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Liquid Cell *in-situ* TEM Capabilities for Lithium Battery Materials

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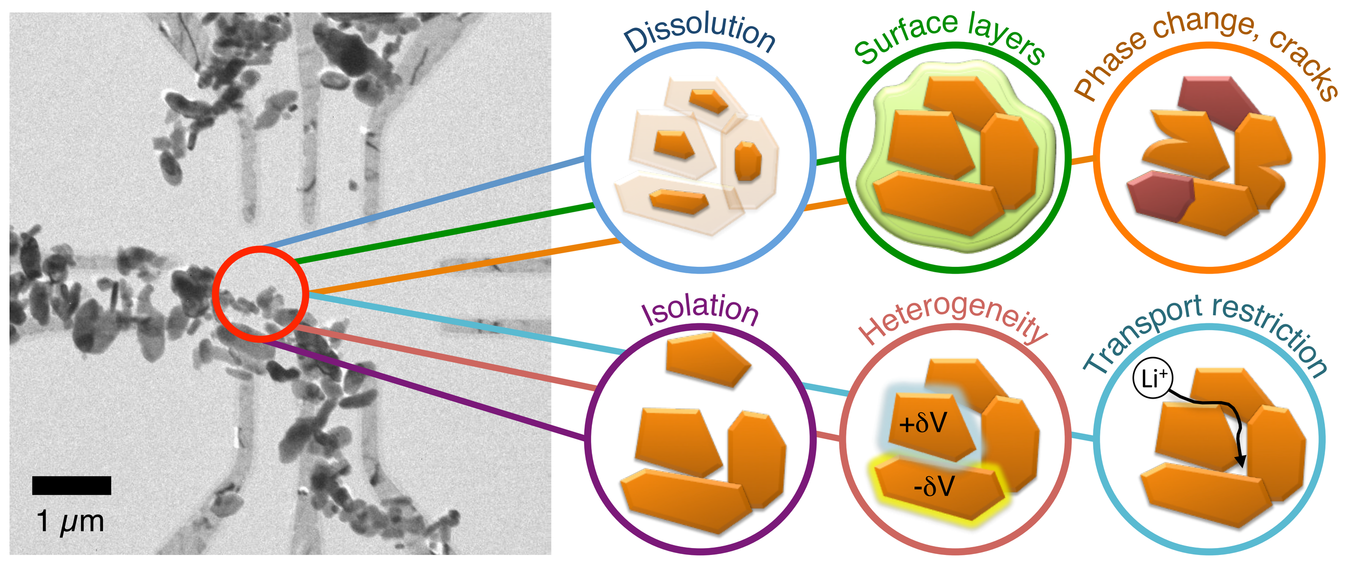
Lithium Battery Degradation

- Lithium ion batteries are widely used in consumer electronics, and increased reliability and safety would enable electric vehicle or power grid applications.
- Degradation mechanisms link to nanoscale materials changes:



TEM image of $LiFePO_4$ particles on liquid cell electrodes.

