and refine the correlations revealed by machine learning is essential. Examples of such approaches have been recently reported.[17]

Thrust 4b: Develop New Concepts for Large-Scale Energy Storage and Conversion

Rather than storing energy in solid electrode materials, energy can instead be stored in redox species dissolved or suspended in a liquid phase, such as redox flow batteries.[25] In a redox flow battery, the cathode and anode materials consist of aqueous or non-aqueous electrolyte solutions (catholytes and anolytes) in which the energy is stored. The anolyte and catholyte are pumped through porous electrodes at each side of a cell stack, where they are separated by an ion-exchange membrane or porous separator to prevent crossover of the active species, while the electrochemical redox reactions occur on the electrode surfaces. (See also the "Flow Systems" sidebar in Panel 1 Report.) The unique architecture and working mechanism allow the energy and power to be controlled independently. The power is defined by the size and design of the electrochemical cell (the stack) whereas the energy depends on the concentration of redox species and the size of the external tanks in which they are stored. In this research thrust, concepts related to the storage of energy within liquid electrolytes will be discussed.

Inspiration from Flow Systems for Novel Chemistries: The unique architecture of redox flow batteries may provide viable solutions to issues inherent in other next generation battery chemistries. As an example, the Li-sulfur battery system, based on the reaction between S_8 and Li (Figure 2.4.2),[26] represents a promising energy storage technology due to high energy density and low cost. However, this battery chemistry falls short of expected performance due to dissolution of lithium polysulfide species, which are intrinsically insulating materials, and the depletion of electrolyte after long-term cycling. Since polysulfides are highly soluble in both water and ether-based solvents, partially liquid batteries based on polysulfides have been explored with the goal of achieving extremely low cost and long cycle life.[27-29] This unique battery design holds promise for addressing the issues of the conventional Li-S battery and can be scaled up for large applications. The key challenges that remain for liquid batteries based on the Li-S chemistry is to understand the solution chemistry and chemical speciation, and to control the dissolution, nucleation, and precipitation cycles. Similarly, aqueous polysulfide-based batteries have also been proposed to circumvent the issue of organic solvents. In a typical aqueous Li-S battery design, for example, electrochemical potential control is employed to take advantage of the reaction between Li_2S_4 and Li_2S, both of which are soluble in water.[30] The higher ionic conductivity of aqueous electrolyte is also appealing to provide high power density. However, the compatibility between the aqueous catholyte and the organic electrolyte in the anode, as well as Li metal protection, still remains to be addressed.

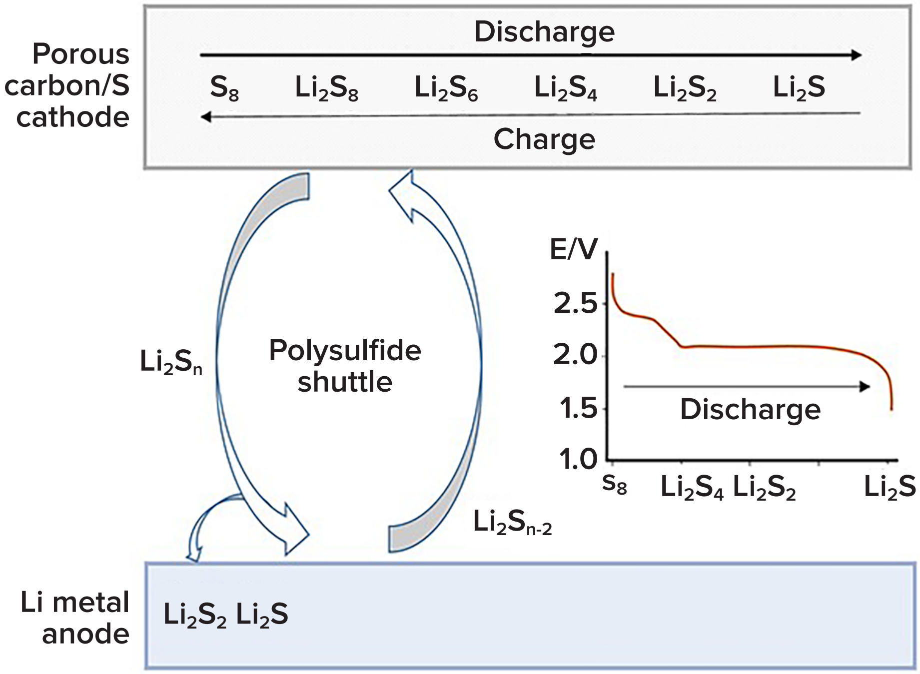


Figure 2.4.2. Working principle of conventional lithium-sulfur battery, which involves the formation of soluble lithium polysulfides and their diffusion in the liquid electrolyte. From Ref. 26. Copyright Elsevier, 2014.

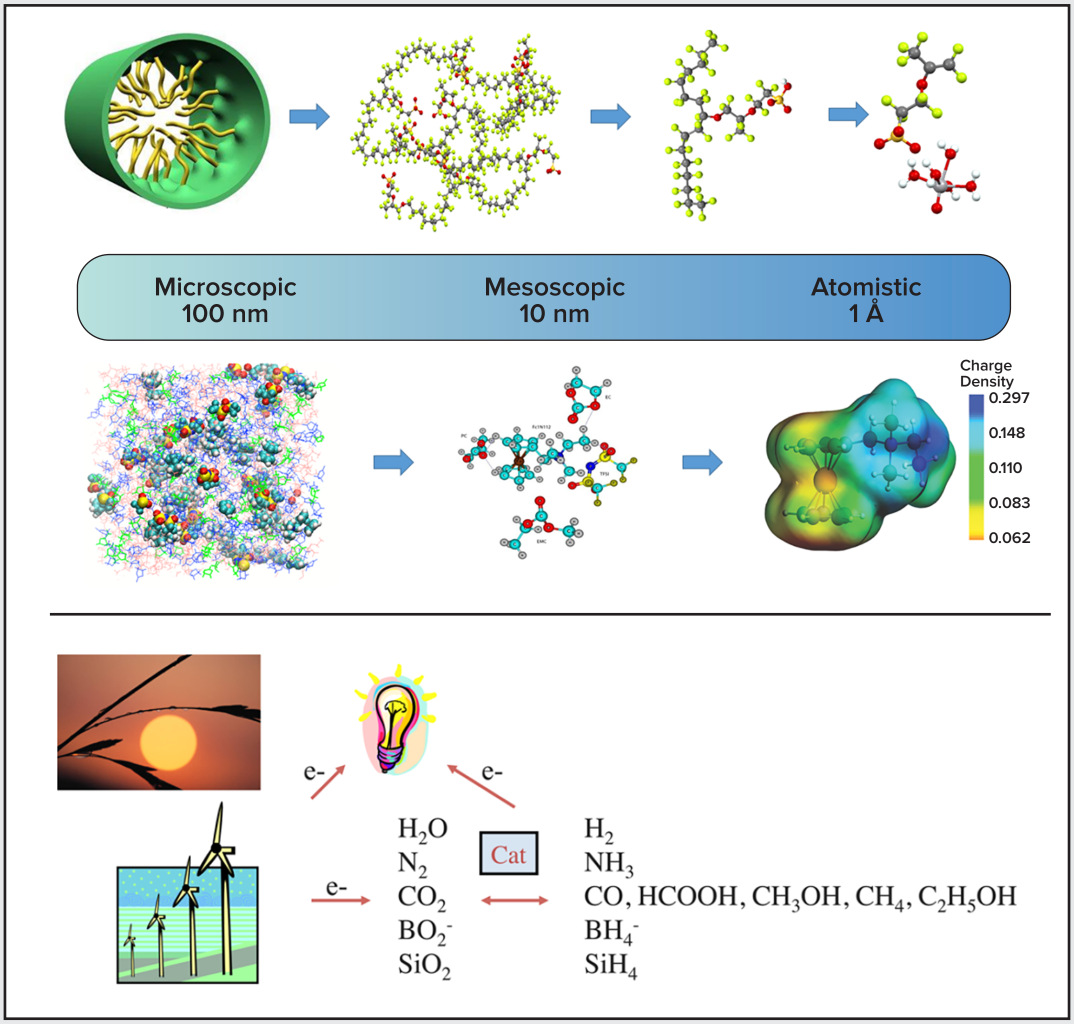
Electrocatalytic Chemical Energy Storage: The redox flow battery architecture opens up possibilities for storing energy over very long periods of time, which is a challenging problem for current electrochemical storage systems. For instance, the redox flow architecture can be configured as an electrochemical conversion and storage system to carry out electrochemically catalyzed reactions of abundant and low cost materials using electricity generated from renewable sources (see sidebar on "Membrane Design, Solvation Mechanisms and Molecular Electrocatalysts for Energy Storage"). The energy would be stored in converted molecules dispersed in the electrolyte, and the chemical energy can be converted back to electricity when needed. In such an electrochemical system, H_2O, CO_2, N_2, and other abundant chemicals are reduced by the electrons provided at the cathode, and oxidation happens on the anode to produce O_2. The efficiency is determined by the charge transfer from the substrate to the molecules, the effectiveness of the catalysts for both the reduction and oxidation reactions, and transport of charged species in the vicinity of the electrodes and catalysts. This energy storage methodology involves a new set of cross-cutting challenges not emphasized in traditional battery systems, such as how to enhance the efficiency of desired electrochemical reactions, as well as how to control the solubility, stability, solvation, and transport of active species. These properties will dictate the cost, energy density, power capabilities, and lifetime of electrocatalytic energy storage systems.

Solvation: Looking beyond the traditional paradigm of a single-atom solute in neat solvents for chemical storage in flow batteries or other molecular systems, it is important to understand how strong interactions (including solvent-solvent, ion-ion, and solvent-ion) influence molecular energy storage systems, and how these interactions can be strategically controlled for energy-intense technologies. Comprehensive understanding of complex solvent systems is needed, especially the interplay between the polyatomic solutes and solvent ions that often possess asymmetric structure and charge distributions, as well as that of competing counter ions. Clear understanding needs to be established regarding the interaction and exact role of location-specific charge allocation with respect to the size and steric effect of the ionic solute molecules. This knowledge will render new strategies to improve the overall functionalities of electrolytes. For example, by preferential solvation or formation of counter-ion pairs, the solubility of the redox active ionic materials can be significantly improved. Such understanding is required across length scales to enable control of solvation with the fundamental electrochemical processes that take place at electrode interfaces. Research opportunities in this area include the critical examination of solvent-mediated ion pair formation in ionic solutions, as well as the manipulation of solvation phenomena to favorably impact overall functionalities and electrochemical processes.[31]

Reaction Processes, Membranes, and Interfaces: Recent progress in nanoscience and nanotechnology has resulted in advances in flow battery design to enhance power density, as well as improved membrane technologies to mitigate crossover and improve stability.[32,33] By decreasing the diffusion path of redox species and enlarging the contact area between the current collector and electrolyte, power performance can be improved. Dramatic advances in power density can also be achieved by better understanding of the reaction kinetics and charge-transfer processes of electroactive species via fundamental electrochemical characterization, which bridges the gap between actual battery performance and the theoretical capabilities of redox-active materials.[34] Advanced redox flow batteries also rely on inhibited crossover of redox species between the anolyte and catholyte compartments; ion-selective membranes have traditionally been used for this function. Rational functionalization of the molecular structure of membranes provides an avenue to reduce the unwanted shuttling of redox species via size tuning[35]; pore size control and charge engineering of the membranes can also mitigate crossover issues.[36] Moreover, to gain a better understanding of the stability of flow systems, analytical techniques coupled with computational transport and kinetics modeling represent promising avenues for study.[37-39] Advances towards the next generation of scalable flow-based energy storage systems will thus be critically dependent on fine molecular tuning and fundamental understanding of both electroactive molecules and membranes.[40] Such investigation will require an interdisciplinary effort integrating expertise in chemistry, materials science, and energy science.

Electrochemical processes occur at the atomic to nanoscale. The transport of electrons and ions links these phenomena to the continuum, where properties are manifested through the overall architecture of the electrochemical cell. In regards to ion transport and charge transfer, research needs include the development of nanostructured electrode surfaces at the liquid/solid interface for fast electron and ion transport in membranes with high selectivity. Nature has the ability to selectively transport molecules through biological cells at rates orders of magnitude higher than any man-made membrane structures, which may provide inspiration to

MEMBRANE DESIGN, SOLVATION MECHANISMS AND MOLECULAR ELECTROCATALYSTS FOR ENERGY STORAGE



Top panel: Predictive understanding of highly correlated structural evolution over spatial and temporal continuum can help tailor the functional properties of membranes and electrolytes. Rational membrane modification can lead to alleviated crossover of redox species and superior ionic conductivity. Elucidating the nature of a redox molecule's solvation process can give rise to high concentration electroactive materials and hence high energy density redox flow batteries. Image courtesy Wei Wang and Vijayakumar Murugesan, Pacific Northwest National Laboratory.

Bottom panel: Storing energy in molecules using electrochemically catalyzed reactions. Efficient utilization of sustainable energy can be further promoted by designing novel battery architectures and new chemistries. In new electrochemical storage systems, the redox-active components can be extended to abundant and low-cost materials, such as H_2O, N_2, or CO_2, based on molecular electrocatalysts. The electrochemical reactions at both the cathode and anode need be fast enough to avoid severe energy losses. Therefore, developing cost-effective, stable, and efficient electrocatalysts will play a critical role in realizing this vision of storing energy electrochemically in molecules within flow battery systems.

From D.L. DuBois, Development of molecular electrocatalysts for energy storage, Inorg. Chem., **2014**, 53 (8), 3935-3960.

fundamentally reinvent engineered membranes beyond simple diffusion or Newtonian fluid flow limitations. Next generation membranes may emerge from the strategic and precise placement of active chemical functionality onto robust material systems, intelligent pore design with signal chemistry, and mechanisms for fast fluid flow and mass transport. The growing research interest in this area in recent years has produced redox active materials other than traditional transition metal ions, such as organic and organometallic redox couples, polymers, and metal ionic liquid complexes.[32,33,41,42] Meanwhile, various charge carrier ions other than protons have been enlisted in many storage systems with new redox chemistries. With the continuous invention of new redox chemistries, there is currently an urgent need to develop new membranes tailored to specific redox chemistries, a variety of charge carrier ions, and various fouling characteristics. Past membrane research has often focused on the compromise between membrane selectivity and conductivity.[43] New membrane materials with high selectivity and fast transport mechanism should be developed and investigated.

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2.5 PRD 5 — Promote Self-healing and Eliminate Detrimental Chemistries to Extend Lifetime and Improve Safety

Extending the lifetime and improving the safety of electrical energy storage devices are critical needs for next generation energy storage systems designed for higher energy density and power. Future batteries, for applications such as vehicles or the electricity grid, will require long lifetimes (15-20 years) without significant capacity degradation or catastrophic failure. For many applications, useful battery life is a critical metric: doubling the lifetime effectively cuts the cost in half, a major consideration wherever more cost-effective solutions compete with battery technology. At the same time, catastrophic failure modes (e.g., dendrite shorting) pose critical safety concerns with major liability and market consequences. Successful management of battery design to mitigate degradation, ensure safety, and deliver high performance requires a much deeper understanding of fundamental degradation and failure mechanisms for current and future storage technologies, which can then inform designs that avoid, mitigate, or self-repair these mechanisms.

Electrochemical Complexity Drives Degradation and Failure: The complexity of electrochemical devices opens many avenues for degradation and failure. At the cell level, batteries consist of electrodes, electrolytes, and inert components such as current collectors and separators (Figure 2.5.1), arranged such that ions and electrons move across various interfaces in the devices during charging and discharging. Electrodes are typically porous composites or assemblies of micro- or nano-particles containing binders and conductive (usually carbon) additives to provide uninterrupted percolation pathways for both ions and electrons. Alternatively, electrodes may be monolithic structures, particularly polycrystalline thin films, so that complexity is introduced by the presence of grain boundaries and differing orientations of crystallites.

Whether composites or monoliths, the electrodes may undergo phase and/or volume changes associated with redox processes during cycling, which can lead to fracture and loss of electrical contact within the electrode and from the current collector. Side reactions with electrolytic solutions or inert components can lead to gas evolution, corrosion, and deleterious changes in interfacial properties. These processes are dependent on the state of charge and cycling conditions and may also occur upon storage (static aging) or rest. Abuse conditions such as a dramatic temperature rise during operation or inadvertent over-charge or over-discharge can, at the least, exacerbate side reactions and mechanical changes in the electrodes and, at worst, lead to catastrophic failure. Controlling the consequences of this complexity in a systematic, rational, and quantitative manner is a grand challenge itself and is fundamental not only in designing electrochemical energy storage devices but also in reducing performance fade and extending lifetime.

Degradation Mechanisms: The primary causes of gradual battery degradation and failure are illustrated in Figure 2.5.2.[1] They can be grouped into three generic categories, based on losing electrochemical functionality of the working ion (Li^+ in the case of Li-ion batteries), the active anode material, and the active cathode material. The loss of working ions in the electrolyte can be caused by side reactions that do not directly store or release energy, such as formation of solid-electrolyte interphases, precipitation from reactions with electrolytes, plating on electrode surfaces instead of intercalating into the electrode interior, or trapping in electrode fragments that have separated from the electrode by fracture. Loss of the activity in the anode or cathode material can result from fracture following repeated volume changes or phase transitions, blocking by surface films, isolation from the working ion by grain boundaries, phase boundaries or other defects, loss of electrical contact to the current collector, or dissolution in the electrolyte.[2]

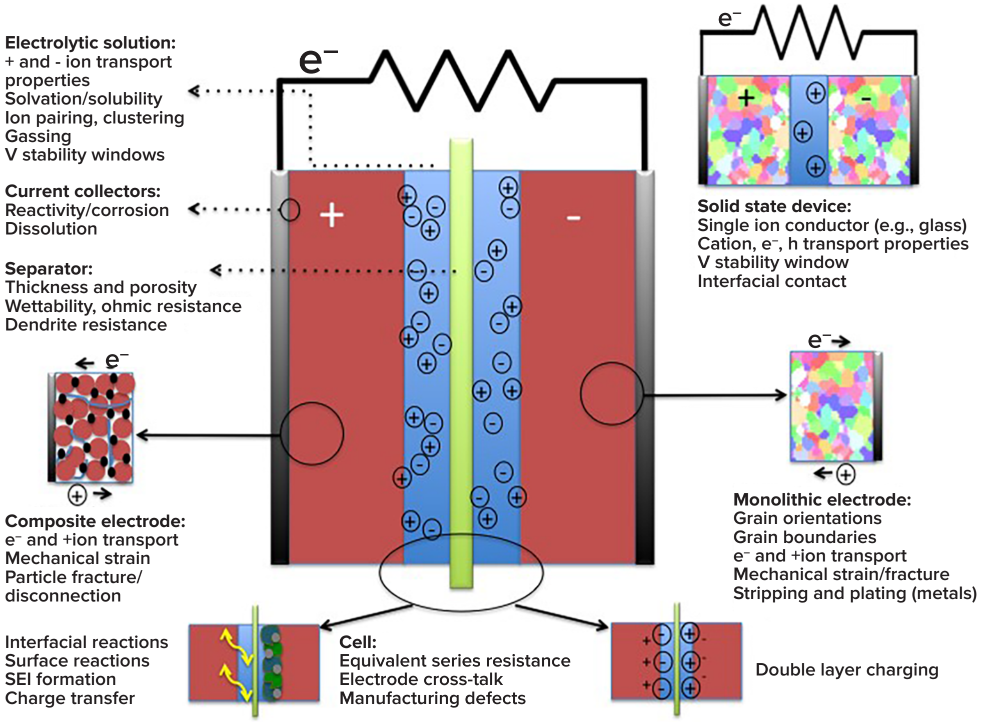


Figure 2.5.1. Schematics of generic electrochemical devices. Although they consist of only a few components, the phenomena that govern their behavior are complex and can contribute to many failure modes. From F. Lin et al., Synchrotron X-ray techniques for studying materials electrochemistry in rechargeable batteries, *Chem. Rev.*, 2017, DOI: 10.1021/acs.chemrev.7b00007.

Longer-term degradation: Batteries often exhibit degradation modes as gradual loss of capacity with charge/discharge cycling, during periods of rest, or periods at higher power/current. Behavior is also influenced by states of charge and thermal environments. While kinetics typically plays a significant role, degradation mechanisms that occur during times of rest or open circuit can result from thermodynamic instabilities of the cell components.[3] Degradation phenomena include self-discharge, increasing interfacial impedance, and an increasing fraction of inactive material phases. Interaction between the cathode, anode, and electrolyte can all contribute to the mechanisms and the kinetics underlying the degradation mode, making it considerably more challenging to study and identify the mechanisms. The diversity of degradation scenarios is exemplified for a graphite anode in Li-ion cells in Figure 2.5.2. Large differences in polarization resistance are found when cathodes are aged at different states of charge at elevated temperatures.[3] Simply immersing a cathode material into a non-aqueous electrolyte for a period of time can result in surface reconstruction,[4] although the role this plays in degradation at different temperatures and states of charge remains unclear.

Catastrophic failure: Catastrophic failure by “sudden death” degradation mechanisms can be more dramatic. For example, dendrites formed on pure metal anodes can grow through a liquid or solid electrolyte, produce a short circuit to the cathode, and cause immediate failure and the risk of fire. Thermal runaway is a second form of sudden death, triggered by heating above a threshold temperature that decomposes the cathode (~150°C for cobalt-based cathodes in Li-ion batteries, higher for $FePO_4$ cathodes), releasing oxygen that reacts with the flammable electrolyte. The reaction is exothermic, so the heat it releases raises the temperature and accelerates the rate of reaction in a positive feedback loop. Thermal runaway reactions are hard to stop, often running until the reactants are exhausted and the battery fully destroyed. This sudden death failure mode presents a major safety hazard.

Battery Chemistries: Despite the pervasive presence of Li-ion batteries in use today, fundamental understanding of degradation and failure is rather rudimentary, without benefit of controlled experiments to prove/disprove hypotheses. Yet, the battery world is increasingly pursuing “beyond Li ion” technologies to achieve the higher performance demanded by large-scale applications. Clearly, mechanisms for degradation and failure are even less understood in these domains, as illustrated in the examples below.

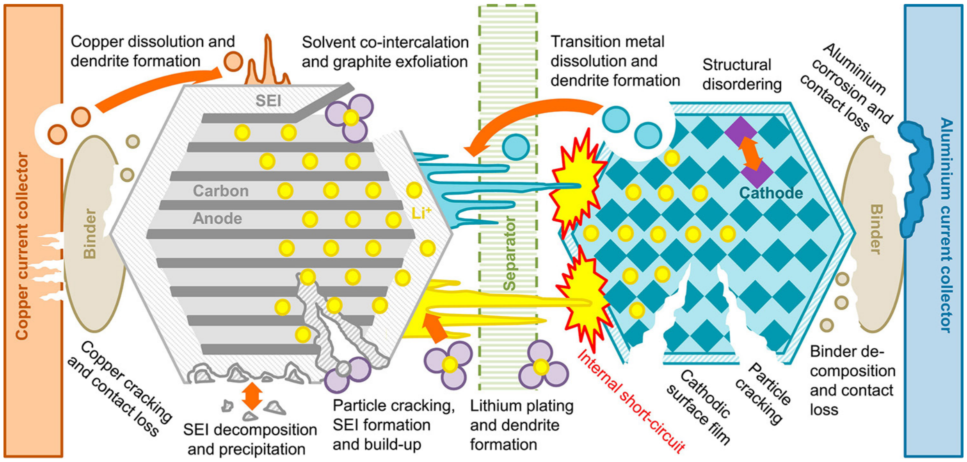


Figure 2.5.2. Degradation and failure modes depicted for Li-ion batteries. From Ref. 1.

Lithium metal anodes: Rechargeable batteries with lithium metal anodes have been earnestly pursued for decades because they promise very high energy densities, but their commercial deployment has been limited. The tendency to form dendrites or mossy deposits upon repeated stripping and plating of lithium has severely limited the cycle life of these devices and presents serious safety hazards. The use of solid rather than liquid electrolytes ameliorates these problems. Thin film devices utilizing glassy LiPON electrolytes have been cycled successfully thousands of times,[5] but they do not completely eliminate these tendencies. Despite intensive investigations of Li-metal batteries, their challenges have not yet been solved. In addition to the aforementioned issues with Li stripping and plating, they have not yet been able to meet practical demands. Advanced Li-polymer batteries can achieve extended performance of 1-10 mAh/cm^2 at currents of 1 mA/cm^2 with a minimum of excess Li metal, but only at elevated temperatures. Upon extended cycling, Li metal anodes have been reported to form hard impurity agglomerates in Li/polymer batteries[6] or wavy ridges leading to islands in Li thin-film batteries.[7]

Sulfur and air cathodes: In addition to problems at the anode, processes occurring at the cathode may contribute to premature failure of batteries utilizing Li metal anodes. In the case of sulfur[8] or air[9] electrodes, for example, insoluble and insulating products of the redox reactions, such as Li_2S or Li_2O_2, deposit on electrode surfaces, eventually preventing passage of current. The factors that limit lifetimes of “beyond lithium ion” battery systems such as Na-ion[10] or those based on multivalent ions[11] are less well-understood and highly system-specific.

Thin film solid-state batteries: Thin film batteries based on the LiPON glassy electrolyte are largely constructed with $LiCoO_2$ cathodes and Li anodes, although a host of other anode and cathode materials have been used in laboratory research.[5] Such thin film batteries are, in some ways, simpler than Li-ion batteries, with fewer components, simple layered geometry, and stable performance of the electrolyte over a wide voltage range. Because LiPON does not react at cell voltages up to 5 V, the electrolyte is not consumed as it is for the liquid-electrolyte cells, avoiding degradation pathways associated with SEI formation. Figure 2.5.3 compares a thin-film Li/LiPON/$LiMn_{1.5}Ni_{0.5}O_4$ cell with solid electrolyte to a cell having the same electrode films with a standard organic electrolyte.[12] Such a comparison is valuable for demonstrating the intrinsic stability of the disordered $LiMn_{1.5}Ni_{0.5}O_4$ spinel cathode for extended cycling. In general, comparing thin film batteries with solid electrolytes to Li-ion batteries with liquid electrolytes may provide ways to distinguish liquid-electrolyte contributors to degradation from more electrode material processes related to cycling, such as phase changes and lattice stresses.

Electrochemical capacitors: Capacitors play an important role in storage technology, providing high power and long cycling advantages compared to batteries. Double layer capacitors exhibit significant self-discharge, believed due to the relatively weak interaction between the electrode and the electric double layer.[13] Issues of self-discharge also plague pseudo-capacitive materials despite the fact that they also store charge via faradaic reactions.[14] Electrochemical capacitors may also fail abruptly due to mechanical breakdown of electrode materials. For example, in some metal oxides, repetitive insertion/deinsertion of Li ions causes strain hardening, fatigue, and fracture of the oxide, leading to separation from the current collector and loss of reversible capacity. This leads to a limit in cycle life of 5,000-10,000 cycles for electrochemical capacitors utilizing these materials.

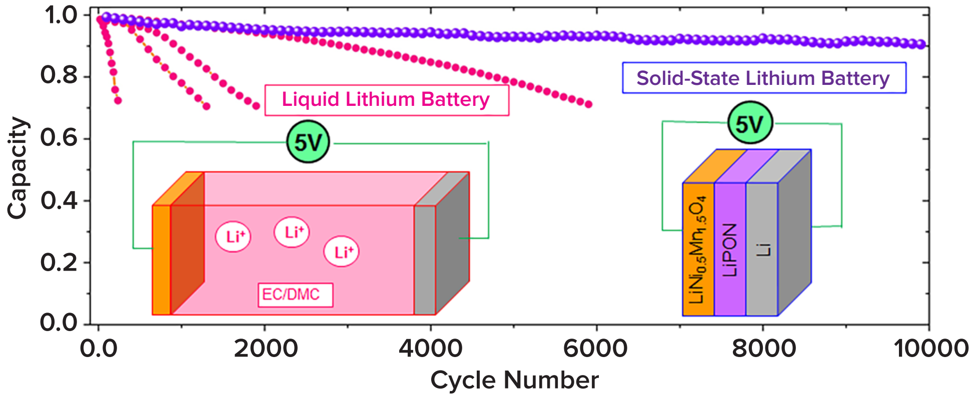


Figure 2.5.3. Comparison of the cycling behavior of Li/LiMn$_{1.5}$Ni$_{0.5}$O$_4$ cells with either liquid or solid electrolytes. From Ref. 12.

2.5.1 SCIENTIFIC CHALLENGES

Why don't electrochemical devices last forever? Why do batteries lose capacity or fade, requiring more frequent recharge? Or worse, why do devices occasionally fail suddenly, sometimes catastrophically, raising concerns about safety? Some failures may be traced back to flaws and errors in manufacturing or design, some are due to gradual loss of electrochemical activity for working ions or active electrode material during cycling, and some are due to catastrophic sudden death such as thermal runaway or dendritic short circuits. Currently, the strategy to extend cycle and calendar life for a storage device is simply to include extra capacity in the battery. This approach avoids having to understand degradation mechanisms, but this is at the expense of increased volume and weight.

What is needed is a new approach to understanding the fundamental mechanisms responsible for degradation, accompanied by a prediction and validation strategy that uses this understanding to evaluate battery designs for degradation mitigation as well as performance. This approach would provide insights into not only what degradation pathways occur during battery life, but also when and where degradation events occur in the device, how rapidly they advance, and how effective are new approaches to slow or stop them and to design around them. The vision is that with systematic and precise study, new tools and sensors, and more sophisticated simulation, researchers in the future will be able to develop safer and more robust devices without sacrificing energy density or performance.

Significant scientific obstacles challenge this vision:

- Storage devices are complex, composed of numerous materials and components.
- Phenomena are coupled, with processes simultaneously driven by electrochemistry, chemistry, mechanics, and thermal behavior.
- Active interfaces and materials are buried and are difficult to probe.
- Evolution of the materials may be very slow and sensitive to duty cycle, thus evading practical real-time observations.
- "Sudden death" events like internal shorts caused by dendrite formation are rare and spatially localized, making it difficult to reproduce in the lab.

Overcoming these obstacles and obtaining a full understanding of the degradation and failure modes of batteries and electrochemical capacitors—and how to mitigate them—require two significant advances. The first is a coordinated portfolio of complementary experimental techniques that provide new levels of observation of degradation phenomena in both model and practical battery systems, enriched by high resolution imaging, dynamic/*operando* observations, and the ability to "see" buried interfaces. The second is a computational framework that emphasizes continuum modeling capable of revealing the evolution of degradation processes while incorporating the fidelity of molecular-level modeling into a larger framework. Emphasis on continuum modeling is critical for its capability to address the behavior behind mesoscale aggregates of molecular, particle, or nanostructure components.

Developing a multimodal array of sophisticated characterization techniques with improved specificity, resolution, and sensitivity, combined with multiscale frameworks converging in continuum modeling, can provide critical scientific insights for significantly improving function, safety, and robustness of electrochemical devices across a broad range of chemistries and architectures. In turn, these insights may stimulate creative approaches to mitigate degradation in the form of electrolyte additives; coatings on active material particle surfaces; entirely new materials, electrodes, or cell architectures; or other approaches not yet identified. Not only will this result in longer calendar and cycle lifetimes, but it can also potentially enable the adoption of energy storage devices with much higher energy densities than currently available, without compromising safety. Furthermore, this approach can result in shorter lab-to-market timelines for new chemistries or architectures with superior properties, as simulations validated by experiment provide lifetime and degradation predictions that reduce the need for extended and time-consuming accelerated testing.

2.5.2 RESEARCH THRUSTS

Thrust 5a: Multimodal *In Situ* Experiments to Quantify Degradation and Failure

Goal: The goal of this thrust is to develop multimodal, *in situ* and *operando* experimental tools with sufficient space and time resolution to see the individual steps in the degradation pathway, understand the cause-and-effect relationships among these coupled phenomena, and thus map the degradation pathway from start to finish to define directions that indicate how battery redesign, choice of materials, or other features can be successful in mitigating the degradation. The emphasis on multimodal techniques reflects the scientific importance of relating degradation metrics to the broader, causal behavior that drives degradation in the materials and architectures employed in the battery. The emphasis on *in situ* and *operando* approaches recognizes that *ex situ* characterization is not sufficient, as it sees only the static outcome of part of the degradation pathway and misses the history of the dynamic interactions of phenomena as they develop. While significant research advances have been made in the last decade in exploiting *in situ* and *operando* tools, they have generally not been applied to characterizing degradation pathways in batteries or deployed in multimodal characterization to examine multiple aspects of the same interacting phenomena over several length and time scales.

Battery degradation and failure, like battery operation, is a complex interaction of many heterogeneous phenomena,[15] involving numerous coupled electrochemical, chemical, thermal, and mechanical phenomena, each with its own kinetic signature. Figure 2.5.4 summarizes some of the relevant phenomena and their time and length scales.

Leveraging Characterization Strategies to Understand and Mitigate Degradation: In typical practice, the outcomes of many coupled phenomena are lumped into a single performance metric (or related group thereof): for example, voltage-current measurements that can be obtained following different protocols. However, these do not reveal the controlling mechanical, chemical, or thermal origins. Similarly, measured temperature variations arise from several possible contributions, including resistive heating, entropic changes due to electrochemical reactions, and the enthalpy of unwanted side reactions. Anisotropic heat conduction creates non-uniform temperature distributions inside the battery, which, in turn, influence the kinetics of local electrochemical phenomena, mechanical expansion, strain, and possibly fracture. Multimodal characterization of the properties and behavior of the materials as they are configured in the battery architecture is a prerequisite for inferring the origins and evolution of degradation phenomena. Furthermore, since battery electrodes have spatial structure, ranging from abrupt interfaces and grain structure in polycrystalline material to particles in composite electrodes, high spatial resolution of the characterization techniques is an important element in at least some part of the multimodal portfolio.

Moreover, such characterization adds value primarily in conveying a picture of how degradation proceeds. In turn, this places a large premium on *in situ* and *operando* experiments that resolve the individual phenomena and reveal their interactions, uncovering otherwise unknown degradation pathways and providing quantitative behavior to inform predictive continuum models of degradation and failure. Over the last decade, many advanced characterization tools for imaging, spectroscopy, and diffraction based on X-ray scattering, electron scattering, neutron scattering, and nuclear magnetic resonance have been developed for *operando* and *in situ* monitoring of electrodes, electrolytes, and their interfaces. As shown in Figure 2.5.5, this suite of tools covers a wide range of phenomena on time scales from seconds to days and length scales from sub-nanometer at the materials level to millimeter at the device level.

Together these tools provide the basis to achieve critical insights into battery degradation processes, particularly if employed in complementary combinations. Element-selective probes such as NMR spectroscopy allow tracking degradation products from electrolyte decomposition as they migrate from one electrode to the other.[16] To address the breakdown of the organic solvent itself by standard means such as ^{13}C or ^{17}O NMR, it is necessary to use isotopic enrichment of the solvent, as the amount of solid-phase breakdown material on the electrode surfaces is expected to be relatively small.[17]

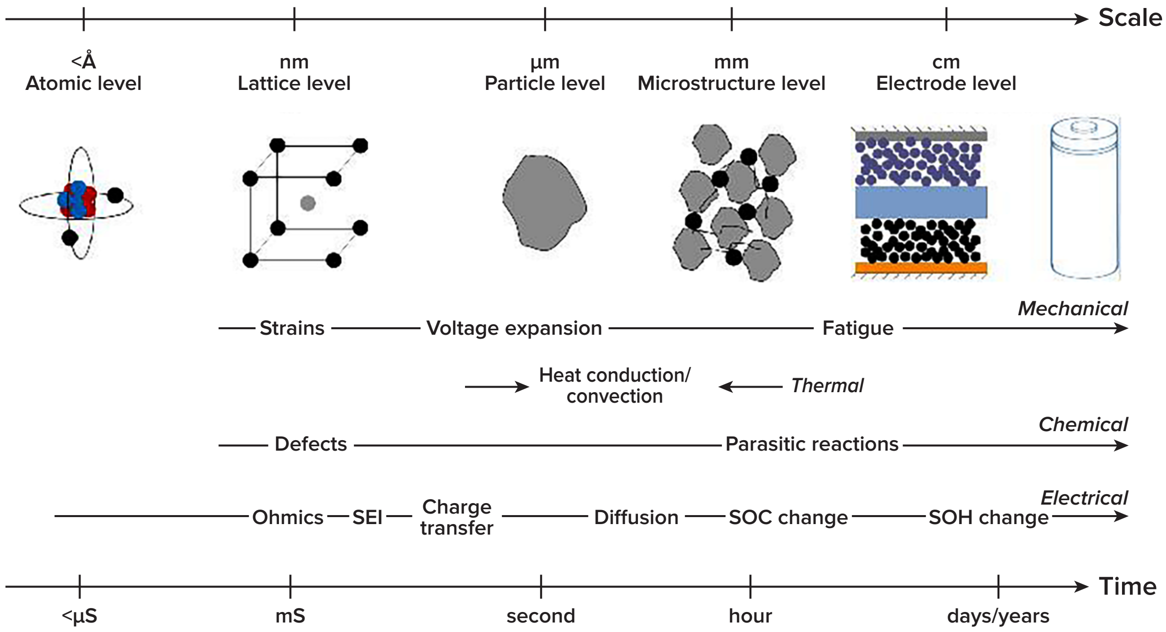


Figure 2.5.4. Understanding irreversible processes across time and length scales in electrochemical cells. This chart shows how the relevant chemical/electrical/mechanical phenomena are coupled across multiple length and time scales. SOC = state of charge and SOH = state of health. Courtesy of Matthieu Dubarry (Hawaii Natural Energy Institute), Boyann Liaw (Idaho National Laboratory), and Craig Arnold (Princeton University).

In situ neutron reflectometry provides a depth profile of buried interfaces in electrochemical cells, with high sensitivity to isotopic variations for several elements, notably Li and H.[18] This technique allows labeling reactants to reveal where they are incorporated into surface layers, often obtaining sub-Ångstrom precision in the size of resolvable features. In comparison, the higher flux of X-rays can provide faster measurements of kinetics and a larger range of momentum change, thereby enabling studies of smaller features. Synchrotron soft X-ray techniques such as X-ray absorption spectroscopy can provide elemental and oxidative state specificity as can photoemission spectroscopy.[19] However, the higher isotopic sensitivity and penetrating power of neutrons allow contrast control in challenging sample environments. Together these techniques are complementary and have the potential for providing greater scientific insights into surface and interface structures if used in a multimodal approach. Particular value may be found in studies of all-solid-state batteries, where probing buried solid/solid interfaces is critical and, in some ways, more amenable than for liquid electrolyte systems.

The value of multimodal characterization has been demonstrated for state-of-the-art layered oxide cathode materials and lithium anodes, exploiting atomic-resolution analytical electron microscopy,[20] coherent X-ray diffraction imaging,[21] X-ray tomography,[22,23] and magnetic resonance imaging[24] to identify defect generation, crack formation, and dendrite growth at particle and electrode levels (see sidebar "Visualizing *In Situ* Dendrite Growth with Magnetic Resonance Imaging"). Nevertheless, how this can be used to develop atomistic/molecular to meso-scale based predictive models for lifetime assessment remains a ripe opportunity. Such detailed information is critical for developing sophisticated and predictive continuum models of battery degradation and failure.

