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NNSA Laboratory Directed Research & Development

Energy Use Impacts and Mitigation

Understanding Battery Life from Atoms to Electrodes

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The challenge: How do we achieve long-life electrical energy storage?

Capturing energy from renewable sources and powering fleets of electric vehicles require the development of affordable, efficient, reliable, and long-lifetime electrical energy storage devices, i.e. batteries.

This work focuses on understanding mechanisms that limit battery lifetime. During normal service life, battery capacity decreases or degrades continuously – either with time (calendar life) or the number of charge-discharge cycles (cycle life). For consumer electronics, such as cell phones, laptops, etc., a cycle lifetime of 1000 cycles is usually sufficient (this is about one charge cycle per day for three years). For powering electric vehicles, we prefer much longer cycle lifetime, 5000 cycles or more, representing a battery lifetime of about 10 years (see Figure 1).

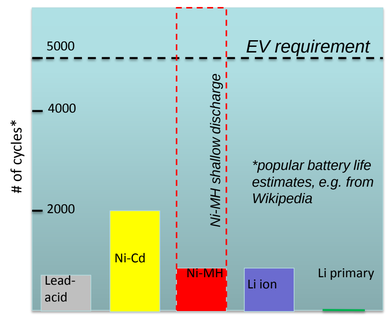

Figure 1. *Most batteries developed for smaller scale applications lack the 5000 cycle lifetime needed for electric vehicles.*

To understand mechanisms of battery degradation, it is necessary to look at length scales from the atomic scale to the scale of the full battery electrode thickness (about 100 microns) and from time scales of chemical reactions (sub-picosecond) to long-term degradation (months). In this work, we have developed new tools and methods to investigate degradation mechanisms over these spatial and time scales. We apply these tools to study Li-ion batteries – the preferred battery to power electric vehicles (see Figure 2). Li-ion batteries have multiple possible mechanisms for degradation (see Figure 3), but the study and identification of these mechanisms is a severe challenge in the battery community and the principle aim of this work.

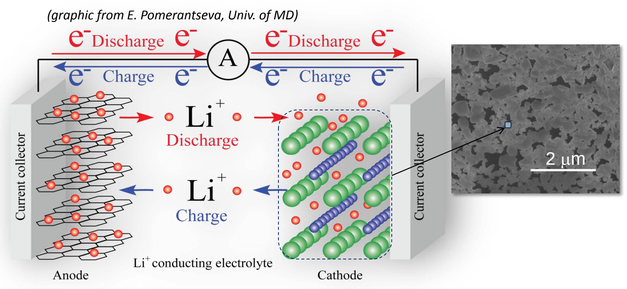

Figure 2. *A schematic of a Li-ion battery. Charge is stored in the form of Li ions that shuttle between anode and cathode. Real batteries (right) are composed of large numbers of small battery particles (over 1 quadrillion particles in an electric vehicle battery).*

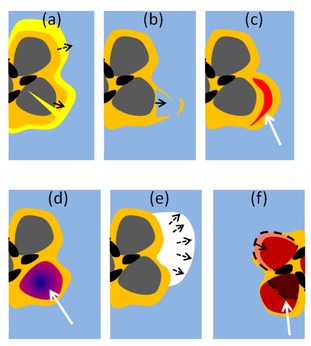

Figure 3. *Schematic representations of possible degradation mechanisms in Li-ion batteries. (a) particle cracking and solid electrolyte interphase (SEI) growth (and dissolution), (b) SEI delamination followed by regrowth, (c) Li plating (white arrow) and SEI growth, (d) active particle stranding (white arrow), (e) blocking of electrolyte channels by precipitates or gas bubbles, and (f) active particle dissolution or phase change (white arrow)*

Our approach: Novel methods to understand battery operation at a fundamental level.

We have developed new *in-situ* electron and x-ray microscopy approaches, miniature sealed batteries with electron and x-ray transparent windows, nanoscale electrochemistry, and atomic-scale modeling for the study of degradation.