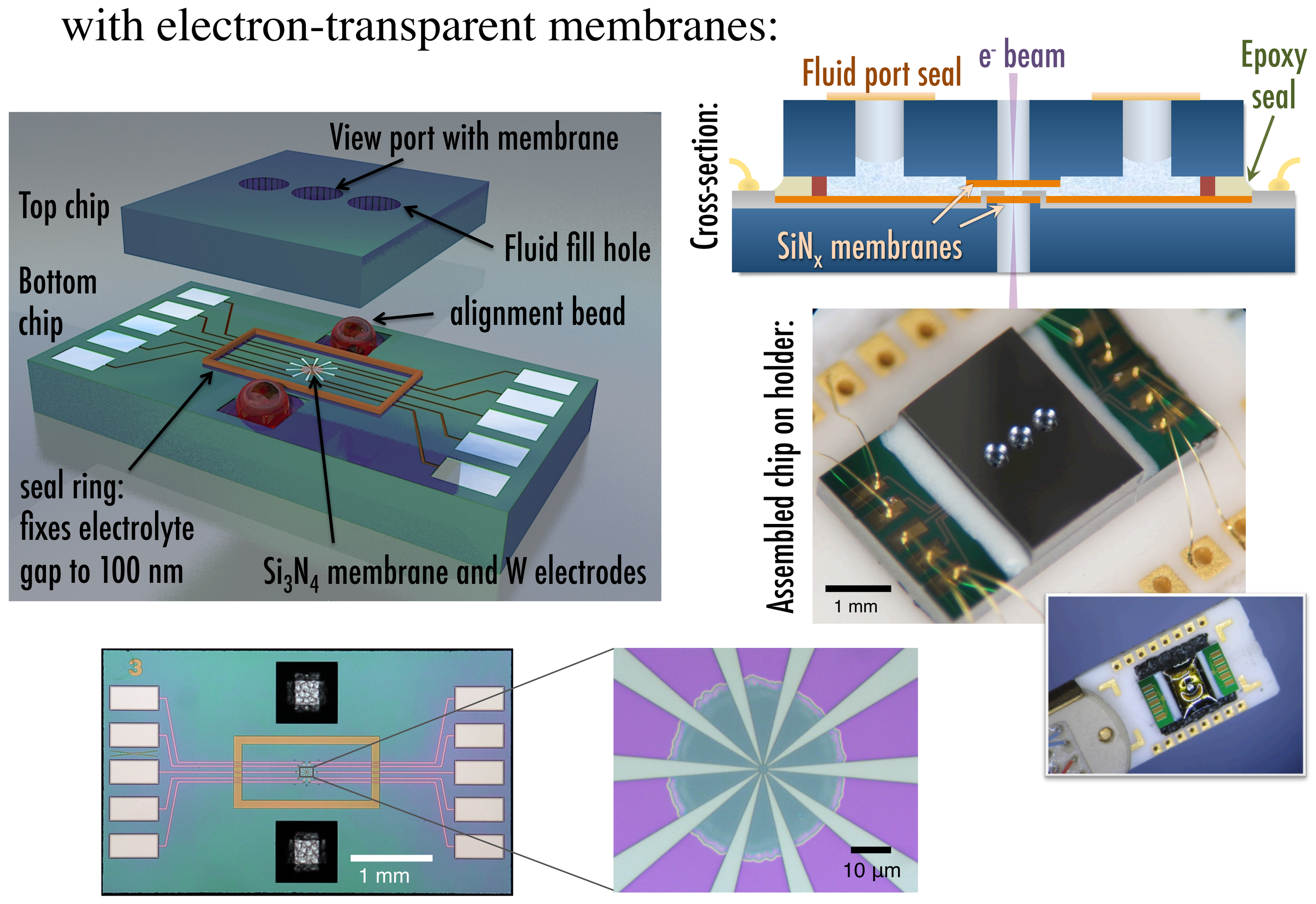
Detrimental effects accompany Li movement during electrochemical cycling.

Imaging nanoscale structures during electrochemical cycling in a transmission electron microscope (TEM) shows battery degradation mechanisms and informs mitigation strategies.

- Lithiation of 3D, 2D, 1D, and 0D structures demonstrated here.

TEM Liquid Cell Design

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

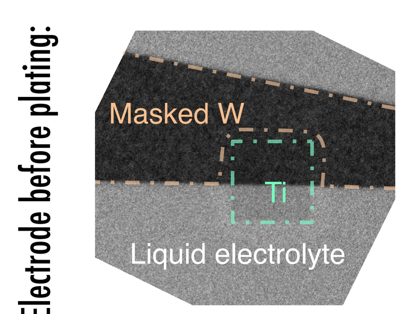


- Quantitative current/voltage control at pA-levels links images to electrochemical signatures.
- Liquid cell amenable to post-processing and lithography to place a wide variety of materials on the electrodes.

Liquid cell priorities: thin electrolyte layer for high resolution, quantitative electrochemistry capability, ability to add active materials, and multiple electrodes for multiple experiments.

3D structure example: Lithium electrodeposition

- Metallic Li is an ideal battery negative electrode, but high-surface-area dendrites cause degradation and safety issues.
- TEM liquid cell enables unprecedented visualization of dendrite initiation conditions and electrodeposition/dissolution dynamics.
- Plate and strip in typical electrolyte (1:1 EC:DMC / 1 M $LiPF_6$) at typical Li-battery current density: 1, 10, and 25 mA/cm^2.

