Liquid Electrochemistry in a TEM: Lithium Cycling

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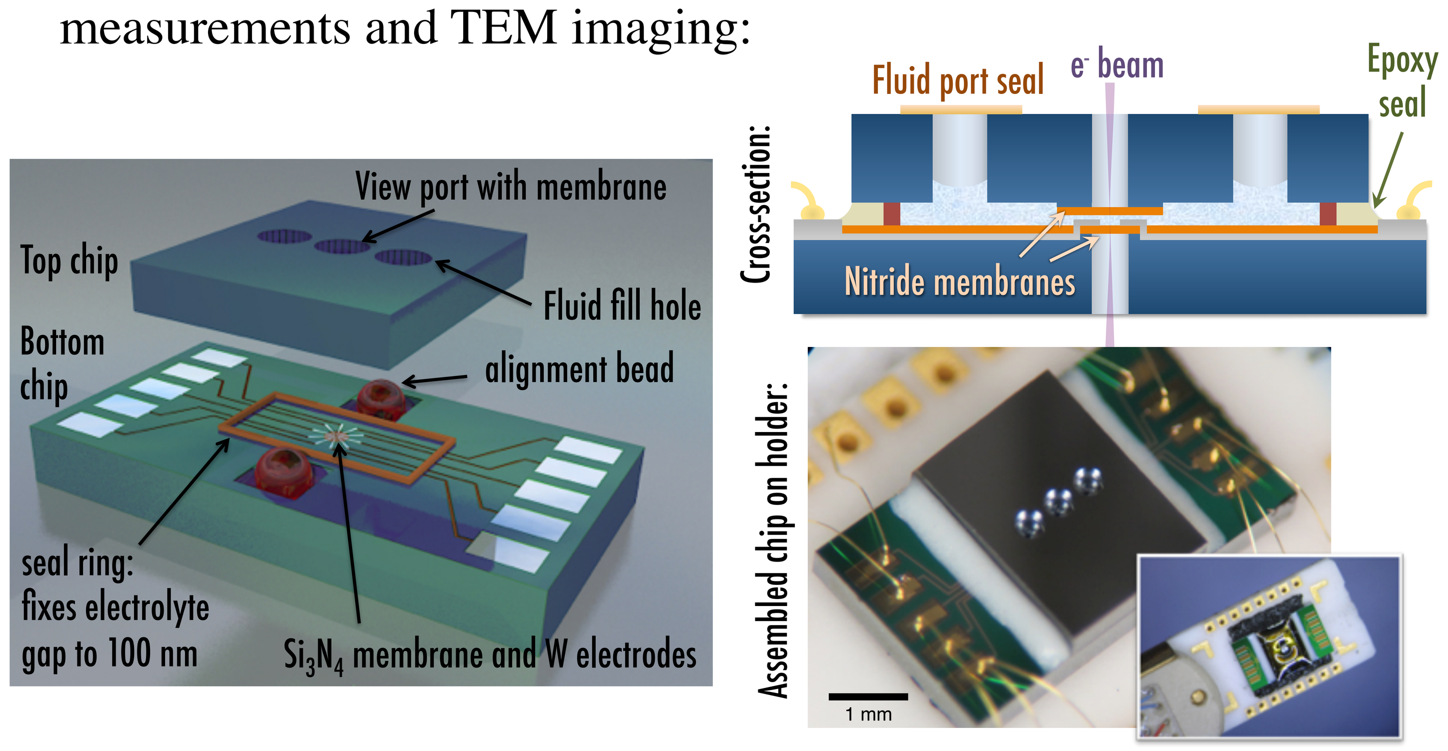
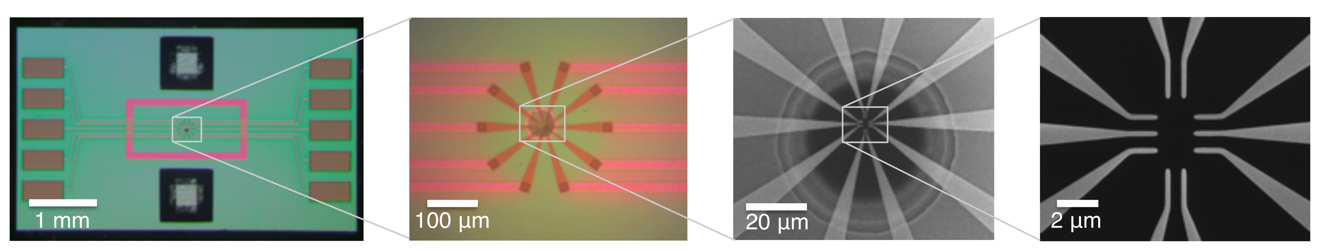
TEM Liquid Cell Design