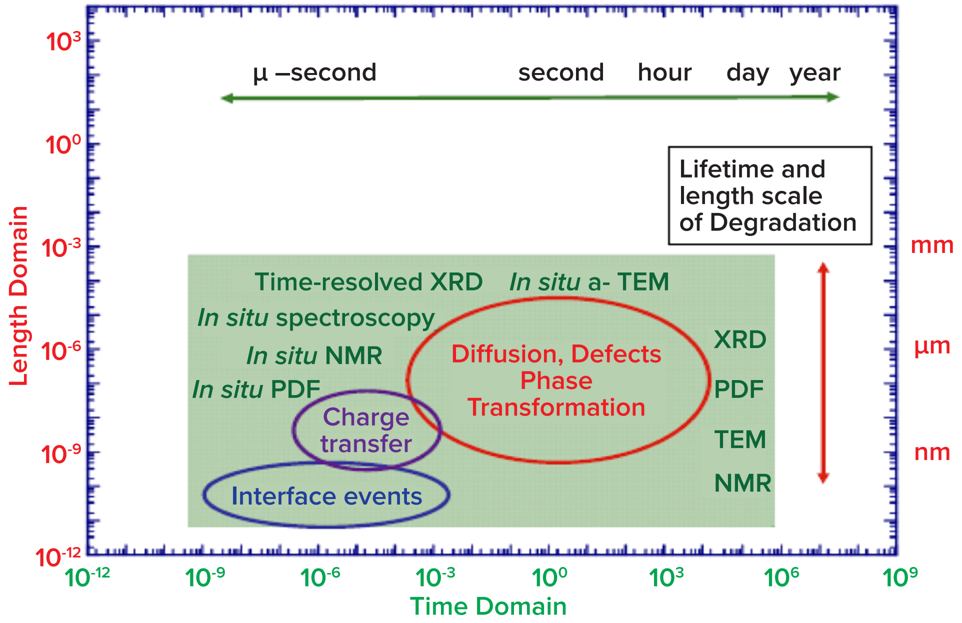


Figure 2.5.5. Spatial and temporal responses of characterization tools. XRD = X-ray diffraction, PDF = pair distribution function, TEM = transmission electron microscopy, and NMR = nuclear magnetic resonance. Courtesy of Shirley Meng, University of California, San Diego, and Northeast Center for Chemical Energy Storage.

Examples: The kinds of synergistic multimodal measurements needed to understand degradation are illustrated by recent studies of heterogeneous spatiodynamics of intercalation examined with *operando* X-ray microscopy (50 nm spatial resolution) in Li_xFePO_4 cathodes.[26,27] The experiments quantified local Li concentration through X-ray spectroscopy of the Fe valence states, revealed local structure through X-ray diffraction, and quantified lithiation kinetics by comparing sequential measurements. The latter revealed that the rate of lithiation within particles varies on nanometer length scales and depends on Li composition. In turn, this variation leads to domains of high and low lithiation, with the inhomogeneity amplified on delithiation and suppressed on lithiation. At equilibrium, such composition changes trigger structural phase transitions, but during lithiation, the kinetics suppress the phase transitions and replace them by a continuous solid solution. Left at rest, the solid solution relaxes to distinct phases with high local stresses at the phase boundaries, a precursor to fracturing. This interplay of composition, kinetics, structure, phase transformation, and stress is central to degradation behavior and may hold a key to fast charging and discharging dynamics in $LiFePO_4$ batteries.

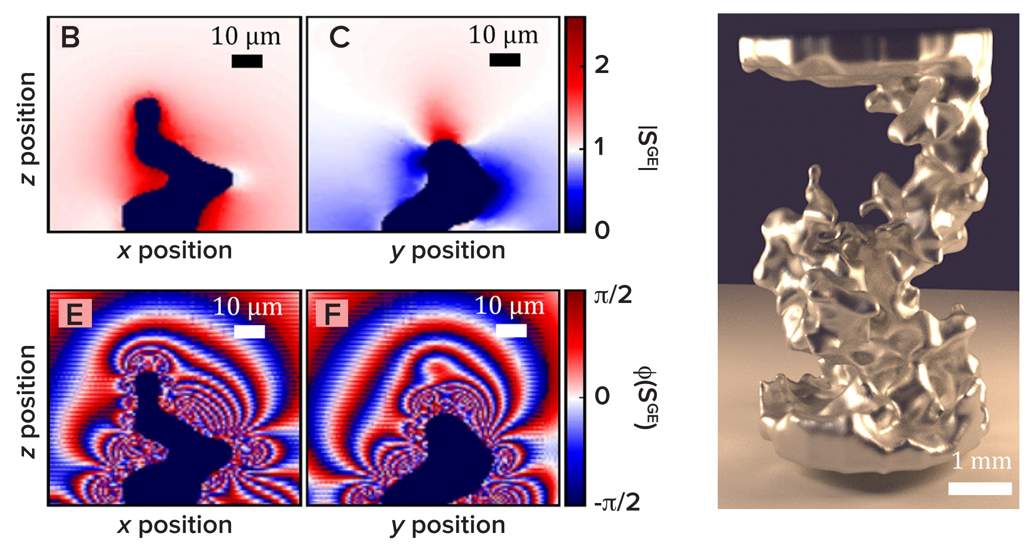
Reaction inhomogeneities induced by electrode structure is another avenue to complexity. In $Li_xMn_{1.5}Ni_{0.5}O_4$, another surprisingly fast charging and discharging cathode, the lithiation rate depends strongly on the exposed crystallographic plane, which is higher for (100) than (111).[25,26] The exposed crystallographic plane creates domains of inhomogeneous lithiation, with up to three distinct lithiation phases with different lattice constants in a single cathode particle. The local strains at the phase boundaries ultimately lead to fracture. As a further example, *in situ* transmission electron microcopy of lithiation-induced strain and fracture[27] showed that, rather than progressing uniformly, lithiation nucleates at a few points and spreads laterally, with continuous grain nucleation occurring along the moving interface. This nucleation creates highly concentrated stresses at the phase boundaries, which ultimately fracture films after a few cycles, though at a stage of degradation before it is reflected in the electrochemical behavior.

For these kinds of multi-phenomena, quantitative experiments only scratch the surface in uncoupling, quantifying, and recoupling the kinetic pathways of battery operation, degradation, and failure. Extension is needed to include thermal effects[28] on ion mobility and defect formation and phase nucleation at nanometer spatial and perhaps femtosecond-picosecond temporal resolution. X-ray free-electron lasers and ultrafast electron microscopy[29,30] enable such comprehensive experiments, capable of mapping the interplay of electronic, structural, electrochemical, mechanical, and thermal kinetics of degradation phenomena.

VISUALIZING *IN SITU* DENDRITE GROWTH WITH MAGNETIC RESONANCE IMAGING

Lithium metal anodes have arguably been a holy grail for battery technology, promising ten times higher charge storage capacity than standard graphite anodes and significantly higher energy density for conventional lithium-ion batteries and next generation lithium-sulfur and lithium-air batteries. The quest for viable Li metal anodes has been thwarted by dendrites, multi-branching tree-like structures that nucleate on the anode, grow across the electrolyte to the cathode on repeated charge-discharge cycling, and thereby short circuit the battery—a serious safety risk with flammable organic electrolytes. Enormous effort has been devoted to solving the dendrite challenge since their discovery in lithium batteries in 1976, so far without success.[53]

Magnetic resonance imaging based on the nuclear magnetic resonance of protons (^{1}H) in the liquid organic electrolyte surrounding the dendrite offers an innovative way to watch dendrites form and grow with higher space and time resolution than previously available.[24] Earlier approaches used nuclear magnetic resonance of ^{6}LI and ^{7}Li, which are only marginally sensitive to distinguishing surface and bulk morphology. The nuclear magnetic resonance of protons in the electrolyte, in contrast, is highly sensitive to the neighboring dendrite surface through shifts in the local steady magnetic field and the radio-frequency field. Isotropic resolution of 180 μm in a 16-min 40-s scan allows real-time 3D tomography, producing movies of dendrite nucleation and growth (see movie S1 in Ref. 24). Such high resolution *in situ* characterization tools offer the promise of observing in 3D and understanding dendrite nucleation on the otherwise flat anode surface and preferential growth of the dendrite tip, the two key phenomena enabling dendrite formation and growth.



(Left) Reconstructed variation of the nuclear magnetic resonance signal around a growing dendrite: (B and C) amplitude $|S^{GE}|$ and (E and F) phase $\phi(S^{GE})$. (Right) Reconstructed dendrite morphology, showing the branching and twisted growth path from anode (bottom) to cathode (top).

Image from A.J. Ilott et al., Real-time 3D imaging of microstructure growth in battery cells using indirect MRI, PNAS, **2016**, 113, 10779-10784.

Rare and Localized Events: Often, degradation and failure are associated with rare and localized events that initiate the process. Dendrite nucleation is an example, an event that cannot yet be predicted and whose origin remains unclear.[31-33] While dendrite nucleation itself is not immediately harmful to battery operation, the inexorable growth of the dendrite on charging and discharging eventually extends the conducting dendrite across the liquid or through the solid electrolyte, reaching the cathode and short circuiting the battery.[34,35] As another example, fracture is a sudden local event releasing accumulated strains that may have built up over tens or hundreds of cycles.[36,37] Exposure to heat, possibly due to local heating in the battery, can trigger a thermal runaway reaction that destroys the cathode and releases oxygen, which then reacts with the flammable liquid organic electrolyte.[38,39] Shown in Figure 2.5.6 are dramatic *in situ* images of thermal runaway, from the development of hot spots to venting of hot gases to ejection of molten liquids and destruction of the battery, as revealed by combined thermal and X-ray tomography.[39] This kind of multimodal dynamic *in situ* characterization allows the origin and combined thermal, electrochemical, and mechanical development of rare degradation events to be comprehensively studied. The safety consequences of such "sudden death" events are often sufficiently severe to stymie commercialization.

The need to understand rare and localized events is common in many areas of materials science, with phenomena such as nucleation, electromigration, and fracture being classic examples where experiment and theory have provided key insights. In the case of nucleation studies, highly sophisticated experimental approaches and advances in both statistical mechanics and density functional theory have led to direct measurements of homogeneous nucleation rates.[40] New advances in imaging of specimens in liquids have led to the direct observation of dendrite formation or "hot spots".[41,42] In the case of electromigration, experimental protocols that allow accelerated aging have been developed and validated, leading to improved approaches to prevent early failure.[28] An entire discipline of fracture mechanics has combined applied mechanics and specially designed testing approaches to yield measurable quantities that accurately describe the statistical nature of fracture failures.[43] Similar methodologies are needed more broadly in the energy storage arena to help classify and quantify how rare events occur, and how they are involved in the overall degradation of electrochemical energy storage materials.

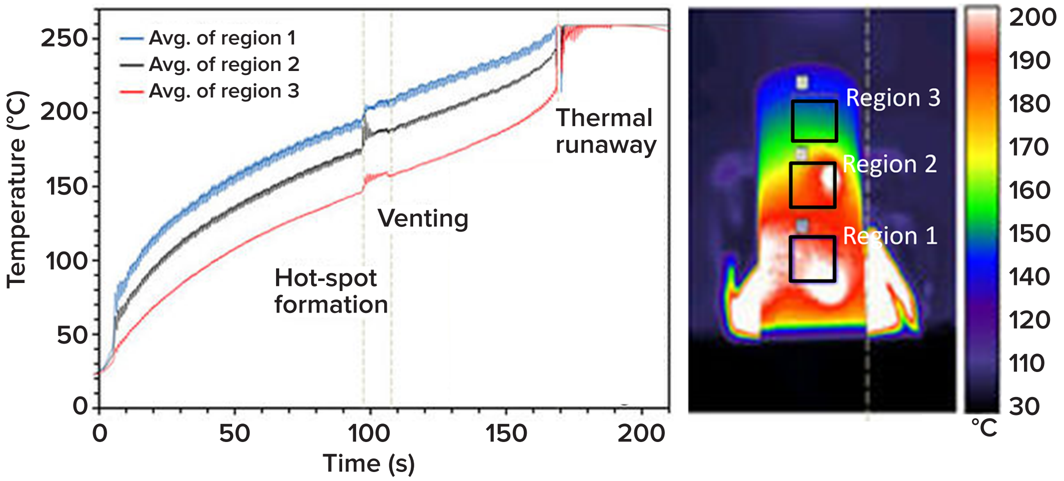


Figure 2.5.6. Real-time, *in situ* multi-modal thermal and X-ray computed tomography of events leading to thermal runaway in a commercial lithium-ion battery. Continuous external heating first produced a slow temperature increase (left), followed by formation of hot spots (right), electrochemical reaction of electrolyte and cathode, venting of hot gases and molten liquids, and finally mechanical destruction of the battery. From Ref. 39.

Thrust 5b: Multi-physics, Multi-scale, Predictive Continuum Models for Degradation and Failure

The various scenarios for battery degradation and failure have their origins in atomistic or mesoscale phenomena such as electrochemical reactions of individual molecules, strain buildup at phase boundaries, or dendrite nucleation at locally favorable sites. Modeling this chain of events requires much more sophisticated continuum modeling than now exists. More sophisticated continuum models capable of faithfully describing 3D meso- and macroscale behavior and coupling phenomena across relevant time and length scales are conspicuous needs for understanding battery operation, degradation, and failure and for identifying promising mitigation strategies. Such advanced continuum models need not be based on first principles as density functional theories typically are; instead, they can utilize empirical properties such as diffusivity or hardness from empirical material measurements or create response surface models from such measurements, which are then incorporated into larger continuum models.

The most common approach to modeling battery operation, degradation, and failure uses simple 1D approximations of electrochemistry, ion transport, mechanical stress, heat generation, and thermal transport at three length scales, as shown in Figure 2.5.7. At the cell level, 1D heat conduction occurs along the through-cell direction (radial for cylindrical cells). At the electrode pair level, mass and charge transport in the liquid electrolyte are described as 1D diffusion. At the particle level, ion transport is described as diffusion in the solid driven by the electrochemical intercalation reaction and a concentration gradient.[44] This model, often called the 1D+1D+1D or the pseudo-3D approach, can describe degradation at charging rates from 0.1 C to 10 C and surface temperatures from 25°C to 60°C, and accounts for energy storage and side reactions, such as SEI formation.[44,45] These modeling approaches, however, are at an early stage of development and certainly do not capture the consequences of 3D geometries that are present at multiple length scales in batteries.

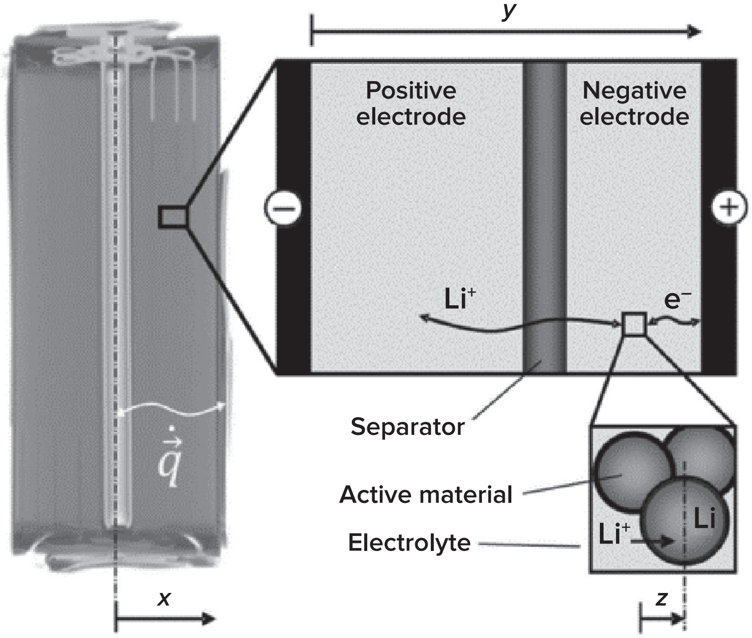


Figure 2.5.7. Three scales for modeling battery operation: macroscopic (cm) at the cell level (left), mesoscopic (100s of μm) at the electrode pair level (upper right), and microscopic (μm) at the particle level (lower right). From Ref. 44.

Solid-electrolyte interphase formation and growth at the graphite anode in Li-ion batteries can be modeled by accounting for initial formation and subsequent growth by slow penetration of solvent molecules through the interphase layer to reach and react with the graphite anode.[46] These kinds of models can account for capacity fade due to loss of working ions to continued formation of the interphase at the anode-interphase boundary, a common cause of gradual long-term degradation. One advantage of such models is their inclusion of reaction kinetics at elevated temperatures, allowing them to motivate the design of accelerated aging protocols. However, as 1D models they do not reflect the temporal changes in SEI structure when volume change in the electrode leads to cracking of the SEI and exposure of fresh electrode surface.

Fracture mechanics of electrodes due to local stresses arising from volume change or phase separation on cycling can be modeled with continuum phase-field approaches coupled to spatial solute distributions and stress profiles.[47] Typically, two-phase regions are intentionally avoided in intercalation cathodes precisely because they lead to local strain and fracture. The downside of avoiding two-phase regions is the significant restriction of theoretical intercalation capacity and reduced practical energy density. However, phase separation is a mesoscale rather than atomistic phenomena, requiring coherence over a finite volume to become energetically favorable. Reducing effective intercalation volumes to tens or hundreds of nanometers dramatically inhibits phase separation. Understanding and deploying this degradation mitigation approach require sophisticated continuum modeling.

Modeling the nucleation and growth of dendrites that can short circuit the battery is a major opportunity and challenge for batteries with pure metal anodes.[31] Continuum models of dendrite nucleation and growth are at a much earlier stage than models of intercalation.[48-50] Nevertheless, they have revealed many features of dendrite nucleation and growth that may lead to effective mitigation strategies, including current density vs. temperature thresholds for diminished dendrite growth, reduced dendrite growth in designed electro-convective flows in liquid electrolytes, and thresholds for dendrite formation as a function of ionic conductivity and current density in solid electrolytes. Modeling dendrite behavior needs to take into account many more phenomena, such as the shear modulus and grain structure of solid-state electrolytes, the conditions for dendrite nucleation, the influence of electrolyte composition and additives, and the role of solid-electrolyte interphases in modulating dendritic nucleation and growth. Self-healing triggered by preferential deposition of inactive cation additives by the higher electric field and potential at a dendrite tip is a promising smart mitigation effect.[31]

While many models deal with observed system-level performance degradation, such as capacity fade, described in terms of system-level diagnostic parameters, they do not consider fundamental local structural, electrochemical, mechanical, and thermal phenomena that govern system-level performance. As advanced *in situ* and *operando* experiments reveal this detailed knowledge, sophisticated multiscale models that incorporate the atomic and mesoscale phenomena into the degradation pathway need to be developed,[51] not only for Li-ion configurations but also for a diverse set of beyond Li-ion chemistries.[52]

A particularly exciting direction, likely facilitated by advances in modeling, would be the design of self-healing components, such as microstructures that gradually align to facilitate more facile ion transport through materials and across interfaces, additives that deploy on fracture to re-establish electrical conductivity among fragments, or materials that expand on heating to interrupt degradation phenomena such as overcharging or thermal runaway reactions. Proposing strategies to actively reverse degradation or enhance performance in real time is a major challenge and opportunity for degradation science.

2.5.4 REFERENCES

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3 Panel Reports for Next Generation Electrical Energy Storage

The *Basic Needs Workshop for Next Generation Electrical Energy Storage* was structured around six panels, including a panel focused on cross-cutting themes:

PANEL 1: PATHWAYS TO SIMULTANEOUS HIGH ENERGY AND POWER

PANEL 2: STRUCTURE, INTERPHASES, AND CHARGE TRANSFER AT ELECTROCHEMICAL INTERFACES

PANEL 3: IN PURSUIT OF LONG LIFETIME AND RELIABILITY: TIME-DEPENDENT PHENOMENA AT ELECTRODES AND ELECTROLYTES

PANEL 4: DISCOVERY, SYNTHESIS, AND DESIGN STRATEGIES FOR MATERIALS, STRUCTURES, AND ARCHITECTURES

PANEL 5: SOLID-STATE AND SEMI-SOLID ELECTRICAL ENERGY STORAGE

PANEL 6: CROSS-CUTTING THEMES

Each panel produced a report on the status of the field, scientific challenges and opportunities, and possible impact. These reports, presented in this chapter, formed the basis for identifying the five PRDs described in Chapter 2.

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3.1 Panel 1 Report — Pathways to Simultaneous High Energy and Power

Both the amount of energy stored, typically defined in terms of the volumetric or gravimetric energy density, and the rate at which that energy is delivered (power density) are critical aspects of electrochemical energy storage systems. The energy density determines how long the system can last between charges, while power density relates to how fast the energy can be extracted from or introduced into the system. Simultaneous high energy and power are required for many applications. For instance, batteries for electric vehicles must contain sufficient energy to enable a long driving range (>300 miles), but they also must feature high power capabilities for acceleration and fast charging (less than 15 minutes). For mobile power sources, consumers also demand extended operation between charging (high energy density) as well as fast charging capabilities. For grid-based energy storage, the energy and power demands vary greatly depending on the specific point of integration within the grid. Fast charging is needed to respond to and accommodate the unpredictable variation of the output from renewable energy sources. Deep charge and discharge cycling is required for load leveling and cyclical day-night storage. Regardless of the application, an exceptionally long cycle life is required to reduce the cost for energy storage. To achieve the goal of simultaneous high energy and power, improved understanding of how energy and power are determined by materials and component behavior across length scales within battery cells is urgently needed.

3.1.1 CURRENT STATUS AND RECENT ADVANCES

Simultaneous high energy and power require deep understanding of fundamental scientific issues. The near-universal relationship between power and energy across a variety of energy storage systems is illustrated in the Ragone plot in Figure 3.1.1.[1] The energy density of a given electrochemical energy storage system is intrinsically governed by the quantity of ions that participate in the electrochemical reactions, the molecular weight or volume of the active materials, and the electrochemical potential difference between different electrodes. The power capability is limited by how quickly ions and electrons can be transported in the bulk and across different interfaces within the system. Ion transport is usually much slower than electron transport and is dependent on a number of factors, including the kinetics of phase transformations within active materials, impedance at interfaces, tortuosity and arrangement of particles within electrodes, and the "transference number" (the fraction of the total current carried either by the anion or the cation) of ions in electrolytes. Conventional high-power batteries are realized by using thin electrodes that include significant volume fractions of electrically and ionically conductive materials, including void spaces to accommodate electrolytes. This formulation balances the diffusion length of the electrons and ions but also decreases the volume available for the materials that are storing energy, thus resulting in lower energy density. High energy systems are produced in a converse fashion, which normally requires increasing the amount of active materials and increasing the electrode thickness, along with reducing the amount of conductive additives and void space. The resulting high internal resistances reduce the available power and increase the possibility of electrode failure. Although a large body of literature has been focused on developing high energy electrode materials, less attention has been paid to the electron and ion transport problems for high energy structures in which the utilization rate of active materials needs to be high.[2-4] There is thus a significant need to advance the synthesis and understanding of stable architectures to simultaneously provide energy and power.

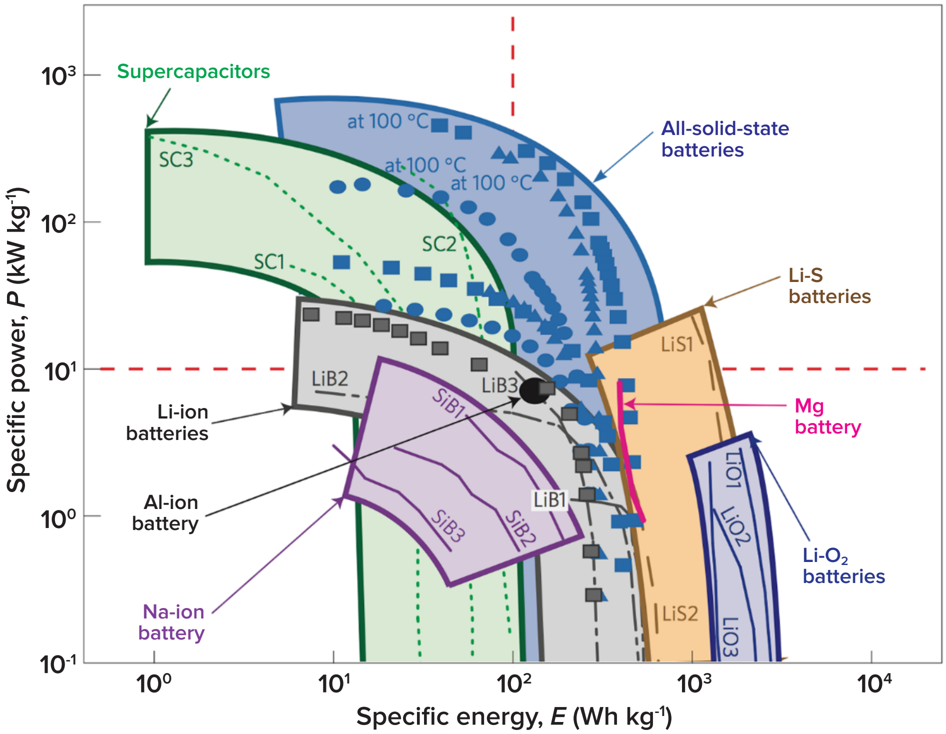


Figure 3.1.1. Ragone plot showing the specific power and energy of a variety of current and emerging electrochemical energy storage systems. From Ref. 1. Reproduced with permission of Nature Publishing Group.

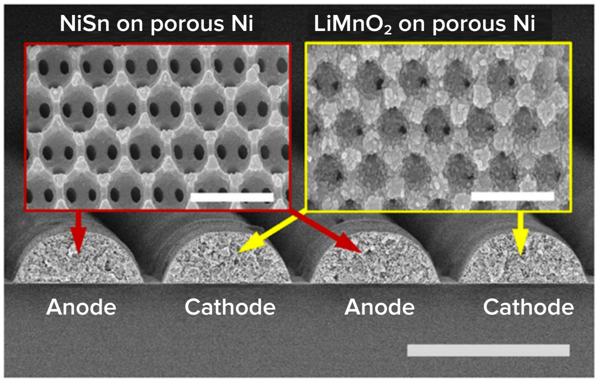
In recent decades, there has been some progress towards energy storage with both high power and energy density. Advances in the discovery and synthesis of solid-state electrolyte materials[5-8] have shown that all-solid-state cells with improved power and energy density compared to Li-ion batteries are a tantalizing possibility, but this success has so far been mostly limited to thin film architectures. Recent advances relating to the addition of interfacial phases between electrodes and solid-state electrolytes to reduce interfacial resistance may provide clues for increasing solid-state battery thickness and energy density.[9] However, a new fabrication and manufacturing paradigm, quite different from the technologies that are used today, is perhaps needed to scale up solid-state battery architectures for energy storage. Several possibilities are emerging or can be foreseen, including thick film/particulate electrolyte and electrode layers, hybrids of thick film structures with thin film interlayers, thin-film 3D structures, and multilayers of solid-state batteries.

In traditional liquid electrolyte-based batteries, new mesoscale electrode architectures have also shown higher power capabilities, and in some cases higher energy density, with both conventional and next generation electrode materials (see “Electrode Architectures” sidebar). Such architectures include alternating lateral mesostructured electrodes,[10] electrodes with aligned porosity[11] and/or active materials that reduce ion diffusion lengths,[12] and microscale secondary particles made up of nanoscale primary active particles.[13,14] Novel electrolyte concepts, such as solvent-in-salt electrolytes, have improved ion transport through electrode/electrolyte interfaces in both aqueous and non-aqueous media.[15,16] Finally, decoupling energy and power via the use of flow cell architectures provides an alternative pathway to balancing and improving energy and power concurrently from a cell design point of view,[17] although the overall energy density of redox flow batteries is much lower than traditional Li-ion batteries.

Despite these recent breakthroughs, simultaneous high power and energy performance sufficient for current and emerging applications has not yet been achieved. It is evident that overcoming energy-power coupling is a complex issue that requires fundamental breakthroughs in materials synthesis and understanding of the charge transport properties and failure modes in complex electrode architectures. Today’s electrochemical systems are limited by relatively long ion/electron transport distances, slow electrochemical reaction kinetics, and the necessary use of separate phases to conduct ions and electrons. To overcome these issues, entirely new concepts and ideas are necessary to develop new multifunctional materials and to integrate nanostructures across multiple length scales to form new architectures. Furthermore, basic research and new techniques are necessary to understand fundamental energy storage mechanisms and dynamic (non-equilibrium) processes within electrochemical systems. As an example, it is critical to develop new methods to design and assemble tailored electrode and system architectures, which will enable improved understanding and control over ion transport kinetics throughout the entire system. Advances towards higher power/energy also require improved understanding of the various aspects that limit kinetics within cells, including structure-property relationships at interfaces, the nature of phase transformations in active materials, and ion/electron transport within complex electrode architectures. Fundamental research to tackle these pressing challenges will establish the scientific basis for the future development of energy storage systems with both high energy and power, as well as the ability to tailor energy/power combinations for a wide variety of applications. As detailed in the “Scientific Challenges and Opportunities” section below, understanding the physical and chemical mechanisms that lead to simultaneous high energy and power will provide rich opportunities for scientific discovery in the years to come.

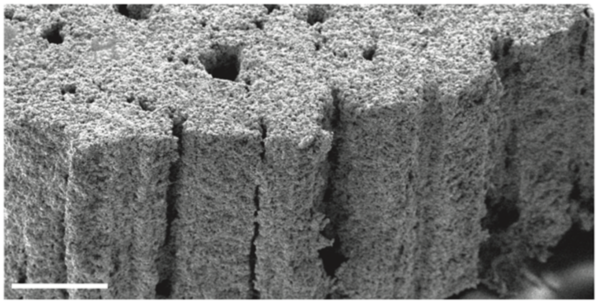
ELECTRODE ARCHITECTURES

Electrode architectures for high energy and power. Novel electrode architectures are being investigated for electrical energy storage with higher energy and power. Examples include:



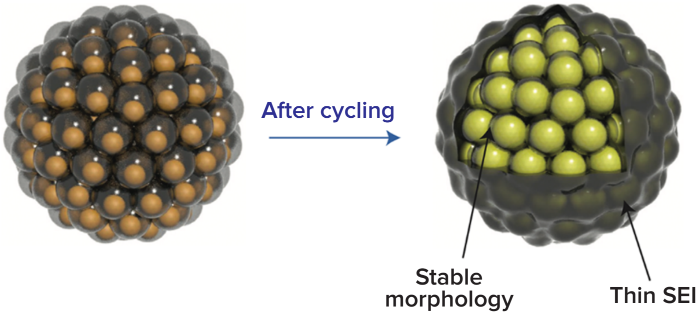
Top: Interdigitated bicontinuous porous electrodes combined on a substrate to form a full lateral battery. Scale bars: 50 μm, inset: 1 μm.

From J.H. Pikul et al., High-power lithium ion microbatteries from interdigitated three-dimensional bicontinuous nanoporous electrodes, Nat. Commun., **2013**, 4, 1732.



Middle: Magnetically-aligned LiCoO$_2$ electrode with controlled porosity. Scale bar: 100 μm.

From J.S. Sander et al., High-performance battery electrodes via magnetic templating, Nat. Energy, **2016**, 1, 16099.



Bottom: Secondary microscale particles containing primary nanoscale particles for mitigating volume changes and enabling long stability and relatively high power in high capacity anode materials.

From N. Liu et al., Pomegranate-inspired nanoscale design for large-volume-change lithium battery anodes, Nat. Nanotechnol., **2014**, 9, 187–192.

3.1.2 SCIENTIFIC CHALLENGES AND OPPORTUNITIES

There are multiple research areas in which sustained effort could result in significant advances towards simultaneous high energy and power performance in next generation electrochemical systems. Three topics with significant scientific challenges and opportunities are discussed here.

New Materials and Architectures for Simultaneous High Power and Energy: One of the most promising pathways to high power and energy is the discovery of new materials and architectures that feature high capacity while also enabling fast ion motion. Fundamental questions that should drive research in this area are as follows:

- ☐ How can materials and architectures be arranged so that ion and electron transport is facile, enabling rapid charge/discharge to enhance power and energy simultaneously?
- ☐ What synthesis and fabrication pathways, from the nanoscale level to mesoscale assembly, can be identified as viable?

These questions pertain to all components of a battery, including active materials, binder, additives, electrolyte, and current collectors. Rethinking the function of each component, designing new materials with multiple functions, and controlling behavior across length scales each have the potential to lead to simultaneous high power and high energy. Various research areas of interest are detailed below.

Controlling nanoscale architecture: A variety of electrode materials with high specific capacity have been developed in recent years, such as $LiFePO_4$ and nickel-rich layered lithium transition-metal oxides. However, their applications for high-power and long-cycle-life lithium-ion batteries have been hindered by kinetic limitations or poor stability. Developing nanostructured electrode materials is a promising way to overcome these drawbacks owing to the unusual mechanical, electrical, and chemical properties of nanomaterials endowed by their confined dimensions.[18] In batteries, nanostructured electrode materials offer the potential for high electrode/electrolyte interfacial area, the ability to accommodate mechanical strain upon lithium insertion, and reduced path lengths for lithium-ion/electron transport through the material, which can lead to high rate capability.[19] For example, the rate behavior of bulk (~1-10 μm dimensions) $LiFePO_4$ materials is significantly restricted by sluggish electron and lithium-ion transport kinetics. Reducing the particle size to the nanoscale (~100 nm) can significantly shorten the diffusion time of Li^+ ions in $LiFePO_4$. When further combined with carbon coating, the power performance of $LiFePO_4$ can be greatly enhanced (Figure 3.1.2a).[20] In another example, to overcome poor thermal stability of nickel-rich layered lithium-transition metal oxides, nanoscale composition gradient structures have been created in which the nickel concentration decreases linearly and the manganese concentration increases linearly from the center to the outer layer of each particle. This complex structure enables high rate capability and cycling stability (Figure 3.1.2b).[21] Although nanomaterials can provide power and energy advantages, their higher specific surface area often results in increased side reactions and lower coulombic efficiency (especially for negative electrode materials). Such disadvantages are a significant challenge that needs to be overcome for maximum technological impact. For examples like this, a worthy goal is to identify design guidelines that prescribe energy and power metrics as a function of the materials distribution in electrode particles.

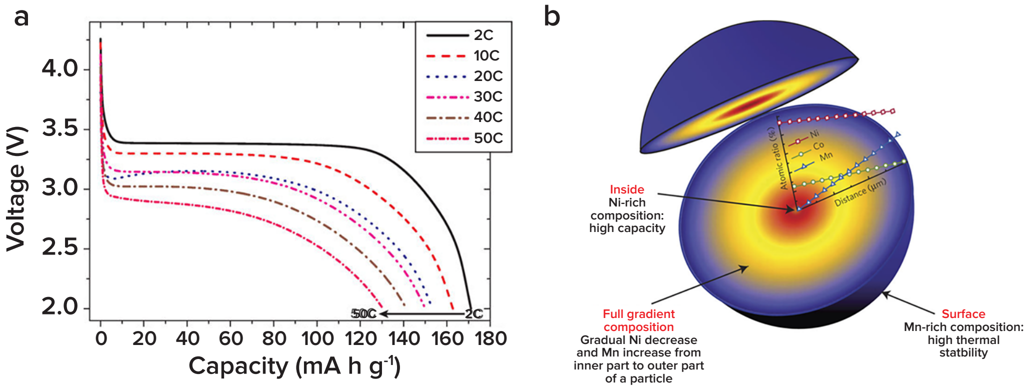


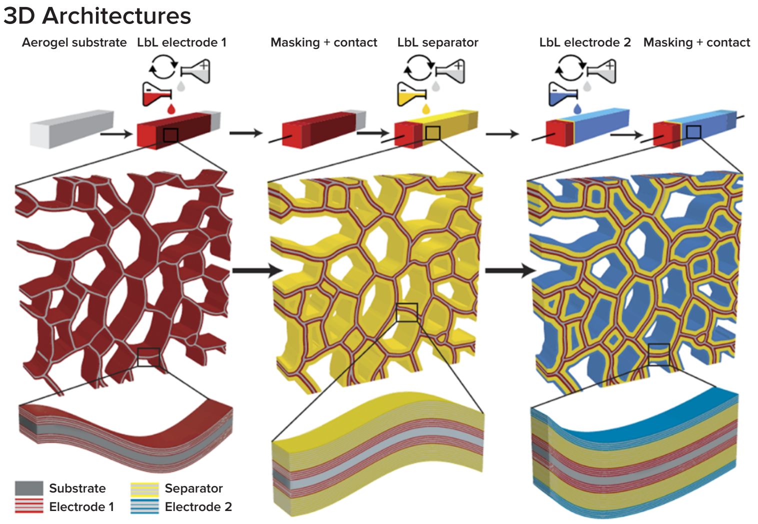
Figure 3.1.2. (a) Galvanostatic discharge curves at different rates for nanoscale carbon-coated $LiFePO_4$. From Ref. 20. (b) Controlled nanoscale composition gradients in a nickel-rich layered lithium-transition metal oxide particle. From Ref. 21.

3D synthesis: Thick electrodes with minimal conductive additives and low porosity are desired for high energy density, but the maximum power is then largely determined by ion transport and reaction kinetics. Reducing the distances for ion and electron transport, as well as maximizing charge transfer kinetics at interfaces, is a highly effective pathway to increased power capability. In current Li-ion battery cathodes, ion transport in electrolytes occurs over distances of ~10 to 100 µm. However, high tortuosity due to randomly packed electrode particles makes the effective transport length 3-5 times longer.[12] Modeling and experiments have established that in sufficiently narrow pores ion transport in electrolytes represents the rate-limiting step that determines battery power,[22] so that reducing tortuosity in porous media is a key to directional transport to improve power. Once pore dimensions rise from nanometers to tens of nanometers, however, ion transport in electrolyte is facile, and electron/ion transport in electrodes becomes limiting.[11]

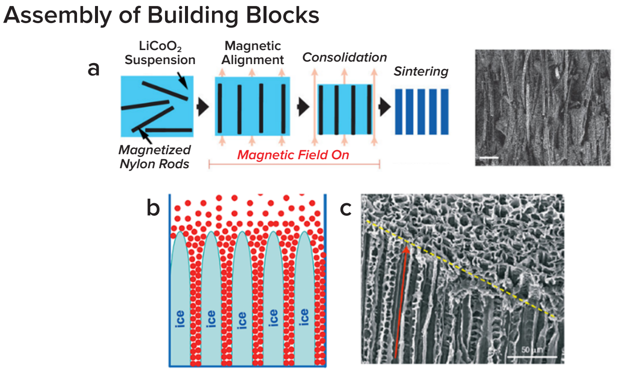
3D ARCHITECTURES AND ASSEMBLY OF BUILDING BLOCKS

The top figure shows a layer-by-layer process to assemble 3D battery electrodes. An electrically conducting scaffold, such as a carbon nanotube aerogel, is coated with electroactive and electrolyte layers using the layer-by-layer process. Such integrated anode/electrolyte/cathode structures can allow for high power.

From G. Nyström et al., Self-assembled three-dimensional and compressible interdigitated thin-film supercapacitors and batteries, Nat. Commun., **2015**, *6, 7259. Reproduced with permission of Nature Publishing Group.*



The lower figure shows processes for assembling nano-to-microscale building blocks into mesoscale electrode architectures. (a) Schematic of magnetic field driven growth of aligned porous structures. Scale bar: 100 µm. (b-c) Schematic of directional freezing and scanning electron microscopy image of the resulting porous structure. Scale bar: 50 µm.



From J. S. Sander et al., High-performance battery electrodes via magnetic templating, Nat. Energy, **2016**, 1, 16099; *H. Zhang and A.I. Cooper, Aligned porous structures by directional freezing,* Adv. Mater., **2007**, 19, 1529-1533 *(copyright Wiley-VCH Verlag GmbH & Co. KGaA, reproduced with permission).*

Reducing ion and electron transport lengths and maximizing the electrode/electrolyte interfacial area while minimizing inactive components necessitate a shift from the conventional layered sandwich structure to a 3D interpenetrating network in which bicontinuous cathode and anode phases are separated by a continuous electrolyte layer.[23,24] Such a concept has been proposed for microbatteries, and fabrication techniques so far are dominated by lithography.[23] These 3D electrode architectures have been realized with lithography or assembled nanomaterials (0, 1, and 2D), but reports on complete devices based on interpenetrating cathode and anode structures are rare. An experimental example of such a structure was formed via colloidal templating of a mesostructured metal foam, which was then coated with an electrochemically active cathode material. This structure provides for fast electron transport and a 3D interconnected pore network for transport of ions, enabling high-power charge and discharge.[2,25,26] However, this structure contains too much porosity and is highly tortuous. The loading of the active material is below that of commercial electrodes, and the metallic current collector is rather heavy; these factors reduce the overall energy density compared to commercial cells. There are now an expanding number of reports that address some of these issues; for instance, one study replaces the metal current collector with a graphene current collector.[27] Another example of 3D battery structure synthesis is shown in the sidebar, “3D Architectures and Assembly of Building Blocks.” Despite progress, much work remains to be done. Infilling high quality electrode and/or electrolyte materials into a 3D architecture is challenging, and scalable approaches for forming 3D structures with low porosity and tortuosity remain to be discovered. Designing scalable bulk fabrication processes for architectured batteries with internal length scales of nano- to micrometers is thus needed.