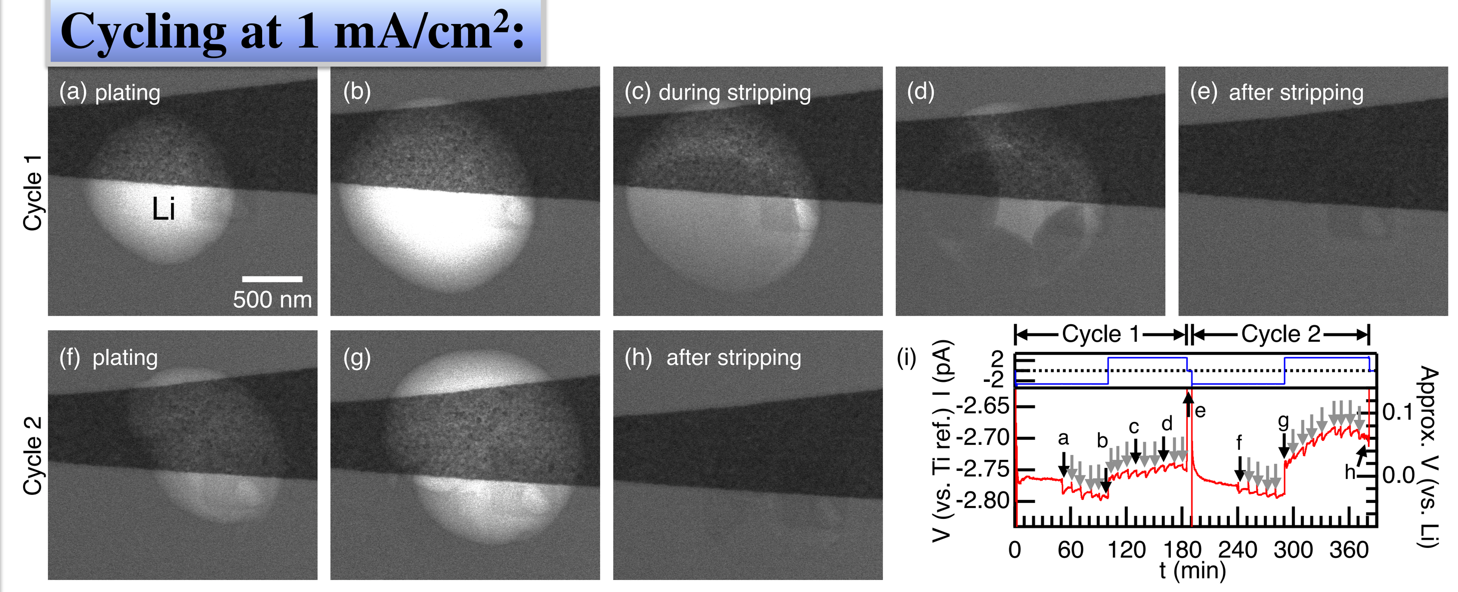


Experiment:

- Apply galvanostatic current to 0.26-μm^2 Ti working electrode to induce Li deposition
- Counter / reference electrodes are 750-μm^2 Ti circles
- Take first image halfway through electrodeposition.
- Image periodically through deposition and stripping.

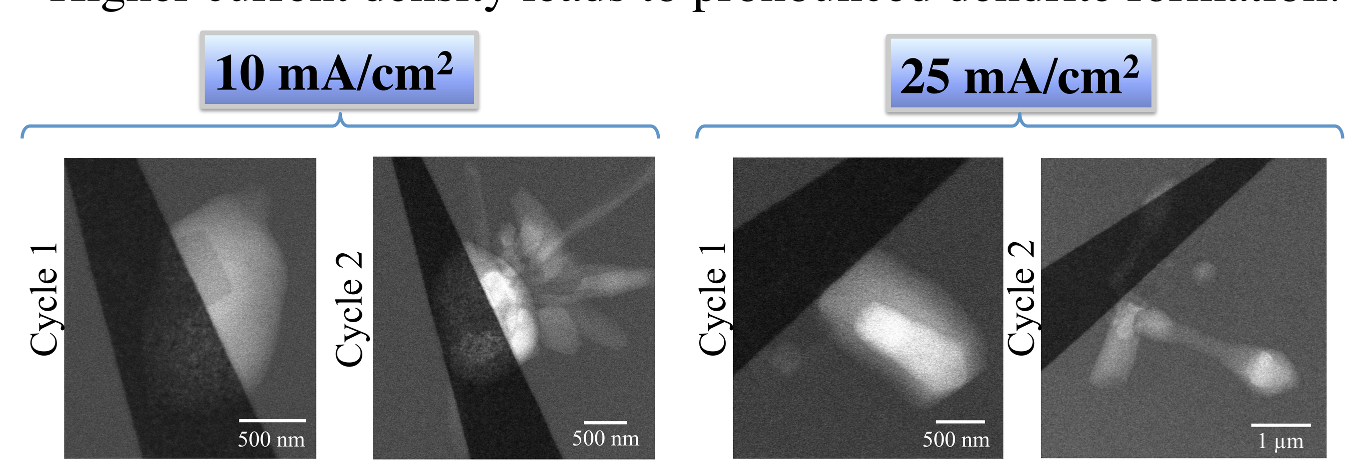
Low-density Li appears light in Brightfield STEM images.

