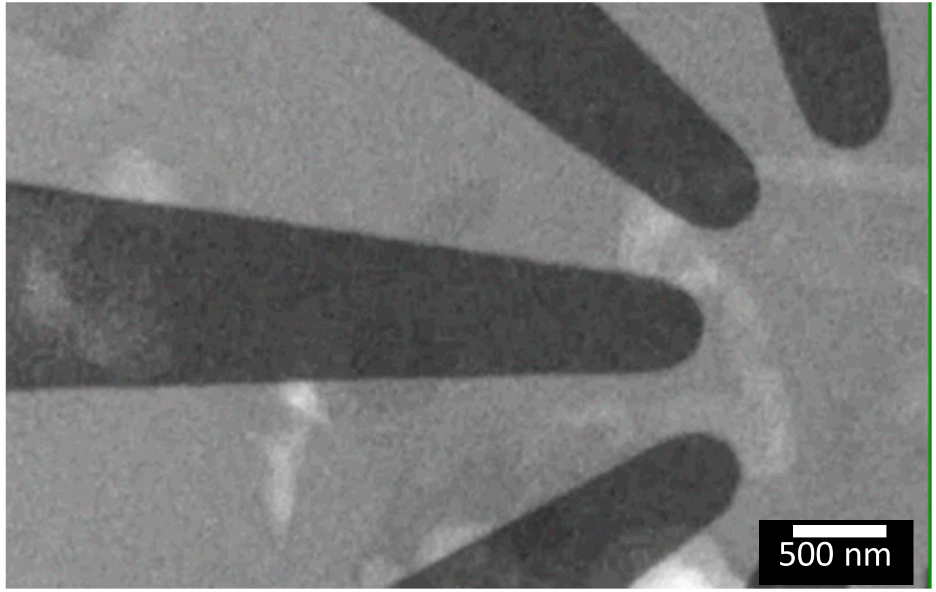
SAND2014-20286C



Li electrodeposition dynamics visualized *in-situ* via a TEM liquid cell

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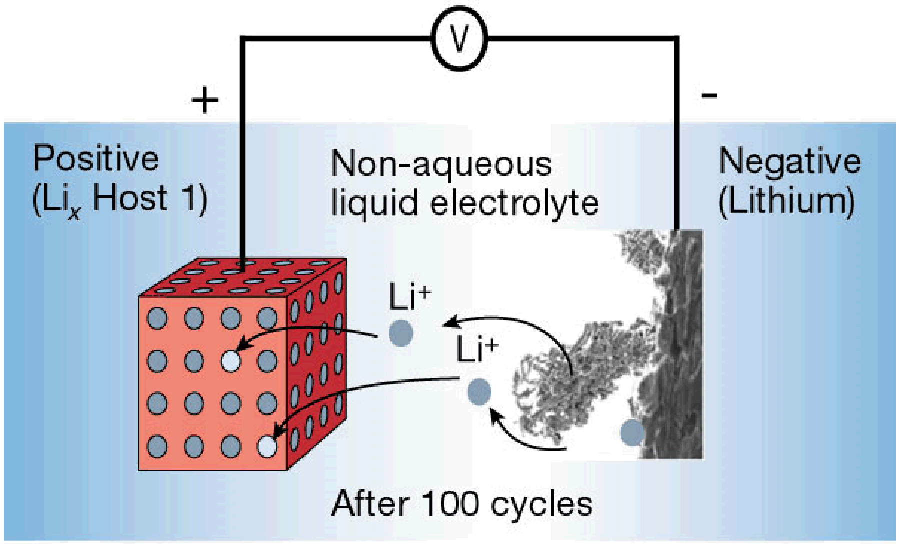
Katherine L. Jungjohann, Kevin R. Zavadil,, and C. Thomas Harris

TEM imaging shows current-density-dependent Li morphology, and electron beam effects emphasize role of interfacial layers.

This work was performed at the Center for Integrated Nanotechnologies, a U.S. Department of Energy (DOE) Office of Basic Energy Sciences user facility. Sandia National Laboratories is a multiprogram laboratory managed and operated by Sandia Corporation, a wholly-owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04- 94AL85000. Portions of this work were funded by the Nanostructures for Electrical Energy Storage, an Energy Frontier Research Center funded by the U.S. DOE Office of Science, and portions were funded by a Sandia National Lab LDRD project.

Li metal batteries: high capacity, cycles poorly



Tarascon, J. M. & Armand, M. *Nature* **414,** 359–367 (2001).