Directional assembly of building blocks into mesoscale architectures: Another approach for high energy and power is thick electrode architectures with oriented materials alignment and porosity.[28] In commercial Li-ion batteries, the repeated electroactive stack consists of porous positive and negative composite electrode films (50–100-μm thick) sandwiched between two current collector foils and electronically isolated by a polymer separator film. The energy density can be improved by increasing the packing density and the thickness of the electrodes. However, progress towards thicker, higher capacity-per-area electrodes has been severely constrained by both transport and manufacturing considerations. Ion transport through the liquid electrolyte-filled pore network is limited in thick/dense electrodes, and high tortuosity is generated due to the calendaring process that compresses electrodes in manufacturing. Structures with anisotropic pores preferentially aligned in the transport direction can solve these problems by enabling faster transport with high structural density and by producing low tortuosity normal to the plane of the electrode.

Aligned porosity can be fabricated with novel synthetic and assembly techniques such as external field-guided alignment (either magnetic, electric, or mechanical) and directional freeze drying. For example, electrodes with directionally oriented electrode materials have been prepared by dispersing a sacrificial magnetic phase in an electrode particle suspension, subjecting the suspension to an external magnetic field to achieve anisotropic ordering, and then removing the sacrificial agents to leave anisotropic porosity (see “3D Architectures and Assembly of Building Blocks” sidebar).[12] Directional freezing has also been used to prepare aligned porous structures.[29,30] A final example is synthesis guided by an electrostatic field, in which the direction and size of growing crystals can be tuned by different electrostatic field directions and intensities.[31] These techniques are a guide for the discovery and development of new guided assembly methods that can enable unprecedented control over electrode mesostructure, with the potential for manufacturability.

Multifunctional materials: Another useful goal for energy storage systems with high energy and power is the development of individual electrode components that intrinsically provide more than one required property or function. The motivation for such work is that a system which simultaneously provides both high energy and high power must contain a maximized fraction of electrochemically active materials while minimizing inactive components (e.g., binder and conductive additives); multifunctional materials are one way to minimize inactive components.

One such example is the development of multifunctional binders for Li-ion batteries. Traditional binders exhibit limited capability to accommodate the significant volume changes that take place during electrochemical reactions of high-capacity active materials within electrodes. A preferred binder for high-capacity electrodes should provide high electronic and ionic conductivity, as well as interfacial adhesion and substantial tolerance to mechanical deformation (Figure 3.1.3a).[32] A new conceptual design for a multifunctional binder was recently developed on the basis of combined chemical synthesis, quantum calculations, and spectroscopic and mechanical experimental tools.[33] The chemical and electronic structures of the conductive polymer binders were tailored by introducing different functional groups for separate purposes (e.g., adhesion vs. electrical conductivity), as shown in Figure 3.1.3b. The resulting polymer exhibits improved electronic and mechanical properties as well as enhanced electrolyte uptake, thus realizing full capacity cycling of the embedded commercial Si particles (3,750 mAh/g). Recently, a multifunctional conductive polymer gel was also adopted as the binder framework to improve the rate capability and cycling stability of high-capacity electrodes. The conductive gel binder promotes electron transport through continuous pathways, facilitates ion transport through hierarchical pores, and improves the electrode dispersity via conformal coating.[34-36] However, despite progress in developing multifunctional binders, more work is needed on discovering binder materials that are elastic enough to maintain stable electrode architectures for large-volume-change anode materials while also binding strongly to surfaces.

Beyond binders, multifunctional active electrode materials with high ionic and electronic conductivity could also enable entirely new battery architectures. For instance, the $LiCoO_2$ cathode material for Li-ion batteries is known to possess sufficient electronic and ionic conductivity to enable the use of large $LiCoO_2$ particles, but conventional batteries still feature composite electrodes ($LiCoO_2$ + carbon black + binder). Recent work has demonstrated that a new direct electrodeposition process can create relatively thick (tens of microns), nearly dense $LiCoO_2$ electrodes that have good power capabilities and superior capacity compared to conventional $LiCoO_2$ cathodes (Figure 3.1.3c).[37] Such innovative synthesis methods and architectures, combined with the development and use of multifunctional materials, could enable breakthrough power and energy performance.

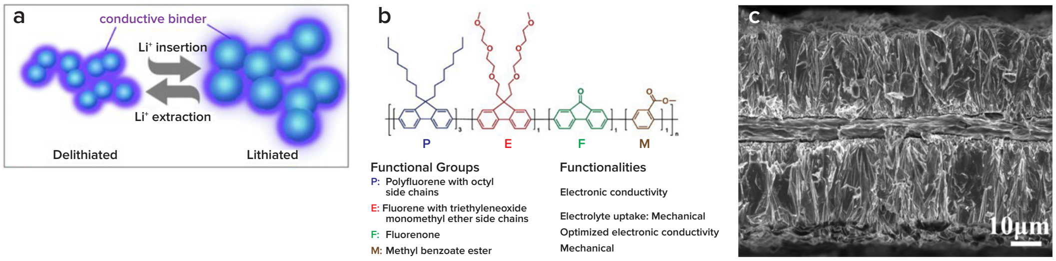


Figure 3.1.3. (a) Schematic of a multifunctional binder system for high-capacity battery electrodes. From Ref. 32. (b) Synthetic scheme illustrating the function of the chemical groups comprising the polymeric binder. From Ref. 33. (c) Thick, nearly dense $LiCoO_2$ films electrodeposited on both sides of an aluminum current collector. From Ref. 37.

Materials Exhibiting Multiple Charge Storage Mechanisms: In an electrochemical energy storage system, energy is stored via ion insertion into a material (faradaic reaction) or by ion adsorption in the electrical double layer at the surface of the electrode material (capacitive reaction). Faradaic insertion reactions traditionally occur in batteries, while capacitive charge storage occurs in electrical double layer capacitors. The kinetics of capacitive vs. faradaic reaction mechanisms gives rise to the different power capability of these different systems, with electrical double layer capacitors exhibiting higher power densities than batteries. However, capacitive storage is restricted to the electrode/electrolyte interfacial area within electrical double layer capacitors, and this, in turn, limits the total available energy stored. Materials that exhibit multiple charge storage mechanisms hold great promise to overcome these conventional boundaries and meet the dynamic power and energy demands of emerging energy storage applications, such as electric vehicles and renewable energy storage. However, utilizing such materials will require improved fundamental understanding of the interplay of different mechanisms, as well as the discovery and development of new heterostructured materials that can operate via different charge storage mechanisms at different rates. A few important research areas are discussed here.

Faradaic insertion reaction mechanisms can be further divided into intercalation, alloying, and conversion reactions. Intercalation involves the insertion and removal of charge-carrying ions within the relatively invariant crystal lattice of a material. Alloying and conversion reaction mechanisms deliver much higher specific capacities, as they involve insertion of ions and complete transformation of an active material to a new phase or phases. They often feature much larger volume changes, and their cycle life has traditionally been inadequate compared to intercalation reactions.[39-41]

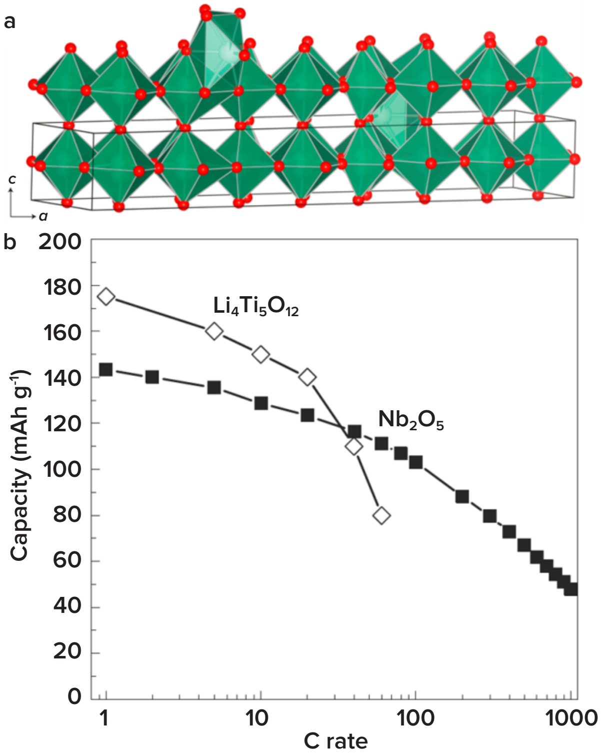


Figure 3.1.4. (a) Crystal structure of T-Nb_2O_5 stacked along the c-axis showing the layered arrangement of O (red) and Nb (inside polyhedra) atoms along the a-b plane. The empty octahedral sites between (001) planes provide natural tunnels for rapid Li^+ ion transport throughout the a-b plane. (b) Comparison of the rate capability of T-Nb_2O_5 with a high-rate lithium-ion anode, $Li_4Ti_5O_{12}$, at various C-rates. From Ref. 38.

An additional charge storage mechanism that has been investigated is known as pseudocapacitance, which broadly describes rapid and reversible Faradaic reactions that feature charge/discharge profiles that mimic those of electrical double layer capacitors.[42] In this sense, pseudocapacitors represent a clear example of materials exhibiting multiple charge storage mechanisms. Pseudocapacitive reactions are often near-surface reactions that occur with fast kinetics, and they can feature higher capacitance than pure double-layer charge storage.[43] Nanostructured materials that are thin enough can exhibit primarily pseudocapacitive behavior, which can result in increased power performance.[44] A related reaction mechanism, intercalation pseudocapacitance, represents a novel type of reaction that combines advantageous features of both high-power capacitors and high-energy batteries.[38] The intercalation pseudocapacitance mechanism involves electron transfer reactions and ion insertion within the bulk with fast, pseudocapacitance-like kinetics. This is enabled by crystal structures that have open transport pathways and negligible structural changes upon intercalation. T-Nb_2O_5 nanocrystals were the first nanomaterials demonstrated to exhibit intercalation pseudocapacitance (Figure 3.1.4), and this list has expanded to include other oxides, nitrides, carbides and metal phosphates.[45-47] Electrode materials that exhibit intercalation pseudocapacitance hold the promise of achieving relatively high capacity (although not as high as alloying/conversion materials) combined with the cycle life and power density of electrical double layer capacitors.

Intercalation pseudocapacitance offers combined high energy and power, but there are a limited number of materials that exhibit this mechanism. A way to expand the number of active materials fundamentally capable of exhibiting high energy and power is to discover and develop individual or heterostructured materials that are capable of exhibiting multiple charge storage mechanisms. These materials would be useful for applications that require different rate capabilities at different times, and their use in a single system would likely result in decreased cost compared to the alternative of separate batteries and supercapacitors. The rational design of heterostructured nanomaterials is a promising strategy to achieve multiple charge mechanisms in single structures.[48,49] One major advantage of designing and using heterostructured materials is the synergistic improvement of the intrinsic properties of each component for better electronic conductivity, faster ionic transport, greater electrochemical reversibility, and overall cycling stability. Owing to these advantages, pseudocapacitive heterostructured materials are currently considered to be potential candidates for electrodes that exhibit simultaneous high power and high energy.[45]

Beyond pseudocapacitance, there is also growing interest in 2D materials for electrochemical energy storage, because they offer fascinating physical and chemical properties that are particularly appropriate for ion storage.[50,51] 2D materials show high redox activity during intercalation processes,[52] but they can suffer from irreversible restacking/agglomeration, which can lead to capacity degradation with cycling and sluggish ion transport. 2D heterostructures may be a possible solution to overcome this major limitation, and pursuit of such materials could open up new opportunities for creating electrodes with simultaneous high energy and power capability. By combining the metallic electrical conductivity of graphene and MXenes (a class of materials that includes 2D transition metal carbides, carbonitrides, and nitrides[53]) with the high redox activity of transition metal oxides or chalcogenides, stacked 2D heterostructures with attractive energy storage characteristics can be realized. Stacked 2D heterostructures containing different active materials have been shown to demonstrate various energy storage mechanisms, including surface adsorption/desorption, intercalation pseudocapacitance, and bulk storage (Figure 3.1.5). Moreover, 2D heterostructured nanosheets with enlarged interlayer distance can also improve the insertion/extraction of large radius (e.g., Na^+ and K^+) or multivalent ions (e.g., Mg^{2+} and Al^{3+}), and they can potentially make the electrodes more tolerant to cycling-induced volume changes.

Novel Materials and Architectures for Decoupled Energy and Power: Traditional batteries are made of solid electrode materials and liquid electrolytes. Several different approaches have been explored to overcome the fundamental barriers to high power associated with thick solid electrode materials. An important research direction that could bypass this challenge involves moving from solid electrode materials towards liquid-like electrode materials.

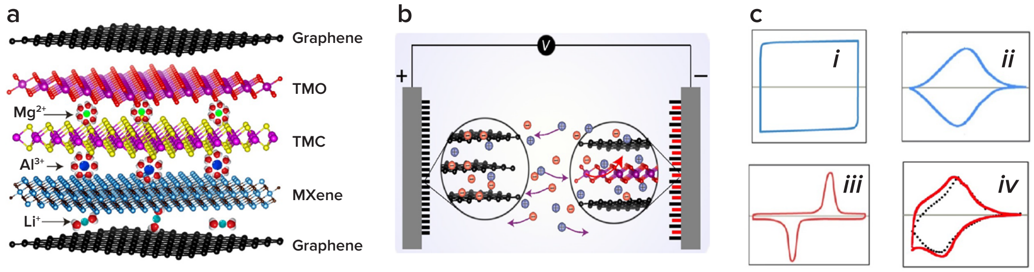


Figure 3.1.5. (a) Schematic of a stacked 2D heterostructured material. 2D transition metal oxide or chalcogenide (TMO or TMC) materials show high redox activity due to their large surface areas and facile ion intercalation, but their electrical conductivity can be limiting. 2D heterostructures combining the metallic electrical conductivity of graphene or MXenes, along with the high redox activity of TMOs/TMCs, can achieve a synergistic enhancement of mechanical, electrical, and electrochemical properties. Furthermore, by incorporating different 2D nanomaterials, different charge storage mechanisms may be exhibited. For instance, graphene nanosheets are promising electrodes for electrical double layer capacitors (b, left electrode), and the corresponding electrical double layer capacitors storage mechanism can be characterized by the classic rectangular cyclic voltammograms (*i* in panel c). 2D heterostructures stacked with graphene and other 2D nanosheets (b, right electrode) that exhibit pseudocapacitive and/or ion intercalation properties (shown by the cyclic voltammogram curves in panel c, *ii* and *iii*, respectively) can efficiently store energy through intercalation pseudocapacitance, demonstrating ion intercalation/deintercalation peaks with large areas enclosed in the cyclic curves (*iv* in panel c). 2D heterostructures with large and fast intercalation pseudocapacitance are expected to achieve battery-level energy density combined with the cycle life and power density of electrical double layer capacitors. Images courtesy Guihua Yu, University of Texas, Austin.

The redox flow battery represents a promising type of energy storage system to manage energy and power.[17] The quantity of energy is determined by the volume of the storage tanks that hold the redox species, and the power capabilities are independently determined by the design of the electrode stack over which the redox species flow (see "Flow Systems" sidebar). Therefore, the energy and power are decoupled in such systems. High energy and power in redox flow batteries critically rely on advanced electrolyte design and electrode-to-system level architectures.[54] Although redox flow batteries have been developed and deployed for grid scale energy storage, more extensive implementation is hindered due to insufficient energy density, power density, coulombic efficiency, and cycling stability. To overcome these challenges, advances in electrolyte design, redox species, and flow cell architectures are necessary.[55] A few promising research directions are discussed below.

Prediction of molecules that exhibit high electrochemical reversibility: Molecules with high redox reversibility are necessary for long cycle life in practical flow batteries.[56] Developing new redox molecules and understanding reaction mechanisms require advanced computational modeling and detailed electrochemical characterization.[57] Elucidating the stability of reaction intermediates and products with computational methods should provide reasonable predictions regarding the reversibility of molecules, which could then be tested experimentally.[56,58]

Membranes with controlled ion selectivity: Membranes play key roles in governing the cycle life, coulombic efficiency, and power density of flow-based energy storage systems. Understanding and precisely controlling pore size, membrane charge, and surface chemistry to influence ion selectivity represent promising methods to meet the strict requirements for next generation flow systems. Research integrating organic chemistry, inorganic chemistry, analytical chemistry, and polymer science is needed for breakthrough advances.[55,59]

Mixed-conducting solutions and suspensions: In addition to conventional flow systems based on high concentration catholyte/anolyte solutions, flow systems can utilize mixed-conducting (ionic and electronic) solutions or even suspensions of solid materials.[60,61] Superior energy density is expected for such systems due to high concentrations of redox species, and exceptional power density is enabled by the mixed-conducting electrolyte with carbon additives. Improved understanding of viscosity, fluid mechanics, and aggregation behavior of suspensions is central to the design of new battery architectures. Such systems could broaden the scientific and technological impact of flow-based energy storage devices.

FLOW SYSTEMS

Flow Systems — Redox Flow Battery

A typical redox-flow energy storage system is composed of two tanks containing redox species dissolved in liquid; these are termed *anolyte and catholyte* (see top schematic to the right). The battery is charged or discharged by pumping the anolyte/catholyte through an electrode stack while separating the anolyte/catholyte with an ion-selective membrane. The performance of such a device is governed by the inherent properties of electroactive species as well as electrochemical engineering of the system. The redox flow battery stands out as one of the most promising candidates for stationary energy storage with high scalability and decoupled control of energy and power. Energy is dictated by the size of the reservoir storing electrolyte, and power is regulated by the electrode stack and the size of current collectors.

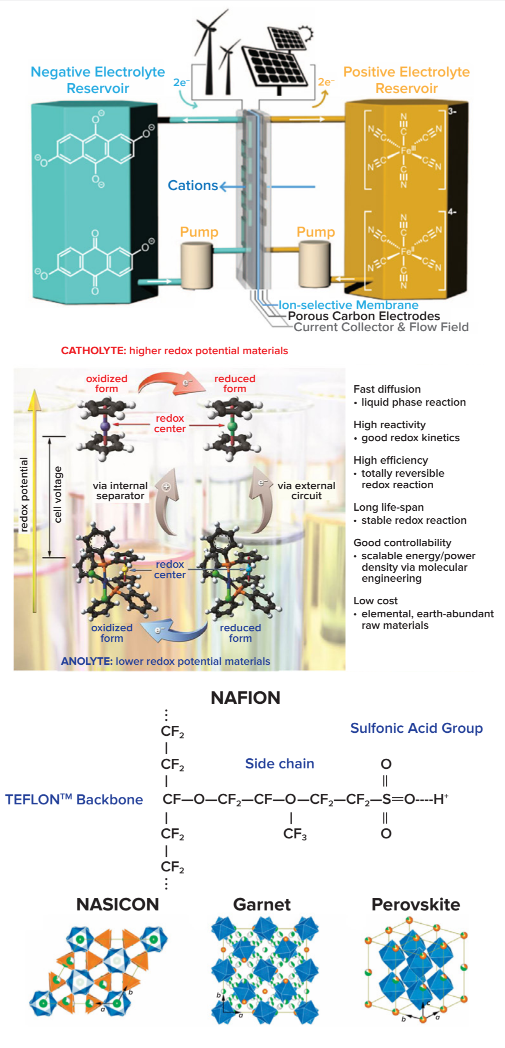
Image from K. Lin et al., Alkaline quinone flow battery, Science*,* **2015**, 349, 1529.

Redox Molecules

The performance of redox flow storage systems is largely determined by the catholyte and anolyte redox species. Electroactive redox molecules must exhibit high diffusion rate, fast reaction kinetics, electrochemical reversibility, stability, scalability, and low cost (see middle schematic to the right, courtesy Guihua Yu, University of Texas, Austin).

Membranes

In addition to the electrode materials, ion-selective membranes are also a critical component of flow batteries. There are two general classes of materials used for membranes: polymer-based separators (e.g., NAFION) and ceramic-based solid-state electrolytes (e.g., NASICON, garnet, and perovskite Li^+ or Na^+ conductors – see structures at bottom of accompanying figure). Future membranes should be designed to incorporate features from these two classes of materials, including the high ionic conductivity and durability of polymers and the high selectivity and rigidity of ceramics.



From Y. Zhao et al., A chemistry and material perspective on lithium redox flow batteries towards high-density electrical energy storage, Chem. Soc. Rev.*,* **2015**, 44, 7968-7996. *Reproduced with permission of Royal Society of Chemistry.*

Expanding solubility windows and tuning reaction kinetics: Recently, organic redox species have emerged as promising electroactive materials for redox flow batteries.[62,63] In addition to the potentially low cost and ease of scalability, the structural and chemical diversity of organic molecules allows for the tailoring of both the chemical and physical properties of electrode materials.[64] For example, the solubility of molecules can be modified by altering functional groups with controlled polarity, and the reaction kinetics is affected by molecular diffusion and electron-transfer processes, both of which are impacted by molecular size and ligand effects.[65]

Designing solid electrolytes to be compatible with anolytes/catholytes: Compared with conventional polymer-based membranes, ceramic solid electrolytes provide increased freedom to select redox species and corresponding solvents while still conducting ions of interest.[8,54] Moreover, ceramic solid electrolytes may significantly reduce crossover of redox species due to their high ion selectivity. To realize wide application of solid electrolytes in flow systems, fundamental research is needed to understand the physical and chemical processes that occur at the interfaces between the solid electrolyte and the anolyte/catholyte.[55]

Semi-solid batteries: Although conventional flow batteries have liquid electrodes, solid electrode materials can be made to flow in suspension. Duduta et al.[61] have explored the semi-solid redox-flow battery architecture using thick suspensions made of Li-ion battery electrode materials in liquid electrolyte.This approach enabled exceptionally thick electrodes ranging from 100 µm to 700 µm, compared to less than 100 µm in traditional Li-ion batteries with solid electrodes. The flowing suspension electrode is also "self-healing" in the sense that it cannot fail under shear stress like a solid. Yet-to-emerge concepts in this vein may yield further scientific breakthroughs in large-scale energy storage.

Molecular-Level Tailoring of Electrolytes and Interphases: The electrolyte is the "blood" of all electrochemical cells and is responsible for ion transport between the two electrodes; however, it is arguably the least understood component in a battery. It is reasonable to say that the overall behavior of advanced batteries is largely dictated by the properties of electrolytes and electrolyte/electrode interphases. In the widely used Li-ion battery system, the power of the cell is often determined by how fast the Li ions are transported across the solid-electrolyte interphase (SEI), as well as through electrode materials. The formation and characteristics of the SEI are key factors that determine the energy, power, and stability of today's Li-ion batteries. To enable simultaneous high energy and power capabilities, researchers face the following scientific challenges: (1) how can the electrochemical window of electrolytes be widened while either controlling or preventing the formation of harmful SEI layers? (2) How can compatible electrolytes be designed with tailored attributes to accelerate ion transport and enhance the compatibility between the electrolyte and electrodes?

To answer these scientific questions, it is critical to fundamentally understand the behavior of solute and solvent molecules in the bulk electrolyte and in the vicinity of the electrode/electrolyte interface. The synergistic action of salt and solvent molecules affects the quality of the SEI derived from an electrolyte. Considering the solvation structure, a Li^+ ion is normally coordinated with three to four solvent molecules in the conventional 1 molar electrolyte solution, which primarily consists of solvent-separated ion pairs and free solvent molecules.[66] In the vicinity of the electrode, the free solvent molecules dominate the inner Helmholtz layer, which dictates the side reactions on the electrode once the electric field is applied. Therefore, the SEI layer formed in regular electrolytes is mainly derived from the decomposition of electrolyte solvents.[67]

Due to the uneven distribution of the electric field on the electrodes, the morphology and composition of SEI layers formed in a functioning electrochemical cell are not uniform. In concentrated electrolytes, however, the overwhelming population of Li salt increases the association among Li^+ ions, anions, and the solvent molecules, which reduces the presence of the free solvent molecules as well as their activity towards the electrode materials. Therefore, when the electrode is polarized, anions have a higher chance of being decomposed, strengthening the anion contribution to the SEI layer.[15] Such changes in the inner Helmholtz layer greatly alter the formation process of the SEI. The SEI layer formed in concentrated electrolyte tends to be thinner and more compact, and it consists of simpler chemical compositions, effectively suppressing further reactions between the active electrode and the electrolyte. A few interesting results featuring concentrated electrolytes have recently been discovered, such as corrosion prevention of aluminum current collectors at high voltages,[68-70] lithium dendrite suppression,[71] and improved cycling stability of Li-S[72] and $Li-O_2$ batteries.[73] Even in aqueous systems, concentrated electrolytes are found to significantly expand the electrochemical stability window to 3 V and beyond, which could lead to new aqueous systems with high energy density.[16]

Although concentrated electrolytes provide new insights on how to stabilize electrolytes by controlling the solvation properties of the organic molecules and preventing SEI formation under high charge/discharge rates, high salt concentrations also increase the viscosity and reduce ion conductivity in electrolytes. These results have a negative effect on the power density of cells. The fundamental question, therefore, is how to understand the interplay between ions and solvent molecules at different length scales, with the goal of increasing the stability of the electrolyte and maintaining high ion mobility (Figure 3.1.6).[74] State-of-the-art computational tools should be used to predict the characteristics and properties of electrolytes from the molecular scale to the mesoscale. Guided by computational studies, rapid synthesis techniques and high-throughput electrochemical measurements should be developed to facilitate the synthesis, selection, and investigation of electrolytes with desired stability, solvation structures, and long-range transport properties. In particular, new computational and experimental tools, including *in situ* and *operando* characterization techniques, are needed to qualitatively and quantitatively describe the kinetic processes of SEI formation and to explain the structures and properties on both the molecular and mesoscale.

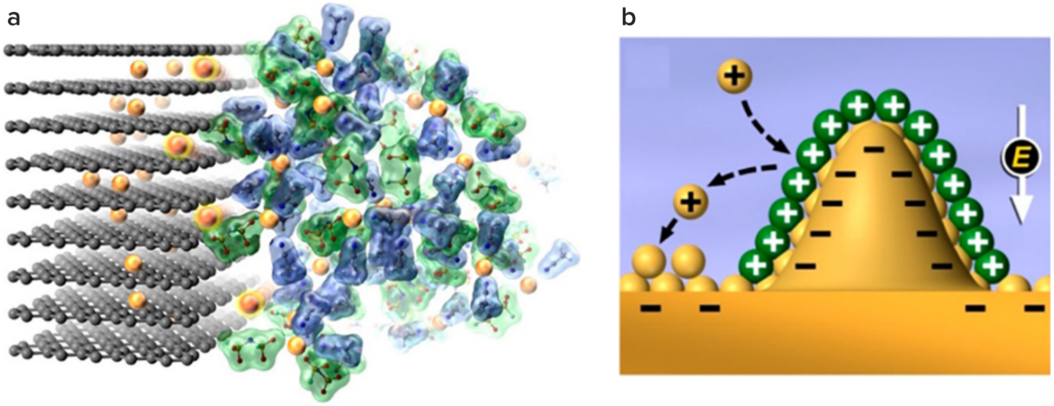


Figure 3.1.6. (a) Improved interfacial stability in non-aqueous superconcentrated electrolyte. From Ref. 15. Reproduced with permission of American Chemical Society. (b) Illustration of Li dendrite prevention mechanisms via the use of an additive containing large cations (Cs^+). From Ref. 74.

3.1.3 IMPACT

The research areas outlined in this panel report are central to the pursuit of electrochemical energy storage with high energy density and power capability. Focused research efforts on new energy storage architectures, multi-functional materials, the electrochemistry of novel molecular and materials-based flow systems, and improved understanding of interphases and electrolytes are key to advancing fundamental science and realizing game-changing energy storage systems.

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3.2 Panel 2 Report — Structure, Interphases, and Charge Transfer at Electrochemical Interfaces

The structure, composition, and evolution of interfaces are critical determinants of the performance of electrical energy storage systems. In all electrochemical devices, charge transfer and, in some cases, charge transport occur across (or along) hetero-material interfaces and interphases. The rates of charge and discharge (power density) achievable in electrochemical cells are, as a consequence, sensitive functions of the morphology and topology of interfaces and the efficiency with which ions, charge, and mass are transported across/along the many interfaces. These interfaces can be either abrupt or evolving. An abrupt interface refers to boundaries between functionally or characteristically different components of an electrochemical cell, such as between the solid electrode and liquid electrolyte or even solid electrolyte (Figure 3.2.1).[1] An evolving interface may arise within cell components dynamically, while they function, e.g., between chemically distinct components in a composite electrode, across or along grain boundaries in polycrystalline electrodes, or between phases under heterogeneous loading (see Figure 2.3.1 in Chapter 2).

Chemistry, electrodynamics, mechanics, and their various couplings at interfaces are likewise known to affect the kinetics and stability of electrochemical processes that determine active material utilization (energy density) and time-dependent performance degradation. There is a critical need for analytical and predictive methods that advance understanding and control of electrochemical processes at interfaces. From an understanding of the processes responsible for SEI formation and function, to those that lead to fast transport of ions in solids, and to morphological and chemical instabilities in electrodes based on high-energy reactive metals such as lithium (Figure 3.2.2),[2] new approaches that enable rational design and synthesis of interphases are required for advances in the field.

Many interfaces in electrochemical energy storage are multiphase junctions consisting of, but not limited to, the active electrodes, separator membrane, and electrolyte, whether the latter is a liquid, solid, polymer, or gel. The presence of binders, conductivity aids, salt, functional additives, and finite amounts of contaminants (sometimes present at low parts per million) in each of these components means that these interfaces are as a rule complex. In some cases, under the action of typical potentials utilized in energy storage devices, these entities may undergo chemical, physical, and/or electrochemical transformation to create self-limiting interphases that couple the bulk electrode subsurface and electrolyte. This SEI can evolve as the potentials of the positive and negative electrodes are frequently operated beyond the electrochemical stability of one or more of the components in the multiphase junction of the surface. In most cases of practical interest, an effective interphase forms through a mechanism that involves contributions of a number of components and cannot be fully identified by isolating the reaction of single components.

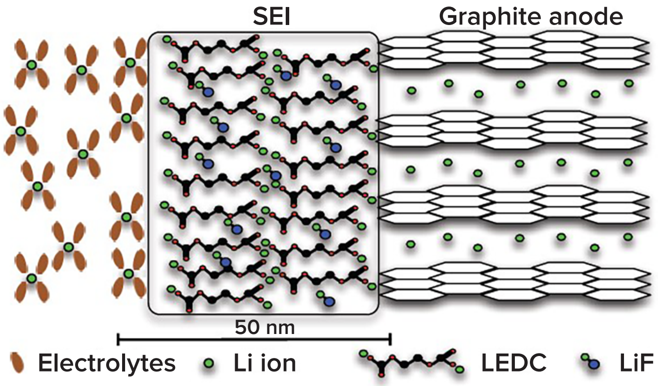

Figure 3.2.1. Illustration of functional electrode-electrolyte interface in electrical energy storage. A binary electrolyte ($LiPF_6$ in ethylene carbonate) generates an initial smooth SEI composed of lithium ethylene dicarbonate (LEDC) and LiF on graphite electrode. From Ref. 1. See also Figure 2.3.11 in Section 2.

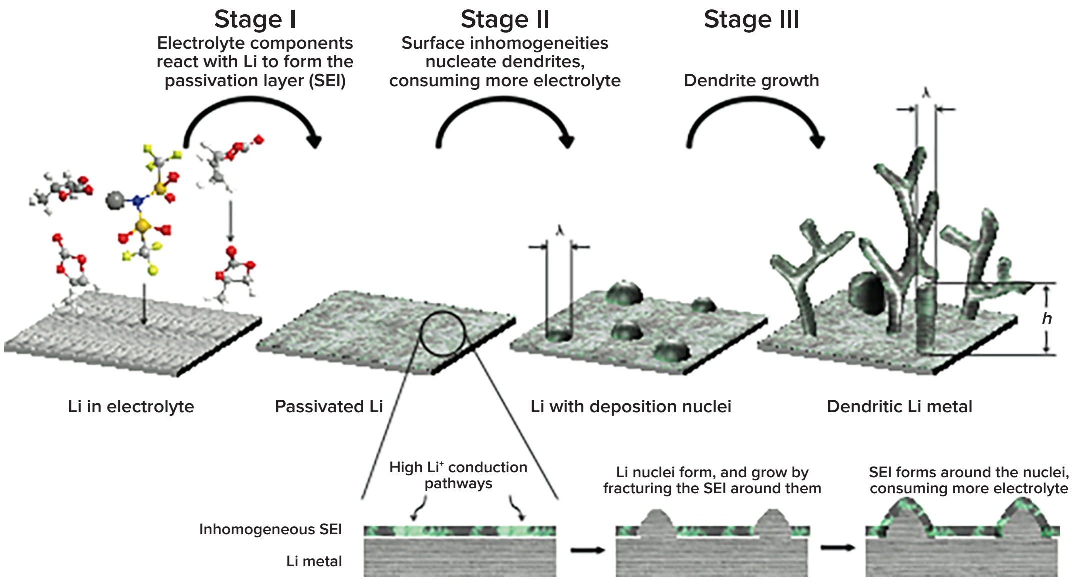

Figure 3.2.2. Stages of failure of a lithium metal anode in a liquid electrolyte. Stage 1: Anode reacts with the metal to form an inhomogeneous solid-electrolyte interphase with a position-dependent interfacial conductivity. Stage II: Lithium deposits preferentially in localized regions to form dendrite nucleates. Stage III: Convergence of electric field lines on the nuclei produces diffusion-limited dendritic growth. Lower panel: A mechanically unstable SEI may crack and buckle, producing fresh sites for parasitic reactions between the metal anode and liquid. Over many cycles, this process consumes the electrolyte, causing the cell resistance to diverge. From Ref. 2.

The following outlines examples of urgent questions that cannot be addressed today, but must be answered for significant technological advances in energy storage over the next decade. What are the design rules for artificial SEIs that enable intrinsically safe electrolytes (e.g., water) at potentials well outside their stability limits for low-cost, high-power, and high-density storage? What is the physics responsible for chemo-mechanical and mechano-transport coupling at solid/solid and liquid/solid interfaces and interphases? How does the research community harness these principles to design and synthesize artificial interphases able to accommodate volume changes associated with alloying and deposition reactions at un-hosted, reactive metal anodes (e.g., Al, Li, Mg, Si, Na, and Sn) or to remediate defects at internal interfaces in solid-state conductors? What are the design rules for electrode materials that, through electrochemical or other means, develop ion and electron transport topologies that maximize interfacial contact between ion- and electron-conducting regions and, thereby, break existing tradeoffs between power and energy density? Is it possible to anticipate the failure modes of protective SEI coatings and to use this information to accurately predict the lifetime of an electrochemical cell designed to last for decades from measurements that span hours or minutes? Even this limited set of questions reveals fundamental gaps in current knowledge, especially related to mechanistic understanding of how coupled processes spanning atomistic to continuum to system-level length scales influence the structure and function of electrochemical interfaces. Answers to yet more fundamental questions concerning the nature of the electrochemical double layer and other interfaces at which charges are transported and where reactions occur in energy storage devices (e.g., solid-solid, solid-liquid, and cathode-electrolyte) promise to simultaneously advance understanding of charged interfaces and to transform our ability to rationally design interfaces for function.

New computational, experimental, and theoretical tools are needed to provide the broad spatial and temporal resolution required for complete answers. It is understood, for example, that development of interface-specific, *operando* analytical techniques operating in realistic contexts are a priority for establishing structure-property-function relationships required for rational design. It is likewise understood that experimental designs that utilize functional model systems of reduced complexity will continue to play a key role in evaluating theoretical predictions of dynamic phenomena, including time-dependent evolution of interface structure and complexity, and for evolving analytical methods that accurately capture molecular details of associated kinetic trajectories across electrified interfaces and over time. Furthermore, because all electrochemical energy storage systems are driven systems, often far from equilibrium and of heterogeneous constitution, it is not yet possible to direct the evolution of the interphase or interface in a component of an electrochemical cell to something that sustains its useful functions indefinitely. Coordinated efforts between experimental, characterization, and modeling approaches, therefore, hold particular promise as they stand to reveal the first links between molecular level processes and bulk electrochemical phenomena, particularly the dynamic origins of long-term cell processes, including degradation.

3.2.1 CURRENT STATUS AND RECENT ADVANCES

Advanced Analytical Characterization Techniques for Probing Interfaces and Interphases: Significant progress has been made in the last 10 years utilizing advanced characterization methods. In particular, *operando* technique development has been enabled by DOE-sponsored facilities and a distributed network of high-energy X-ray and neutron sources facilitating fundamental studies at all scales. X-ray scattering methods that probe the structure of interfaces, such as X-ray reflectivity and X-ray crystal truncation rod analysis, benefit from X-ray penetration through millimeters to centimeters of matter and the ability to obtain angstrom-scale resolution. High-brilliance synchrotron sources not only provide high dynamic range and enable real-time studies, but the energy tunability of these sources can also allow element-specific probes to couple with the excitation of core electrons (e.g., X-ray absorption spectroscopy). Soft and tender X-ray (< 2 keV and 2 keV to 8 keV, respectively) spectroscopies and microscopies have made significant advances in the last few years. Bringing these techniques together with traditional ultra-high vacuum surface science is enabling insight into atomic concentration, chemical properties, and electronic structure in functioning electrochemical interfaces.[3] With the emergence of X-ray transparent windows, differentially pumped analyzers, and tunable synchrotron X-ray facilities, solid/gas,[4,5] solid/liquid,[6-9] and solid/solid[10-12]interfaces are now at the forefront of characterization. For instance, ambient-pressure X-ray photoelectron spectroscopy has been used to probe the electric double layer at the solid-liquid interface, obtain the potential profiles, and discern interfacial chemistry (see Figure 2.3.12 in Chapter 2).[7,8]

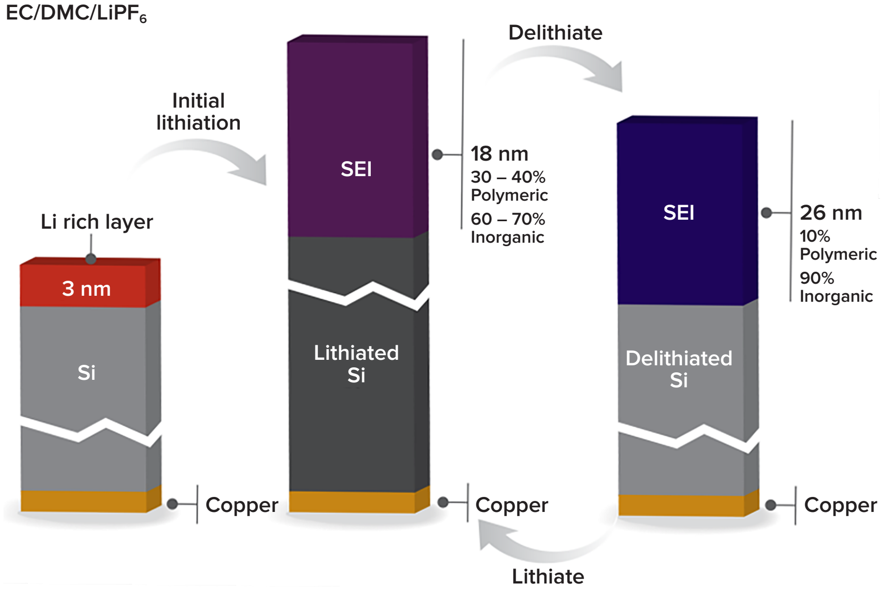

Figure 3.2.3. Results from quasi-elastic neutron scattering to probe lithium transport in amorphous Li_xSi anode materials in electrolyte of $LiPF_6$ and ethylene carbonate/dimethyl carbonate. From Ref. 16.

