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Germanium Nanowire Lithiation Observed *In Situ* Using a Transmission Electron Microscope Liquid Cell

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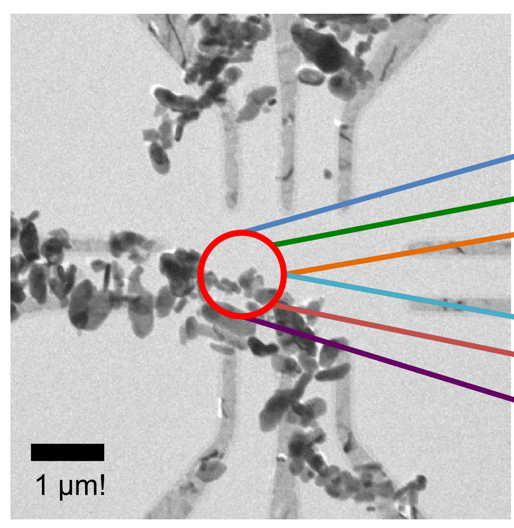
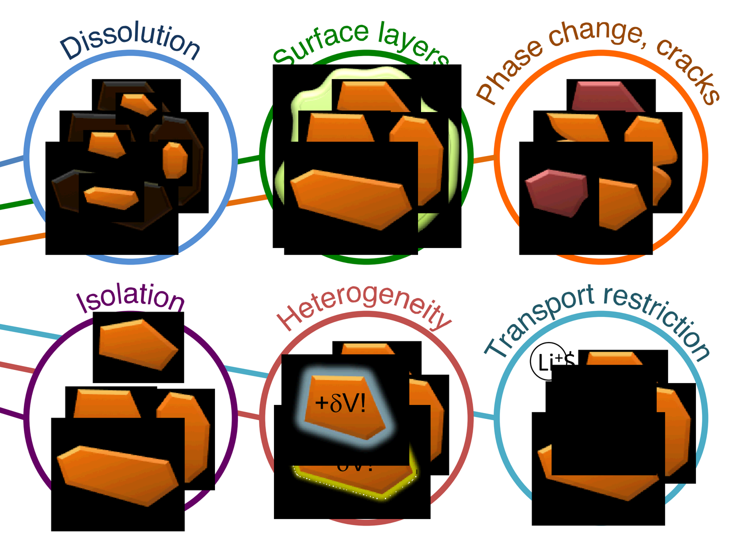
Problem: Degradation in Batteries

- Energy storage in batteries can involve detrimental, irreversible electrochemical processes that are inherently nanoscale.
- What are the degradation mechanisms in rechargeable Li-ion battery electrodes?



Micrograph of $LiFePO_4$ particles on liquid cell electrodes.

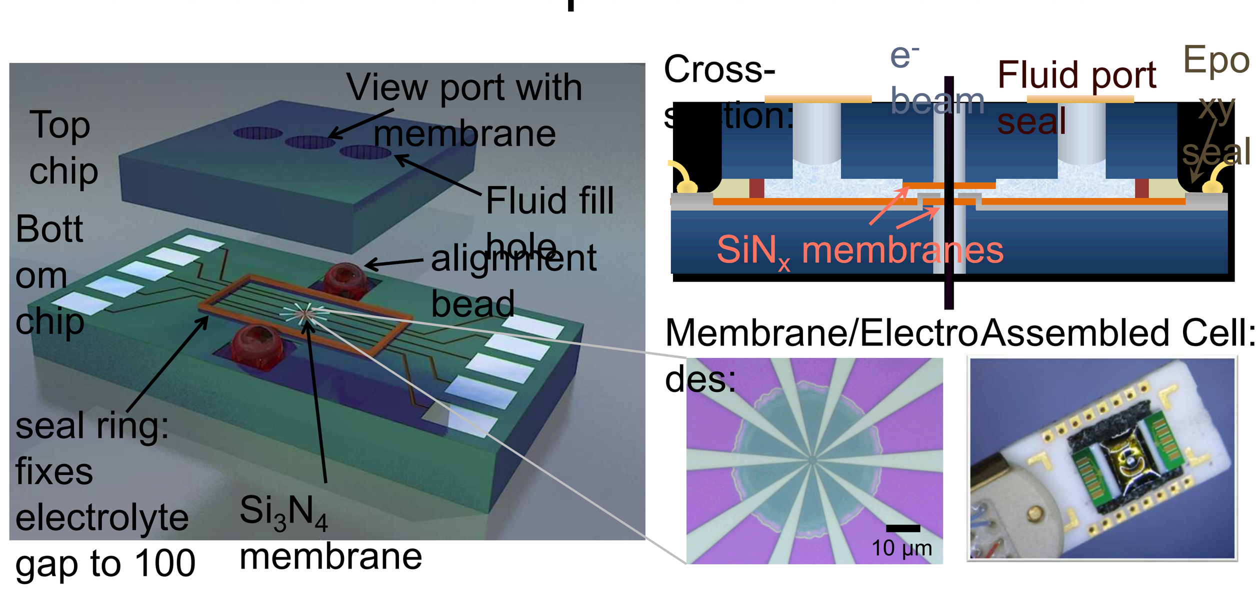


Detrimental effects accompany lithium movement during electrochemical cycling.