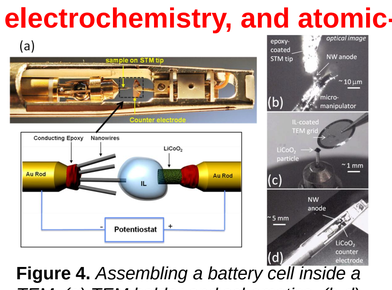

Figure 4. *Assembling a battery cell inside a TEM. (a) TEM holder and schematics, (b-d) anode particle, ionic liquid electrolyte, and counter electrode placed in holder.*

- **In order to observe battery degradation processes in real-time at the atomic scale, we developed *in-situ* transmission electron microscopy (TEM) that allows assembly, operation, and imaging of single-particle electrochemical cells (Figure 4).**
- **Battery degradation is a loss in battery capacity, and this requires new approaches to perform electrochemical measurements at the single particle level – 10 billion times lower current than a normal lab-scale measurement (Figure 5).**
- **Many degradation processes occur at the electrode level where interaction between battery particles is important. We developed an approach to examine full cross-sections of battery electrodes using ultra-microtoming and x-ray and electron microscopy (Figure 6).**
- **Degradation also occurs due to reactions between the electrodes and the electrolyte. To study this behavior, we developed a unique sealed liquid electrochemical cell that is able to operate inside and outside a TEM (Figure 7).**

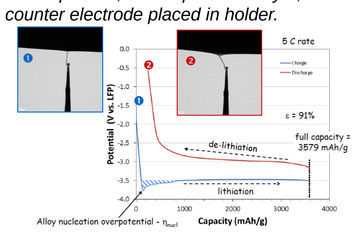

Figure 5. *Performing charge-discharge cycling on a single Si nanowire – a traditional measurement, but now performed at the nanoscale.*

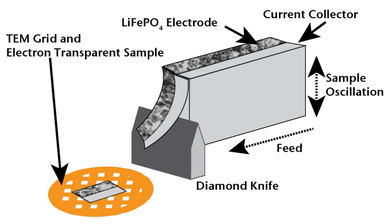

Figure 6. *Ultra-microtome sectioning is able to provide a thin (< 200 nm thick) slice through a full scale battery electrode (100 microns thick), enabling transmission microscopies.*

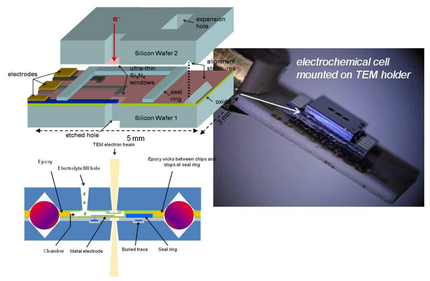

Figure 7. *A microchip-based sealed electrochemical cell enables imaging of battery charging and discharging using conventional volatile battery electrolytes while operating inside a TEM. Left images show a schematic of the cell, which is based on two chips that are aligned with sapphire lenses and that entrap a small volume of liquid electrolyte. Right shows the sealed cell on a TEM sample holder.*

Our results: Atomic to electrode-scale studies reveal new insight into degradation mechanisms.

Our studies on single particles revealed that particle fracture for alloying anodes is strongly size-dependent, and the lithiation process may be highly anisotropic. For a complete electrode, the lithiation process can be highly heterogeneous. Atomic scale modeling reveals that the process of electrolyte degradation is unexpected.

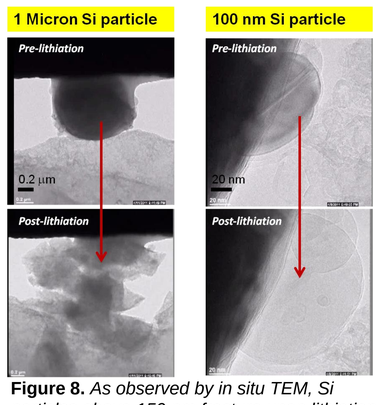

Figure 8. *As observed by in situ TEM, Si particles above 150 nm fracture upon lithiation (left) whereas smaller particles (right) do not.*

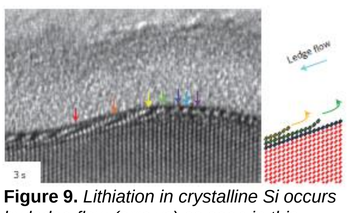

Figure 9. *Lithiation in crystalline Si occurs by ledge flow (arrows) as seen in this atomic resolution TEM image.*