Cycling at 1 mA/cm^2:

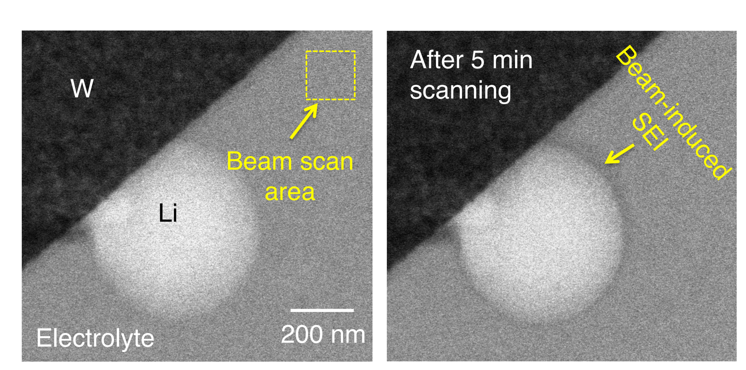


During electrochemical stripping, dissolution initiates from discrete weak points in surface film rather than uniformly.

- Higher current density leads to pronounced dendrite formation:

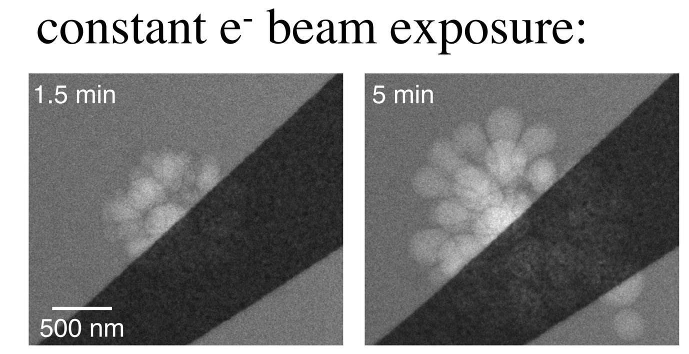


- Electron beam can induce electrolyte radiolysis and create surface films beyond the naturally-formed solid electrolyte interphase ("SEI"):



Imaging dose rate: **10** $e^- nm^{-2} s^{-1}$ for 5 s.
Dose rate in small square: 3,750 $e^- nm^{-2} s^{-1}$.

<u>Consequence</u>: Li morphology different when plated under constant e^- beam exposure:

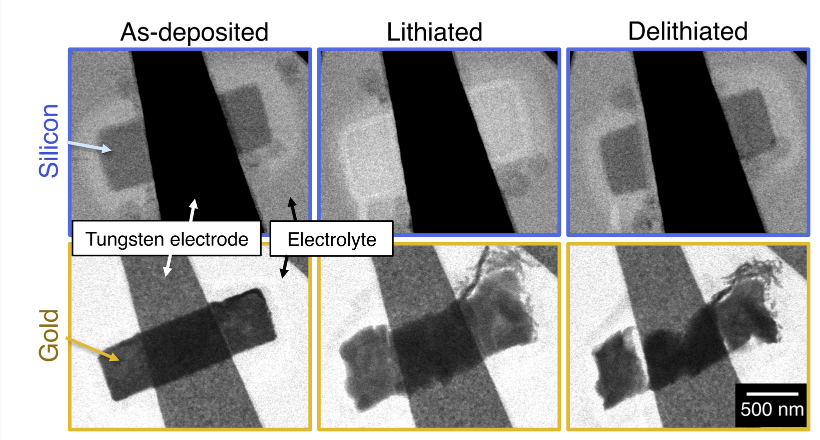


Li plating at 10 mA/cm^2, images taken every 15 s.