Neutrons are sensitive to a large fraction of elements (e.g., Li, H/D, C, O, and F) that are of interest to energy storage applications and are thus ideal probes for *in situ* characterization of interfaces (e.g., neutron reflectometry or small angle neutron scattering). Neutron probes have revealed the complex and dynamic surface chemical features of the SEI and have provided new insights into SEI nucleation and evolution during cycling.[13,14] Furthermore, with anticipated advances in data binning and processing, kinetic measurements of diffusion and reaction processes should become possible. A major historical challenge in designing electrolyte and electrode/electrolyte interfaces for function is determining diffusion pathways. Recent neutron scattering results have defined a path forward for directly measuring intrinsic diffusion distances based on quasi-elastic scattering (for an example, see Figure 3.2.3).[15,16]

Advances have also been reported on laboratory-scale characterization techniques. For example, the use of scanning probe microscopy for electrochemical research is still in its infancy. With the possibility of tens of nanometers of lateral resolution and imaging capabilities, this method holds the potential to bridge the existing gap of characterization techniques on length scales between atoms and devices. Advanced scanning probe microscopy techniques have been used to study Li-ion transport,[17] where temperature-dependent measurements have enabled quantification of the activation energy in single grains of the electrode material $LiCoO_2$.[18] Applying these methods to understand ion transport in interphase layers could lead to valuable new insights into Li pathways, including desolvation dynamics and ion structuring, in these heterogeneous structures. Early efforts to apply scanning probe microscopy techniques have characterized the double layer for room-temperature ionic liquids in electrochemical capacitors (see Figure 2.3.3 in Chapter 2),[19] probed insulating properties and morphological evolution of the SEI on silicon anodes,[20] and studied nucleation events during Li electrodeposition at the SEI.[21]

Raman spectroscopy is a powerful tool for probing and mapping surface chemistry or structural changes of electrodes (Figure 3.2.4) under realistic operating conditions. The method has been successfully used to track interfacial structural changes induced by charge storage in supercapacitor electrode materials[22] and to interrogate phase evolution in SnO_2-based electrode materials for lithium batteries.[23] More important, carefully designed *operando* Raman experiments allow direct correlation between changes in structural features of electrode materials and electrochemical performance, providing normally difficult-to-access information that is vital to understanding the mechanisms of electrode processes required for rational design of electrodes with optimal architectures for fast transport of ions and electrons.

All-solid-state energy storage systems have the advantage of solid or semi-solid electrolytes (i.e., ceramics, polymer, and gel electrolytes as separators and ionic conductors). While these systems are under active investigation as an intrinsically stable storage platform, they fail most often at the electrode/electrolyte interfaces (e.g., due to poor wetting, delamination, or proliferation of metal dendrites). Knowledge of the molecular-scale interfacial processes, including the mechanics of solid-solid interfaces, that enable these systems to function well when they do, or to fail in unexpected ways (e.g., growth and proliferation of metal dendrites along grain boundaries of solids), is still in its infancy. The majority of studies are still reliant upon post-mortem destructive cross-sectional examinations.[24,25] There is thus a critical need for *operando* approaches to analyze interfacial properties and their time-dependent evolution. Recent work demonstrated the feasibility of using an embedded reference electrode to enable *in situ* voltage tracking of each electrode within a solid supercapacitor device using a polymer electrolyte.[25] While this approach allows for each individual electrode to be monitored during cell charging/discharging, localized interfacial information is still missing. If this approach can be combined with other non-destructive *in situ* methods, such as 4D X-ray imaging, more insights could be revealed.

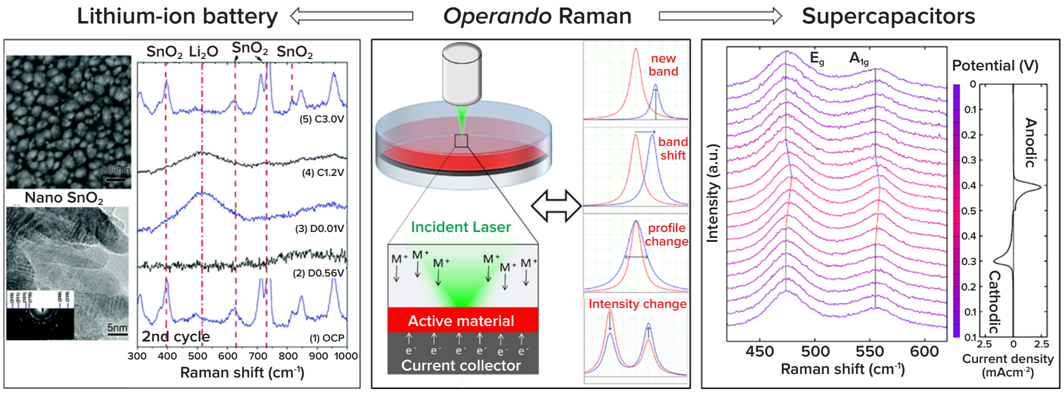

Figure 3.2.4. Probing interfaces using Raman spectroscopy. Schematics of *operando* Raman spectroscopy (center), its application for nanostructured SnO_2 as lithium-ion battery anodes (left), and its application for layer-structured NiO_2H_x as supercapacitors (right). From Refs. 22 and 23.

Theory, Modeling, and Simulations: A wide range of computational techniques, spanning several orders of magnitude of time and length scales, has been applied to understand the complex physical, chemical, and transport phenomena that control the function of electrochemical interfaces. These methods include: molecular dynamics using classical force fields (which deals with nanoscale structure and nanosecond dynamics), density functional theory or quantum chemistry (possibly coupled to implicit solvent methods for modeling chemical/electrochemical reactions, charge transfer, and spectroscopy), and continuum models of transport and chemo-mechanical coupling at interfaces. In this section, the focus is on recent, select developments not covered in previous reviews.[26,27]

The recent, technologically driven surge of interest in theoretical electrochemistry is leveraging advanced tools of computational modeling and simulations. This use of theory is often driven by the need to explain experimental observations, but in so doing misses opportunities to provide guidance about improvements or even fundamental breakthroughs. Likewise, the most recently advanced computational tools (i.e., those based on atomistic or first-principles approaches) are usually applied to simulate specific systems, whereas the fundamental level of the theory, due to its prosaic (more than century old) character concerning classical topics such as ion transport or electron transfer, is left underestimated despite the fact that at that level there is much to be revisited and revised. This state gives rise to a mismatch between the goals and tools. In essence, the aim of theory is to provide:

- ☐ Fundamental limits or characteristics of the processes relevant for the electrochemistry (time and length scales, factors or windows of electrochemical stability, redox potentials, and the maximum energy/work that can be stored/gained);
- ☐ The limits of applicability of the theoretical models (applicable to dilute or concentrated solutions, expressed with respect to concentration vs. activity; mean-field approaches vs. many-body models or the role of correlations; equilibrium vs. non-equilibrium thermodynamics; different regimes of electron/proton transfer, etc.); and
- ☐ The hierarchy of models designed to describe specific phenomena (phenomenological Newman-like models, Marcus theory of adiabatic electron transfer in outer-sphere reactions, etc.).

In the recent literature, especially works dealing with the atomistic description of interfaces, those aspects not well formulated might make the outputs somewhat open to interpretation when compared with experiment.

By nature (or historically), the key parameters (“descriptors”) used to define the fundamental limits of the electrochemical systems are determined in the frameworks of classical thermodynamics or classical/quantum statistical mechanics operating with continuum equations. Due to the more recent trend towards atomistic simulations of specific systems of interest, the fundamental aspects become elusive, and much of what was developed earlier is either forgotten or not used. Specifically, the continuum description of interfaces (including electrochemical ones) has been well developed in the framework of stochastic hydrodynamics[28] and classical DFT.[29] Fluids with particles (ions) interacting via short- and long-range (Coulomb) potentials were extensively studied in the 1960s.[30] In addition, a series of non-equilibrium kinetic equations of ionized plasma (solvated ions) was derived. Regimes were isolated wherein, due to dynamical effects, the Debye screening potential is no longer valid to describe the evolution of the system.

Continuum theories are of particular interest for modeling electrochemical interfaces, because when applied in concert with atomistic description/simulations, they allow for establishing the limiting characteristics of molecular setups and for avoiding time-consuming equilibration of slow molecular subsystems of the electrochemical interface. They can also be used to revisit the basic and universally applied assumptions of equilibrium thermodynamics, thus benefiting both fundamental science and technologically relevant applications.

Interfacial charge transfer kinetics in liquid electrolytes requires fundamental understanding of desolvation processes and ion mobility at the electrolyte/electrode interface. Force-field based molecular simulations have determined the structure and dynamics of various electrolyte

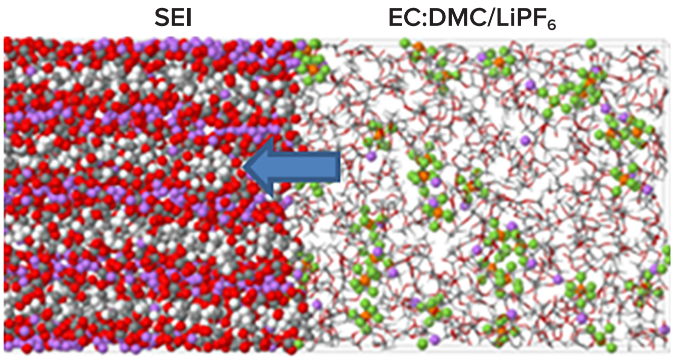

Figure 3.2.5. Simulating the SEI to analyze transport barriers. The structure and dynamics of the electrolyte (EC:DMC/LiPF$_6$) at an electrified interface was studied and the activation energy computed for the desolvation of Li$^+$. From Ref. 33.

solvents at the electrified interface (see Figure 3.2.5 for example with electrolyte of $LiPF_6$ salt and ethylene carbonate/dimethyl carbonate solvent).[31-33] These techniques can potentially explore the role of grain boundaries and other defects in accelerating transport. Including atomic polarizability in the force field should significantly improve the accuracy of the simulated activation energies, allowing comparison to experiments.

Molecular dynamics based on DFT, combined with rigorous statistical mechanical potential-of-mean-force techniques, is more suited for the final step involving Li-ion entry into the anode to “combine” with an electron.[34] Advanced computational platforms and algorithms that offer improved processing speed will advance the level of realism that may be preserved in future large-scale simulations. DFT methods, including joint DFT, are particularly suited for elucidating the activation energies associated with SEI formation mechanisms. Proton transfer from solvent to material surfaces upon oxidation of ethylene carbonate molecules in the electrolyte has been predicted even under moderate voltage conditions.[26,35] This explains previous experimental observations.[36] Interfacial diffusion properties have also been successfully predicted using electronic structure methods. Joint DFT calculations have recently been used to compute activation energies for in-plane motions of Li and Na ad-atoms on minimal, halide-salt models for the SEI in acetonitrile to understand how these species influence transport in the SEI. Notably, activation barriers for Li ad-atom diffusion in SEIs composed of halide salts were found to be substantially lower than for salts, such as Li_2CO_3, that form spontaneously in the SEI on a lithium anode.[2,37,38] Indirect confirmation of these predictions has been reported from experiments in which the stability of Li electrodeposition in SEI enriched in halides salts was compared with deposition in a spontaneously formed SEI.[39,40]

Electric double layers develop at electrified interfaces in mobile dielectric media,[41] and their effects on transport and electrochemical reactions (such as SEI formation) are not well understood. The solvent composition and salt concentrations in the electrolyte at the Helmholtz layer are different from the bulk. Moreover, even the bulk speciation in complex organometallic electrolytes is not well known. Currently, there are only a few studies on this topic.[42] Application of the large external fields in energy storage devices may also cause non-equilibrium ion[43,44] and solvent distributions, producing gradations in ionic conductivity across an electrolyte. For example, enrichment of ethylene carbonate solvent at the interface and in the Li solvation shell in mixed electrolytes can explain why it is preferentially reduced to form the SEI (Figure 3.2.6). Further, the electrolyte composition has been shown to depend on the electrode potential in multicomponent liquid electrolytes. As the potential is decreased, the interfacial electrolyte layer is enriched with ethylene carbonate while the dimethyl carbonate is depleted.[45] Changes in Li^+ solvation structure upon application of a potential bias have also been predicted.

Manipulation of the double layer structure and interfacial ion composition, through changes in the SEI-formation potential and ion concentration, presents new opportunities for tailoring electrochemical reactions and stability. These effects are not limited to lithium-ion batteries. The highly nontrivial solvation shell of magnesium salts in diglyme/oligomer electrolyte has, for example, been elucidated in combined DFT modeling and measurements.[46] Additionally, recent continuum models show that they couple in non-trivial ways to the mechanics of other components in an electrochemical cell (e.g., separator and electrode) to either enhance or exacerbate the stability of metal deposition processes at electrified interfaces.[2,47,48] Intriguingly, the inner Helmholtz layer dominated by bis(trifluoromethanesulfonyl)imide anions at high salt concentrations was an important factor in preventing aluminum current collector corrosion.[49] Likewise, permanently anchoring a fraction of such anions in a liquid electrolyte has been reported to improve interface conductivity at high potential biases and to stabilize otherwise unstable electrodeposition of metals such as Li, Na, and Al. These considerations give us confidence that rational design of electrochemical interfaces can be used to advantage in managing chemical and physical kinetic processes at interfaces.

Fundamentally, the spatial inhomogeneity of the phases (solid-liquid) and reduced dimensionality of the interfacial phase are the key factors that limit the applicability of universal thermodynamic concepts. For inhomogeneous phases, the boundary conditions that determine the initial and end points are not well defined. This, in turn, invokes the details of the process (e.g., its path), which eventually define the details of the interfacial chemistry (otherwise overlooked in bulk-phase thermodynamic studies) as a reflection of the fact that something may happen at the interface and at the interface only. The interfacial speciation and the deformation of the solvation structures of ions in the interfacial regions are manifestations of the same idea.[26]

The above considerations have a profound impact on the atomistic methodology for studying interfacial processes. Any attempts to set up the parameters of the interface (treated atomistically) according to equilibrium thermodynamics will encounter problems. Due to the finite size of the system, idealized conditions, etc., thermodynamic characteristics may not be realizable at all. As a consequence, there will be a problem with comparisons of the computationally estimated parameters with experimentally measured ones. In particular, many discrepancies between theory and experiment in electrochemical deposition of divalent metals are rooted here. Extremely high estimates of activation energies for the first electron transfer hindered by the strongly bound solvation sphere of the divalent ions lead to gigantic overestimates of deposition overpotentials,[50] which can result from ignorance of the interfacial inhomogeneity.

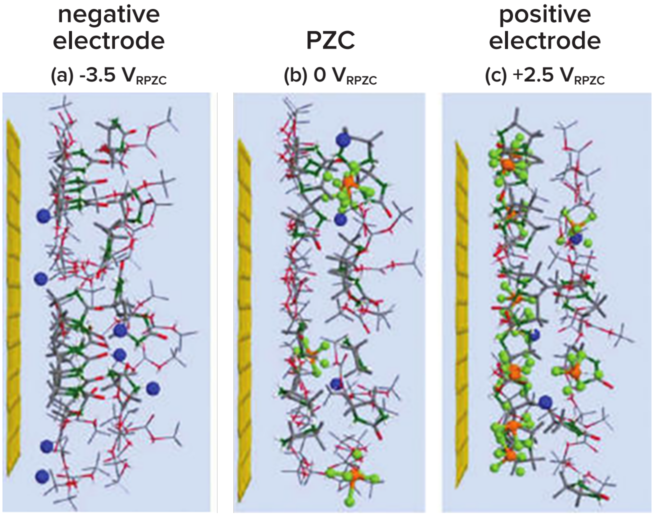

Figure 3.2.6. The interfacial structure of electrolyte (salt of $LiPF_6$ and solvent of ethylene carbonate mixed with dimethyl carbonate) at the negative electrode, point of zero charge (PZC), and positive electrode, calculated from molecular dynamics simulations. Voltages are relative to potential of zero charge (RPZC). From Ref. 45.

Electrochemistry, on the other hand, involves intrinsically non-equilibrium electron distributions, which conflict with the ground-state Kohn-Sham DFT formulation. Constant-voltage DFT calculations are, therefore, demanding. They require referencing the Fermi level to some external potential. For the hydrogen fuel cell and electrochemical capacitor applications, this has been achieved by using specialized boundary conditions that combine DFT and implicit solvent-like methods such as the effective medium approach and joint DFT.[51-56] As an example, the effective medium method references the metallic electrode Fermi level to the standard hydrogen electrode and is held constant in molecular dynamics simulations with an extended Lagrangian, enabling DFT/molecular dynamics simulations of potential-dependent interface/interphase electrochemical reactions. Currently adapted potentiostat schemes either introduce the grand-canonical approach at the expense of eliminating the interface per se[57] or introduce artificial boundary conditions[53,55] that ignore, to some extent, the response of the electrolyte and thus simulate non-equilibrium situations.

Mechanistic Understanding of Interfaces and Interphases: The structure and function of the SEI in Li-ion battery anodes have been under investigation for over 30 years, and a general understanding of the primary components of the SEI has emerged from characterization experiments.[58-66] During the initial lithiation cycles, an SEI forms on the anode surface due to the electrochemical instability of electrolyte components, including additives and salt. In favorable situations, the reactions that form the SEI are self-limiting, preventing continuous loss of electrolyte components that form the SEI. An ideal SEI allows interfacial Li-ion transport at rates comparable to what can be achieved in the bulk. It must be mechanically stable and electrically insulating, inhibiting further reduction of the electrolyte. Formation of the SEI is now understood to be one of the most important and fundamental reactions in Li-ion batteries and is critical to attaining reversible cycling performance. Electron microscopy, spectromicroscopy, scanning probe techniques, etc.—often implemented in parallel on the same electrodes—have been instrumental for understanding the SEI structure and its time-dependent structural evolution in an electrochemical cell.[1,67] There are, nonetheless, persistent gaps of knowledge regarding interface/interphase structure-property relationships, which inhibit our ability to effectively design interfaces with explicit, desirable function.

Towards Rational Design of Interphases and Interfaces: Better understanding of interphase formation in energy storage, and the critical components required to obtain interfaces with desired reactivity, can enable their rational design. An effective interphase, whether be it synthesized via *in situ* or *ex situ* chemistry, displays the following properties: it is electronically insulating, has high ionic conductivity, displays self-passivating growth, and is stable towards dissolution.[68] There have already been many demonstrations of "artificial interphases" through coating electrodes with very thin (1-50 nm, but typically 1-3 nm) insulative films that mimic the effect of an *in situ* derived interphase. These coatings (e.g., Al_2O_3, B_2O_3, SiO_2, ZrO_2, and polymers)[69-72] are deposited by various techniques ranging from solution casting to atomic layer deposition and have been shown to be highly effective for stabilizing the cycling of cathodes in Li-ion batteries at very high potentials, where anodic decomposition of electrolyte is a dominant failure mode. These coatings can also be effective in protecting reactive metal anodes where electrolyte consumption by parasitic reactions with the metal is an important mode of failure. That being stated, an effective *ex situ* derived interphase need not be electronically insulating,[73] especially when the electrode surface is catalytic and triggers the electrolyte decomposition. In this case, replacing the catalytic surface of the electrode with a non-catalytic electronically conductive surface will effectively eliminate the degradation-related surface decomposition. The importance of this approach is that the electronic charge transfer to the external circuit is maintained. Further, recent studies have also shown that surface "layers" need not be distinct chemical or physical phases, but surface regions that are rich in extrinsically introduced ions or that enable strong composition gradients,[74-76] leading to improved interfacial properties and electrolyte stability.

3.2.2 SCIENTIFIC CHALLENGES AND OPPORTUNITIES

Advanced Analytical Characterization Techniques for Probing Interfaces and Interphases: A key challenge is unravelling the complexity of coupled processes that control the function of heterogeneous electrochemical interfaces. New approaches are required that use combinations of tools for complementary insights. At one end of the spectrum, opportunities exist for studies that take advantage of well-controlled model systems in which the functional aspects of the electrochemical cell are preserved to enable detailed understanding of how interfaces of well-defined chemistry contribute to overall function. At another extreme, opportunities exist for approaches that enable *operando* interrogation of specific features of a heterogeneous interface to unravel structure-function relationships in both explicit and buried interfaces. Each of these approaches brings obvious drawbacks; however, strategies for overcoming them are not unfamiliar in the chemical physics community. For example, well-controlled model systems can provide a wealth of valuable information about particular interfacial components or particular configurations of multiple components, but there is a gap in applying that knowledge to much more heterogeneous realistic electrodes if these model systems are designed to be so ideal that the electrochemical context is lost. There are also questions related to the best ways to corroborate the results obtained from multiple studies, particularly for specialized *in situ* setups. For example, how "universal" are the results? In this regard, round-robin studies of the same model systems by multiple teams of researchers must be encouraged. *Operando* investigations overcome the most serious drawbacks of model-system studies, but require more intensive, longer term commitment to instrument development and large-scale collaborative efforts among tool and subject matter experts.

Additionally, there is poor understanding of the impact of interphase heterogeneities within the cell as it relates to spatiotemporal aspects of charge transfer associated with a cell's accessible energy density and lifetime. Tools are needed to elucidate how ions transport at phase boundaries and how processes such as desolvation and non-specific surface binding influence the energetics of interfacial transport across length and time scales. There is, likewise, no concrete understanding of how the electric field in a liquid in contact with a solid electronic conductor is altered by separating the liquid and solid with a leaky dielectric, insulator, or semiconductor of nano-sized thickness that may permit some ingress of the liquid. *Operando* investigations and time-dependent studies are likewise needed to fully understand the potential of interfaces to evolve over time. To provide the required insights, such measurements should be performed under relevant conditions to enable coupling to *ex situ* observations and connections to bulk electrochemical observables to be determined. Beyond these specific needs, there is a critical overarching need for new methods suitable for isolating the role that electrochemical interfaces play in device degradation and for enabling accelerated analyses for predicting device failure and lifetime.

All-solid-state energy storage devices present characterization challenges, as it is difficult to unravel contributions from the multiple solid-solid interfaces that can be present in a single device. Further, the accessibility and mechanism of ionic species transport from solid or semi-solid electrolytes to electrodes are still unclear, especially in materials with high porosity that may host a bound solution phase in the pores. The effect of aging, mechanical stresses, inevitable processing defects, and thermal history on stability and transport processes at the solid-solid interface is still not well understood. More important, no theory or methodology can predict degradation pathways, service life, or failure modes of all-solid-state devices.

Theory, Modeling, and Simulations: Part of the electric field, and therefore the potential drop/rise, may occur within the solid-solid interface due to lithium insertion into and/or depletion from the SEI/electrode interface. As solid-state transport is much slower than liquid state transport, this creates a time-scale mismatch for molecular dynamics simulations. A related challenge is that Li^+ insertion and electron flow involve modifying the surface charge by an integer number,[77] unlike on pristine metallic electrodes where fractional changes suffice.[51-54] This is particularly true for small-polaron conductors like spinel $Li_xMn_2O_4$; adding a fractional electron violates the relevant small-polaron physics that drives Jahn-Teller distortions. To this end, quantum mechanics/molecular mechanics approaches incorporating an implicit solvent, in conjunction with grand canonical Monte Carlo techniques for both electron and lithium content, can make tremendous progress.[55,56] Joint DFT predictions of surface mobility have already motivated successful efforts by experimentalists to design simple halide-salt rich SEIs that impart improved function.[39,40] There is opportunity to develop the underlying solvent models to more quantitatively describe ion-solvent coordination and to determine how ion desolvation dynamics influences interfacial transport.

Studying buried solid-solid interfaces[78-82] is at the frontier of energy storage modeling and requires mastery of the complex interfacial energy landscapes featuring multiple local minima. As liquid electrolyte batteries also exhibit SEI-electrode solid-solid interfaces, such modeling effort will have universal impact on all energy storage devices. Foundational work on pristine electrode-vacuum interfaces is a pre-requisite for such studies.[83] However, the modeling of spatial inhomogeneities, defects, and grain boundaries on atomic length scales may prove crucial to quantitative predictions of passivation breakdown and metal deposition. Finally coupling coarse-grained modeling techniques, such as phase-field methods,[84] will be crucial for predicting mesoscale behavior.

Of particular promise are cohesive studies that combine state-of-the-art and emergent experimental analysis with state-of-the-art and emergent theoretical work to unravel the complex physical, chemical, and mechanical processes responsible for function at electrochemical interfaces. Ambient pressure X-ray photoelectron spectroscopy of flash-freezing liquid electrolytes, Auger and high-resolution electron microscopy, and *operando* studies of interface evolution by means of soft X-rays, neutrons, and light microscopy are among the methods that hold greatest promise for coupling experiments with modeling. As discussed earlier, because relevant battery interfaces are generally too complex for complete modeling studies, experimental designs focused on model systems with a simplified but functional SEI will provide more meaningful correlation with theory. Likewise, experiments based on scanning probe microscopy or high-resolution electron microscopy provide opportunities for isolating components at a complex interface for rigorous studies on length scales readily compatible with advanced simulation methods. Along these lines, the philosophical approach underlying modeling/experimental collaboration should be clarified. The value inherent to directly model one particular measurement needs to be balanced with creating a broader framework of comparison that allows modeling to provide inspiration for new experiments. Theory should ideally propose novel “descriptors” of relevant but hidden atomic-length physics that provide guidance about what needs to be measured. These descriptors would, in turn, inform the experimental technique that should be used. They can include local mean field and fluctuation-induced properties such as potentials-of-mean force, local dielectric responses, speciation, and nucleation probabilities at interfaces. Both theoretical and experimental efforts should define their relevant precision limits and time/length scales to facilitate comparison. There is also a need for theoretical/simulation approaches to directly interpret measurements on complex systems, particularly those with overlapping signals, as in probability density function analysis, or measurements when probing vibrational or electronic structure via interfacially sensitive spectroscopy.

Mechanistic Understanding of Interfaces and Interphases: Design rules are needed to better connect the interphase composition along with structure and functionality, particularly for the SEI. Obtaining better control of interphases in energy storage systems is complicated by the fact that electrodes are heterogeneous systems composed of multiple components. Numerous interfaces exist even when considering only the active materials (particle-particle, particle-binder, particle-conducting additive, particle-electrolyte, etc.). The specific form of the interphase will dictate the exact free-energy landscape for migrating charges. These landscapes, which have origins at the atomic level, are collectively responsible for the cell's energy efficiency, rate capability, and stability. Further, the so-called "inactive" conducting additives and binders may also affect interfacial processes and the nature of the SEI that is formed on electrodes.[85-87]

Fundamental, mechanistic understanding is required to elucidate how individual components of the SEI contribute to the functional properties of this interphase. Individual components of the SEI (e.g., LiF, Li_2CO_3, and alkyl carbonates) have been studied in isolation, but their synergistic effects have only begun to be addressed. How multiple components and processes interact together is still not well understood. There is also the possibility that the behavior of individual components may not be "additive", and that the interphase properties are a product of the heterogeneity, which cannot be captured through studying individual components in isolation. Hence, while a need exists for fundamental studies on model systems of reduced complexity to understand chemistry-structure-property-function relationships for individual components, a complementary need exists for detailed studies of realistic systems in which coupled contributions to overall SEI function are preserved.

Addressing the challenge requires that electrolyte formulations be modified to vary the structure of the SEI in a systematic fashion. These components must be fully experimentally characterized, with the use of multiple tools to extract information regarding coupled and synergistic relationships. Such measurements would enable the development of a fundamental understanding of the structure and function of the SEI on lithium-ion battery anodes and enable the use of reactive metals, such as Si, Sn, Li, Na, and Al, as anodes for high capacity storage.

New methodologies to elucidate the complexity of fully formed interphases are also needed, particularly if interphase formation occurs through the contribution of a number of components. There is especially a need for methods that take advantage of specific labeling, such as radio-isotopes,[88-90] to track chemical species throughout the reaction pathway, thus allowing realization of their role in the development of the final interphase product. An example of isotope tagging[88] is the direct observation of solid-phase electrolyte products resulting from decomposition of acetonitrile solvent on the mesoporous activated carbon positive electrode of a non-aqueous asymmetric hybrid supercapacitor by ^{13}C, ^{1}H, and ^{15}N solid-state nuclear magnetic resonance. At least two of the observed nuclear magnetic resonance signals could be assigned to acetamide and a lithium-based carbon derivative, suggesting that the Li salt interacts with the acetonitrile solvent, leading to accumulation of decomposition products on the electrode particle surface. Such approaches can be used to understand true interphase development.[89] A parallel computational investigation (e.g., the ionic-conducting properties of the known components as a function of different nano-structures) is also required to understand the structure-function relationship of the SEI.

Towards Rational Design of Interphases and Interfaces: Metal anodes represent the most efficient use of mass and volume as the penalty of a host material (e.g., graphite, Si, or Sn) is eliminated, but the absence of a host scaffold results in the formation of a physically unsupported SEI.[91] Attempts to create artificial SEIs through thin film growth on Si (Figure 3.2.7) and lithium anodes using coating techniques, including atomic and molecular layer deposition, have improved lithium anode stability with cycling.[71,72,87, 92-95] Ultimate success for these or new approaches must solve both the coulombic efficiency and dimensional control (dendrite) problem. Management of the local volume change within a cell that employs a metal anode must also be addressed. Discharge of the anode produces local volume loss and threatens the ability to maintain a coherent, low-impedance interface with the artificial SEI membranes and films integrated with the anode. One solution to this problem is to design for volume change through an appropriately sized host scaffold (e.g., using porous structures), where the scaffold mass and volume are minimal relative to the metal.

There are vast opportunities in materials synthesis/processing and electrode fabrication to direct interfacial reactions beyond the use of surface coatings to act as artificial SEIs. Such architectures could be designed to more efficiently use advances in materials synthesis (e.g., highly faceted nanostructures) and fabrication (e.g., 3D printing and self-assembly) to control interfacial processes and introduce adaptable interphases. All-solid-state thin film batteries have been fabricated with well-defined and stable interfaces. Recent work on the 5-volt Li/LiPON/$LiMn_{1.5}Ni_{0.5}O_4$ micro-battery revealed that it can cycle over 10,000 cycles with greater than 90% capacity retention with the formation of the right interfacial structure[96] (see Figure 2.3.4 in Chapter 2). These results indicate that under specific circumstances, it is possible to cycle lithium metal and an advanced high-energy cathode that would not be stable within a liquid electrolyte cell; however, there is still a lack of fundamental understanding of the composition and morphology of these interfaces. Efforts to advance such understanding will potentially enable design of suitable bonding motifs that yield low-impedance interfaces and provide pathways for new materials development.

Energy storage systems can also benefit from the recent advances in nanomaterials synthesis and fabrication approaches that enable the preparation of well-faceted and/or morphology-controlled materials. For instance, several theoretical and experimental studies have shown that different crystalline silicon surfaces display very different reactivities to the electrolyte,[97,98] which can play a role in the first-cycle coulombic efficiency of silicon anodes through the formation of different types of interphases. Scanning probe measurements on different facets of $LiNi_{0.5}Mn_{1.5}O_4$ crystals also indicated facet-dependent SEI formation.[10] The facet-dependent reactivity for other processes, such as O_2 evolution at elevated temperatures due to thermal instability[99] and transition metal ion dissolution[100] in Li-ion battery cathodes, is also becoming more apparent. Key to these studies is the validation of theoretical models through coupling of experimental techniques and computer simulations. Taking advantage of materials with an abundance of facets that catalyze the formation of “good” interphases over undesirable ones could be a promising approach for future directions. Computational studies of such reactions on different facets will greatly aid this design effort.

Additionally, configuring active interfaces (switchable, reconfigurable, etc.) to respond to local cues in the cell provides new opportunities to control charge transfer and transport. This has recently been demonstrated through the use of redox-active binders and cathode hosts in Li-S battery cathodes.[101,102] Success in this regard hinges upon the ability to advance new concepts, chemistries, and cues within the cell, e.g., at specific potentials. The goal is to initiate or arrest the formation and growth of the interphase or to manipulate the chemistry at an interface responsible for the energetic barriers to charge transfer.

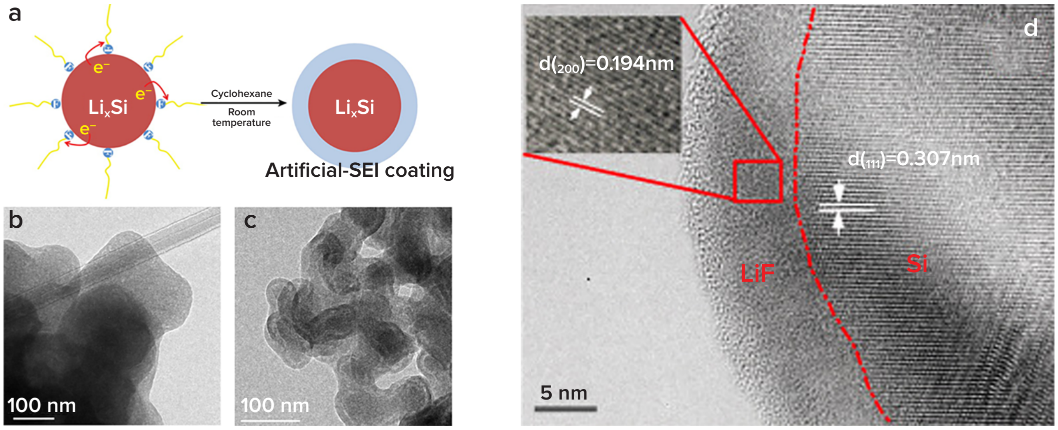

Figure 3.2.7. Design of artificial SEI to stabilize Si anodes. (Left) Lithiated silicon is coated with a conductive polymer coating that buffers structural changes during lithiation and delithiation of the active anode material. From Ref. 94. Reproduced with permission of American Chemical Society. (Right) LiF is used as an effective coating for Si anodes. From Ref. 95.

3.2.3 IMPACT

Advanced Analytical Characterization Techniques for Probing Interfaces and Interphases: The development of advanced characterization tools and associated experiment designs will impact our ability to rationally design electrochemical interfaces for function in at least three specific ways. First, they will enable molecular-scale definition of functioning electrochemical interfaces in their full electrochemical context. This will allow the field to move beyond cartoon descriptions of important functional interfaces, such as the SEI, to more informed descriptions compatible with developing minimal physical and theoretical models required for rational design. Second, they will allow the complex physical, chemical, and mechanical processes and their couplings, which control function of these interfaces, to be unraveled and their roles in determining function and failure determined. Third, these tools will provide rich data sets on well-characterized systems that are good targets for evaluating theories and computational analyses of interface structure, transport phenomena, and evolution. By advancing fundamental understanding of chemistry-structure-property-function relationships across all scales relevant in energy storage applications, they will accelerate progress towards realization of safe, lightweight, and cost-competitive storage of electrical energy across the spectrum of energy storage applications. Additionally, electrified liquid-solid and solid-solid interfaces are critical in many electrochemical systems beyond energy storage technologies, such as fuel cells, sensors, and electrochromic displays.

Theory, Modeling, and Simulations: Accurate modeling of interfacial transport, charge transfer, and electrochemical reactions is particularly suited for focused examination of hypotheses and decoupling of competing mechanisms at multifunctional materials/interfaces. Future modeling efforts should look to fully embrace all the complexities of solid-solid and solid-liquid interfaces, as well as interphases coupling both of the interfaces. Although many challenges remain in computational methods, calculating reaction activation barriers (within a well-specified set of assumptions) can be readily applied to study degradation processes. This will greatly benefit experimental study of degradation and alleviate the demands on accelerated testing of battery lifetimes at elevated temperature and harsh conditions. The coupling of DFT techniques to longer length scales, implicit solvent treatments, and Monte Carlo simulations will be a foundational advance that also benefits basic research needs for fuel cells, flow batteries, and other energy storage and conversion technologies.

Mechanistic Understanding of Interfaces and Interphases: Surface structure, reaction products, potential profiles, and interfacial chemistry all contribute to the nature of the interface, and the relationships should be discerned. Better understanding of the mechanistic aspects could enable active (rather than passive) control of chemical structure and composition at interfaces, which may facilitate new electrode development and the establishment of more resilient interfaces. This fundamental understanding will also enable a more rational design of energy storage systems to identify the best combinations of components (electrode interface structure, electrolyte composition, additives, etc.) as novel materials are discovered and developed. Control and realization of better interfaces can lead to significant improvements in the energy density, rate performance, low-temperature performance, and calendar lifetime of energy storage systems.

Towards Rational Design of Interphases and Interfaces: The ability to design and adapt electrochemical interfaces at will for a desired function can have far reaching impacts in the ability to control the free-energy landscape and offer unprecedented management of the directionality of charge transfer and transport. More robust synthetic methodologies and linking structure-property-functionality relationships of electrochemical materials and interfaces will enable the family of materials suitable to energy storage to be significantly expanded. Self-healing approaches may preserve interface function and thus present opportunities for increased safety, enhanced lifetime, and adaptable systems.

3.2.4 REFERENCES

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3.3 Panel 3 Report — In Pursuit of Long Lifetime and Reliability: Time-Dependent Phenomena at Electrodes and Electrolytes

Electrochemical storage devices do not last forever. Failure mechanisms differ depending on the device chemistry, mode of use, and details of storage. Electrochemical cells may degrade gradually, or experience "sudden death" events that result in catastrophic failure, which can present safety hazards. These failure mechanisms are many and varied, but result in shorter device cycle lives and lifespans than generally desired. Premature failure is common to all types of devices, but the issues are particularly well delineated for lithium-ion batteries, as outlined below. These findings broadly illustrate the challenges involved in attempting to understand the key and often inter-related factors that influence device lifetimes and the commensurate need to develop solutions for them.

The evolution of rechargeable lithium batteries dates back to the 1950s when Carl Wagner began the discussion of fast ionic conduction in solids.[1] In the 1960s, the work was expanded to studies of topotactic reactions in certain unique crystal structures, and in the 1970s, to the concept of intercalation of alkali ions into these structures as cathode materials for rechargeable alkali metal batteries.[2] In the 1980s, commercialization of intercalation electrode-based cell designs was pursued, and in the 1990s, early lithium-ion batteries with a "rocking-chair" functional concept were successfully commercialized.[3] In the 2000s, the energy density and costs of the lithium-ion battery cells were progressively improved with significant market penetration, and in the present day, mature cell designs are being adopted to consumer electronics, electric vehicles, and electrical grid energy storage applications.

3.3.1 CURRENT STATUS AND RECENT ADVANCES

Despite astonishing improvement in the performance for lithium-ion batteries, the advancement of the technology continues to face significant challenges. There exists significant complexity associated with the long-term behavior of lithium-ion batteries either in storage or under use. For example, the same material composition used in the battery may exhibit different long-term behavior depending on the syntheses, electrode processing techniques, cell fabrication methods, and aging conditions. Thus, variability in performance cannot be easily traced back to its fundamental origins. In other words, the differences cannot be easily identified by the discrimination of materials variations in syntheses, electrode processing conditions, or cell fabrication methods. These issues highlight the need for basic understanding of such complexity at the systems level.

This panel recognized the importance of degradation mechanisms in determining the viability of the energy storage systems. Major challenges for longer life for electric energy storage in a closed system with high energy density are developing the ability to probe, identify, and quantify unwanted reactions, which are often subtle and happen at the electrode/electrolyte interfaces, and unraveling the atomic-to-mesoscale mechanistic mysteries that appear to impose strong dynamic limits on storage reversibility and lifetime. The need to mitigate any irreversible changes during the charge-discharge cycle calls for *operando* and/or *in situ* characterization methods, as well as advanced modeling and simulation, that can reveal time-dependent behavior in both the electrodes and electrode/electrolyte interfaces.