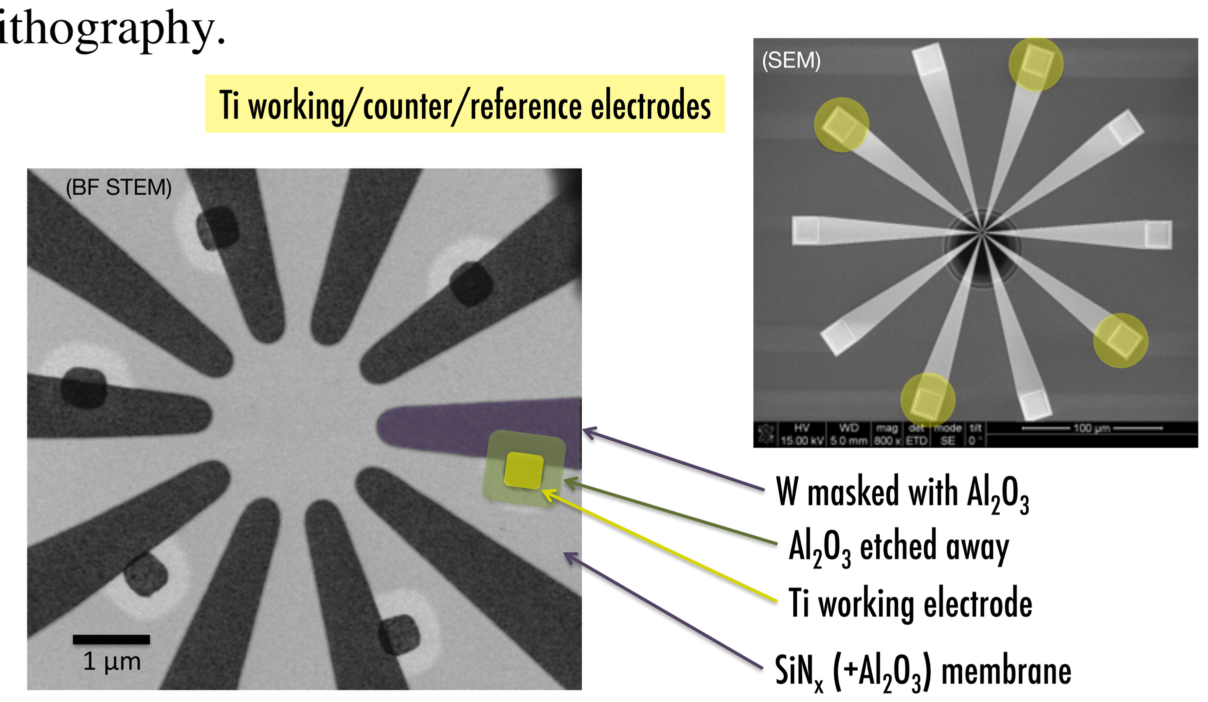
- A sealed liquid electrochemical cell enables unique *in-situ* experiments on a transmission electron microscope (TEM) in standard volatile electrolytes.
- To link observed morphological changes in electrodes to standard electrochemical cells (e.g. batteries), quantitative current/voltage control is required at fA-pA levels.
- We developed a electrochemical platform optimized for nanoscale measurements and TEM imaging:



Our priorities: narrow electrolyte gap for good resolution, quantitative electrochemistry capability, ability to add active materials, and multiple electrodes for multiple experiments.

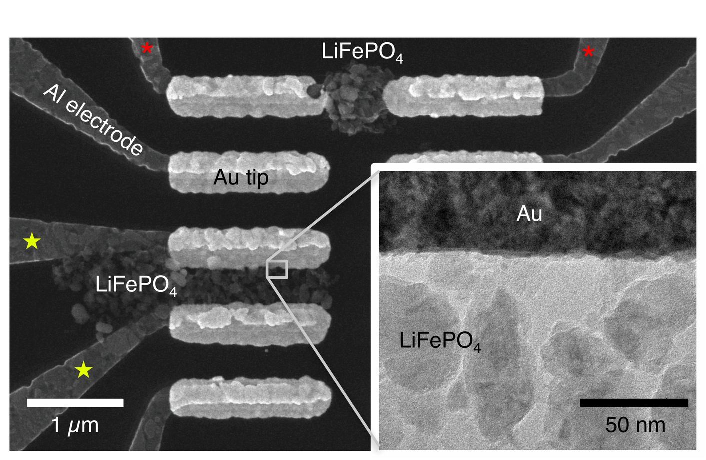


- To localize electrochemistry to viewable area, electrodes are masked with ALD Al_2O_3 and patterned using electron-beam lithography.