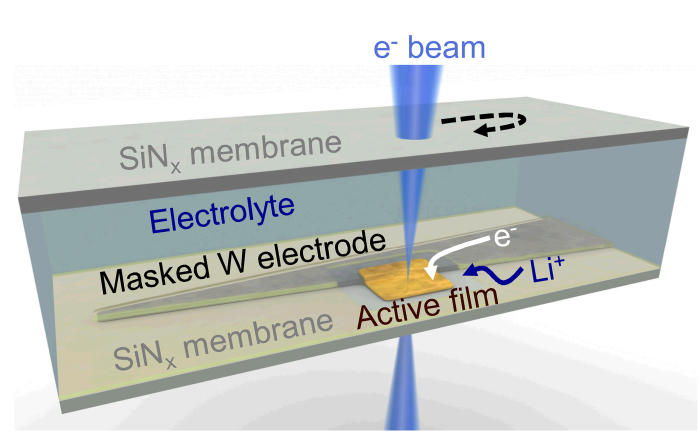
Imaging nanoscale structures during electrochemical cycling in a transmission electron microscope (TEM) informs mitigation strategies.

Approach: Microfabricated TEM Liquid Cell

High-resolution TEM imaging of materials in **standard liquid electrolytes** enabled by a custom microfabricated, sealed cell with electron-transparent membranes.



Materials of study are placed on electrodes; cell filled with ~100-nm thick liquid layer.

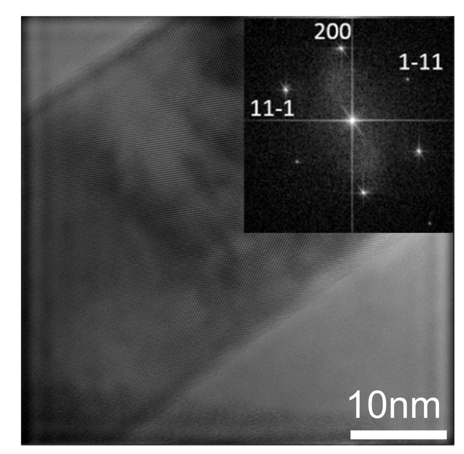


Controlled rate links images with electrochemical signatures.

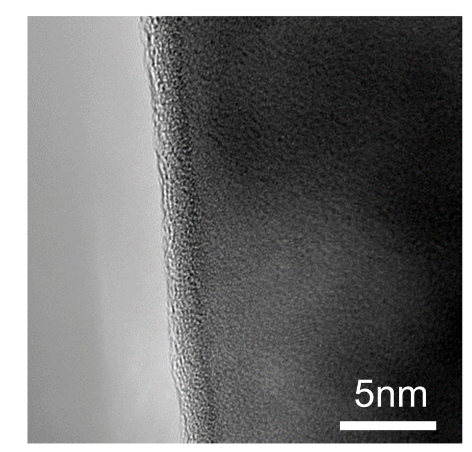
Electrolyte: 1:1 EC:DMC + 1M $LiPF_6$.

Material System: Germanium Nanowires

- Want to understand mechanical failure mechanisms in high-capacity anode materials, to improve battery performance and life (Ge = 280%, Si = 300%, cf. graphite).
- Nanowires can potentially permit higher charging rates and accommodate more stress without cracking compared to bulk.
- Compared to Si, Ge possesses higher Li diffusivity, higher electrical conductivity, and undergoes isotropic expansion during lithiation. However, Ge is more expensive.
- With a higher atomic weight (w.r.t., Si), Ge is a more favorable materials system for *in-situ* TEM electrochemical studies.

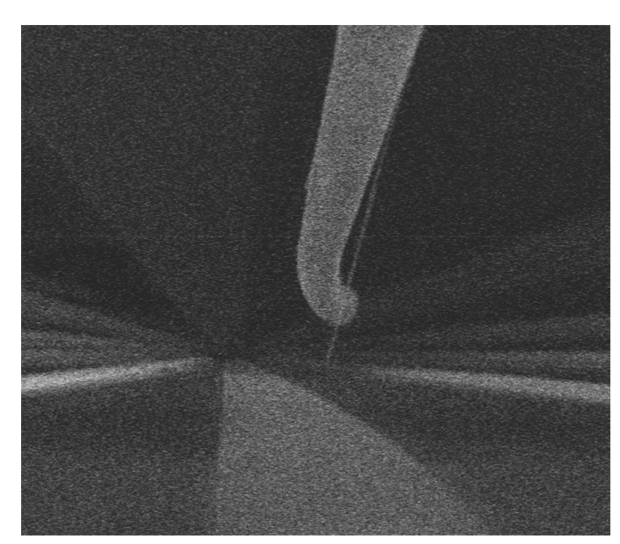


HR-TEM image of [111] Ge NW with the electron diffraction pattern shown in the inset.