More specifically, this panel concluded that the following aspects are critically relevant to the improvement of energy storage performance: (i) electrochemical energy storage reversibility, stability, degradation, corrosion, and reliability issues; (ii) electrochemical-mechanical coupling phenomena; (iii) side reactions and subtle rate-limiting reactions (through proper measuring, characterizing, modeling, predicting, and mitigating approaches); (iv) phase transformations in solid electrode particles and architectures; and (v) stripping and plating mechanisms of alkali metals at liquid/solid and solid/solid interfaces. Also needed is better understanding of (i) safety issues associated with the formation of dendrite-like structures during battery operation, and possible solutions with adaptive materials and structures, and (ii) battery operation at high temperature and its effect on the corresponding rates of degradation, and possible mitigation strategies for any adverse changes.

The panel also recognized that the complexity and the dynamic nature of the relationship between cell preparation and performance could be captured in time-dependent behaviors if a better characterization and understanding of such behavior can be established in future research. It is important to realize that these time-dependent behaviors occur across a very significant time domain and a large range of spatial distributions in the physical landscape (see Figures 2.2.1 and 2.5.4 in Chapter 2).[4] For instance, the time domain and the spatial distributions could range from picoseconds to years and from atomic level to the entire cell, respectively.

More importantly, in an electrochemical system, the chemical, electrical, mechanical, and thermal properties and their gradient distributions couple with the time-dependent phenomena, yet each coupled process has a specific time constant in response to a driving force that causes the changes in such a process. These time constants may spread over a significant range in the time domain. The perturbations in properties can also percolate at different spatial scales, from atomic distances to the entire cell dimensions. These complex and interrelated temporal and spatial correlations pose challenges in gaining a consistent understanding of the causes of the variations in the energy storage device behavior. To overcome these technical barriers, this panel concluded that a suite of characterization techniques and modeling capabilities, with high sensitivity, high resolution, and/or high accuracy is critically needed to solve these mysteries. The characterization techniques should cover the entire temporal and spatial ranges with sufficient resolution to provide accurate information. The systems that are studied should range from actual batteries (to capture unknown processes) to model systems (that can apply greater precision and isolate the effects of specific sets of variables on degradation phenomena). This information then can be used to feed models and analytics to obtain quantifiable parameters and metrics. From this, a high-fidelity and consistent model framework can be developed to allow quantitative understanding of the observations and provide predictive capabilities that can be validated by further experimentation. Such a cross-cutting approach that combines experimental characterization and computation and modeling to provide consistent results would lead to a deeper understanding of energy storage characteristics with basic principles quantitatively defined to facilitate future developments from the materials level to cell design.

The panel recognized that the current approaches, particularly based on empirical methods, do not fully capture the multi-dimensional scale and multi-temporal effects in the bulk of the materials and electrodes and at the electrode/electrolyte interfaces in energy storage systems. The understanding of the short-term mechanisms that enable the energy storage performance does not lead to insights about the long-term impacts on the degradation and the behavior of the materials, electrodes, and the cell. Non-uniformities, inhomogeneities, and anomalies in the energy storage performance, which often occur on a localized scale, are not captured properly to ensure the durability, reliability, and safety of the device. Impacts from chemical impurities cannot be easily quantified. The issues associated with mechanical incompatibilities among different components in the cell cannot be identified and quantified as well. More importantly, the defect structures and concentrations in the materials and electrodes cannot be quantified properly at present. These different aspects associated with energy storage performance and cycle life are vital information for design and development, yet the assessment and characterization methods to facilitate progress in understanding them are lacking.

With the understanding of the complex interactions within and between electrodes, researchers need to address the coupling of mechanical/structural, electrochemical, chemical, thermal, and electronic properties in the electrode and electrolyte materials, electrode architecture, and cell design in relationship to the performance characteristics. They also need to address the impacts from impurities and other cell attributes that include the crosstalk between the electrodes and multi-dimensional impacts from the cell design metrics.

3.3.2 SCIENTIFIC CHALLENGES AND OPPORTUNITIES

Mechanisms that limit lifetime are poorly understood. Degradation phenomena lead to insufficient lifetimes as well as safety issues for all electrochemical systems, from commercialized to emerging chemistries, from electrochemical capacitors to batteries. Degradation phenomena are often poorly understood because degradation arises from the interplay between multiple properties, and its effects can exist over multiple time and space scales. There is generally a lack of guided mitigation strategies for long lifetimes. The ultimate scientific challenge posed in this panel is: “Is there a practical limit to the lifetime of electrochemical energy storage devices?”

Degradation Arises from the Interplay between Multiple Properties: Degradation phenomena depend upon multiple variables within the electrochemical environment, for example, the electrode material composition, local structure, architecture, energy storage mechanism, and electrolyte. Additional complexity comes from the dynamic coupling of these phenomena with the mechanical, thermal, and electrical properties.

There is an opportunity to develop multi-modal techniques that can measure multiple properties at the same time: for example, measurement of the mechanical and electrochemical properties of materials as a function of state of charge and cycling. There is also an opportunity to fully understand coupled degradation pathways. Another example would be to measure several properties of an interface layer (i.e., structure, composition, and conductivity) as a function of numerous independent variables (i.e., potential, cycle life, calendar life, the presence of additives or impurities, and counter electrode composition).

Degradation Effects Can Exist over Multiple Time and Length Scales: Achieving a detailed understanding of degradation mechanisms is elusive without validated accelerated lifetime testing. Many of these phenomena are present at different time and length scales, making them difficult to detect. Some degradation phenomena occur when the cell is in a state of rest (also called “static aging”), and the state of charge is likely to dictate the degradation pathway.

There is a need for multi-scale models that address degradation mechanisms. There are opportunities for new characterization techniques such as *in situ* time-resolved imaging probes and validated accelerated lifetime testing. An example of this approach is shown in Figure 3.3.1. Cells containing lithium anodes and either $Ag_2V_4O_{11}$ (SVO) or $Ag_2VO_2PO_4$ (SVPO) cathodes were discharged over the course of a year. Pulse testing at the end of the year showed that the cell with SVO performed much worse than the one with SVPO. Elementally specific X-ray microfluorescence mapping of lithium anodes harvested from the cells showed that a larger amount of vanadium had deposited on the anode surface when SVO was used compared to SVPO. This difference was attributed to dissolution from the cathode. Vanadium is present both in the outer layer of the solid-electrolyte interface, where it is present in ionic form, and in the inner layer, where it is reduced to the element. The end result is inhibition of lithium-ion diffusion and higher interfacial impedance, explaining the faster degradation of the cell with the SVO electrode.[5] Notably, the inhibited lithium-ion diffusion is apparent only under a high discharge rate (pulse testing, bottom right image in Figure 3.3.1), and not under the low discharge rate (upper right image), illustrating an additional complexity—the link between time-dependent degradation phenomena and use conditions.

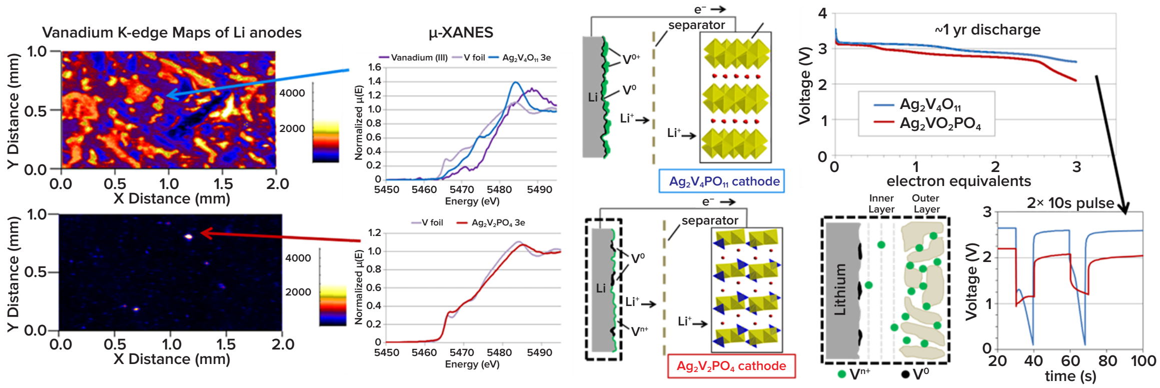

Figure 3.3.1. (Left) X-ray microfluorescence maps of vanadium species on lithium anodes harvested from $Li/Ag_2V_4O_{11}$ (Li/SVO) (top) or $Li/Ag_2VO_2PO_4$ (Li/SVPO) (bottom) cells discharged at a 1-year discharge rate. Arrows indicate selected regions on the maps where microbeam X-ray absorption near edge structure spectra were collected to determine the oxidation states of the metal centers resident in the SEI on the electrode surface. The data were used to develop a conceptual model for the SEI on the Li anodes, where the presence of vanadium cations inhibits facile movement of positively charged lithium ions during discharge. The model rationalizes the higher resistance of anodes from $Li/Ag_2V_4O_{11}$ (Li/SVO) cells, as reflected by the poorer pulse performance (right). From Ref. 5.

Lack of Guided Mitigation Strategies: Current approaches to improve lifetime are often based upon an Edisonian trial-and-error approach because of the lack of fundamental understanding how different mitigation strategies work. For example, electrolyte additives are often used to allow cycling to higher potentials,[6] thus improving the energy density of cells. Likewise, surface coatings of various materials, from carbons to polymers to oxides, are used to suppress unwanted reactions between active particles and electrolytic solutions.

Significant opportunity exists for the rational design of degradation mitigation strategies that are guided by fundamental understanding. Strong collaboration between synthesis, characterization, and modeling is required to solve this problem. This scientific challenge is to inspire the design of resilient and robust electrodes and other cell components.

3.3.3 IMPACT

Successful formulation and mitigation strategies should result in suppression and prevention of unwanted processes. An example of a recent successful strategy is given in Figure 3.3.2.[7] In some metal oxide electrodes, repetitive insertion/deinsertion of Li ions cause strain hardening, fatigue, and fracture of the oxide, leading to separation from the current collector and loss of reversible capacity. This leads to a limit in cycle life of 5,000-10,000 cycles for electrochemical capacitors. This research demonstrated that poly(methyl methacrylate)/propylene carbonate gel electrolytes extend the cycling stability of MnO_2@Au nanowires to >100,000 cycles.

Prevention or control of “sudden death” events may also lead to greater safety as well as longer lifetime. It is known, for example, that short circuits do not necessarily always result in catastrophic events. What leads to these slow short circuits, and can they be made reversible? If this can be understood, battery engineers can more aggressively pursue high energy density chemistries without compromising performance or adding expenses at the system level to guarantee safety. Along these lines, solid electrolytes offer potential for improved resistance to lithium dendrite formation in batteries with lithium metal anodes, but lithium metal can deposit at grain boundaries, resulting in device failure. Lithium formation depends on the local electrochemical potentials formed within the cell. Understanding metal deposition, as well as the phases that form at electrode-electrolyte interfaces and grain boundaries, and controlling electrolytes and interfaces would result in more resilient devices, which can fully exploit the high energy density that use of lithium metal promises. To date, the promise of lithium metal electrodes has not been fully realized due to safety concerns.

Devices may also fail more gradually due to slow processes in the cells, such as parasitic side reactions or cumulative mechanical strain, as active materials undergo repetitive volume changes during cycling. These effects may take a long time to manifest and may not be adequately captured by accelerated lifetime testing protocols. Successful quantification of such phenomena in the kinetic regime by appropriate models would result in predictive capabilities that reduce the need for extended and time-consuming testing. Characterization techniques with sufficient resolution and precision to deconvolute and decouple the thermal-mechanical-electrochemical phenomena that occur will provide information that allows solutions to be found quickly. These solutions could be in the form of electrolyte additives, coatings on active material particle surfaces, or entirely new materials, electrodes, or cell architectures or other approaches not yet identified. This enhanced design space could result in parallel improvements in storage and lifetime. In addition to the potential for greatly improved electrochemical storage devices, these approaches will provide a needed integrated understanding from the atomic to macroscopic scales in a consistent framework of multi-dimensional spatial and temporal resolutions with temporal correlation to facilitate material-to-system designs.

Interfacial processes, including formation of SEIs at anodes and cathode/electrolyte interfaces, can often determine the immediate and long-term electrochemical properties of cells, especially their lifetimes. SEI formations are often very complex and have properties that depend on cycling conditions, specifically current densities and temperature. Good interfacial contact between components in solid-state cells can be difficult to maintain, yet this is critical to their function. Rational design and optimization of these interfaces would result in more resilient devices that are less sensitive to abuse conditions such as temperature excursions. Intelligently designed interfaces may allow battery engineers to incorporate new, high-capacity electrode materials based on (for example) oxygen redox processes more easily. Surface oxygen reactivity, if unmanaged, can result in surface reconstruction and formation of chemical species, which can reduce lifetimes by either depositing on the cathode or, if soluble, shuttling to the anode. Mitigating this degradation will be the key to being able to utilize these compounds in safe and robust electrochemical cells.

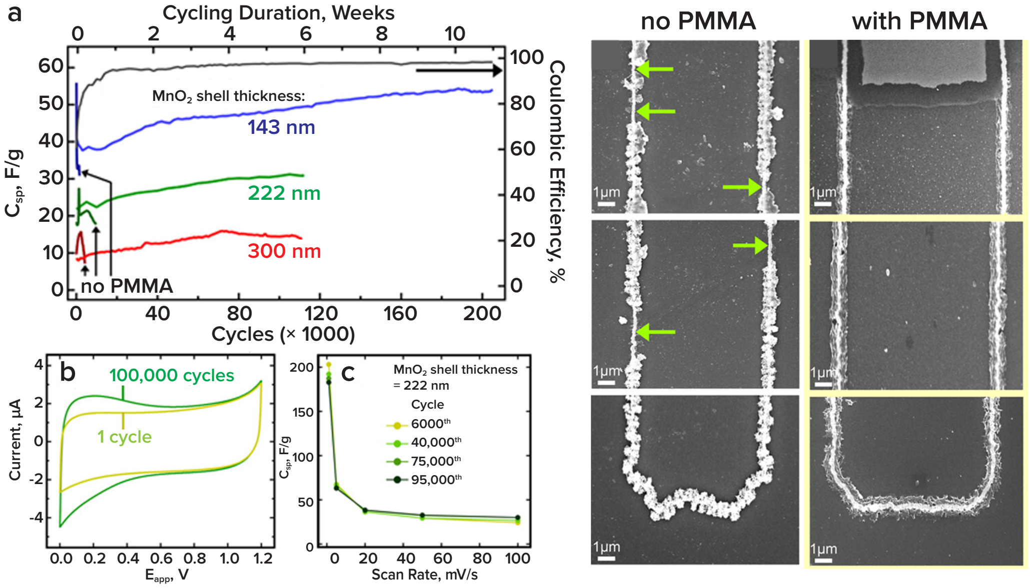

Figure 3.3.2 (a) Electrochemical cycling of MnO_2@Au supercapacitor devices, showing greatly enhanced cycling for devices containing poly(methyl methacrylate) (PMMA). The term C_{sp} indicates mass-normalized specific capacity. (b) Cyclic voltammogram for improved device at cycles 1 and 100,000. (c) Variation of capacitance with scan rate as a function of cycle number. Right: images of devices showing loss of metal oxide due to embrittlement from nanowires after cycling in the absence of PMMA, and intact device when PMMA is used. From Ref. 7.

In short, applying an array of sophisticated characterization techniques with improved specificity, resolution, and sensitivity, as well as developing multi-modal approaches, combined with multi-scale modeling efforts can provide insights that can lead to new paradigms for improving performance, safety, and robustness of electrochemical devices, across a broad range of chemistries and architectures. Not only will this result in longer lifetimes and cycle lives, but also it can potentially enable the adoption of energy storage devices with much higher energy densities than currently available without compromising safety. While a number of possible approaches and solutions have been discussed as examples, there are likely many unexplored approaches that merit significant fundamental inquiry.

3.3.4 REFERENCES

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3.4 Panel 4 Report — Discovery, Synthesis, and Design Strategies for Materials, Structures, and Architectures

This panel discussion summarizes the status of advances in the fields of prediction, synthesis, and characterization of energy storage materials. By no means does this serve as a complete review, as it is intended to highlight important future research opportunities. In particular, it calls for a collaborative multilevel approach to identify new tailored architectures by using novel synthetic routes guided by input from theory and computational predictions.

3.4.1 CURRENT STATUS AND RECENT ADVANCES

What Is Known and What We Need to Know: Batteries are complex electrochemical reactors. Their theoretical performance is determined by the redox-active materials at each electrode and is broadly enabled by ion conduction by the electrolyte. Although battery technology has been deployed commercially for many years, the fundamental science and engineering of batteries—both of its individual components and the overall architectures—is still lacking fundamental understanding. Traditionally, the push for more efficient energy storage has been mainly driven by the search for new active materials and electrolyte formulations for Li-ion technologies. Although some promising alternative chemistries are currently extensively investigated, a commercially proven game-changer that replaces Li-ion chemistry has not yet emerged.[1] With energy storage on the threshold of transformational change, there is an urgent need to continue the search for alternatives. Newer scientific approaches that are strongly centered on computational efforts have been successful in providing candidate materials and suggesting alternative research directions that cannot be achieved by purely empirical (trial-and-error) synthesis routes. These and new emerging computational approaches are leading to discovery of increasingly complex, highly functional materials for battery components. Importantly, these materials may, in part, exist as metastable phases, of which some are only present during operating conditions. Moreover, one of the key questions is how one would synthesize these new materials, as traditional routes may not be adequate, especially if metastable phases and/or complex architectures are to be realized. Thus, there is an urgent need for further integration between experiment and theory and computation to accelerate materials discovery and theoretically guided synthesis.

But how far away is the current state from achieving these objectives? A brief tour through the main battery components will clarify the way and point out the challenges. The following sections review the state-of-the-art in the main battery components: electrodes, electrolytes, and interfaces. Characterizing and designing each of these components and their assemblies are of utmost importance for realizing a new generation of high performance batteries.

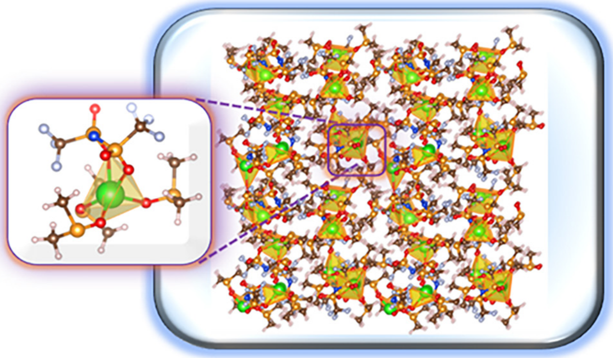

Figure 3.4.1. Unique solvated structure in superconcentrated electrolyte of sodium bis(trifluoromethanesulfonyl)imide in dimethyl sulfoxide. From Ref. 6.

Electrolytes: from Liquids to Solids through New Concepts: Recent studies in Li-based batteries have demonstrated that high salt concentrations can help reduce the parasitic reactions between the electrolyte and electrodes during electrochemical cell cycling, thus extending battery life.[2,3] This is due to changes in solvation structure around Li^+ ions and interfacial reactions with electrodes. Furthermore, the 1.23-V electrochemical window of aqueous electrolytes is increased to 3 V by the “water-in-salt” approach.[2]

This concept has been generalized to Na-based batteries[4,5] and Na-O_2 batteries with superconcentrated electrolyte of sodium bis(trifluoromethanesulfonyl)imide (TFSI) in dimethyl sulfoxide (DMSO) (Figure 3.4.1).[6] A unique solvated structure of loosely crosslinked $(DMSO)_3$-Na^+-TFSI basic units binds a significant proportion of the DMSO solvent molecules, leaving only a few available for parasitic reactions. This implies that to minimize solvent decomposition from volatile side reactions yet maintain full utilization of the electrolyte, one can reduce the fraction of "free solvent" (i.e., non-fully solvated solvent molecules) in dilute electrolytes by increasing the salt concentration. However, to generalize this novel concept and apply it to diverse solvent and salt systems, better fundamental understanding about the nature of superconcentrated electrolytes is essential.

The electrolytes used in electrochemical energy storage are either liquids, as in the case of lithium-ion batteries, or solids, as in solid-state batteries. They are very rarely a combination of the two. This is unfortunate because an ideal electrolyte is one that has the conductivity of a liquid but the thermal, chemical, and dimensional stability of a solid. Recently, researchers have used the sol-gel process to prepare materials by using an ionic liquid as the solvent phase.[7] The final material consists of an interconnected porous inorganic network that effectively holds the ionic liquid phase by capillary forces, as the pore size is on the order of 10 nm. This material, termed an "ionogel," has been adapted so that the ionic liquid is ionically conducting through the addition of a lithium-based salt. Moreover, because the ionic liquid has extremely low vapor pressure, the liquid phase is completely stable in ambient conditions. The resulting composite material is solid-like in its appearance but has much greater ionic conductivity because of the liquid-phase character of the ionic liquid domains. The ionogel approach is just at the proof-of-concept stage but already shows great promise. Because of the continuous liquid phase, ionogel conductivities are in the range of 10^{-3} S/cm at room temperature, only 2 to 5 times less conductive than the corresponding ionic liquid but many orders of magnitude greater than solid electrolytes. However, a key question that has yet to be fully answered is whether the electrolyte/electrode interface will have much lower impedance than that of solid electrolytes. If the presence of the liquid phase produces a low interfacial resistance, as occurs in liquid electrolyte systems, this will overcome one of the limitations of solid-state battery technology.

Interfaces: Where All the Action Is…The various battery components interact through physical interfaces. Lately, new experimental methodologies with ultrafast time resolution have become available for investigating the molecular structure of bulk electrolytes, interfaces, and solids: in particular, those exhibiting fast dynamic behavior. These new ultrafast techniques, coupled to computational analyses, are starting to answer unresolved questions in electrochemical energy storage. For example, vibrational sum frequency generation has been combined with cyclic voltammetry to investigate the formation of the solid-electrolyte interphase on anode surfaces.[8] Other femtosecond time-resolved spectroscopies have been used to investigate the structure and dynamics of bulk electrolyte solutions.[9,10] Interestingly, the experimental findings provided by these techniques can be used not only to bridge the gap between other structural methodologies with lower time resolution such as nuclear magnetic resonance, but also to generate databases of experimental observables required for methodologies such as machine learning. Other electrochemical research communities have helped in the advancement of the understanding of solid-liquid interfaces. For example, analysis of the interfacial water on gold electrodes studied by X-ray absorption spectroscopy and first-principles calculations revealed that the interfacial water molecules have a different structure from those in the bulk.[11] Recently, studies have also started unravelling the electrochemical double layer by direct probing of the solid-liquid interface (see Figure 2.3.12 in Chapter 2) by means of ambient pressure X-ray photoelectron spectroscopy performed under polarization conditions.[12] These newly emerging experimental techniques are opening up many possibilities and enabling comparison, validation, and benchmarking of theory and computational approaches.

Charge Transport and Storage: The Pulse of the Battery: Our current understanding of ionic diffusion in the solid state is that the basic process occurs through migration of ions between empty interstices or vacancies in the lattice.[13] This motion of ions is strongly influenced by the nature of the bonding in the host framework because of electrostatic interactions that occur between the positively charged alkali ions and the negatively charged anions.[14-16]

In oxides, the distortions that occur as Li ions are inserted or removed can induce severe changes in the structural framework. In the classic $LiCoO_2$ material, as Li is removed from the parent structure, the electrostatic repulsion between the neighboring layers of CoO_6 results in an elongation along the *c*-axis of the unit cell.[16,17] This expansion continues up to the point where all the Li is removed (i.e., CoO_2 remains) and the compound irreversibly distorts to a CdI_2-like structure. This new polymorph is completely incapable of Li-ion insertion because the Li site shares a face with the CoO_6 octahedra, an environment that is energetically unfavorable due to the strong coulombic repulsion between the Li and Co ions.[18] Similarly, the framework of spinel $LiMn_2O_4$ is known to undergo a structural distortion that causes an elongation along the c-axis of the cubic cell and lowers the symmetry to the tetragonal polymorph of λ–MnO_2.[19]

While polyanionic materials also experience distortions to their frameworks, the complex ways that their rigid oxoanionic subunits can pack offers an endless number of unique structural topologies for designing new intercalation hosts. The many advantages of polyanionic electrodes include robust structures that provide long-term stability over thousands of cycles, the ability to tune redox potentials through inductive effects, and rich compositional phase diagrams.[20] These materials also offer advantages over oxides because polyanionic compounds do not typically release O_2 on thermal decomposition, which can exacerbate thermal runaway when cells fail.

Charge-storing materials (carbons, metal oxides, etc.) are now available in a wide range of nanoscale forms and have been incorporated in complex electrode architectures that have shown improved electrochemical performance. With these new materials, the traditional lines between capacitor-like and battery-like behavior are being blurred, both in terms of the current–voltage characteristics and the charge/discharge time scale.[21,22] For example, conventional battery materials, such as $LiCoO_2$, may exhibit a capacitor-like (pseudocapacitive) current–voltage response when synthesized in crystallites sized <10 nm.[23] Alternatively, nanocrystalline $LiMn_2O_4$, when incorporated as a thin coating on an ultraporous conductive carbon architecture, exhibits energetically well-defined Li^+-insertion peaks as would be found in a typical battery, but the resulting $LiMn_2O_4$—carbon electrode architecture delivers charge on a few-seconds timescale that is typical of supercapacitors.[24] There are many other such examples, including individual materials exhibiting multiple charge-storage mechanisms that operate at different time regimes, from few-second pulses (supported by double-layer capacitance or redox pseudocapacitance) to long-term/high-capacity operation (battery-like ion insertion). These new materials and electrode architectures promise to provide new functionality to the electrochemical devices into which they are ultimately incorporated. Yet, a sufficient understanding of the structural characteristics that give rise to such behaviors is lacking.

A Holy Grail: Lithium Metal as a High Capacity Negative Electrode: The development of Li metal anodes is generally considered critical to enable rechargeable battery systems with high energy density, including those that go beyond Li-ion, such as Li-S. However, Li metal anodes suffer from well-known challenges such as low coulombic efficiency, instability against most electrolytes, and formation of dendrites. Many reports focus on approaches that mitigate the symptoms of poor performance (i.e., suppression of dendrites) without addressing the underlying root cause of why they form and how they evolve. By looking beyond performance-based metrics, a more fundamental understanding of why a certain methodology is successful (or not) can be gained.

Recent advances in *operando* analysis, combined with computational modeling, allow for an understanding of the coupled morphological, electrochemical, chemical, and mechanical behavior of Li metal anodes during cycling. This coupling between multiple variables (i.e., morphology, electrochemical activity, and mechanical stresses) is critical to understand the origins of poor performance, which allows for rational design of new solutions. In the example shown in Figure 3.4.2, *operando* video microscopy of Li metal morphology is coupled with galvanostatic voltage vs. time traces.[25] This correlation between morphology and electrochemical properties provides insights into dendrite and pit formation.

Another concern with Li-metal and Li-alloy materials is the effect of the solid-electrolyte interphase generated due to unwanted reactions at the electrode surface. These materials undergo significant mechanical volume expansion and contraction during lithiation-delithiation.[26] Due to this volume change, the solid-electrolyte interphase continuously breaks and reforms during cycling. This repeated breakage and reformation consume both the active materials and the electrolyte, resulting in low cycling efficiency and poor cycling life. A number of efforts have been made to stabilize the solid-electrolyte interphase.[27-33] Some of the more common approaches include optimizing solid-electrolyte interphase compositions by tuning electrolyte components, developing a protective layer on the material surface to circumvent the poor interfacial chemistry between Li-alloy materials and electrolyte, and using surface modification techniques to construct an artificial solid-electrolyte interphase layer to protect both electrode material and electrolyte. Despite these efforts, the solid-electrolyte interphase problem persists, and there is a critical need to develop a stable and functional solid-electrolyte interphase that can withstand mechanical volume expansion and contraction.

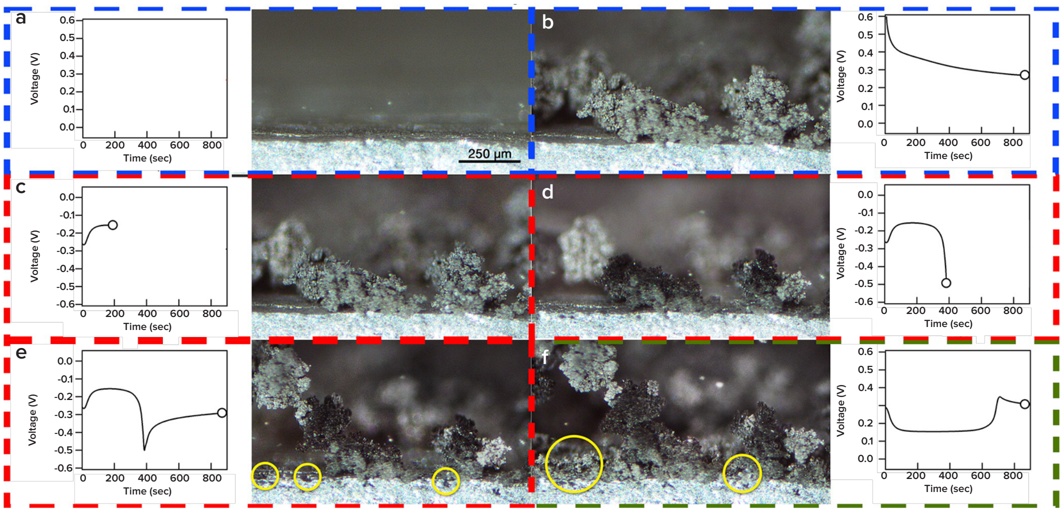

Figure 3.4.2. *Operando* video microscopy illustrating correlation between the morphological evolution of Li metal and galvanostatic voltage traces. From Ref. 25.

The extreme reactivity of Li metal anode surfaces has also been examined with *ab initio* molecular dynamics simulations and density functional theory. This study includes analysis of solvent and salt decompositions in concentrated solutions,[34-36] the consequences of highly interconnected battery chemistries,[37,38] and the effect of artificial solid-electrolyte interphase layers.[39] The combination of *in situ* advanced characterization techniques with *ab initio* methods[40] is a promising avenue for integrating insights and obtaining a more complete picture of complex interfacial phenomena.

A Better Understanding Starts at the Atomic and Molecular Level: The use of first-principles computations to characterize electrode/electrolyte interfaces is beginning to receive increasing attention within the community. This section briefly reviews activities in two vibrant areas: interfaces with lithium and the electrical double layer in capacitor systems.

Electronic structure and atomistic force-field models have been used to investigate the chemistry at the electrode-electrolyte interface. Quantum chemical methods have been applied to elucidate solid-electrolyte interphase reactions since the early 2000s.[41] These studies provided the potential energy pathways for decomposition of the main organic carbonate solvents, including the prediction of most of the solid-electrolyte interphase products that were previously or later discovered with experimental techniques. However, the surface effects were incorporated much later[42] and have now become routine in the analysis of electrode/electrolyte interfaces. *Ab initio* molecular dynamics simulations have given new insights into the initial stages of solid-electrolyte interphase formation on lithiated silicon anodes (Figure 3.4.3) at varying degrees of lithiation, emulating different states of charge. [43,44] They have been also applied to characterizing reaction mechanisms of complex electrolytes [45,46] and side reactions, such as cation dissolution at the cathode/electrolyte interface.[38] First-principles-constrained density functional theory calculations have shown great value in estimating the electron tunneling rate between an electrode and a solvent molecule across an insulating oxide layer and other related phenomena at electrochemical interfaces.[47] The stability of the solid-electrolyte interphase products has also been investigated by density functional theory and *ab initio* molecular dynamics methods.[48,49] Thus, current electronic structure methods can examine the thermodynamics of surface chemistry and can look at small local models of the interaction of the surface with the electrolyte. Recent development of methods that marry electronic structure of the local electrode/electrolyte description with a continuum model of the electrolyte beyond the first 2-3 layers holds some promise to capture chemistry in this interfacial region. Classical force-field models can better handle longer range behavior, allowing for examination of ion distributions and the impact of electric fields on electrolyte structure.[50] However, reactive processes such as ion association/dissociation and surface reaction are poorly captured by most classical force fields, and reactive force fields[51] typically include charge equilibration schemes where handling the charged interface is a challenge.

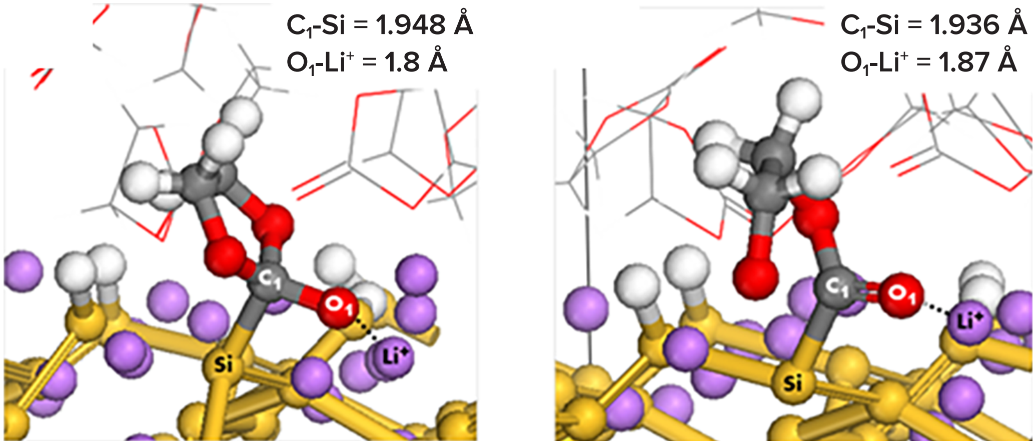

Figure 3.4.3. Decomposition of ethylene carbonate at the lithiated silicon surface/electrolyte interface. The image shows the adsorption of a solvent molecule at the electrode surface, followed by a C-O bond breaking. From Ref. 43.

For capacitive energy storage systems, where charge transfer and surface reaction do not occur, atomistic and electronic structure methods have made considerable advances in considering interfacial structure. Advancing upon conventional interfacial double-layer theory (Helmholtz, Gouy-Chapman, and Gouy-Chapman-Stern models), a more accurate interfacial description has been obtained analytically.[52,53] These models can determine the differential capacitance vs. potential for different ionic concentrations next to a planar electrode. Coarse-grained models, such as classical density functional theory [54,55] and grand canonical Monte Carlo theory,[56] have provided more accurate microscopic insights into the ionic response and electrochemical double layer structure and have allowed one to examine how ion size, ion valence, solvent dipole, ion concentration, and the electrode pore size/geometry influence the capacitive performance (for example, Figure 3.4.4). To capture the role of electrode chemistry and electronic structure, electronic density functional theory for the electrode has been integrated with implicit solvation models via the joint density functional theory framework[57] to address quantum capacitance and dielectric screening in single-layer to few-layer graphene electrodes.[58] Different from electrochemical double layer capacitors, surface redox and ion-intercalation pseudocapacitors are more complicated and difficult to simulate. A 1D continuum transport model was used to describe the hybrid pseudocapacitor based on the lithium intercalation and diffusion in metal oxide,[59] while joint density functional theory was applied to study the protonation reaction and surface redox pseudocapacitance of the RuO_2(110) surface.[60]

From the Components to the Device: Architectural Design and Control: While the active material and electrolyte have often been the focus of innovation, battery performance also depends on a series of support components that enhance charge transport and mechanical stability. These components include carbon additives and binders. Coatings are increasingly being used to impart interfacial stability. Emerging concepts of self-healing and thermal shutdown require adding yet additional materials that can deliver this function, which remain to be fully defined. Lastly, ion transport at the electrode is ensured by the formation of a porous structure that ultimately needs to be as thick as possible (certainly, over 100 mm). Industry has made notable incremental advances by tinkering with the processing of current materials into cells. At this point, it is evident that future breakthroughs will require a holistic strategy where all components of the battery are rationally designed, and whose final architecture requires that all components, redox-active or supporting, are located precisely in the exact amounts and location for optimum function. Animated by the explosion of nanotechnology, materials chemists and engineers have developed an impressive ability to assemble heterostructures at the level of single nanocrystals (Figure 3.4.5),[62] secondary particles,[63] electrolytes,[64] and even electrodes.[65] These contributions provide the basis for creating novel electrode and battery architectures.

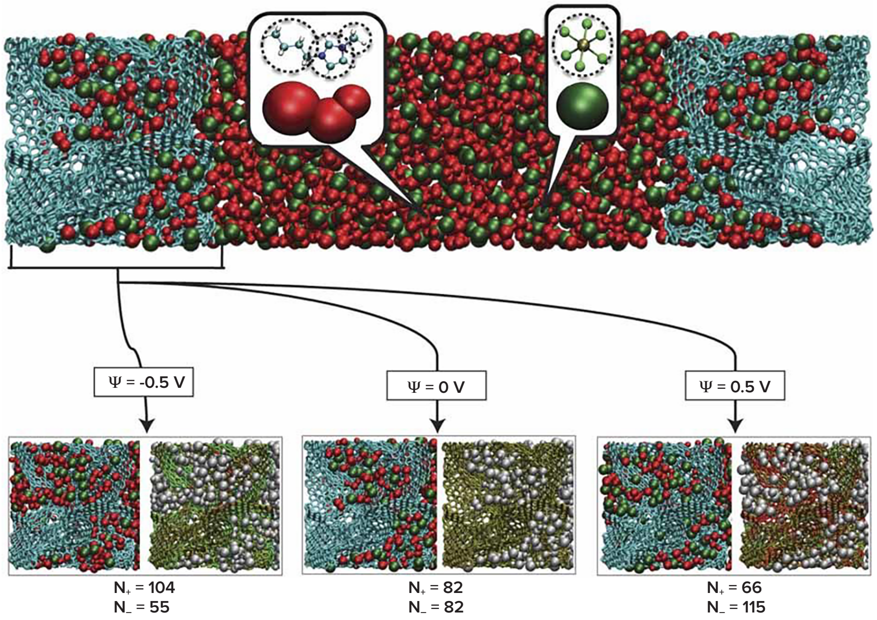

Figure 3.4.4. Simulation of an electrochemical double layer capacitor cell comprising two realistic carbon models at the end with a bulk coarse-grained ionic-liquid electrolyte in the middle from a constant-potential molecular dynamics simulation. From Ref. 61. Reproduced with permission of Nature Publishing Group.

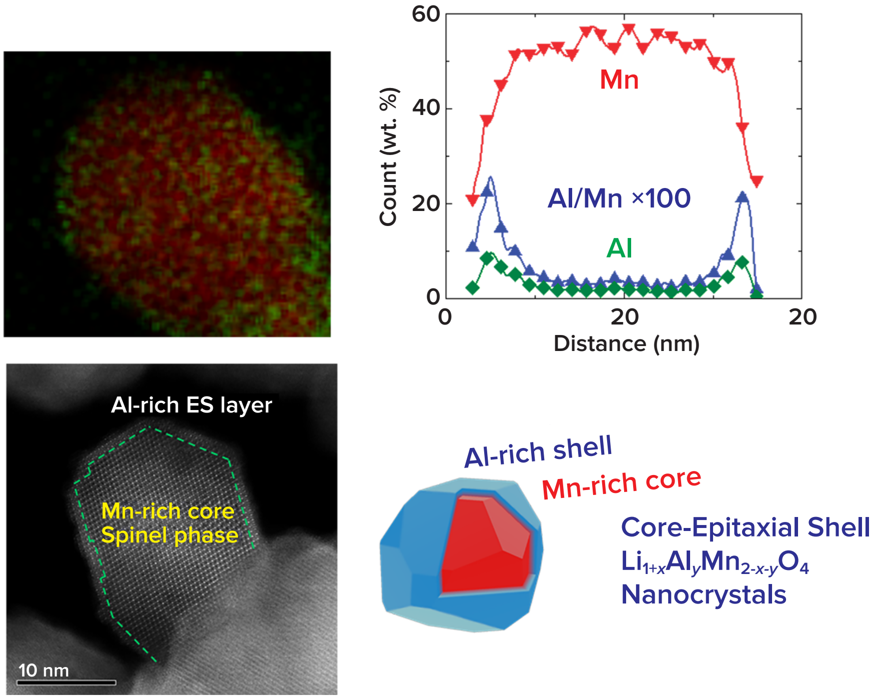

Figure 3.4.5. (Top left) Energy dispersive X-ray spectroscopy of Mn (red) and Al (green) with (top right) corresponding line scans of core-epitaxial shell $LiMn_2O_4$/$LiAl_xMn_{2-x}O_4$ nanocrystals. (Bottom left) Scanning tunneling electron microscopy image of a core-epitaxial shell crystal, demonstrating the epitaxial character of core and shell, and (bottom right) schematic representation of the heterostructure. From Ref. 62.