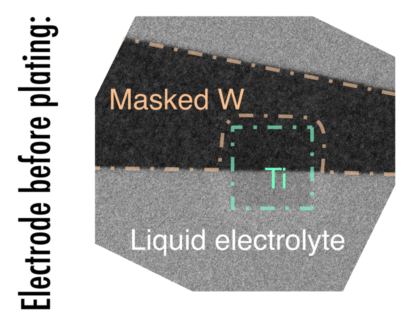
Nanoparticle assembly also possible:

Dielectrophoresis between starred electrodes resulted in localized immobilization of nanoparticles at electrode tips from a dispersed solution.



Lithium Electrodeposition and Stripping

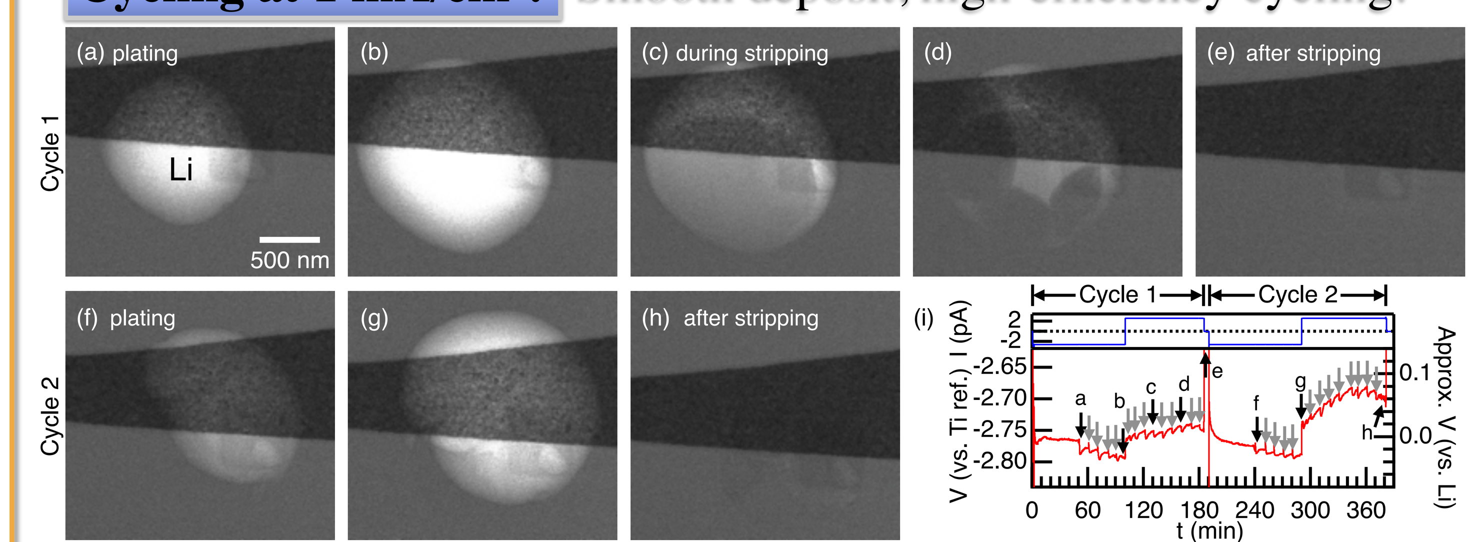
- Metallic Li is an ideal battery negative electrode, but high-surface-area dendrites cause degradation and safety issues.
- TEM liquid cell enables unprecedented visualization of dendrite initiation conditions and electrodeposition/dissolution dynamics.
- Plate and strip in typical electrolyte (1:1 EC:DMC / 1 M $LiPF_6$) at typical Li-battery current density: 1, 10, and 25 mA/cm².



Experiment:
- Apply galvanostatic current to 0.26-µm² Ti working electrode to induce Li deposition
- Counter / reference electrodes are 750-µm² Ti circles
- Take first image halfway through electrodeposition.
- Image periodically through deposition and stripping.