Li dendrite initiation visible in TEM liquid cell. Both electrodeposition and stripping influenced by presence of a passivating surface film from electrolyte breakdown.

2D structure example: Lithiation of Si and Au thin films

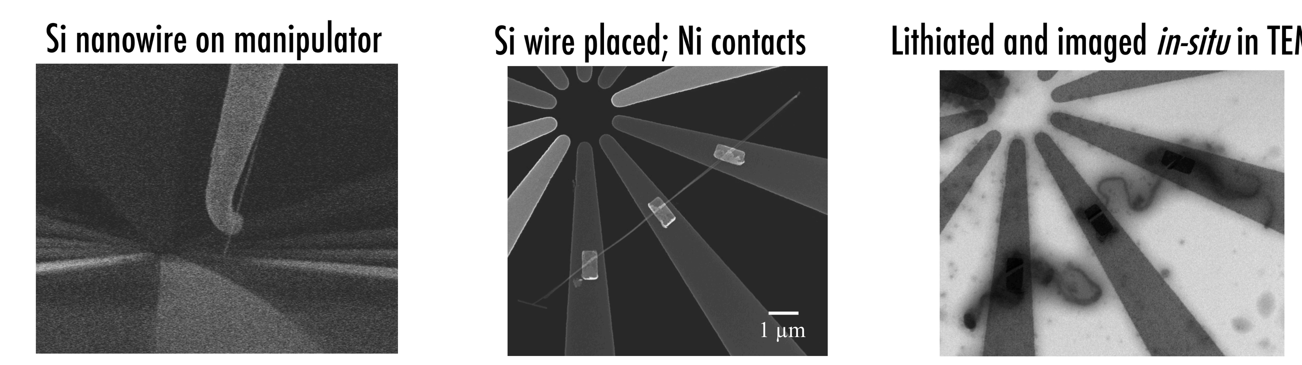
- Propagation of phase changes in Li-alloying materials can cause nonuniformities and localized stress.
- TEM shows nucleation and growth of heterogeneous domains in thin film electrodes during lithium insertion and extraction.



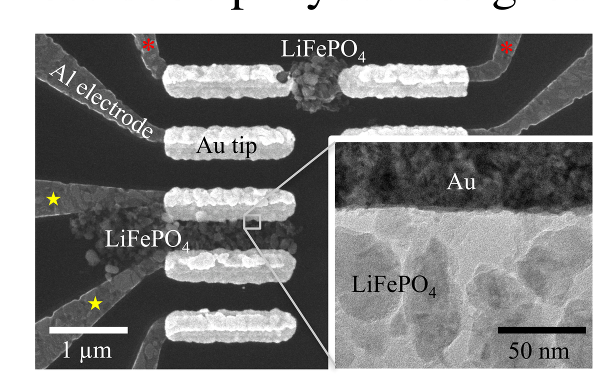
- Electron-beam lithography used to pattern thin film (50-100 nm) of active material on inert, passivated W electrode.
- Liquid cell filled with EC:DMC / $LiPF_6$ electrolyte and galvanostatic current applied to lithiate and delithiate electrodes.
- Amorphous Si lithiation uniform and reversible
- Crystalline Au pulverizes due to nonuniform phase change propagation

1D and 0D structure examples: Si wire, $LiFePO_4$ particles

- Pick-and-place manipulation possible for single-nanowire testing.



- Electrode tip layout designed for nanoparticle dielectrophoresis:



- Liquid cell immersed in $LiFePO_4$ nanoparticle suspension
- AC voltage applied between starred electrodes resulted in assembly near tips
- Experiments ongoing in TEM and STXM on nanoparticle assemblies

Summary

- CINT TEM liquid cell platform enables visualization of challenging Li plating, alloying processes in volatile liquids.
- Small exposed electrode area allows quantitative electrochemical measurements, linking observed nanoscale phenomena to bulk electrochemistry.
- Needle-like Li dendrites visible in TEM, more pronounced at higher current density, influenced by surface films.
- Incorporation of thin films, nanowires, and nanoparticles possible to image structure change upon lithiation.

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