A Key Step: *In-situ* Monitoring Synthesis Processes: Conventional syntheses of materials, especially for inorganic solids, are often done using solid-state reactions, flux growth, or solvothermal methods. The synthesis of novel compounds, however, often becomes limited by trial-and-error synthesis techniques, unable to benefit from the effectiveness gained by using modeling and other experimental methods. This is often due to the lack of direct knowledge and information of the chemical processes that take place during the synthesis. It is well established that synthesis methodologies can have a significant effect on the properties of materials. Understanding the synthesis mechanisms can also help design better strategies, reduce cost of starting materials, and provide ways to scale up for commercial production. Computational approaches can predict structures of both stable and metastable compounds with desired properties, but the synthesis route is often too expensive or not known. To solve this problem there is a need for the *in situ* monitoring of synthesis. Some work has been done in various fields, such as mesoporous materials,[66] oxides, and phosphides using different types of synthesis procedures,[67] as well as *in situ* monitoring of crystallization pathways (Figure 3.4.6) oriented toward controlled synthesis.[68-70]

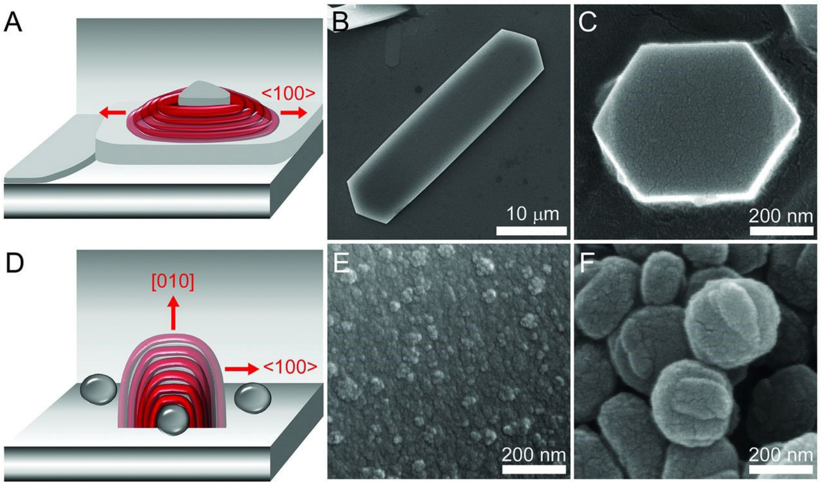

Figure 3.4.6. Schematics of two-dimensional layer growth (A) and three-dimensional island growth (D), depicting proposed mechanisms of silicalite-1 crystallization at high and low temperature, respectively. (B and C) Scanning electron microscope images of crystals prepared by either seeded (E) or nonseeded (F) crystallization, which exhibit rough surfaces and spheroidal shapes. From Ref. 70. Reproduced with permission of AAAS.

The Ultimate Goal: Prediction of Materials Structure and Behavior: Computation and modeling have over the last decade become essential tools in advancement of energy storage technologies, providing a mechanistic rationale to guide material, component, and device design. Modeling approaches applied to electrochemical energy storage systems range across electronic structure methods, atomistic simulations, microstructural simulations, and continuum-scale reaction and transport models.

Computational materials screening, based on first-principles electronic structure methods, has been applied to discover new materials with desired properties for battery components as well as in electrocatalysis, heterogeneous catalysis, and photocatalysis. When it comes to batteries there have been a number of computational atomic-scale predictions of electrode materials and electrolytes based on the Materials Genome approach. See for example the recent reviews.[71,72] First-principles methods can be used to predict discharge voltages, [73,74] ion diffusion rates, and material stability by calculating bulk phase diagrams[71] and surface reactivity.[28] First-principles computational studies of electrolytes can determine electrochemical stability windows and ion-association energies to identify potential new formulations.[75] History-dependent lithiation algorithms have captured key aspects of the transition of crystalline-Si surfaces to amorphous-Si surfaces during electrochemical lithiation (Figure 3.4.7).[76] However, the characterization of the state of the electrode surface in direct contact with the electrolyte and its evolution during battery cycling still remains a challenge.

There have also been important advances in modeling phenomena at longer length and time scales. Macro-homogeneous approaches in modeling battery electrodes, [77] as well as coarse-grained mesoscopic [78] and continuum-scale models,[79] have become important tools in understanding how materials properties can translate into battery behavior and performance. Over the last decade, there have been many efforts in the area of continuum modeling. Currently, multi-physics, multi-scale models coupling electrochemical-thermal-electrical simulation tools are being developed and used by the battery community to predict performance of cells and packs.[80] These models span architectures from the electrode to the cell level to modules to packs and can even be linked to vehicle performance. Efforts are also underway to link mechanical and structural models to these electrochemical-thermal-electrical models to predict the safety behavior of electrodes, cells, modules, and packs[81] under a crash-induced crush.

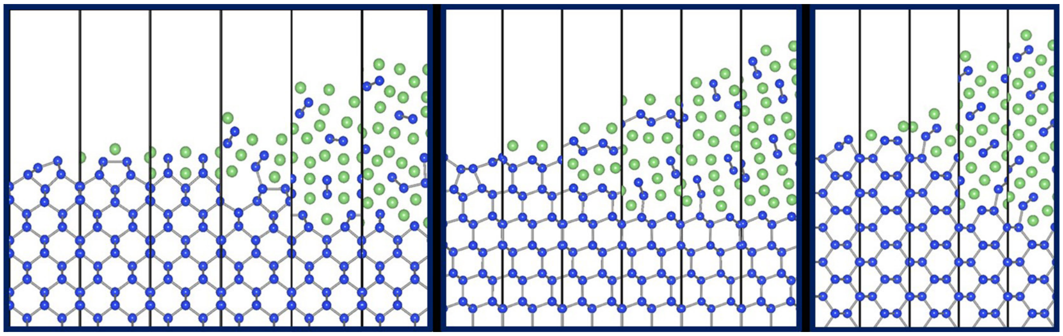

Figure 3.4.7. Electrochemical lithiation of single-crystal Si surfaces, as determined by a history-dependent lithiation algorithm. Decreasing electrode voltage from left to right for each surface. Green spheres, Li atoms; blue spheres, Si atoms. From Ref. 76.

In recent years, there has been significant interest in building on the porous electrode model by performing 3D microstructure-based simulations[82] with detailed representation of the porous nature of the battery electrodes, obtained by various techniques, including focused-ion-beam scanning electron microscopy and X-ray tomography. Microstructure modeling is underway to ultimately understand the interplay among active material structure, particle distribution, binder, conductive additives, and electrolyte to design better electrodes. Coupled electrochemical-thermal-electrical-mechanical models[83] are being applied to the microstructures to understand the behavior of electrodes. Testing and characterization of electrodes with various properties are used to inform and validate the microstructure models. Attempts to model anisotropic reactions between particles have moved the field away from the core assumption of the macro-homogeneous approach that all particles in the porous electrodes are equivalent. Of high interest to battery researchers is mesoscale modeling development to probe the effects of the cathode composition, the ratio of active material, conductive additive, and binder content on the electrochemical and mechanical properties and performance.

3.4.2 SCIENTIFIC CHALLENGES AND OPPORTUNITIES

Battery performance ultimately depends on a series of interrelated components that synergistically enhance transport and mechanical stability. Our discussion above suggests that breakthroughs in performance will require a holistic strategy where all components of the battery are rationally designed, but also one where the formation of the final architecture is done in such a manner that all components, redox-active or supporting, are located precisely in the exact amounts and location for optimum function. In the end, the goal must be to maximize the amount of redox-active material over all other components, thus maximizing the energy density and specific energy of the final device. It is not currently possible to build controlled porous electrode architectures beyond a few micrometers, at best, which is an order of magnitude below application requirements. Despite significant improvements in the design and local manipulation of materials, precise control of chemistry and structure remains to be achieved. More importantly, the design of physicochemical rules for each component in the ideal architecture has yet to be achieved. The development of such design rules requires a much deeper understanding of the fundamental coupled processes involved in affecting reversibility and reliability of electrical energy storage systems.

Understand, Predict, and Guide the Synthesis Routes: With the development of faster and higher flux instruments at user facilities with X-ray, neutron, and electron analytical tools capable of collecting data on the time scale of synthesis reactions, it is now possible to routinely follow synthesis with these tools.[84-86] To date, however, very little work has been done in this area for energy storage materials, but in the next decade it is anticipated that following the synthesis reactions will become routine and allow researchers to access intermediate phases, fully identify their synthesis conditions, and follow the growth of materials from amorphous to crystalline or vice versa by using total scattering methods. Understanding the reaction mechanism will allow researchers to improve our material synthesis, assist in better predictive modeling, and enhance the ability to discover new materials.

Exploit Blended Capacitor/Battery Functionality: For realization of the next generation electrode materials, a detailed fundamental understanding is needed of the composition/structure/architecture relationships that determine their current–voltage curves and time response. One particularly important area of interest is the role of structural defects/vacancies and the disorder that often accompanies this blended capacitor/battery behavior. Such materials are often difficult to characterize by conventional methods that rely on crystallinity/structural periodicity. However, newer tools using synchrotron-based techniques offer the promise of unraveling the structural complexity of poorly ordered or defective materials that otherwise display intriguing charge-storage characteristics.[87] *Ex situ* characterization will provide baseline information on material structure, but the ability to perform such measurements *in situ* or *operando* will be critical in elucidating the charge-storage mechanisms that may be at play in such systems. Further, because the materials in question will support electrochemical processes occurring on the order of a few seconds, the tools used to characterize them must be able to measure dynamically at such time scales. Advanced characterization should also be coupled with computation/modeling of such solid-state structures.

Modeling of pseudocapacitors is still in its infancy. There are currently no good models to describe these materials due to the complexity of the interfacial physical chemistry. There are multiple considerations here as the surface structure, surface reaction pathway, reaction kinetics, overpotential, solvent effect, and electrolyte pH are all able to greatly influence pseudocapacitive behavior, which is characterized by surface redox reactions. It is likely that a multi-scale approach is necessary. Moreover, modeling at the microstructural level should assist in directing the design of porous electrode architectures that deliver high capacity/energy, but on supercapacitor-like time scales.

Design Effective Electrodes, Electrolytes, and Interfaces: Understanding how densely packed solids facilitate the motion of positively charged ions through their lattices is crucial for accelerating the design of next generation intercalation hosts and solid electrolytes that can transport next generation elements like Na or multivalent cations. This is particularly challenging for materials consisting of compositions with a mixture of rigid covalent and more flexible ionic bonds, as in polyanionic compounds.[88,89] These structural deformations are not only critical for influencing the rate of ionic diffusion, but also have direct consequences for the mechanical properties and the potential for particle fracture over extended cycling. Developing better experimental and computational methods to characterize the nature of cooperative structural distortions is an area that would greatly facilitate the prediction of local stresses that can build inside the intercalation hosts during (de)insertion while simultaneously building the fundamental understanding of how to accelerate the transport of ions through materials.

Superconcentrated electrolytes are destined to emerge as a vital factor in advancing electrochemical energy storage. This is because specific solution structures (both bulk and at electrode/electrolyte interfaces) associated with these chemistries may have great beneficial impact on the mitigation of unwanted reactions that cause major safety problems in batteries. This field of electrolytes has received only a limited amount of study. The opportunity here is to integrate data mining with advanced atomic-scale simulations and *in situ* high-level characterization, which can then be used to guide experimental studies directed at structure/property relations. A key issue to be considered with these electrolytes, both computationally and experimentally, is their unique solvation properties, which can then be used to provide new chemical insights. A well-defined challenge with these studies will be to extract design rules from a vast chemical space for electrolyte design and development.

Ionogels present a tantalizing opportunity in which to achieve liquid-like ion transport and interfacial transport in a solid-state matrix. Their incorporation in solid-state batteries can be transformative to this technology if the presence of the local liquid phase produces a low interfacial resistance, as occurs in liquid electrolyte systems. This may result in extended battery lifetimes. Moreover, designing appropriate mesoporous host matrices may yield materials with reduced dimensionality and with confined liquid phases that can operate at low temperatures.

Making the Use of Li Metal Anodes a Reality: There is a critical need for improved *operando* analysis of Li metal anodes, which will increase our understanding of the coupled electrochemical, morphological, and mechanical behavior of the negative electrode and its interface. Combining experimental work with multi-scale modeling will enable the research community to move towards experimentally informed design, and away from empirical approaches based on qualitative or semi-quantitative concepts. One of the most important challenges is to develop a tailored solid-electrolyte interphase for the high-volume-change Li-alloy materials. Some of the basic scientific questions that need to be addressed are: What are the origins of the spatial/temporal variations in chemical composition and impedance of the solid-electrolyte interphase during cycling? What are the chemical and mechanical origins of hot spots where solid-electrolyte interphase fracture and dendrite nucleation occur? Another important direction concerns stable solid-electrolyte interphase formation. How can good tolerance to volume change occurring from charging and discharging be achieved without compromising electrical contact properties or mechanical integrity? Also, how can the solid-electrolyte interphase be designed to prevent such effects as gas formation, and how can ionic conductivity be maintained throughout the changes in volume? To address these issues, new research directions are needed that lead to the interfacial assembly of functional components with precisely controlled structures. One opportunity here is computational design that guides the synthesis of new interfacial ion-conducting materials to accommodate the change of volume.

Rational Discovery of Smart Materials and Architectures: The transfer of electrons and ions at the electrode/electrolyte interface challenges first principles and atomistic modeling approaches, and significant advancement remains necessary to allow such modeling to guide rational design. At the interface, electrode charge and electrolyte countercharge are distributed at a length scale that challenges first-principles methods. Studying bond-breaking and -forming reactions, involving both electron and ion transfer, necessitates the use of electronic structure methods that can accurately capture the energetics of the processes involved. However, directly incorporating the effect of potential while reactivity is changing, coupled with the complexity of the electrode and electrolyte microstructures, poses new challenges. These challenges leave an opportunity for developing new, integrated approaches with the combined advantages of electronic structure and force-field modeling to simulate the dynamic and reactive behavior of electrochemical interfaces. Such models would find application in investigating interfacial ion transfer in battery components and interfaces, solid-electrolyte interphase formation, electrocatalytic reactions in regenerative fuel cell systems, and surface chemistry in pseudocapacitors.

Beyond current approaches, computational strategies could be directed into multimodal inverse design, where a collection of functionalities is targeted not only to identify materials, but also architectures that are composed of assemblies of individual materials. The ultimate goal is to provide detailed guidance to synthetic efforts, which will require further development of multiscale models and experimental *in situ* monitoring of materials evolution under both synthesis and operation conditions, as well as novel algorithms to describe environment-dependent atomistic structures of multicomponent interfacial phases. Machine-learning and data mining approaches combined with refined experimentation and first-principles modeling to generate consistent and broad databases are highly promising approaches to achieve these objectives. [90]

Computational strategies to treat ion insertion into amorphous electrodes, together with genetic algorithms describing interfaces with variable electron and ion counts, are beginning to emerge. Coupling of these and related strategies to growing databases of electrode/electrolyte surface structures will permit development of general predictions of potential-dependent interfacial structures. As an example, a grand canonical genetic algorithm[91] has recently been developed that permits identification of ordered phases of two-dimensional materials with fixed chemical potentials. These and other algorithms should be extended to provide unbiased searches of configurational space of near-surface structures resulting from ion insertion (or removal) at variable chemical potentials. It would be crucial also to identify history-dependent aspects of these processes that would lead to novel structures at different insertion (removal) rates or to hysteresis between insertion and removal processes. Such phenomena are common in battery components and are not understood.

3.4.3 IMPACT

The following impact is possible from pursuing the basic research described above:

- ☐ Rational design and synthesis of materials and architectures yielding energy-dense, long lasting, and safer electrodes (and thus much improved energy storage devices).
- ☐ Rational design and synthesis of materials and architectures addressing volume expansions and making electrodes self-healing and resilient (and thus much improved energy storage devices).
- ☐ Greater understanding of reaction mechanisms leading to point failure at the mesoscale level. This will enable design of new classes of energy-relevant materials with orders of magnitude improvements in durability.

□ The design and development of new charge-storing materials and electrode architectures that are capable of operating under many different charge/discharge regimes, including complex duty-cycle demands, such as repetitive-pulse discharge/charge, deep discharge levels, and many-cycle operation. This will ultimately reduce the complexity of energy-storage systems, resulting in lower cost and less environmental impact.

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3.5 Panel 5 Report — Solid-State and Semi-Solid Electrical Energy Storage

Solid-state energy storage differs from the preponderance of commercial energy storage devices in wide use today (i.e., in portable electronics) in one important respect—the use of solid, rather than liquid, electrolytes. This distinction has profound implications.[1,2] First and foremost, solid electrolytes significantly minimize the safety risks associated with high volatility and flammability of liquid organic electrolytes.[2,3] Second, they diminish the propensity to form Li dendrites that can short circuit the electrodes—a catastrophic failure mechanism observed in liquid-electrolyte-based batteries[3]—and thereby enable the use of high-capacity Li-metal anodes. Third, new electrode and cell architectures become possible with solid electrolytes, enabling control of the geometric and spatial arrangement of one electrode with respect to the other.[4-6] Fourth, the nature of the interphases formed at the solid electrode/solid electrolyte interface can differ substantially from conventional liquid/solid systems, engaging such phenomena as space charge regions and electronic Fermi level pinning at the interface as well as short-range dipole layer formation.[7] And fifth, the transport properties of the solid electrolyte can be substantially different from those of liquid electrolytes.[2,8]

Many of the challenges slowing the adoption of solid-state energy storage are centered on the solid electrolyte and its interfaces with electrode materials. Ionic conductivity is highly important, with only a small number of solid compounds exhibiting values comparable to liquid organic electrolytes.[8] For such reasons, liquid electrolyte systems dominate most applications, while solid-state storage plays a role in niche applications and in some consumer devices.

3.5.1 CURRENT STATUS AND RECENT ADVANCES

Evolution of Solid Ion Conductors: The origin of solid-state ionics dates back to the 19th century, when Faraday discovered ionic conductivity in metal sulfides and fluorides. [9] At the end of that century, Nernst reported one of the first uses of solid ion conductors in the zirconia-based glow lamp,[10] which relied on the transport of oxygen anions under an applied electrical voltage to emit light. Though fast-ion conductivity was known to occur in AgI and derivatives thereof since the early 20th century, it wasn't until the latter half of that century that the first solid-state battery was developed using Ag and RbI_3 electrodes and a solid electrolyte based on $RbAg_4I_5$. [11,12] Facile transport of Ag ions through $RbAg_4I_5$ allowed for the first room temperature discharge of an all solid-state battery. [12] The same concept was extended to the lithium-iodine system using the ionic conductor LiI. At present, Li-I_2 solid-state batteries are used in pacemakers and in applications requiring low rate, but reliable, discharge with negligible self-discharge.[13,14]

While these first-generation solid-state batteries were pioneering discoveries, the appeal of rechargeability and high rate cycling comparable to liquid-based batteries inspired the development of molten alkali batteries employing fast-ion conducting solid electrolytes.[15,16] In these batteries the physical states of the electrodes and electrolyte are inverted compared to conventional batteries, i.e., the electrodes are liquid and the electrolyte is solid. For example, a sodium beta alumina electrolyte, when paired with a molten sodium anode and sulfur cathode at 300°C, enabled the development of industrial-scale grid storage batteries in use today.[17] These molten alkali batteries demonstrated for the first time that solid electrolytes can enable high-capacity, commercially viable batteries.

Emergence of Modern Solid-State Batteries: In the 1980s and 1990s, the potential of all-solid-state batteries using Li metal and an intercalation host cathode ($LiCoO_2$) was realized in thin film format.[18-20] As in previous examples, the discovery of a new electrolyte led to the development of a new battery configuration: in this case, based on the thin film electrolyte known as LiPON (lithium phosphorous oxynitride), which is a glass with Li-ion conductivity of ~10^{-6} S/cm.[18] Because its conductivity is relatively low compared to fast-ion conductors (also three orders of magnitude lower than conventional liquid Li-ion electrolytes), it must be made relatively thin (~1 μm), which is easily achievable through thin-film deposition processing. These commercially available batteries demonstrated unprecedented energy density at the cell level, very long cycle life (> 20,000 cycles), and high-rate cycling stability; perhaps most importantly, they showed that the Li metal interface could be successfully stabilized with a solid electrolyte.[18] Note, however, that the thin film format employs fabrication techniques (e.g., physical vapor deposition) foreign to conventional, large-scale commercial battery manufacturing, with consequences in material and architectural characteristics that invite a new set of scientific questions. Consequently, fabricating large-format batteries would benefit from the development of solid electrolytes manufactured using traditional bulk-scale synthesis and manufacturing techniques. Presumably, the same or similar processes could be used to fabricate solid-state batteries.

Given the myriad properties and manufacturability of solid electrolytes, a series of radar plots can be used to compare the properties of the common material classes, as shown in Figure 3.5.1.[8] Three specific classes of materials—sulfides, oxides, and polymers—are discussed below.

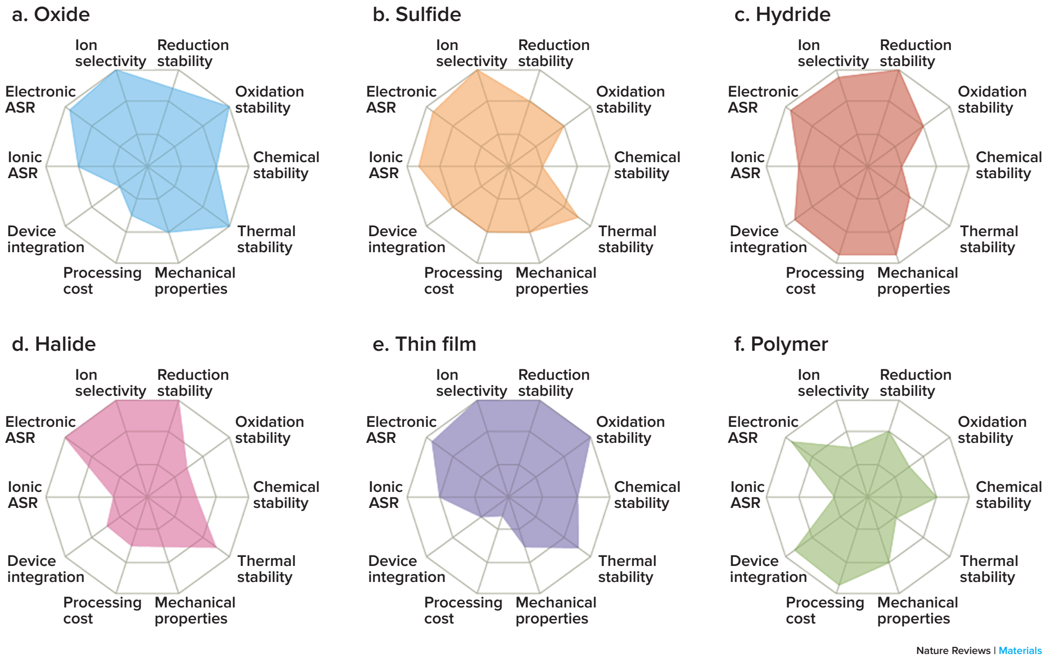


Figure 3.5.1. Radar plots comparing the properties of several common classes of solid lithium ion conductors. From Ref. 8.

Inorganic/Ceramic Solid Electrolytes: The last decade also saw the resurgence in discovery of solid-state electrolyte materials, notably Li-ion-conducting sulfides and oxides. For example, Kamaya et al.[21] and Mizuno et al.[22] discovered crystalline $Li_{10}GeP_2S_{12}$ and glass Li_2S-P_2S_5, both exhibiting Li-ionic conductivities comparable to liquid electrolytes. Compared to oxides that typically require high temperature densification, the sulfide electrolytes can be densified at room temperature. Recently, Kato et al. demonstrated that bulk-scale solid-state batteries can be fabricated at ambient temperature, with specific energies of several hundred Wh/kg while cycling at relatively high rates for hundreds of cycles.[23] A solid-sulfide electrolyte was used owing to its high ionic conductivities and ease of consolidation at ambient temperature under relatively high pressure (> 100 MPa) (Figure 3.5.2).[23] Undoubtedly, the ionic conductivities and ease of processing offered by the sulfides mark an important milestone in solid-state battery development.

Another important discovery occurred in 2007, when Weppner et al. reported a new oxide bulk-scale Li-ion conductor based on the garnet mineral structure, $Li_7La_3Zr_2O_{12}$ (aka LLZO).[24] When doped with Al or Ta to stabilize the cubic polymorph, LLZO is one of the few bulk-scale electrolytes to simultaneously exhibit stability against metallic Li, fast-ion conductivity, and Li electrode/electrolyte interfacial resistance (at 25°C) comparable to liquid-based cells.[24-26]

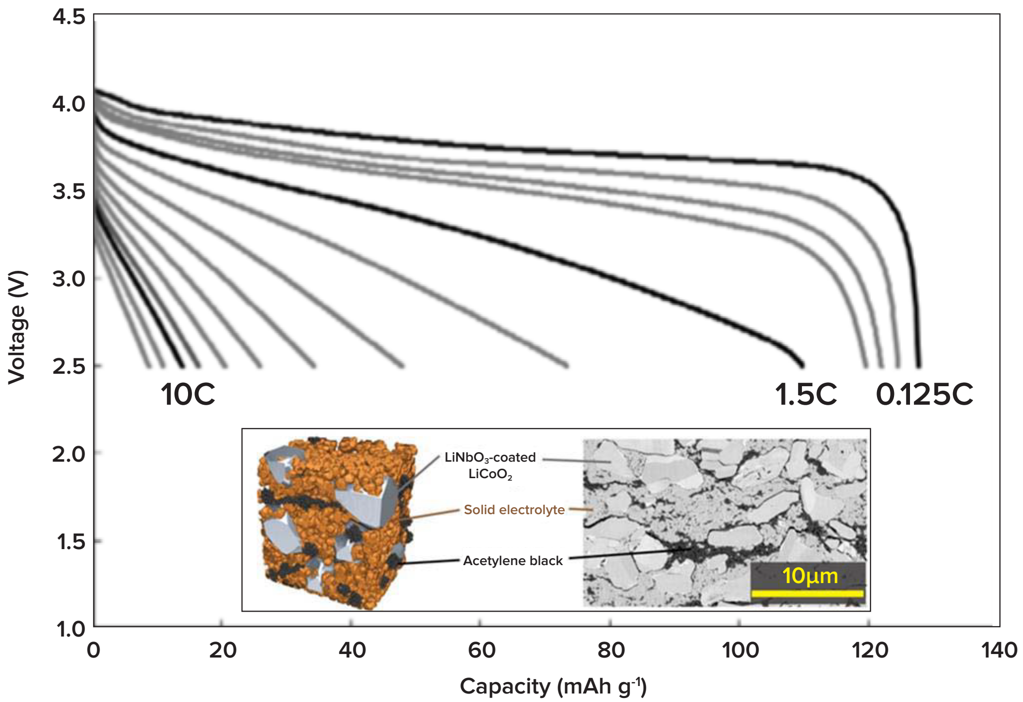


Figure 3.5.2. Discharge curves at various discharge rates from slow (0.125C) to fast (10C) for all solid-state bulk-scale Li battery based on sulfide-based electrolyte. From Ref. 23. Reproduced with permission of Nature Publishing Group.

Polymeric Solid Electrolytes: In polymer electrolytes – another class of solid electrolytes – lithium salts are dissolved in high molecular weight polymer solvents. Electron donor groups on the polymer chains solvate the Li cations, leading to salt dissolution and the generation of mobile charge carriers. The archetypical formula for a polymer electrolyte is PEOn:LiX, where PEO stands for polyethylene oxide, *n* denotes the ratio of ethylene oxide functionalities to Li cations, and X is a soft anion with delocalized negative charge to aid dissolution in the polymer matrix.[27] As lithium mobility in these systems is correlated to segmental motion and, consequently, lower stiffness, the tradeoff between conductivity and mechanical stiffness is a fundamental challenge. Material design strategies have been developed over the past 30+ years to address this trade-off and identify optimized materials for integration into practical cells. Examples include the fabrication of polymer electrolyte composites, where stiff inorganic fillers are dispersed into the polymer matrix,[28] and the design of block copolymers such as poly(styrene-b-ethylene oxide), where the styrene microphase-separated block provides mechanical reinforcement, and the ethylene oxide block conducts lithium.[29]

Comparing the entire class of polymer electrolytes to the sulfides and oxides (see radar plots in Figure 3.5.1), polymers have inferior transport properties (lower ionic conductivities and lithium transport numbers), but have advantages in low-cost processability and integration into cells. Since the early 1980s, there have been several demonstrations of full lithium-ion battery cells with good capacity retention over several hundred cycles. Typically, elevated temperatures (80-100°C) are required to achieve full electrode utilization due to the modest ambient ionic conductivities of the polymers.[30,31]

Comparison with Current Technology: Conventional Li-ion technology (i.e., based on liquid electrolytes) is widely used in portable electronics and is slowly making inroads into low-volume electric vehicles (plug-in hybrid and battery electric) and niche high performance vehicles. Large-scale adoption of electrified powertrains would, however, strongly benefit from lower cost, higher performance, and safer batteries. The opportunity to realize these improvements has created the impetus to pursue bulk-scale all-solid-state batteries employing an alkali metal as the negative electrode. Owing to their low mass, low electronegativity, and high volumetric and specific capacity, alkali metals are highly attractive negative electrodes. However, short-circuit failures caused by the formation of dendrites have limited the widespread use of rechargeable batteries using alkali metal negative electrodes coupled with liquid electrolytes. Consequently, one of the most appealing features offered by solid-state batteries is the prospect of stabilizing the alkali metal electrode (i.e., suppressing dendrites), which would enable cell-level energy densities substantially higher than current technology (≥ 1,000 Wh/l).

3.5.2 SCIENTIFIC CHALLENGES AND OPPORTUNITIES

The first decade and a half of the 21st century brought about a renaissance in solid-state electrolyte research, perhaps bringing the scientific community to the verge of a new era in electrochemical energy storage. The need for advanced batteries is a frequent topic of news reports and, more often than not, is coupled with the expectation that solid-state batteries will provide for safer, more robust, more wearable, and more energy dense devices. Given the urgency for advancing high-performance, commercially viable energy storage technology, a focus on key barriers will be critical for accelerating the scientific learning process.

The steady stream of reports of new solid electrolytes with high ionic conductivities (10^{-3} S/cm) has created a sense of excitement within the solid-state ionics community. How ions can move so rapidly through a solid material is fascinating and raises the grand challenge to provide an equally fast response of the electrodes. However, there are yet few compelling demonstrations of successful integration of solid electrolytes into viable solid-state cells. This integration requires much more than a high ionic conductivity and presents great challenges to achieving compatibility with other components, reliable and scalable fabrication, and stable and long-lived performance. Much is left to understand about how ions move along and across solid interfaces, how materials behave and evolve when far from equilibrium, how defects either lead to failure or ensure rapid kinetics, and how thermodynamics drives reactions toward equilibrium to deliberately passivate interfaces or find metastable structures. Continuous advances in computation, materials synthesis and characterization, and *in situ* analyses provide optimism that these technical challenges can be overcome.

The following four research areas describe the key scientific challenges and research opportunities for next generation solid-state ionic research. First, in the last decade a few viable solid-state electrolytes have been discovered exhibiting some, but not all, of the the necessary properties to enable the next generation of solid-state batteries. These materials will aid in the development of design guidelines (or “descriptors”) that will accelerate the discovery of the next generation of materials. Second, solid-state ionic conductors involving alkali metals are typically reactive and, therefore, difficult to synthesize. Moreover, metastable materials or glasses represent an important class of solid-state electrolytes but are typically less stable than their crystalline counterparts, leading to additional synthetic challenges. New synthesis routes and *in situ* tools to characterize phase formation and microstructure are needed and will complement the materials discovery thrust. Third, capitalizing on the discovery of advanced solid-state electrolytes requires integration with electrodes to form solid-solid interfaces. Little is known about such solid-solid interfaces and the factors that govern their stability and kinetics. Comprehensive knowledge of solid-solid interfaces is needed to overcome the challenge of stabilizing, in particular, the alkali metal-solid electrolyte interface. Fourth, solid-state interfaces are difficult to characterize because they are buried. Novel *in situ* characterization techniques are required to access solid-solid interfaces without disturbing them. Taken together, these thrusts elaborate the science needed to realize the potential offered by solid-state electrochemical technology.

Discovery of High Performance Solid Electrolytes: Historically, the search for new solid electrolytes has relied on intuition and serendipity. While this approach has recently generated a small number of promising materials, it remains highly inefficient. Rational strategies are needed for the discovery of new electrolytes and for the improvement of the properties of known, but flawed, compounds. The development of these strategies will accelerate the commercialization of viable solid-state batteries by eliminating the trial-and-error aspects of present approaches.

Strategies to advance the state of the art can be divided into two categories. The first involves mitigating the shortcomings of known ionically conductive materials through the development of measures to counteract their flaws. For example, in the case of LLZO, a recently uncovered performance limitation is short-circuiting,[32] which arises from penetration of lithium metal along the grain boundary network of the polycrystalline membrane. Eliminating this failure mode might be possible by using surface coatings, altering the intrinsic interfacial chemistry, or manipulating grain boundary properties and would constitute an important step towards making LLZO-based cells viable. Unfortunately, a full understanding of which failure modes are likely within different classes of solid electrolytes does not yet exist. Thus, development of rational countermeasures currently can only proceed *after* failure modes have been identified.

An alternative strategy is to identify totally new solid electrolytes that do not exhibit these flaws. Unfortunately, the prediction of stable crystal structures based on a specified composition or property remains an unmet challenge. Nevertheless, computational techniques based on atomic-scale simulations can definitely aid in this search. A more practical, but still challenging strategy would involve screening of existing databases of known (or hypothetical) materials, such as the Inorganic Crystal Structure Database.[33] Given a composition and crystal structure, arguably the most straightforward way to determine whether the corresponding compound exhibits high ionic conductivity is through molecular dynamics simulation. A drawback to this approach, however, is its limited throughput. *Ab initio* molecular dynamics although highly accurate, can typically access only a few picoseconds of simulation time due to its extreme expense, resulting in limited transport statistics. In contrast, classical molecular dynamics, which uses a prescribed interatomic potential, can access much longer simulation times, typically on the order of nanoseconds. Nevertheless, classical molecular dynamics remains moderately expensive, and the determination of accurate interatomic potentials that are transferrable across materials classes can pose a challenge. In summary, while molecular dynamics is well-suited for careful characterization of the transport properties of a small number of compounds, it is not amenable to high-throughput screening. Other methods for screening candidate solid electrolytes are needed.

Rapid screening becomes possible when design rules or “descriptors” for ionic conductivity (and other key properties) are identified. In principle, these descriptors can then be evaluated with low-to-moderate computational expense for many candidate materials.[34] In the case of ionic conductivity, correlations between ion mobility and several other structural or chemical features have been discussed.[35,36] These include the topology of the migration channel, ionic radius and volume effects, ionic polarizability, bond valence, and phonon modes.[35] To cite one example related to crystal topology, Figure 3.5.3 illustrates energy barriers associated with Li-ion migration within prototypical crystal lattices based on three anionic crystal structures: hexagonal close packed (hcp), body-centered cubic (bcc), and face-centered cubic (fcc).[36]

At present, the importance and generality of any single descriptor from the preceding list remain a matter of debate, as opportunities for validation are limited by the dearth of experimental data. Thus, the speed at which computationally guided discovery can proceed will be influenced by the availability of high-quality measurements drawn from diverse materials.

In addition to high ionic conductivity, a viable solid electrolyte should also exhibit chemical and electrochemical stability with respect to the electrodes,[37-39] have a wide electrochemical window,[37] and display suitable mechanical properties[40-42] and microstructural features. Not all of these requirements are well-defined (e.g., mechanical and microstructural); moreover, the sheer number of criteria complicates the discovery process. Although many of these properties can be calculated, doing so is expensive in some cases. At present, little or no effort has been devoted to identifying descriptors for these properties. A comprehensive strategy for the discovery of viable solid electrolytes must take these properties into account, and not focus solely on ionic conductivity.

Key scientific challenges for discovery of new solid electrolytes include the following: identify what chemical and structural features provide for efficient ion transport properties, stability with electrodes, and dendrite suppression; predict electronic and ionic transport processes from computational methods, in concert with *ab initio* crystal structure prediction algorithms; develop and apply new *in situ/operando* experimental probes of interfacial stability, reaction, and interphase formation in model materials; and accelerate materials discovery through rapid synthesis and characterization protocols.

While the mainline approach to enhanced solid electrolytes places a premium on high ionic conductivity materials, another route to high performance solid electrolytes is through much thinner (<100 nm) solid electrolytes. Basic principles of diffusion dictate that in such cases the charge/discharge rates are determined by diffusivity in the electrodes, so that electrolytes with inherently lower (10-100X) ionic conductivity can be tolerated in such thin layers. This route poses a different kind of synthesis challenge, based on vapor phase chemistry for materials growth under self-limiting surface reaction conditions employed in atomic layer deposition. Syntheses of LiPON[43,44] and LLZO[45] solid electrolytes by atomic layer deposition have been reported, with LiPON having been employed as an ultrathin (~40-100 nm) electrolyte in solid-state batteries.[44]

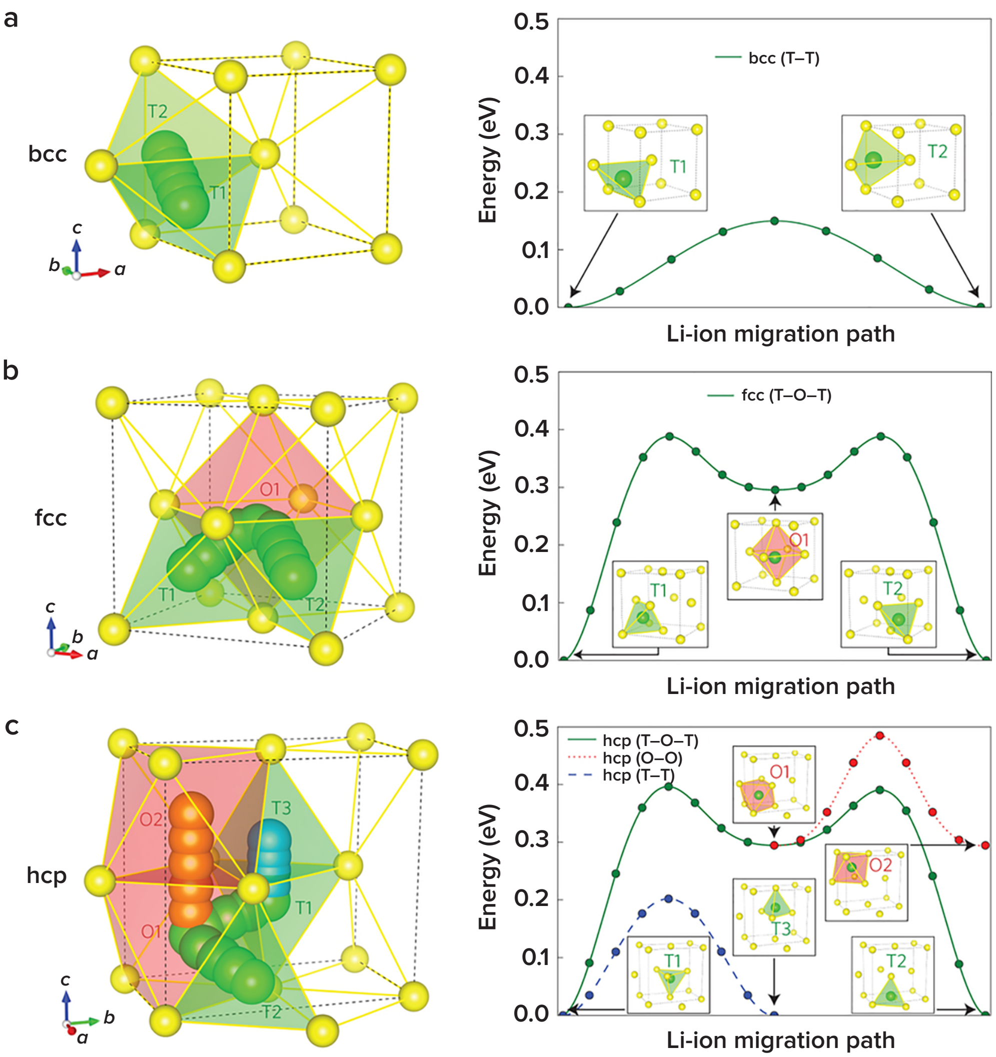


Figure 3.5.3. Examples of Li-ion migration barriers calculated for three prototypical lattices: bcc (top), fcc (middle), and hcp (bottom). Octahedral and tetrahedral interstitial sites along the migration path are labeled with the symbols "O" and "T," respectively. From Ref. 36. See also Ref. 44.