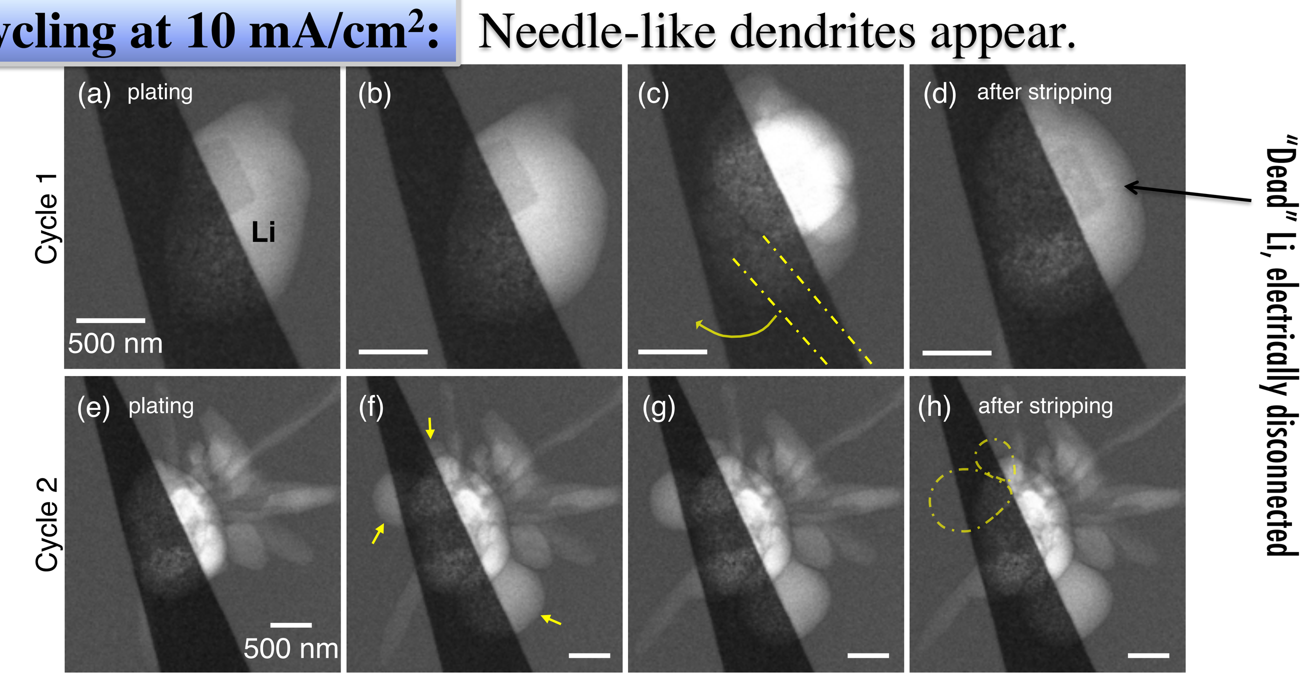
Low-density Li appears light in BF STEM images.

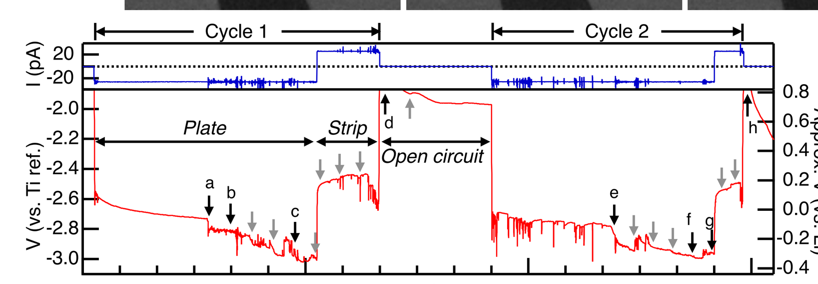
Cycling at 1 mA/cm²: Smooth deposit, high-efficiency cycling.