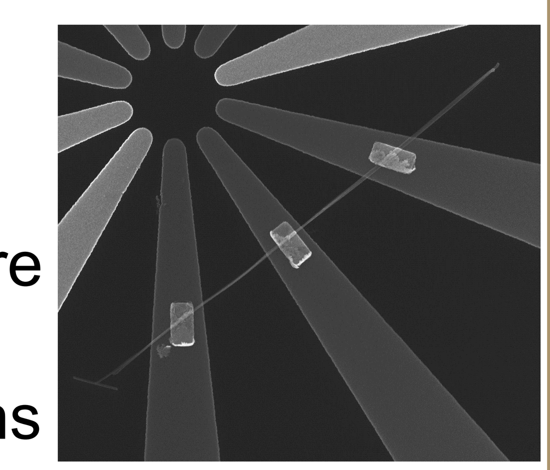


An image showing the amorphous oxide layer, with a nominal thickness of 3nm on the NW surface.

Single Nanowire Device Fabrication

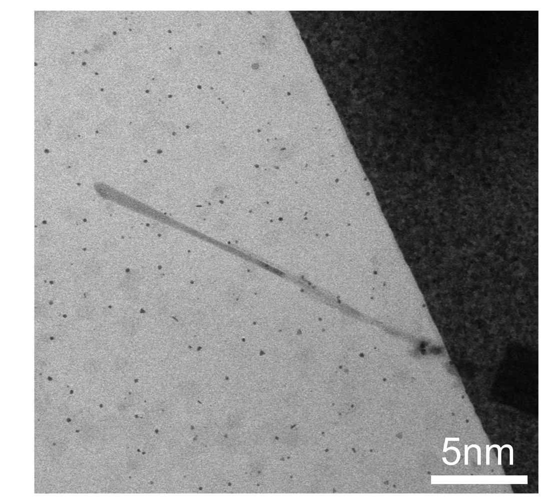


Single nanowires are harvested from the growth substrate and placed onto electrodes using a dual-probe nanomanipulator embedded in an SEM.

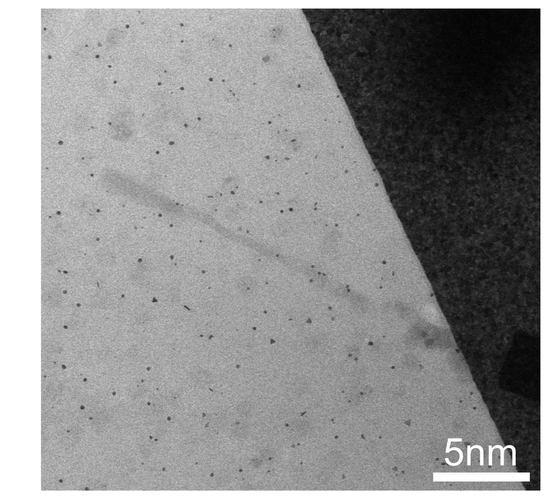


Metal contacts are patterned onto the wires using e-beam lithography (EBL). The entire structure is then passivated with Al_2O_3 with selected regions of the wire opened with EBL and wet etching.

In-situ Electrochemical TEM: Galvanostatic cycling of Ge NWs

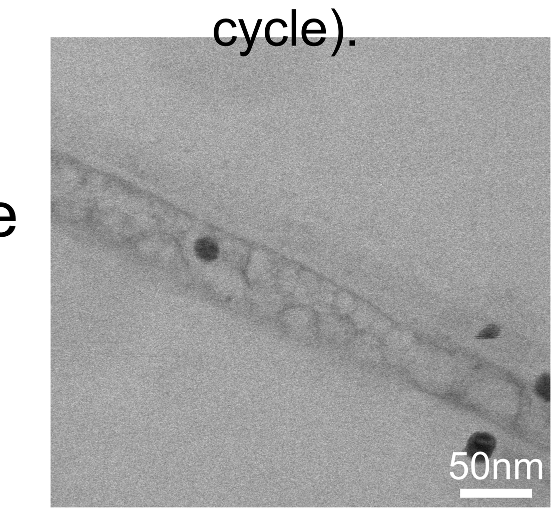


The wire before cycling.



The wire fully lithiated (1st cycle).

Galvanostatic cycling at 1pA. When fully lithiated the single crystalline wire becomes amorphous and faint in contrast. After multiple cycles the wire becomes porous.



Void formation after multiple cycles.

Results and Observations

- The Sandia-microfabricated TEM liquid cell enables an unprecedented view of Li-ion battery electrode behavior and provides a versatile platform for imaging a variety of immersed materials.
- Individual Ge nanowires can be cycled multiple times without failure.
- These wires exhibit porosity after numerous cycles, where the void size appears to be a function of the wire diameter.

Published Papers:

Leenheer *et al.*, *J. Microelectromech. Syst.* **2015**. DOI 10.1109/JMEMS.2014.2380771

Leenheer *et al.*, *ACS Nano.* **2015**. DOI 10.1021/acsnano.5b00876

Impact: Energy Security, Electricity Storage

- Electricity storage is a key technology for energy independence and security.
- Batteries are expensive and short-lived; by understanding degradation pathways, future batteries can use less expensive, more robust, higher-capacity materials.

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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NEES II NANOSTRUCTURES *for* ELECTRICAL ENERGY STORAGE