Modeling and materials discovery are also closely linked with the other three research areas identified by this panel and discussed below. These include the search for alternative synthesis and fabrication, the refinement of interfaces for rapid ion transfer and electrochemical stability, and the evaluation of bulk and thin film electrolytes for both flaw tolerance and robustness with repetitive cycling.

Understanding Synthesis and Creating Idealized Interfaces. As advances in computational chemistry identify novel solid electrolyte compositions with highly desirable properties, such as superionic conductivities and electrochemical stabilities, there is a concomitant need to advance the science of synthesis. These novel materials may exist at their thermodynamic equilibrium, or they may need stabilization at a metastable state far from equilibrium. Because synthesis is typically done on a trial-and-error basis, theoretically promising compounds may never be synthesized even in small quantities for property evaluation, let alone for a viable industrial-scale production. Improvements in predictive synthetic strategies are required to realize these new compositions and phases. Key scientific challenges include 1) achieving exquisite control over material compositions and structures by developing a comprehensive understanding of the chemical and physical phenomena of synthesis, 2) understanding how to consolidate loose electrolyte powders into dense solid electrolyte membranes while retaining key desirable properties, 3) establishing clear design principles for the integration of solid electrolytes into electrochemical cells with technologically-relevant electrochemical performance, and 4) developing fabrication strategies and cell designs that can accommodate the conflicting requirements at the composite cathode/electrolyte and metal anode/electrolyte interfaces.

To facilitate material discovery, *in situ* monitoring of the synthesis process may help chart chemical phase evolution pathways and identify metastable phases far from thermodynamic equilibrium. For example, *in situ* electrochemical impedance spectroscopy integrated with solid-state synthesis of $Li_7S_3P_{11}$ has been used to identify degradation processes at high temperatures, leading to the formation of undesired phases and reduced ionic conductivities (Figure 3.5.4). With this information, the authors were able to identify optimal synthesis conditions.[46] Moreover, simultaneous determination of structure and properties of target and intermediate compounds will allow fast experimental screening of materials. *In situ* techniques, including X-ray diffraction,[46] Raman spectroscopy,[47] X-ray photoelectron spectroscopy,[48] electron microscopy,[49] and solid-state nuclear magnetic resonance,[50] have been recently employed to create "panoramic" reaction maps and accelerate the discovery of efficient synthesis routes for many classes of materials.

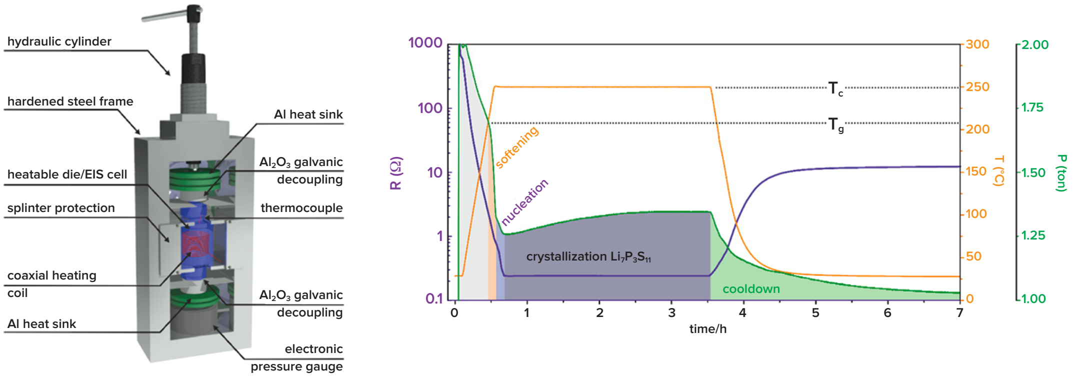


Figure 3.5.4. (Left) Schematic of hot press apparatus designed for real-time acquisition of process parameters (pressure and temperature) combined with electrochemical impedance spectroscopy. (Right) Synthesis diagram showing the evolution of $Li_7S_3P_{11}$ resistivity during thermal treatment. Sample temperature (orange), pressure (green), and resistance (purple). From Ref. 46. Reprinted with permission of American Chemical Society.

Sintering to consolidate loose electrolyte powders into dense layers is another challenge and is traditionally accomplished by solid-state diffusion at high temperatures. The process is controlled by the slowest moving species and can thus require several hours at temperatures above 1000°C to achieve densification. Ironically, the high diffusivity of Li ions at room temperature, which is desired in solid-state electrolytes, causes loss of Li during sintering. Thus, from a practical perspective, sintering is often a bottleneck in ceramic processing that must be overcome to dramatically improve manufacturing throughput and lower costs. Recent advances in ceramic processing science have the potential to address these challenges. Spark plasma sintering is one example of field-assisted sintering techniques that hold promise in consolidating ceramic electrolytes to full density without a significant change in composition and phase.[51] This method has been used in the preparation of NASICON,[52] garnet,[53] and $Li_7P_3S_{11}$[54] electrolytes, in addition to the assembly of complete solid-state electrochemical cells.[52] Other advanced material processing capabilities, such as rapid thermal annealing, laser processing, and rapid quench processing, also offer opportunities to control the morphology of solid-state materials. For example, glassy phases can be kinetically trapped as the thermal quench outpaces crystallization. These processing techniques will provide a rich foundation for a full range of basic research on synthesis and should enable revolutionary advances in structures and properties.

As promising solid electrolytes with high ionic conductivities and enhanced electrochemical stabilities have been developed over the past decade, efforts to demonstrate solid-state energy storage in practical devices have highlighted fundamental challenges in fabrication. Literature demonstrations of solid-state cells typically show non-optimized designs where the solid electrolyte is several hundreds of micrometers thick. However, the solid electrolyte should be as thin as possible to minimize its volume and mass contribution to the cell. Thinness is a critical design parameter in terms of transport as well. For solid-state cells to have rate performance comparable to that of conventional lithium-ion cells, the area-specific resistance of the solid electrolyte should be on the order of 10 $\Omega\cdot cm^2$. Therefore, solid lithium conductors with relatively high conductivities of 10^{-4} and 10^{-3} $S\cdot cm^{-1}$ need to be fabricated with thicknesses on the order of 10 and 100 μm, respectively. For materials with inferior lithium conductivities, the solid electrolyte layer thickness must be further minimized to accommodate the area specific resistance requirement. Advanced film or coating fabrication technologies, such as various solution casting approaches and physical or chemical vapor deposition, can provide these capabilities. These transport requirements also highlight fundamental challenges in integrating these thin solid electrolyte layers with energy-dense composite cathodes and alkali metal anodes. The electrolytes must be thin yet also mechanically robust to accommodate various stresses from integration with other cell components, assembly and packaging into a full battery module, and cyclic dilation during cycling.

Conventional wisdom suggests that the alkali metal/electrolyte interface should be free of inhomogeneity, e.g., defects that can lead to non-uniform current densities and formation of lithium dendrites.[55,56] A fundamental question for fabrication is whether a planar interface is a general requirement for the lithium-electrolyte interface. An alternative approach is to fabricate high surface area or 3D structures to reduce current densities at the interface.[57] Also, it is unclear how inhomogeneity at the interface governs electrochemical phenomena. It is critically important to understand how much inhomogeneity can be tolerated in solid-state cells without appreciably compromising cell performance, a question that is fundamental to mesoscale science.[58] At the cathode, on the other hand, the solid electrolyte must be mated to a solid-state composite (porous) cathode. While compliant sulfide and polymer electrolytes have been successfully integrated with porous cathodes, this integration is much more difficult to achieve with stiff ceramic oxide materials. Future research should seek to balance the development of feasible fabrication approaches with studies of how these approaches shape the physical and chemical nature of the electrode-electrolyte interface.

More generally, the domain of solid-state storage presents qualitatively different structural permutations whose consequences in design and synthesis are profound at the mesoscale, posing a host of scientific questions. Thin film synthesis, already common in commercial solid-state cells, provides relatively smooth, predictable surfaces and films, but with greater limitation on material complexity. Thick film synthesis, typically formed from powders by sintering, accesses complex combinations of elements and stoichiometries but produces less controlled microstructure (particle shape and size) and varying tortuosity of transport paths. One can envision mixtures of the two as well, exemplified by thin film atomic layer deposition of an alumina layer to enable wetting of garnet electrolyte pores for successful in-filling of Li anode material.[59] Given these considerations, what architecture and synthesis strategy can realize high performance and stability in the resulting storage structures?

These outstanding questions emphasize the need for rational design principles to identify solid-state architectures for efficient charge capacity utilization, long-term cycleability, and mechanical robustness in electrochemical cells. Developing these design principles requires relevant model systems that allow study of correlated physical, chemical, and electrochemical phenomena during cell operation. Lithium thin-film batteries are exemplary systems and provide inspiration for these model systems.[60] As progress in solid-state electrolytes continues and they are integrated into practical solid-state electrochemical cells, relevant model structures for these novel materials and devices must be developed. For example, a model structure could be a single crystal of a polycrystalline ceramic or a bi-crystal consisting of a crystalline electrode and crystalline electrolyte. Ideally, these structures should allow the interrogation of how material properties and structural features (such as crystal orientation, aliovalent substitutions, impurity phases, and interfacial layers) govern the correlated phenomena. Electrochemical system modeling coupled to these experimental observations is also needed. In particular, modeling of solid-state mechanics is especially important to understand the evolution of material and interfacial stresses associated with cycling and to discover how the cell architectures can be designed to accommodate reversible volume changes with each charge/discharge cycle. As the computational capabilities progress for model systems, an important challenge will be extending the coupled physics to cell architectures of real, practical solid-state devices. *Operando* characterization of solid-state cells will be useful in validating these computational models.

Interaction of Chemistry and Mechanics of Solid-Solid Interfaces: While there have been recent advances in solid ion conductors exhibiting conductivities comparable to liquid electrolytes, how to best translate these materials into viable solid-state batteries is not currently known. What are the design rules? How are solid-solid interfaces formed? How does charge transfer occur at interfaces? What mechanical stresses arise during fabrication and during cycling?

Essentially, there are two interfaces of interest, distinguished by the electrode type—the alkali metal electrode and the ceramic electrode. Several key scientific challenges related to these two interfaces must be addressed to mature solid-state batteries. First, despite the impact that metallic anodes could have on energy storage technology performance, very little is known about the chemical, electrochemical, and mechanical stability of the alkali-metal/solid electrolyte interface. It has been shown that relatively soft alkali metals can penetrate relatively hard ceramic electrolytes at high current density.[32] Ostensibly, this seems to defy physics; however, there must be an explanation. Understanding the underlying mechanisms that allow this unusual phenomenon to occur could guide future efforts to mitigate it. Second, intrinsic to their design, solid-state batteries require a chemical and physical union between the cathode, which is typically a ceramic, and the solid electrolyte. Because the approach to construct a rechargeable, bulk-scale, solid-state battery is unknown territory, it is important to understand how the transport of ions and electrons occurs across these solid interfaces, and how mechanical stresses are generated when the electrode changes volume during cycling while the solid electrolyte does not. Lastly, the development of new *in situ* characterization techniques tailored for the analysis of advanced solid-solid interfaces could facilitate understanding by observing phenomena in real time and without the artifacts frequently created by postmortem analyses, especially with air-sensitive materials. Acquiring a fundamental understanding related to these aspects will accelerate the development of solid-state batteries.

In summary, the key scientific challenges for enabling solid electrolyte/solid electrode interfaces are: understand what limits the stability and kinetics of the alkali-metal/solid electrolyte interface, understand charge transport and the mechanical stability of the ceramic cathode/solid electrolyte interface, and develop *in situ* techniques to analyze solid-solid interfaces.

Alkali Metal Solid-Electrolyte Interface: One of the most promising approaches to enable a step increase in battery energy density is to stabilize the alkali-metal/solid-electrolyte interface.[61,62] Solid inorganic, polymeric, or ceramic/polymeric composite electrolytes could act as a physical barrier to block the formation of dendrites, thereby stabilizing the alkali metal electrode surface during cycling.[1,32,53,63] Additionally, the solid electrolyte must be compatible with the alkali metal while possessing high ionic conductivity and mechanical and electrochemical stability.[37-39,43,64] Of particular importance is achieving facile and stable charge transport across the alkali-metal/solid-electrolyte interface at meaningful current densities.[53,65] Though there are some hypotheses and models that analyze the alkali-metal/solid-electrolyte interface, none has been validated.[66,67] Similarly, there are limited experimental studies that precisely determine what governs the maximum current density of the alkali-metal/solid-electrolyte interface.[53,68] Currently, for example, it is believed that Li penetrates grain boundaries in polycrystalline LLZO electrolyte (see Figure 2.3.5 in Chapter 2) at current densities above a few tenths of a mA/cm^2.[32,69] Why this occurs is currently not understood. Thus, the need to understand the underlying mechanisms that govern the stability of the alkali-metal/solid-electrolyte interface is clear (Figure 3.5.5).

***In-Situ* and *Operando* Characterization of the Solid-Electrolyte Interface:** Though computation can predict electrochemical stability, solid-electrolyte interphases often form between a metal electrode and solid electrolyte.[37,70] The effects of the alkali-metal/solid-electrolyte interface can be benign, detrimental, or beneficial.[64,71] Nevertheless, because the alkali-metal/solid-electrolyte interface can affect interface kinetics, stability, and durability, efforts are needed to better understand all solid electrolyte-electrode interactions at the atomic, molecular, and microstructural level (Figure 3.5.6).[71,72] Our knowledge of heterogeneous ionic interfaces, however, is very limited, mainly because of the complexity of interfacial structure and chemistry in real materials systems, where not only chemical inter-diffusion, lattice strain, defects, and chemical reactions can occur, but space charge effects may also complicate analysis .[73-77]

As these phenomena are correlated, all associated microscopic factors (i.e., lattice, electrons, polarons, and ions) must be simultaneously considered when studying the effects of spatial, temporal, and space charge. Analyzing these effects requires atomic-scale resolution, which creates the need for the fabrication of a precise model for all solid interfaces. Because crystallographic orientation could affect charge transport, fabrication of bicrystals[78] with control over atomic plane alignment and composition at interfaces will be necessary. New characterization techniques, which could analyze all these factors simultaneously under relevant and simulated operating environments, are therefore needed.

In summary, the discovery of numerous viable solid electrolytes could allow for a paradigm shift in battery technology. However, little is known about their integration with electrodes and into solid-state batteries. Myriad barriers related to the all-solid interface remain but may be overcome through a galvanizing and holistic effort bringing together the fields of materials science, solid-state electrochemistry, mechanical engineering, computation, physics, and materials characterization.

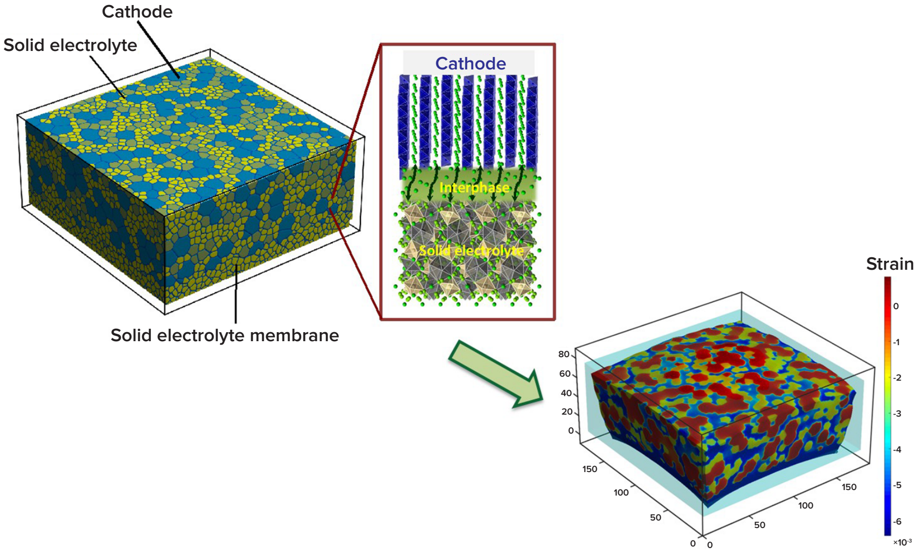


Figure 3.5.5. Schematic of structure and mechanical stresses across ceramic electrode/solid electrolyte interface in all-solid-state batteries (where all constituents are solid and chemically bonded). Understanding charge transport and the mechanical stresses across ceramic electrode/solid electrolyte interface will be key in enabling 3D composite cathodes with high areal capacity capable of operating at meaningful current densities over thousands of cycles. Courtesy of Jeff Sakamoto and Katsuyo Thornton, University of Michigan.

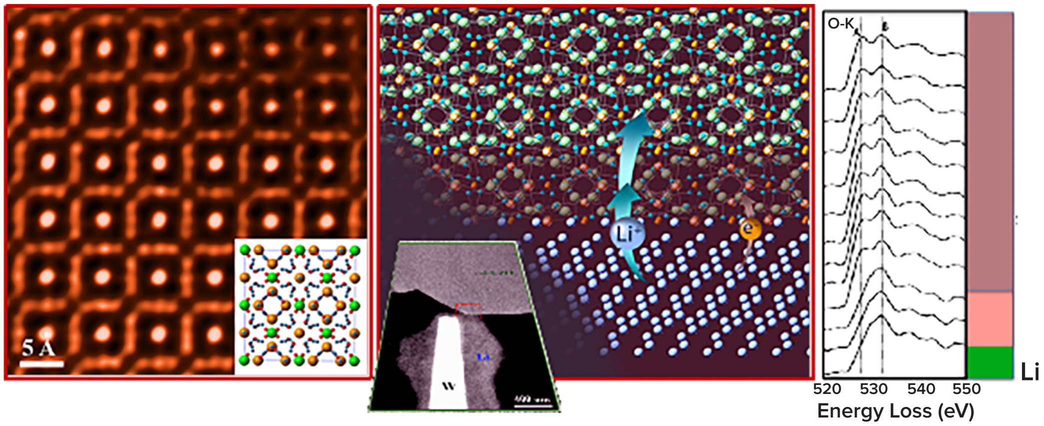


Figure 3.5.6. Atomic-scale chemical and structural evolution at the Li-metal/cubic-LLZO interface (center) as revealed by *in situ* electron microscopy (left) and electron energy loss spectroscopy. Spontaneous injection of Li^+ and electrons induced a self-limiting, stable alkali-metal/solid electrolyte interface. Such a passivation layer may be preferred compared to what is formed through chemical decomposition whereby multiple reactant phases may introduce inhomogeneous current distribution that limits the maximum tolerable current density. Taking advantage of intrinsic phase transformations in materials may be a strategy to enable the formation of stable and conductive interfaces leading to safe and high-performance solid-state batteries. From Ref. 72.

Evolution of Materials and Interfaces with Cycling in the Solid State: The rate and mass of ions transported through a battery over its lifetime are staggering, so it is little wonder that the materials and interfaces and microstructures evolve with time. Generally, this leads to a degradation of performance and eventual failure, but does it need to be so? Is it possible for materials and architectures to be stable or even improve with cycling? This may depend on whether the initial performance approaches the theoretical or optimal capacity and rates. Also, there may be active ways to regenerate or renew degraded battery components that can be developed for next generation electrical energy storage. These are grand challenges.

With solid-state batteries, evolution differs greatly from that of liquid electrolyte cells. The liquid can mediate reactions at the electrodes including dissolution, surface diffusion, gas evolution, Ostwald ripening, and shape changes. The dense structure and solid/solid interfaces, however, may be more sensitive to mechanical stresses and degradation due to cycling, leading to creep, migration, fatigue, and fracture processes. Spatial inhomogeneity in current density and temperature may also contribute to the stresses and accelerate changes in solid materials and interfaces.

Key scientific challenges include the following: identify how structures and defects direct the flow of ions in crystalline and disordered materials and across boundaries, understand how extended cycling of a solid-state cell leads to evolution of the electrode and electrolyte materials and interfaces, and understand how electrochemical and mechanical phenomena interact to govern stability, especially at high current densities. The opportunities that grow from addressing these scientific challenges may lead to the discovery and creation of novel means to prevent degradation and even improve stability.

New capabilities in materials characterization, manufacturing, and computation provide routes to address the challenges. Characterization is particularly challenging when the active interfaces and materials are buried, when they are difficult or impossible to disassemble, and when the evolution occurs over long times and many cycles. New probes that can penetrate materials—discerning subtle changes that occur at short times and visualizing the ionic current distribution at multiple length scale—are needed. Computations that simulate and predict the accumulation of changes over hundreds and thousands of cycles will rely on an accurate and precise understanding of the chemical and physical processes.

As an example of the subtle changes in the electrode materials that evolve dramatically over many cycles, Figure 3.5.7 shows the wavy structure that appears from an initially smooth Li film sandwiched between LiPON and parylene to form a thin film Li/LiPON/ $LiMn_2O_4$ battery.[79] This structure emerges gradually over 3150 cycles (equivalent to >100 turnovers of the available Li) at room temperature.[80] Between the ridges, the LiPON surface is visible. The interesting twist is that this occurs far more slowly for a $LiCoO_2$ cathode.

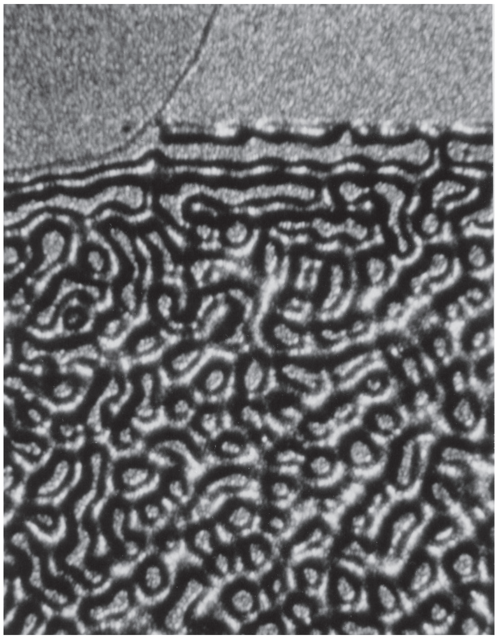


Figure 3.5.7. Wavy structure of Li anode after 3150 cycles of alumina/Pt/$LiMn_2O_4$/LiPON/Li/parylene thin film battery. The inactive Li tab is still smooth as shown in upper right. Scale is ~2 mm across. From Ref. 79.

Intercalation cathodes evolve to different extents with cycling in solid-state batteries. For several thin film cathodes that are fully crystalline and single phase, the structure and interface can be very stable for solid-state batteries even after many cycles.[81] This finding is surprising when using a glassy solid electrolyte, given that changes in the lattice parameters accompany the cycling. If cathodes are cycled at voltages exceeding their stability window, the rate of deterioration is reduced in a solid-state battery, but degradation is not eliminated. The evolution of a thin film $LiCoO_2$ cathode with LiPON electrolyte cycled to 5 V has been monitored by transmission electron microscopy.[82] Examples where cathodes of a solid-state battery actually improve with extended cycling include the gradual evolution in the crystallinity of the $LiMn_2O_4$ cathode with cycling[80] and the increasing specific capacity of MoO_3 cathodes upon extended cycling at 150°C in a Li/LiPON battery.[83] For a Mn spinel cathode, both X-ray diffraction and the voltage profile of the charge/discharge curves demonstrated that an initially amorphous cathode gradually becomes more crystalline with cycling. Seeking mechanisms to stabilize and renew battery materials, short of replacement, is an opportunity for future research.

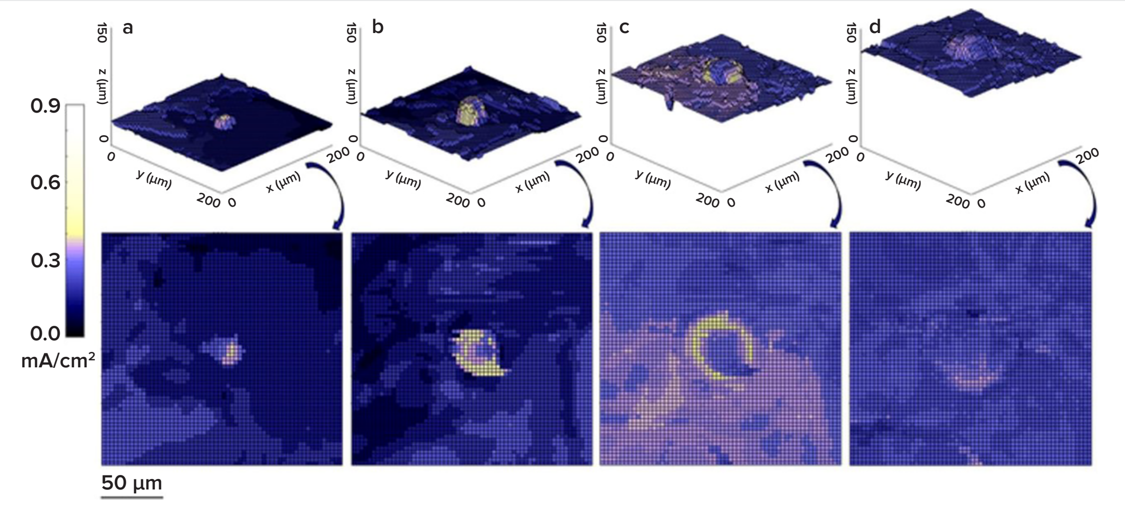
Cell failure is often a localized event. A prominent example is dendrite failure in lithium metal batteries. Synchrotron X-ray micro tomography (see sidebar, "*In Situ* Analysis of Buried Alkali-Metal/Solid Electrolyte Interfaces") is one approach for determining local current density at the electrode. Time-resolved tomograms can be used to determine the evolution of the shape of the electrode as the lithium metal is electrodeposited. The difference between two tomograms can be used to calculate the rate of local lithium deposition, and each mole of deposited lithium carries charge given by Faraday's constant. This enables determination of local current density. In large portions of a well-made cell, the current densities and deposition rates are uniform.

IN SITU ANALYSIS OF BURIED ALKALI-METAL/SOLID ELECTROLYTE INTERFACES

Electrode topography and current density maps have been obtained from a symmetric lithium-polymer-lithium cell.[84] Charge was passed from the top electrode (not shown for clarity) through a solid block copolymer electrolyte toward the bottom lithium metal electrode. The topography of the electrode (top) was determined from the tomograms while the local current density was obtained from differences between tomograms at different time points using Faraday's law. The average current density was controlled to be 0.18 mA/cm^2 using a potentiostat.

A small protrusion is evident at early times. The current density, as anticipated from elementary electrophysics, is maximal at the tip of the protrusion. In a liquid electrolyte, this inhomogeneity in current density would amplify deposition at the tip, resulting in unstable dendrite growth. In a solid, however, the maximum deformation is also located in the vicinity of the tip of the protrusion. This elastic deformation slows down growth at the tip. The current density maximum is in the form of a ring well removed from the tip of the protrusion. This results in flattening of the protrusion. Note that dendrites, the classical mode of failure in lithium metal electrodes, can be averted by the use of a solid electrolyte.

Methodologies for elucidating the local events that cause failure of batteries are essential for understanding and preventing them. Local probes such as X-ray micro tomography and scanning probe microscopy are essential for finding the "needle in the haystack" that causes battery failure. Measurement of local current density complements measurement of local potential, as discussed elsewhere in this document.



Local current density maps on a lithium metal electrode determined by time-resolved synchrotron X-ray microtomography.

Image from K. J. Harry et al., Influence of electrolyte modulus on the local current density at a dendrite tip on a lithium metal electrode, J. Electrochem. Soc.*,* **2016***,* 163, A2216-A2224.

3.5.3 IMPACT

Lithium-ion technology could be reaching its fundamental limits of performance and safety, thus restricting opportunities for further improvement. To keep pace with the ever-increasing demands for high performance energy storage, new approaches, cell chemistries, and cell configurations are necessary. In principle, solid-state batteries at the cell level can achieve high energy densities (> 1000 Wh/l) while using non-flammable electrolyte to improve safety. In addition, some solid-state electrolytes can be synthesized in air to reduce fabrication costs. For high energy/power applications such as electric vehicles, the intrinsic stability and substantially wider operation temperature, enabled by certain solid electrolytes, can reduce the mass, volume, cost, and complexity of the battery management system to further improve pack-level performance.

Altogether, a concerted effort to close current knowledge gaps through multi-disciplinary fundamental research will accelerate the maturation of solid-state battery technology. Given the current state of the development in combination with the current level of commercial interest, it is possible that overcoming the fundamental barriers described above will have significant technological impact.

3.5.4 REFERENCES

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3.6 Panel 6 Report — Cross-cutting Themes

The design of energy storage devices for tailored applications is a balancing act among competing performance metrics such as energy, power, lifetime, safety, and cost. This section summarizes the "cross-cutting" panel discussions regarding how to push the basic science frontiers forward and rapidly translate basic science to technology.

3.6.1 EMERGING METHODS IN MULTIMODAL CHARACTERIZATION OF ENERGY STORAGE WITH *OPERANDO*, *IN SITU*, AND *EX SITU* EXPERIMENTAL TOOLS

Improving the performance and lifetime of electrochemical energy storage systems necessitates a significantly better understanding of the electrochemical processes that take place within the storage device and the failure and degradation mechanisms of the storage system. Characterization of atomic, nanoscale, and mesoscale phenomena—especially at interfaces during charge and discharge—is essential. The inherent complexity of energy storage systems requires multiple techniques, as they must embrace diverse length and time scales and span many phenomena. In addition, there is a need to couple *in situ/operando* with *ex situ* studies, as they have different levels of data fidelity and interrogation power. Similarly, it is important to explore model systems that are designed to distinguish behaviors and reveal correlations. The important outcome of this characterization is a rational design of improved electrical energy storage systems. Over the past decade, much progress has been made in using particle- and photon-based spectroscopy, scattering, and imaging techniques to characterize electrical energy storage systems.[1-4]

Probes Sensitive to Light Elements Reveal Interface/Interphase Chemistry and Dynamics: In the last ten years, significant advances have been made in characterization tools suitable for probing interfaces and dynamics of ion motion, with high temporal and spatial resolution. These tools include electron microscopy, neutron and X-ray scattering, and spectroscopy methods, each of which brings unique chemical specificity and sensitivity. Preliminary results and planned improvements demonstrate the type of data that can be derived from these experiments and anticipate new opportunities to derive fundamental insights and drive the predictive development of stable and resilient interfaces.

One major opportunity involves the use of neutrons, which probe the low atomic number elements (e.g., Li, H, C, O, F) that dominate interface chemistry and ion transport. By virtue of their scattering cross section, neutrons are excellent probes for *in situ* characterization studies of interfaces through the use of neutron reflectometry and small angle neutron scattering, inelastic neutron spectroscopy and quasi elastic neutron scattering, and muon spin resonance. These probes, when combined with X-ray and electron characterization, provide important complementary physical and chemical insights. See sidebar on "Neutron Scattering."

In situ neutron reflectometry has revealed a complex dynamic surface chemistry of the solid-electrolyte interphase layer and is providing insights into interphase formation and dynamics.[5-7] For example, in silicon and $LiMn_{1.5}Ni_{0.5}O_4$ electrode chemistries, a 3-nm Li-rich layer forms on the electrode surfaces when exposed to a battery electrolyte. This is far thicker than an electrochemical double layer and represents the initial stages of interphase nucleation: it directly influences Li transport and desolvation at the interphase during charging and cycling. This layer expands with lithiation (~20 nm) and becomes polymer-rich. Upon charge-discharge cycling, the layer reversibly thickens and thins while changing from polymer- to inorganic-rich in a process described as "breathing". These foundational studies demonstrated the ability to determine interface structures, chemistries, and dynamics and should be extended to systems such as solid-solid and solid-polymer interactions. With advances in data collection time, kinetic measurements of diffusion and reaction processes become possible.

These will enable experimentally validated structure and composition data to build theoretical models and simulations of interfacial phenomena. Other methods include the use of small angle neutron scattering, which can follow interphase formation within the pore structure of a hard carbon anode.[8] In this study proton/deuterium

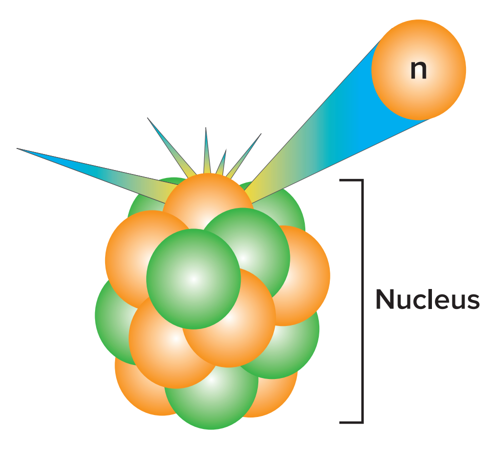
NEUTRON SCATTERING: A VERSATILE SUITE OF PROBES OF STRUCTURE AND DYNAMICS FOR ELECTRICAL ENERGY STORAGE

Major U.S. Neutron User facilities include:
High Flux Isotope Reactor (https://neutrons.ornl.gov/hfir)
NIST Center for Neutron Research (https://www.ncnr.nist.gov/)
Spallation Neutron Source (https://neutrons.ornl.gov/sns)

Neutrons can be exploited to probe the structure and dynamics of materials in a way that is complementary to electrons and photons. Unlike those probes, neutrons do not scatter from the electron cloud but interact with the nucleus. Hence, the scattering power of neutrons is not directly proportional to the atomic number. As a consequence, neutrons can detect light elements in the presence of heavier elements, distinguish between two different isotopes of the same element, and have very different scattering lengths for adjacent elements in the periodic table. The isotope effect is widely used to control (enhance or eliminate) contrast and label reactants of interest. The neutron's spin makes it a powerful direct probe of magnetism.

In addition, because neutrons have zero charge, they are highly penetrating and non-destructive of the sample being analyzed. As a result, regions of interest buried within a sample can be interrogated, exact quantitative data analysis is simplified, and *operando* and multi-modal measurements can be made more realistic, robust, and uncomplicated.

Because of the neutron's mass, its energy (at pertinent wavelengths) is similar to, and can be exchanged with, many excitations in a material. Thus, inelastic and quasi-elastic scattering can be used to probe a wide variety of dynamic phenomena. Indeed, structural neutron probes can span over nine orders of magnitude in length scale, while inelastic neutron scattering probes can span four orders of magnitude in length and seven in time.



Neutron Diffraction: This technique can be used to follow phase transition as a function of any stimulus, e.g., variations in temperature or charge-discharge rate. As such, the structural evolution, growth process, phase fraction can be followed during synthesis or *operando* processes involving electrode or electrolyte materials. In addition, peak shapes and peak displacement in diffraction patterns can be used for the study of microstructure, such as stacking faults or degradation mechanisms.

Neutron Depth Profiling: This technique determines the elemental mass as a function of depth into the sample—even in composite structures. It is suitable for characterizing a few select elements in most any solid material to depths of micrometers with resolution as fine as several nanometers. Most commonly determined elements are ^{6}Li, ^{10}B, and ^{14}N. In Li-ion batteries an entire cell or a small portion can be interrogated for total Li content, the Li concentration over a depth range, the 3D spatial Li distribution, or the Li distribution change in one-minute intervals over many hours.

Neutron Reflectometry: This technique determines interfacial structures buried within samples (including *operando* electrochemical cells) with nanoscale resolution in one dimension. Features as thin as 0.5-4 nm can be determined with sub-angstrom precision. Thus, neutron reflectometry is ideal for precise measurements of the structure and transport though a solid-electrolyte interface and other surface coatings, plating and stripping, crossover reactions, interdiffusion and self-diffusion, and other interface structures.

Inelastic and Quasi-Elastic Neutron Scattering: These two techniques are uniquely useful for probing the bonding, diffusion, motions, and other energetic processes in solid-state materials. Inelastic scattering is complementary to infrared or Raman spectroscopy. However, with neutrons there are no dipole-selection rules, so all vibrational modes are observable. As with other spectroscopic techniques, inelastic scattering can identify both crystalline and amorphous hydrogenous phases in materials. Quasi-elastic neutron scattering probes low-energy localized or diffusive atomic motions or molecular reorientations.

Small Angle Neutron Scattering: This technique determines nanoscale structures, particle shapes and sizes, and inter-particle correlations in a wide variety of samples from solids to powders to suspensions by analyzing the scattered intensity in two dimensions as a function of the small angle relative to the incident direction. It is used to study the evolution of electrode particles/grains and the structure and morphology of electrolytes (liquids, gels, suspensions, and polymers). Combined with *in situ* electrochemical rheology, it is a powerful technique to understand the operation of flow batteries.

Neutron Imaging: This technique has been used extensively to measure water concentrations from anode to cathode in polymer electrolyte membrane fuel cells due to the large neutron cross section for hydrogen and the low cross section for many other elements that allows for deep penetration in industrial-sized objects. Neutrons also have a similar sensitivity to Li due to the large cross section of ^{6}Li. By imaging non-uniform lithium concentrations, it is possible to aid development of simplified models of battery degradation for field use. Furthermore, by identifying, pinpointing, and characterizing localized rare events using *operando* probes, one can bring to bear other probes to further understand conditions that lead to battery degradation, such as the growth of dendrites and other phenomena.

labeling studies were able to identify interphase heterogeneity and order within the pores as a function of potential. Beyond interfacial studies, neutron tomography has been used to follow ^{6}Li diffusion within electrode structures and to demonstrate the transport kinetics in composite electrodes.[9]

Other neutron techniques include quasi-elastic neutron spectroscopy, which is suitable for measuring diffusion rates, similar to nuclear magnetic resonance studies, but with the added benefit of determining a hopping distance.[10] With crystal diffraction data, one can directly determine diffusion pathways in energy storage materials, which would enable simulation work and modeling methods to predict optimal crystal structures and bonding.