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

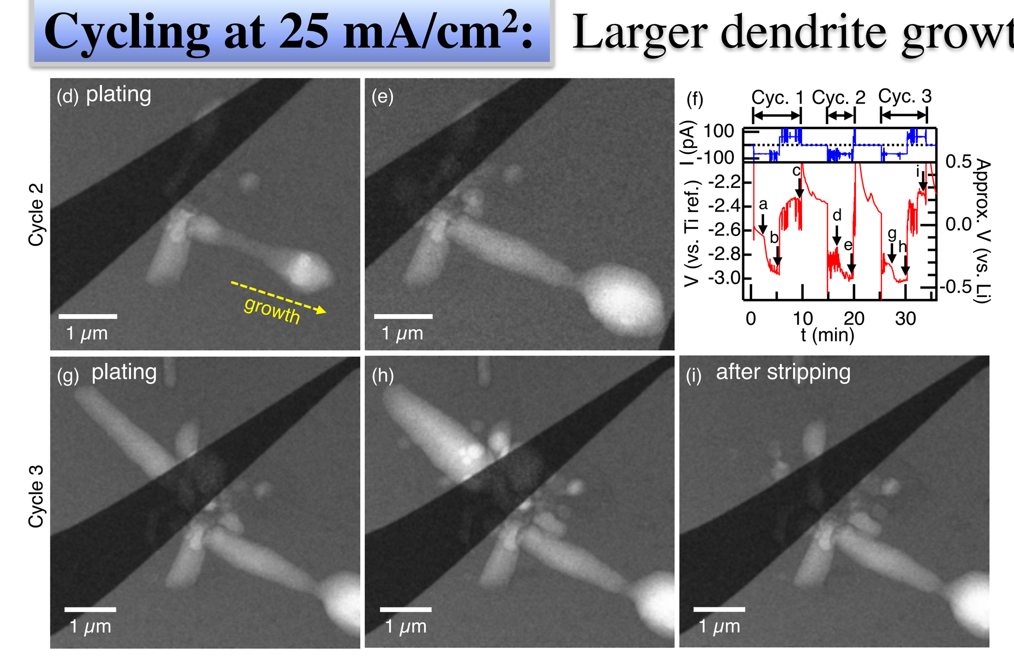
Cycling at 10 mA/cm²: Needle-like dendrites appear.





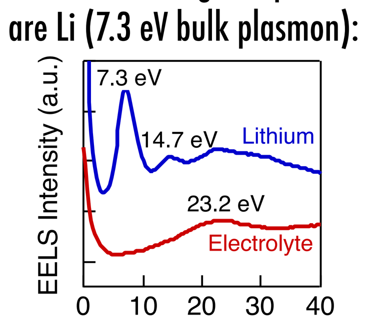
Dendrites appear on later cycles, likely due to formation of passivating surface films from electrolyte breakdown (solid-electrolyte interphase, SEI)

Cycling at 25 mA/cm²: Larger dendrite growth, poor efficiency.



Some Li needles observed to grow from the base, not just from the tip.

EELS confirms light deposits are Li (7.3 eV bulk plasmon):