- **Battery anodes based on silicon can exhibit degradation due to particle fracture (Figure 8). This process is highly size-dependent. Our *in-situ* TEM studies show that particles below approximately 150 nm in size do not fracture upon lithiation, while particles above this size do fracture. In both cases, large volume expansion > 300 % is observed. Particle fracture leads to degradation for two reasons: (1) the fracture creates fresh electrode surface which leads to an increase in electrolyte reduction and formation of the solid electrolyte interphase (SEI), and (2) fracture may lead to electrical isolation of the particle from the matrix, resulting in a net loss of active material.** *Ref: X. Liu, et al., ACS Nano 6, 1522 (2012).*
- **For the first time, it is possible to observe the lithiation mechanism in a Li-ion battery anode in real-time with atomic scale resolution (Figure 9). We observed the lithiation of a crystalline silicon particle, and it was found that lithiation proceeds by ledge flow of surface steps located on (111) planes. This leads to highly anisotropic lithiation where the volume expansion is greater in some directions than others. This anisotropy can induce particle fracture due to stress concentration, but the anisotropy can be reduced through the use of amorphous silicon.** *Ref: X. Liu, et al., Nature Nanotech 7, 749 (2012).*
- **A new approach to map the charging and discharging process as a function of depth in a full-scale battery electrode was developed. The approach uses scanning transmission x-ray microscopy performed at the Advanced Light Source at Lawrence Berkeley Labs. The sample is prepared by microtoming a thin wedge < 400 nm thick out of an electrode. Using x-ray absorption spectroscopy the charge state of each particle is mapped with 20 nm resolution. The STXM is combined with TEM to give spatial resolution down to the atomic scale. When a $LiFePO_4$ battery cathode was examined, it was unexpectedly found that the charging process was highly heterogeneous and almost independent of depth and particle size (Figure 10). The charging rate was found to be controlled by nucleation.** *Ref: Chueh, et al. Nano Lett. 13, 866 (2013).*

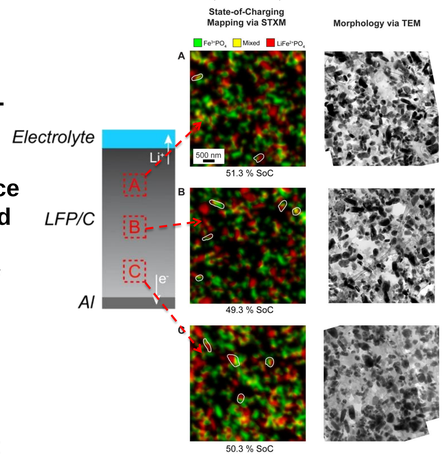

Figure 10. *STXM (middle) and TEM (right) reveal that charging is highly heterogeneous in a $LiFePO_4$ electrode, but almost independent of position (left) or particle size.*

- **Degradation due to electrolyte reduction was modeled from first principles using *ab initio* molecular dynamics. Unexpectedly, it was found that electrolyte reduction on a bare lithiated graphite anode predominantly occurs by 2 electron transfer to the ethylene carbonate molecule (Figure 11). The reaction byproducts are different by this reduction compared to the expected 1 electron process, and this suggests new experimental signatures and electrochemical conditions for detecting electrolyte breakdown.** *Ref: Leung, et al. submitted (2013).*

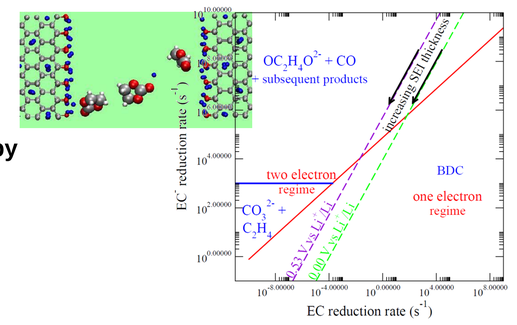

Figure 11. *Ab initio MD (upper left) shows that 2 electron reduction of EC dominates over much of the electrochemical range (right).*

Impact: This study offers tools to understand the origins of degradation and how to reduce it.

The approaches developed here enable the measurement of degradation mechanisms that limit battery life. Several degradation mechanisms were observed and modeled. Specific suggestions to reduce degradation can be made, and this could enable long lifetime batteries, extending the range and lowering the cost of electric vehicles (ultimately leading to increased electric vehicle ownership and utilization).

- **Mechanical, surface, and chemical forms of degradation were observed or modeled on battery anodes and cathodes. These findings suggest that controlling particle size and the application of surface coatings would be beneficial to extending life.**
- **Battery lifetime is a key to increased adoption of electric vehicles. Electric vehicles are desirable* (Figure 12), but limited range and high purchase price are the biggest barriers to increased adoption. ***http://money.cnn.com/2013/05/09/autos/tesla-model-s-consumer-reports/

Figure 12. *The Tesla S electric vehicle is the highest rated vehicle from Consumer Reports.*

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