Advances in Electron Microscopy to Enhance Understanding of Battery Materials and Systems: The technique of electron microscopy has seen tremendous advances during the last decade, and these advances have significantly contributed to our mechanistic understanding of electrochemical energy storage materials and systems (Figure 3.6.1). For example, dramatic improvements in spatial resolution in scanning transmission electron microscopy, transmission electron microscopy, and electron energy loss spectroscopy have allowed elucidation of degradation mechanisms in cathodes,[11,12] the origin of high grain boundary resistivity in solid electrolytes,[13] and lithiation mechanisms in electrodes.[14] The recent development of annular bright field detectors for scanning transmission electron microscopy enables the direct imaging of light elements, such as Li^+ and H^+, and greatly enhances our ability to understand the relationship between structure and chemistry in energy storage materials.[15] In addition to the dramatic improvements in spatial resolution and detection limits in scanning transmission electron microscopy, the recent development of *in situ* electrochemical cycling capabilities has had a major impact on understanding the lithiation of electrode materials. Two *in situ* configurations—open cell[16] and closed cell[17,18]—have provided significant insight into the dynamic structural and chemical changes that occur under simulated cycling conditions. The former method utilizes a portable scanning probe within the transmission electron microscope or a membrane-based electrical device for establishing contact, and has the advantage that the full range of atomic-resolution transmission electron microscopy techniques can be exploited. The open cell configuration, mainly used to study lithiation and delithiation behavior in electrodes,[16] has been employed to understand the interfacial stability of a solid electrolyte against lithium metal.[19] The closed cell approach exploits recent advances in liquid cell microscopy[18] and microfabrication technologies to build a quasi battery system within the electron microscope.[12] This approach has the advantage that it can integrate a liquid electrolyte into the system, but the spatial resolution and analytical signal are compromised due to scattering from the confining silicon nitride windows, as well as the liquid layer itself.

New and emerging electron microscopy techniques to benefit energy storage research: Recent advances in electronics and optics have stimulated the development of new experimental microscopy techniques. Integrating and optimizing these emerging techniques so that they may be applied to energy storage research will remain an area of significant interest. One of the most important instrument advances in recent years has been the invention of direct electron detectors, which enable high-speed imaging with a frame rate of over 4,000 frames per second. Such fast imaging has significantly enhanced the temporal resolution for *in situ* characterization and has also improved low-dose imaging capabilities.[24] One significant advantage of these fast cameras is that they enable dramatically improved ptychographic imaging.[25,26] Scanning transmission electron microscopy-based ptychography records a full series of "ronchigram" (or convergent beam electron diffraction) patterns as a function of the probe position, resulting in four-dimensional datasets, two in reciprocal space and two in real space. Such 4D datasets have recently been used to reconstruct internal electric or magnetic fields in a specimen at atomic resolution.[27] This means that with the integration of *in situ* electrochemical cycling, electron microscopy may be able to map local electric potential simultaneously with chemical and structural analysis at the atomic scale. This new capability will significantly enhance our understanding of the behavior of solid-solid interfaces and boundaries, where multiple, simultaneous phenomena spanning chemical, electrochemical, mechanical stability, and space charge effects contribute to the overall performance. It must also be mentioned that interfaces are three-dimensional, non-centrosymmetric structures, and their spatial and temporal behavior must be interrogated in 3D at the nanometer to atomic scale. As a result of newly developed atomic-scale tomography, reconstructing the 3D atomic structures of such embedded features is now feasible,[21] and dynamic, nanometer-scale chemical tomography has also been demonstrated.[28] Thus, it may eventually be possible to combine determinations of both the local electric potential and the 3D atomic structure under *in situ* cycling. As a result, state-of-the-art scanning and transmission electron microscopy methods will allow us to develop a comprehensive microscopic understanding of the critical interfacial phenomena at the same spatial and temporal coordination, under *in situ* electrochemical conditions.

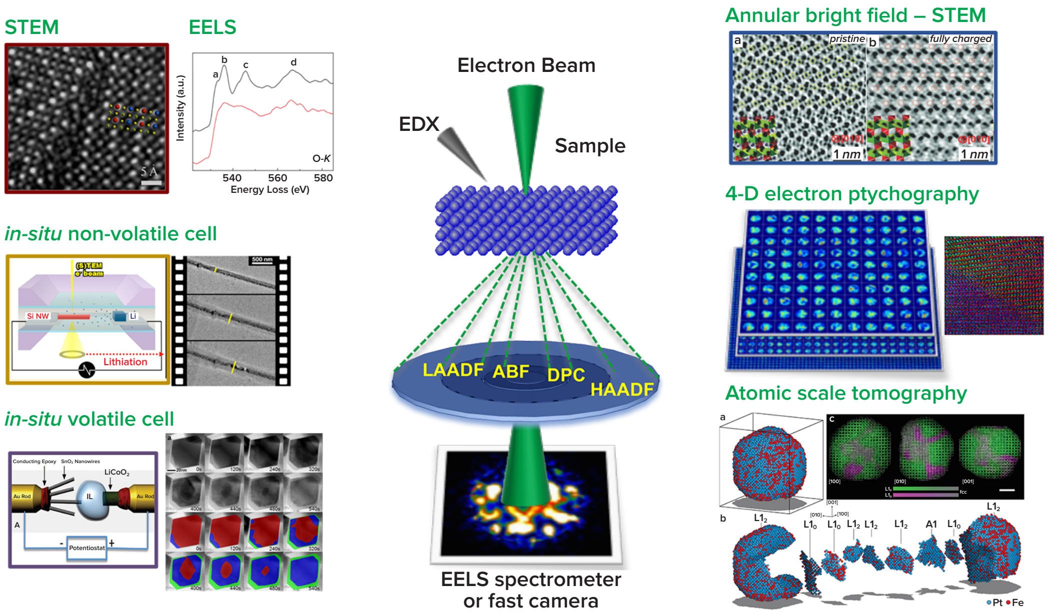


Figure 3.6.1. State-of-art and emerging STEM-based techniques and their applications to battery research. STEM = scanning transmission electron microscopy; EELS = electron energy loss spectroscopy; EDX = energy dispersive X-ray analysis; LAADF = low-angle annular dark field; ABF = annular bright field; DPC = differential phase contrast; HAADF = high-angle annular dark field. From Refs. 13, 17, 20-22. Image on upper right from Ref. 23, with permission of American Chemical Society.

Future development of electron microscopy techniques: Despite these recent technique developments, the fundamental limits of spatial, energy, and temporal resolution, as well as dose, speed, and chemical sensitivity, have not yet been fully realized. Future microscopy development is needed to address grand scientific challenges in electrical energy storage research. For example, simultaneous high spatial and temporal resolution cannot be achieved, and thus the transport of charge carriers cannot be traced directly at the atomic scale. Energy resolution is not sufficient to probe intermediate electronic states, which dictate electrochemical stabilities of electrode-electrolyte interfaces (although sub-10 meV resolution has recently been demonstrated).[29,30] Because very different electron doses are required for imaging hard ceramics and soft matter, hard-soft matter interfaces, which play a significant role in future lithium metal batteries, cannot yet be routinely characterized at the atomic scale. Furthermore, it remains challenging to link local nanoscale features to both the bulk properties and the overall function of a material. Integrated characterization techniques, which measure various key parameters (not only structure and chemistry, but also function), and which cover different length scales simultaneously, will be critical to providing a holistic characterization of how batteries function. Overcoming these challenges will not only require significant advances in instrumentation, such as highly stable control electronics and power supplies, but also the integration of new computing algorithms and data science.

Advances in Mechanical Property Measurement: There is a strong connection between the ion concentration and mechanical properties of materials such as material volume, mechanical stresses, and stiffness. This electrochemical-mechanical coupling can follow from a change in the unit cell[31,32] or a change in solid-liquid interaction under confinement in pores or between layers of quasi-2D materials.[33-36] The solid-liquid interaction will be strongly determined by the ion size, as well as solvation and surface chemistry. In turn, the mechanical properties and dimensional constraints can limit ionic transport, an important but still unexplored area. The electrochemical-mechanical coupling can be considered in multiple ways. The volume change caused by electrochemically induced stoichiometry changes can lead to local stress and mechanical degradation. On the other hand, electro-chemo-mechanical coupling may also provide new opportunities to characterize materials by measuring the stress/strain generated by the stoichiometry change. There is a great opportunity to design new *in situ* detection and imaging strategies on mesoscopic length scales, which are largely missing, and to implement testing strategies for full battery cells. In the first case, contact resonance scanning probe microscopy can be used to image the ion insertion pathways through changes in Young's modulus when Li^+ and K^+ are electrochemically driven into layered materials such as MXene (see Figure 2.3.9 in Chapter 2).[37] This approach reveals where the ions cross the solid-liquid interface and where they are incorporated into the electrode. In the latter example, electrochemical-acoustic time-of-flight analysis was used to study changes in elasticity of full commercial cells.[38] Approaches like this have the potential to image the state of charge of batteries and track the development of interphase formations during electrochemical operation over a long cycle life.

Advances in X-ray Imaging: Much progress has been made over the past five years in using photon-based imaging techniques applied to energy storage materials, as highlighted in recent publications.[39,40] These have proven useful both *operando* and *ex situ* and include transmission X-ray microscopy, micro-computed tomography, and scanning transmission X-ray microscopy. The two imaging modalities, morphological (including 3D morphology) and chemical using spectro-microscopies, can be used separately or in combination. The latter is especially powerful as this allows mapping phase changes in both primary and secondary particles. Full field transmission X-ray microscopy and micro-computed tomography of most energy storage materials employ hard X-rays, while scanning transmission X-ray microscopy of such materials primarily uses soft X-rays. Soft X-rays are more chemically sensitive and so provide greater fidelity. In contrast, *operando* and *in situ* investigations are much easier with transmission X-ray microscopy and tomography using hard X-rays, although there has been recent development of *in situ* scanning transmission X-ray microscopy with soft X-rays but at some sacrifice in resolution.[41] While most imaging is 2D, the 3D imaging that is inherent to micro-computed tomography and achievable in transmission X-ray microscopy can be much more informative in some cases.[42]

Advances in Use of Model Systems: Over the past decade, researchers have adopted a reductionist approach by using model, but still relevant, systems to obtain a detailed understanding of energy storage phenomena, especially related to interfaces and interphases. Typically, this involves *in situ* characterization using single crystals such as Si thin films,[43] or open cell geometries for nanostructured electrodes as used for transmission electron microscopy (see above). This methodology uses techniques such as surface X-ray and neutron scattering and transmission electron microscopy to provide exquisite details on interface structure and chemistry at length scales less than 1 nm. Due to the simplicity of the experiment, direct comparison to theory is often more straightforward than for more complex, but more realistic (closed) half-cells. Often, highly idealized geometries and *in situ* cells are used, with the knowledge gained being transferable to real cells. For example, X-ray and neutron reflectivity have provided insight into phase transformations and the formation and "breathing" of the solid-electrolyte interface on silicon.[44]

3.6.2 TRANSLATION OF BASIC SCIENCE TO TECHNOLOGY INNOVATION

Bridging the different time and length scales enables the transformation of the discovery process for new materials and technologies. Computation-based science and engineering offers an unusual opportunity for technology innovation through reduced design time and accelerated development cycles of new materials and processes. Over the past decade, substantial research has been devoted to the development and application of a powerful collection of tools for computational modeling, which has been followed by synthesis, processing, and characterization of emerging energy storage materials and interfaces. These simulation and characterization tools, which include X-ray and neutron spectroscopy, electron microscopy, nuclear magnetic resonance, and high-performance computation, provide an unprecedented view of the atomic-scale structure and dynamics of materials, and also the molecular-scale basis of reaction processes. Rational strategies for material design and discovery can now be implemented for complex systems that previously were not tractable. This will be a key enabler for future technology innovations.

Integrated computational materials engineering has already shown the capability to accelerate the introduction of new materials and processes into the industrial product development cycle by minimizing testing requirements, reducing failures, and increasing quality. Other key parts of this integration require the development of experimental capabilities, the development of a robust and sustainable supporting infrastructure, and the assembly of a cross-functional team of scientists and engineers to implement the integration and infrastructure. Early successes in several industry sectors have already demonstrated significant return on investment and reduced development times. Combining integrated computational materials engineering with accelerated discovery of new materials and processes offers additional opportunities to incorporate new materials earlier into the product design cycle, thereby increasing performance and shortening the materials development cycle to better align with product development.

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Appendix A: Workshop, Panel, and PRD Participants

Chair: George Crabtree, University of Illinois-Chicago/Argonne National Laboratory

Co-chairs: Gary Rubloff, University of Maryland
Esther Takeuchi, Stony Brook University/Brookhaven National Laboratory

BASIC ENERGY SCIENCES TEAM:

Linda Horton, Craig Henderson, Gregory Fiechtner, Bruce Garrett, George Maracas, Natalia Melcer, Charles Peden, Thomas Russell, Andrew Schwartz, Michael Sennett, John Vetrano

Katie Runkles (administrative)

Plenary Speakers:
Yi Cui, SLAC National Accelerator Laboratory National Accelerator Laboratory and Stanford University
Linda Nazar, University of Waterloo
Jean-Marie Tarascon, Collège de France
Karen Thomas-Alyea, Samsung Research America
M. Stan Whittingham, Binghamton University

PANEL NOTES:

(1), (2), (3), (4) and (5) indicates the PRD discussion panel in which the individual participated following the thematic panel reports on Tuesday morning. (*) indicates the PRD discussion panel leads. (CC) indicates a panel participant assigned to the crosscutting panel. (w) indicates a participant who contributed as a designated writer for the panel on Wednesday afternoon.

PANEL 1: PATHWAYS TO SIMULTANEOUS HIGH ENERGY AND POWER

Leads:
Paul Braun, University of Illinois (1*)
Jun Liu, Pacific Northwest National Laboratory (4*)

Yet-Ming Chiang, MIT
Ping Liu, University of California-San Diego (4)
Ram Manthiram, University of Texas-Austin (4)
(w) Matthew McDowell, Georgia Tech (4)
Hailong Ning, Xerion Advanced Battery Company
Eric Wachsman, University of Maryland
David Wesolowski, Oak Ridge National Laboratory (1,4)
(w) Jie Xiao, University of Arkansas (1)
Kang Xu, Army Research Labs
Jihui Yang, University of Washington (1)
(w) Guihua Yu, University of Texas-Austin (4)
Jason Zhang, Pacific Northwest National Laboratory (1)
Mei Cai, General Motors (CC)
Venkat Srinivasan, Argonne National Laboratory (1,2)
Feng Wang, Brookhaven National Laboratory (4)
Babu Chalamala, Sandia National Laboratories (4)
Alan West, Columbia University (CC)

PANEL 2: STRUCTURE, INTERPHASES, AND CHARGE TRANSFER AT ELECTROCHEMICAL INTERFACES

Leads:

Lynden Archer, Cornell University (3*)
David Prendergast, Lawrence Berkeley National Laboratory (3*)

Glenn Amatucci, Rutgers University (1-5)
Nina Balke, Oak Ridge National Laboratory (CC)
(w) Robert Baker, Ohio State University (3)
Oleg Borodin, Army Research Labs
(w) Candace Chan, Arizona State University (3)
Ethan Crumlin, Lawrence Berkeley National Laboratory (2,3)
Paul Fenter, Argonne National Laboratory (3)
Hong Gan, Brookhaven National Laboratory (3)
(w) Brett Helms, Lawrence Berkeley National Laboratory (3)
(w) Kevin Leung, Sandia National Laboratories (3)
Keryn Lian, University of Toronto (3)
Meilin Liu, Georgia Tech University (3)
Brett Lucht, University of Rhode Island
Chris Mundy, Pacific Northwest National Laboratory (2)
Minoru Otani, AIST, Japan
Nikhilendra (Nik) Singh, Toyota (3)
Gabriel Veith, Oak Ridge National Laboratory (CC)
Kevin Zavadil, Sandia National Laboratories (3)

PANEL 3: IN PURSUIT OF LONG LIFETIME AND RELIABILITY — TIME-DEPENDENT PHENOMENA AT ELECTRODES AND ELECTROLYTES

Leads:

Shirley Meng, University of California-San Diego (5*)
Jay Whitacre, Carnegie Mellon University (4*)

Craig Arnold, Princeton University (2,5)
Veronica Augustyn, North Carolina State University (5)
Daniel Buttry, Arizona State University (1,4)
Long-Qing Chen, Penn State University (5)
(w) Marca Doeff, Lawrence Berkeley National Laboratory (5)
Matthieu Dubarry, Hawaii Natural Energy Institute (5)
Joe Dura, National Institute of Standards and Technology (2,3)
Jeffery Fergus, Auburn University (5)
Katherine Jungjohann, Sandia National Laboratories
Robert Kostecki, Lawrence Berkeley National Laboratory (2)
(w) Bor Yann Liaw, Idaho National Laboratory (5)
Amy Marschilok, Stony Brook University (5)
Reg Penner, University of California-Irvine (5)
Oleg Shpyrko, University of California-San Diego (5)
Dan Steingart, Princeton University (CC)
Andy Sun, University of Western Ontario (2)
Johanna Nelson Weker, SLAC National Accelerator Laboratory (CC)
Ralph White, University of South Carolina (2)

PANEL 4: DISCOVERY, SYNTHESIS, AND DESIGN STRATEGIES FOR MATERIALS, STRUCTURES, AND ARCHITECTURES

Leads:
Perla Balbuena, Texas A&M University (1*)
Amy Prieto, Colorado State University (1*)

(w) Bart Bartlett, University of Michigan (1)
Jordi Cabana, University of Illinois – Chicago (1-5)
Guoying Chen, Lawrence Berkeley National Laboratory (1)
Neil Dasgupta, University of Michigan (1,2)
(w) Bruce Dunn, University of California-Los Angeles
Timothy Ellis, RSR Technologies (1,4)
R. Edwin Garcia, Purdue University
Ashfia Huq, Oak Ridge National Laboratory (CC)
Brian Ingram, Argonne National Laboratory (1,3)
(w) Michael Janik, Penn State University
De-en Jiang, University of California-Riverside (2)
Daniel Kuroda, Louisiana State University (2)
Jeff Long, Navy Research Lab (1)
Brent Melot, University of Southern California (1)
Ahmad Pesaran, NREL
(w) Aleksandra Vojvodic, University of Pennsylvania (1)
Donghai Wang, Penn State University (1,4)
Yiying Wu, Ohio State University (4)

PANEL 5: SOLID-STATE AND SEMI-SOLID ELECTROCHEMICAL ENERGY STORAGE

Leads:
Nancy Dudney, Oak Ridge National Laboratory (5*)
Jeff Sakamoto, University of Michigan (3*)

Paul Albertus, ARPA-E
Nitash Balsara, University of California -Berkeley
Miaofang Chi, Oak Ridge National Laboratory (CC)
Will Chueh, SLAC National Accelerator Laboratory (CC)
Yan Yan Hu, FSU National Mag Lab (1)
Boris Kozinski, Bosch USA (1)
Bryan McCloskey, University of California – Berkeley (4)
Lincoln Miara, Samsung (CC)
Yifei Mo, University of Maryland (2,5)
Rishi Raj, University of Colorado-Boulder (1)
Daniel Scherson, Case Western Reserve University (2)
(w) Don Siegel, University of Michigan
Alec Talin, Sandia National Laboratories (3)
(w) Wyatt Tenhaeff, University of Rochester (3)
Chungshen Wang, University of Maryland
Will West, Jet Propulsion Lab (4)
Jeff Wolfenstine, Army Research Labs

CROSSCUTTING THEMES:

Lead:

Yue Qi, Michigan State University (2*)
Eric Stach, Brookhaven National Laboratory (5*)
Mike Toney, SLAC National Accelerator Laboratory (2*)

Nina Balke, Oak Ridge National Laboratory (3)
(w) Mei Cai, General Motors (2)
(w) Miaofang Chi, Oak Ridge National Laboratory (2)
Will Chueh, SLAC National Accelerator Laboratory
Ashfia Huq, Oak Ridge National Laboratory (3)
Lincoln Miara, Samsung
(w) Dan Steingart, Princeton University (2)
Gabriel Veith, Oak Ridge National Laboratory (2,3)
(w) Johanna Nelson Weker, SLAC National Accelerator Laboratory (2)
Alan West, Columbia University (2)

BASIC RESEARCH NEEDS FOR NEXT GENERATION ELECTRICAL ENERGY STORAGE

Invited Participants (alphabetical)

Paul Albertus, ARPA-E
Glenn Amatucci, Rutgers University
Lynden Archer, Cornell University
Craig Arnold, Princeton University
Veronica Augustyn, North Carolina State University
Robert Baker, Ohio State University
Perla Balbuena, Texas A&M University
Nina Balke, Oak Ridge National Laboratory
Nitash Balsara, University of California -Berkeley
Bart Bartlett, University of Michigan
Oleg Borodin, Army Research Labs
Paul Braun, University of Illinois
Daniel Buttry, Arizona State University
Jordi Cabana, University of Illinois - Chicago
Mei Cai, General Motors, Inc
Babu Chalamala, Sandia National Laboratories
Candace Chan, Arizona State University
Long-Qing Chen, Penn State University
Guoying Chen, Lawrence Berkeley National Laboratory
Miaofang Chi, Oak Ridge National Laboratory
Yet-Ming Chiang, Massachusetts Institute of Technology
Will Chueh, SLAC National Accelerator Laboratory
George Crabtree, Argonne National Laboratory
Ethan Crumlin, Lawrence Berkeley National Laboratory
Yi Cui, Stanford University
Neil Dasgupta, University of Michigan
Marca Doeff, Lawrence Berkeley National Laboratory
Matthieu Dubarry, Hawaii Natural Energy Institute
Nancy Dudney, Oak Ridge National Laboratory
Bruce Dunn, University of California-Los Angeles
Joe Dura, National Institute of Standards and Technology
Timothy Ellis, RSR Technologies
Paul Fenter, Argonne National Laboratory
Jeffery Fergus, Auburn University
Hong Gan, Brookhaven National Laboratory
R. Edwin Garcia, Purdue University
Brett Helms, Lawrence Berkeley National Laboratory
Yan Yan Hu, National High Magnetic Field Lab, FSU
Ashfia Huq, Oak Ridge National Laboratory
Brian Ingram, Argonne National Laboratory
Michael Janik, Penn State University
De-en Jiang, University of California-Riverside
Katherine Jungjohann, Sandia National Laboratories
Robert Kostecki, Lawrence Berkeley National Laboratory
Boris Kozinski, Bosch USA
Daniel Kuroda, Louisiana State University
Peter Lamp, BMW
Kevin Leung, Sandia National Laboratories
Keryn Lian, University of Toronto
Bor Yann Liaw, Idaho National Laboratory
Jun Liu, Pacific Northwest National Laboratory
Ping Liu, University of California –San Diego
Meilin Liu, Georgia Tech University

Jeff Long, Navy Research Lab
Brett Lucht, University of Rhode Island
Ram Manthiram, University of Texas-Austin
Amy Marschilok, Stony Brook University
Bryan McCloskey, University of California-Berkeley
Matthew McDowell, Georgia Tech
Brent Melot, University of Southern California
Shirley Meng, University of California-San Diego
Lincoln Miara, Samsung
Yifei Mo, University of Maryland
Chris Mundy, Pacific Northwest National Laboratory
Linda Nazar, University of Waterloo
Johanna Nelson Weker, SLAC National Accelerator Laboratory
Hailong Ning, Xerion Advanced Battery Company
Minoru Otani, AIST, Japan
Reg Penner, University of California-Irvine
Ahmad Pesaran, National Renewable Energy Laboratory
David Prendergast, Lawrence Berkeley National Laboratory
Amy Prieto, Colorado State University
Yue Qi, Michigan State University
Rishi Raj, University of Colorado-Boulder
Gary Rubloff, University of Maryland
Jeff Sakamoto, University of Michigan
Daniel Scherson, Case Western Reserve University
Oleg Shpyrko, University of California-San Diego
Don Siegel, University of Michigan
Nikhilendra (Nik) Singh, Toyota
Venkat Srinivasan, Argonne National Laboratory
Eric Stach, Brookhaven National Laboratory
Dan Steingart, Princeton University
Andy Sun, University of Western Ontario
Esther Takeuchi, Stony Brook University
Alec Talin, Sandia National Laboratories
Jean-Marie Tarascon, Collège de France
Wyatt Tenhaeff, University of Rochester
Karen Thomas-Alyea, Samsung Research America
Mike Toney, SLAC National Accelerator Laboratory
Gabriel Veith, Oak Ridge National Laboratory
Aleksandra Vojvodic, University of Pennsylvania
Eric Wachsman, University of Maryland
Feng Wang, Brookhaven National Laboratory
Donghai Wang, Penn State University
Chungshen Wang, University of Maryland
David Wesolowski, Oak Ridge National Laboratory
Alan West, Columbia University
Will West, Jet Propulsion Lab
Jay Whitacre, Carnegie Mellon University
Ralph White, University of South Carolina
Stan Whittingham, Binghamton University
Jeff Wolfenstine, Army Research Labs
Yiying Wu, Ohio State University
Jie Xiao, University of Arkansas
Kang Xu, Army Research Labs
Jihui Yang, University of Washington
Guihua Yu, University of Texas-Austin
Kevin Zavadil, Sandia National Laboratories
Jason Zhang, Pacific Northwest National Laboratory

BASIC RESEARCH NEEDS FOR NEXT GENERATION ELECTRICAL ENERGY STORAGE

Invited Observers (alphabetical)

Jianming Bai, Brookhaven National Laboratory
Enrique Batista, Los Alamos National Laboratory
Ali Belkacem, Lawrence Berkeley National Laboratory
Andrés Eduardo Moctezuma Berthier, IMP, Mexico
Gilbert Bindewald, DOE Office of Electricity
Chris Bradley, DOE Office of Science, Basic Energy Sciences
Phil Britt, Oak Ridge National Laboratory
Tony Burrell, National Renewable Energy Laboratory
Karen Chen-Wiegart, Brookhaven National Laboratory
Ben Davis, Los Alamos National Laboratory
Dennis Dees, Argonne National Laboratory
Jack Deppe, DOE Office of Energy Efficiency and Renewable Energy
Tom Devereaux, SLAC National Accelerator Laboratory
Tien Duong, DOE Office of Energy Efficiency and Renewable Energy
Eric Dufek, Idaho National Laboratory
Peter Faguy, DOE Office of Energy Efficiency and Renewable Energy
Peter Fischer, Lawrence Berkeley National Laboratory
Bruce Garrett, DOE Office of Science, Basic Energy Sciences

Bonnie Gersten, DOE Office of Science, Basic Energy Sciences

Robin Hayes, DOE Office of Science, Basic Energy Sciences

Craig Henderson, DOE Office of Science, Basic Energy Sciences

Linda Horton, DOE Office of Science, asic Energy Sciences

Dave Howell, DOE Office of Energy Efficiency and Renewable Energy

Aravinda Kini, DOE Office of Science, Basic Energy Sciences

Harriet Kung, DOE Office of Science, Basic Energy Sciences

George Maracas, DOE Office of Science, Basic Energy Sciences

Nenad Markovic, Argonne National Laboratory

Michael Markowitz, DOE Office of Science, Basic Energy Sciences

Steve Martin, Ames Laboratory

Natalia Melcer, DOE Office of Science, Basic Energy Sciences

Raul Miranda, DOE Office of Science, Basic Energy Sciences

Jamie Morris, Oak Ridge National Laboratory

Karl Mueller, Pacific Northwest National Laboratory

Bill Parks, DOE Office of Electricity

Mick Pechan, DOE Office of Science, Basic Energy Sciences

Charles Peden, DOE Office of Science, Basic Energy Sciences

Thomas Russell, DOE Office of Science, Basic Energy Sciences

Andy Schwartz, DOE Office of Science, Basic Energy Sciences

Viviane Schwartz, DOE Office of Science, Basic Energy Sciences

Eric Schwegler, Lawrence Livermore National Laboratory

Michael Sennett, DOE Office of Science, Basic Energy Sciences

Thomas Settersten, DOE Office of Science, Basic Energy Sciences

Patricia Smith, DOE Office of Energy Efficiency and Renewable Energy

Vince Sprenkle, Pacific Northwest National Laboratory

Glen Teeter, National Renewable Energy Laboratory

Tony van Buuren, Lawrence Livermore National Laboratory

John Vetrano, DOE Office of Science, Basic Energy Sciences

Rigaiy Zidan, Savannah River National Laboratory

Appendix B: Workshop Agenda

Basic Research Needs Workshop for

Next Generation Electrical Energy Storage

Gaithersburg Marriott Washingtonian Center – March 27-29, 2017

Chair: George Crabtree, University of Illinois-Chicago/Argonne National Laboratory

Co-chairs: Gary Rubloff, University of Maryland
Esther Takeuchi, Stony Brook University/Brookhaven National Laboratory

Monday, March 27, 2017

7:00 a.m.	Registration/Breakfast

Opening Plenary Session (Salons E-G)

8:00 a.m.	Welcome and Workshop Charge *Harriet Kung, Associate Director of Science for Basic Energy Sciences*
8:15 a.m.	Chair Welcome and Workshop Structure *George Crabtree, Argonne National Laboratory/University of Illinois - Chicago*
8:30 a.m.	Introduction to Plenaries *Esther Takeuchi, Stony Brook University/Brookhaven National Laboratory*
8:45 a.m.	Electrical Energy Storage: Where have we come from and the scientific challenges still facing us? *M. Stan Whittingham, Binghamton University*
9:15 a.m.	High-energy batteries: a systems perspective *Karen Thomas-Alyea, Samsung Research America*
9:45 a.m.	Challenges for Solid State Batteries *Linda Nazar, University of Waterloo*
10:15 a.m.	Break
10:45 a.m.	State of Energy Storage Technologies for Transportation *David Howell, Vehicle Technologies Office, Energy Efficiency and Renewable Energy, Department of Energy*
11:15 a.m.	State of Energy Storage Technologies for the Grid *Gilbert Bindewald, Office of Electricity Delivery and Energy Reliability, Department of Energy*
11:45 a.m.	Panel Introductions *Gary Rubloff, University of Maryland*
12:00 p.m.	Working Lunch

1:00 – 5:30 p.m. Parallel Panel Sessions

Panel 1 — Pathways to simultaneous high energy and power – Lakeside 1
Paul Braun, University of Illinois Urbana-Champaign
Jun Liu, Pacific Northwest National Laboratory

Panel 2 — Structure, interphases, and charge transfer at electrochemical interfaces – Lakeside 2
Lynden Archer, Cornell University
David Prendergast, Lawrence Berkeley National Laboratory

Panel 3 — Time-dependent phenomena of electrodes and electrolytes – Salon A/B
Shirley Meng, University of California, San Diego
Jay Whitacre, Carnegie Mellon University

Panel 4 — Discovery, synthesis, and design strategies for materials, structures, and architectures – Salon C
Perla Balbuena, Texas A&M University
Amy Prieto, Colorado State University

Panel 5 — Solid state and semi-solid electrochemical energy storage – Salon D
Nancy Dudney, Oak Ridge National Laboratory
Jeff Sakamoto, University of Michigan

Crosscutting Themes — Salon E-G (meets after dinner and on Tuesday)
Yue Qi, Michigan State University
Eric Stach, Brookhaven National Laboratory
Mike Toney, SLAC National Accelerator Laboratory National Accelerator Laboratory

3:00 – 4:00 p.m. Refreshments available

5:30 p.m. Break for Dinner (on own)

9:00 p.m. Parallel Panel Discussions (continued);
Crosscutting Theme group meets in plenary session room, *Salon E-G*

Tuesday, March 28, 2017

7:00 a.m.	Breakfast

Plenary Session (Salons E-G)

8:00 a.m.	Nanoscience for Energy Storage: Success and Future Opportunity *Yi Cui, Stanford University*
8:30 a.m.	Material science for electrochemical storage: Achievement and new directions *Jean-Marie Tarascon, Collège de France*
9:00 a.m.	Break and move to panel sessions
9:15 a.m.	Parallel Panel Sessions for discussion/preparation of preliminary reports
10:30 a.m.	Break and move to plenary room for panel reports (Salon E-G)
10:45 a.m.	Report from Panel 1 — Pathways to simultaneous high energy and power
11:00 a.m.	Report from Panel 2 — Structure, interphases, and charge transfer at electrochemical interfaces
11:15 a.m.	Report from Panel 3 — Time-dependent phenomena of electrodes and electrolytes
11:30 a.m.	Report from Panel 4 — Discovery, synthesis, and design strategies for materials, structures, and architectures
11:45 a.m.	Report from Panel 5 — Solid state and semi-solid electrochemical energy storage
12:00 p.m.	Report from Crosscutting Themes
12:15 p.m.	Working Lunch (Meeting of Chair, Co-Chairs, and Panel Leads in Salon A-B)
1:30 – 5:30 p.m.	Initial PRD discussions (as revised March 28, 2017; PRD assignments given out to participants after lunch)
3:00 – 4:00 p.m.	Refreshments available
5:30 p.m.	Break for Dinner (on own)
7:00 – 9:00 p.m.	PRD Discussions (continued) & Preparation of PRD reports

Wednesday, March 29, 2017 (as revised March 28, 2017)

7:00 a.m.	Breakfast

Plenary Session (Salons E/F/G)

8:00 a.m.	Report from PRD 1 — Holistic design and synthesis of materials and structures *Paul Braun, Perla Balbuena, Amy Prieto*
8:30 a.m.	Report from PRD 2 — Bridging scales: time, length, and phenomena *Yue Qi, Mike Toney*
9:00 a.m.	Report from PRD 4 — Discovery of alternative energy storage chemistries and structures *Jun Liu, Jay Whitacre*
9:30 a.m.	Break
9:45 a.m.	Report from PRD 3 — Inspired interfaces/interphases *Lynden Archer, David Prendergast, Jeff Sakamoto*
10:15 a.m.	Report from PRD 5 — Mitigating unwanted processes, degradation *Shirley Meng, Nancy Dudney, Eric Stach*
10:45 a.m.	Discussion
11:15 a.m.	Closing Remarks *George Crabtree, Argonne National Laboratory/University of Illinois – Chicago*
11:30 a.m.	Workshop Adjourned

Writing Session (Lakeside #1/#2)

12:00 p.m.	Working Lunch — Chairs, panel leads, and designated writers only
1:00 p.m.	Writing — Chairs, panel leads, and designated writers
5:00 p.m.	Departure

Appendix C: Abstracts for Plenary Talks

ELECTRICAL ENERGY STORAGE: WHERE HAVE WE COME FROM AND THE SCIENTIFIC CHALLENGES STILL FACING US?

Professor M. Stanley Whittingham

Binghamton University

Electrical energy storage has come a long way in the last 45 years, enabling portable electronic devices, electrification of transportation and renewable energy. However, there are several key scientific hurdles that must be overcome to allow electrochemical reactions to fulfill their full promise. These challenges, including understanding metal electrodeposition and highly conducting (ionic and electronic) cathodes will be described.

HIGH-ENERGY BATTERIES: A SYSTEMS PERSPECTIVE

Dr. Karen Thomas-Alyea

Samsung Research America

Materials that offer a dramatic increase in energy density exhibit significant volume change with state of charge and are not thermodynamically stable with most electrolytes. We will discuss the design requirements for materials that exhibit volume change, along with the status of mathematical models for design optimization. We will also discuss the unique requirements for commercialization of rechargeable lithium metal, which must have robust safety even in the presence of manufacturing tolerances.

CHALLENGES FOR SOLID STATE BATTERIES

Professor Linda Nazar

University of Waterloo

All solid state batteries are highly anticipated to provide new opportunities for higher energy density, safer batteries in the future but they also pose many challenges. This talk will focus on those issues, including the choice of the negative electrode material: can lithium metal provide a solution? Can dendritic growth be controlled and what are the required properties for solid state electrolyte membranes to prevent this while fulfilling other material requirements? Other topics that will be covered include approaches to search for new solid state ion conductors, the role that computation can play in that search, and new tools necessary to probe the all-important problem of interfaces.

NANOSCIENCE FOR ENERGY STORAGE: SUCCESS AND FUTURE OPPORTUNITY

Professor Yi Cui

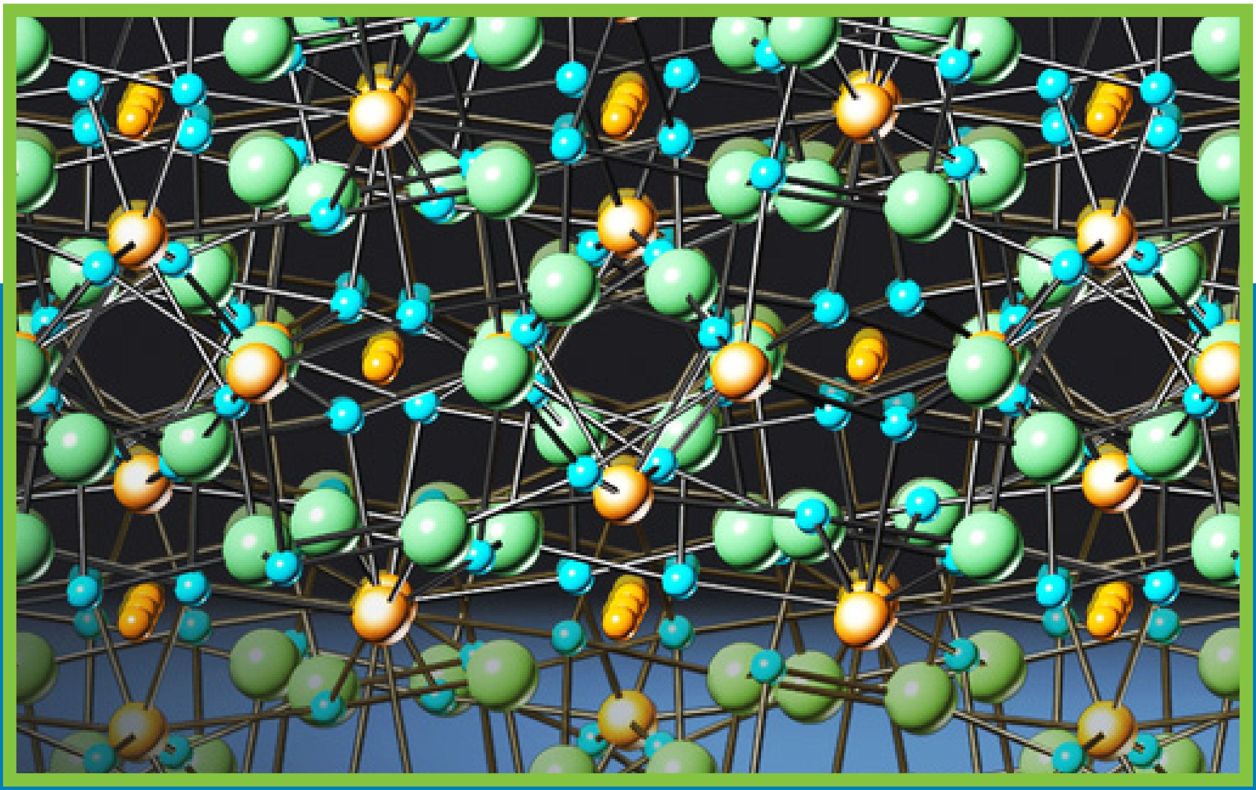
Stanford University and SLAC National Accelerator Laboratory National Accelerator Lab

Emerging electric transportation and large-scale stationary applications call for new materials and chemistries for low-cost, high energy, fast and safe operation of electricity storage. Nanoscience has afforded new ideas and tools to understand, design and test materials across multiple length scale from atom, nano to macro scale. Selected past successful examples will be highlighted. Future research opportunity will also be discussed.

MATERIALS SCIENCE FOR ELECTROCHEMICAL STORAGE: ACHIEVEMENTS AND NEW DIRECTIONS

Professor Jean-Marie Tarascon
Collège de France, Paris

Materials have been essential for improving any energy related technologies including batteries. Identifying new phases, tuning their morphology and mastering their processing into electrodes via the help of evolving analytical techniques have contributed to the success of the Li ion technology, which will be illustrated via recent achievements. Will pursuing the same way be sufficient to meet tomorrow's highly evolving demands linked to automotive mobility and others? This is what this presentation will attempt to answer. As personally perceived, the future of battery offers new opportunities for materials scientists as long as we are willing to explore new risky paths.



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