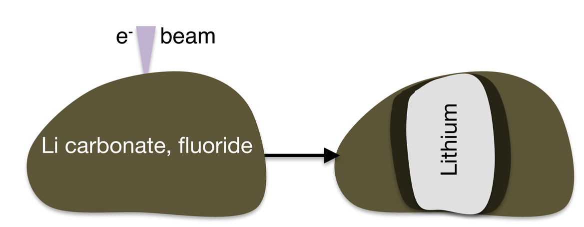


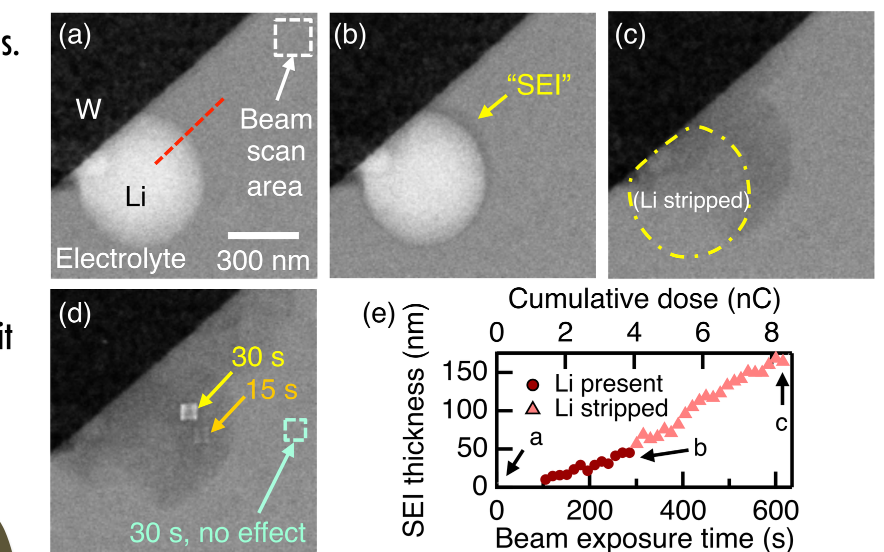
Electron Beam Effects

- Electron beam induces radiolysis in electrolyte that can interfere with the intended electrochemistry even at minimal dose rates.
- For reactive metal plating, surface films (solid-electrolyte interphase, SEI) critically affect deposition location/morphology.
- Test beam effect: scan in electrolyte near Li at high dose rate, and do plating/stripping with nearly constant imaging.

Imaging dose rate: **10 e⁻ nm⁻² s⁻¹** for 5 s.
Dose rate during test: 3,750 e⁻ nm⁻² s⁻¹.

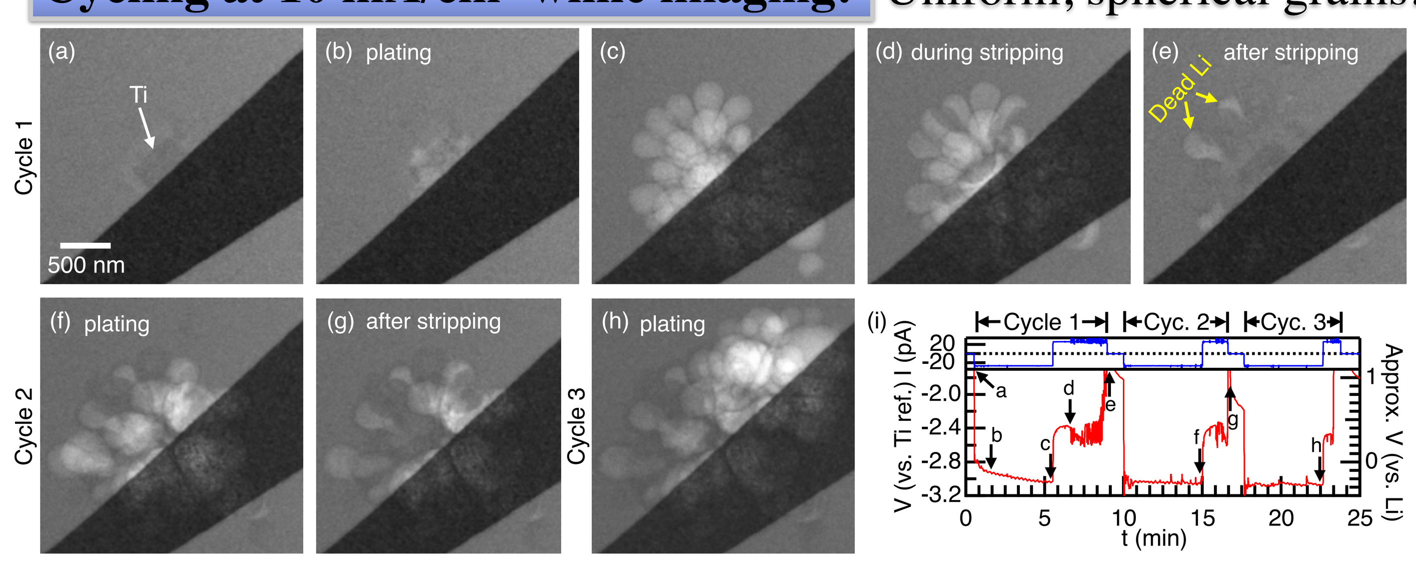
- Beam creates a SEI surface film upon extended exposure.
- Beam-induced film continues to grow without Li present.
- Scanning beam in dark deposit reduces it back to light-colored Li:





Note: Little beam effect while scanning in electrolyte away from Li.

Cycling at 10 mA/cm² while imaging: Uniform, spherical grains.



Compare to deposition morphology without beam exposure.
Beam mediates Li nucleation and growth even with minimal beam current.

Summary

- CINT TEM liquid cell platform development enables visualization of the difficult Li plating process.
- Small exposed electrode area allows quantitative electrochemical measurements, linking observed nanoscale phenomena to bulk electrochemistry.
- Initiation of needle-like Li dendrites visible in TEM and are more pronounced at higher current density.
- Electron beam exposure induces a surface film and modifies the Li plating morphology, causing spherical grains rather than crystalline needles.

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