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VIEWPOINT

The Role of Nanoscale Science for Advancing Batteries

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We are entering into an age of massive electrification driven by the transition to cleaner energy sources, and this will require enormous shifts in the ways we use, store, and convert energy. A key aspect of electrification is the use of batteries to efficiently and reversibly store electrical energy. Although batteries have been known for over 200 years, the last two decades have seen dramatic advances in both the energy storage capabilities and the scale of production of Li-based batteries. This progress has been driven by the need for batteries that will power our society's current and future electric vehicles, hybrid-electric aircraft, and portable electronics, as well as to support the electric grid. These applications require batteries that can store more energy and deliver it more rapidly while remaining low in cost.

> Understanding transformation and degradation behavior of battery materials at the nanoscale is a key driver for future development of batteries with improved performance.

Materials science plays a foundational role in battery science and technology, as electrode materials and their interfaces must be carefully designed and engineered for optimal electrochemical transformations and long-term stability. Over the past 20 years, control of materials at the nanoscale has become an important enabler in advancing battery technology. As an example, engineered materials with nanoscale dimensions have shown promise and have been widely investigated for batteries,[1,2] as highlighted in Whittingham's recent Viewpoint in *Nano Letters*.[3] Specific advantages of nanoscale materials for batteries include shorter ion diffusion lengths and improved resistance to mechanical degradation,[4] as demonstrated in commercialized $LiFePO_4$ cathode materials and high-capacity Si-based anode materials. While useful, nanoscale materials are not a panacea for batteries, as the higher surface area of nanomaterials can cause reduced efficiency and limited cyclability, and the manufacturing cost of such materials can be high. But nanoscience has not only influenced the energy storage landscape through the use of engineered nanomaterials. Instead, an arguably greater impact has arisen from our vastly improved abilities to characterize, understand, and ultimately control the transformation mechanisms of a wide variety of battery materials at the nanoscale level. This leap forward in our ability to understand and direct transformations in battery materials is a direct result of the nanoscience community's two-decade emphasis on attaining precise nanoscale control of materials. Already, such efforts have guided the engineering of batteries with improved performance, and further advances in this area are sure to power battery development into the future.

UNDERSTANDING BATTERIES AT THE NANOSCALE

Charge and discharge of batteries cause complex evolution of the materials inside a cell; there is structural transformation of active materials, diffusion of ions, evolution of local strain and stress, and the formation of new phases at interfaces. Characterizing dynamic processes in batteries is important for understanding how the structure, chemistry, and morphology of materials and interfaces affect electrochemical behavior, as well as how materials change and degrade over time, which can lead to decay of charge storage capacity. When coupled with synthetic methods that allow for nanoscale control over material structure and chemistry, the knowledge of how materials evolve in batteries provides critical information for how to create new materials that enable improved energy, power, and long-term stability.

The past decade has seen an explosion of tailored experimental methods for studying the dynamic evolution of battery materials down to the nanoscale.[5] These techniques have been driven by advances in instrumentation, adaptation of methods from other fields, as well as by pure scientific ingenuity. Since batteries are closed systems that often include air-sensitive materials, custom methods must be developed that are suitable for their investigation. A variety of X-ray imaging methods has been used to study nanoscale dynamics in battery materials, including X-ray tomography for imaging particle transformations,[6,7] Bragg coherent diffraction imaging to detect movement of individual dislocations in active particles,[8] scanning X-ray spectroscopy and imaging,[9] and scattering techniques to detect strain in individual particles during battery reactions.[10,11] Transmission electron microscopy (TEM) has also become an essential tool for exploring battery materials. *In situ* TEM has revealed nanoscale reaction mechanisms in solid and liquid environments in a wide variety of technologically important active materials,[12−16] and the recent development of cryogenic TEM methods has proven useful for understanding the atomic-scale structure of fragile battery materials such as lithium metal and its interfaces.[17,18] Other important techniques providing nanoscale insight include nuclear magnetic resonance[19] and X-ray spectroscopies,[20] among others.

■ NANOSCALE SCIENCE FOR THE NEXT 20 YEARS OF BATTERIES

The key needs for batteries for electrified transportation are increased energy content and reduced cost along with improved safety and longevity/durability. In the near term, ongoing work will continue that is focused on replacing Li-ion battery electrode materials with other materials that can store more Li per volume and/or weight within the Li-ion battery architecture. These new materials include alloy anodes, lithium metal anodes, conversion cathodes, and high-Ni or Li-rich oxide cathodes. Much of the nanoscale characterization of the past few years has focused on understanding the transformation mechanisms and degradation behavior associated with these new materials. Building on this intensive research and development, some of these materials are being successfully implemented in commercial Li-ion batteries.[21] Additionally, sodium-ion-based materials and systems are being developed, which may have cost advantages.[22]

Beyond these efforts, a major opportunity to advance battery technology lies in the creation of new battery architectures for energy storage. One such architecture is the solid-state battery, which could exhibit higher energy density while improving safety and durability.[23] These batteries are made of all-solid-materials and therefore do not contain the flammable liquid electrolyte that is necessary for Li-ion batteries. While this technology has been known for decades, accelerated efforts in recent years have focused on developing the materials and interfaces necessary for the creation of cells that can rival or exceed Li-ion battery energy and power characteristics. The all-solid nature of these systems presents a fundamental challenge, however, as the necessary chemical and structural changes of materials during charge and discharge can cause exacerbated capacity degradation. Although many of the same active materials can be used in solid-state batteries as in Li-ion batteries, the solid-state architecture is a completely different environment that causes distinct material and interface transformations. For further development of solid-state batteries, there is a critical need over the next few years to fundamentally understand transformation and degradation mechanisms in materials and at interfaces, and nanoscale characterization will play an important role. Indeed, state-of-the-art materials characterization has recently revealed unique interfacial transformations compared to conventional liquid-based batteries,[24−26] with more exciting breakthroughs on the horizon.

An important goal of battery material characterization is to build up enough knowledge to be able to directly link the measured output of a battery cell (e.g., voltage or current) to the internal material transformations and degradation mechanisms. This connection is necessary since it is useful to understand the state of the materials inside an operating battery based on a simple measurement of battery output. The next step beyond this basic correlation is to understand how the initiation of degradation in materials across length scales in a battery is linked to subtle changes in output voltage, temperature, volume/pressure of a cell, or other externally measurable parameters. This understanding would allow for more precise monitoring of cells during use within a pack that contains thousands of individual cells, and cell state-of-health based on these measurables could be linked to the state-of-health of the materials inside. This is a challenging proposition since degradation of an individual cell often involves rare events, such as Li metal deposition at the anode or excessive local interphase formation. Understanding the conditions that cause these rare circumstances at the nanoscale level will require a combination of experimentation, data analytics, and modeling. Early work in this area has already shown the value of systematic analysis of voltage outputs from many cells in identifying early stage degradation mechanisms.[27]

Nanoscale engineering of materials has been a major boon for battery research and development, and our improved capabilities to characterize and understand materials at the nanoscale have played a key role in these efforts. Electrochemical energy storage is poised to play an essential part in our increasingly electrified world, and the materials and nanoscience communities will continue to uncover the fundamental aspects of battery operation that provide the foundation for development and commercialization of this technology.

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Notes

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