<u>Li metal offers 10x higher gravimetric capacity than graphite.</u>

But, cycling creates high-surface area Li resulting in:

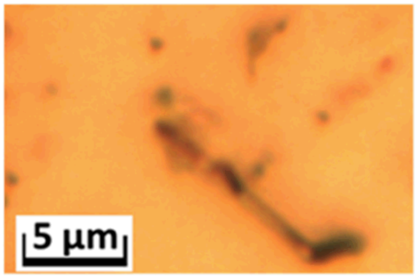
1. Continual electrolyte reduction: Irreversible growth of "SEI" (solid electrolyte interphase)
2. Disconnected Li and capacity loss
3. Possible electrical shorts

Imaging Li deposition *in-situ* guides models for Li dendrite growth and strategies for suppression.

Microscopy shows Li growth details *in-situ*

Optical microscopy

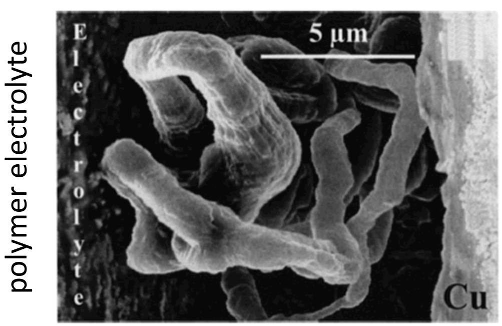
Drawback: diffraction limit



Steiger, J., Kramer, D. & Mönig, R. *J. Pow. Sources* (2014). doi:10.1016/j.jpowsour.2014.03.029

Scanning electron microscopy

Drawback: no liquid electrolyte

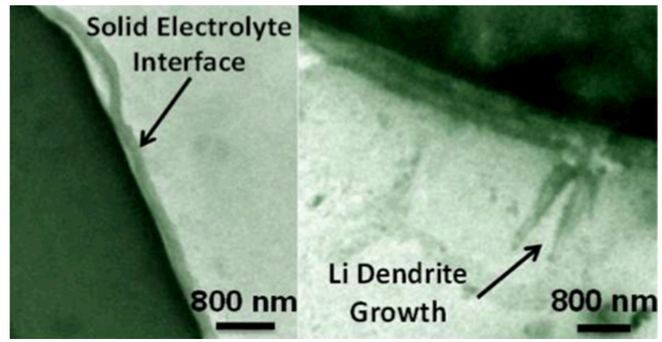


Dollé, M., Sannier, L., Beaudoin, B., Trentin, M. & Tarascon, J.-M. *Electrochem. Solid-State Lett.* **5,** A286 (2002).

Transmission electron microscopy

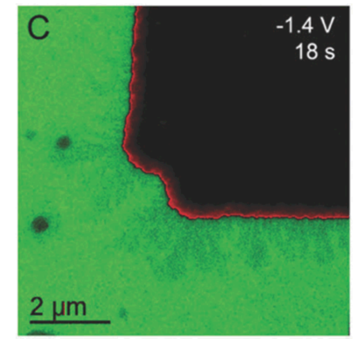
View submicron features immersed in liquid electrolytes.

SEI, Li dendrites on Au



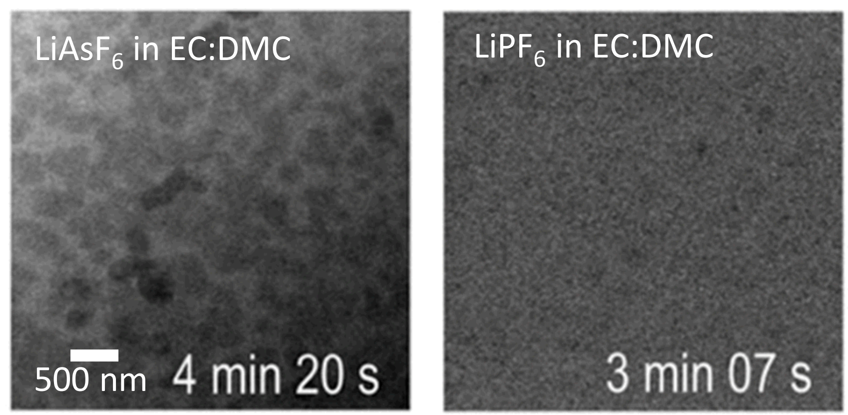
Zeng, Z. *et al*. *Nano Lett.* (2014). doi:10.1021/nl403922u

"SEI" dendrites



Sacci, R. L. *et al. Chem. Commun.* **50,** 2104–2107 (2014).

Electrolyte degradation (probed with electron beam)

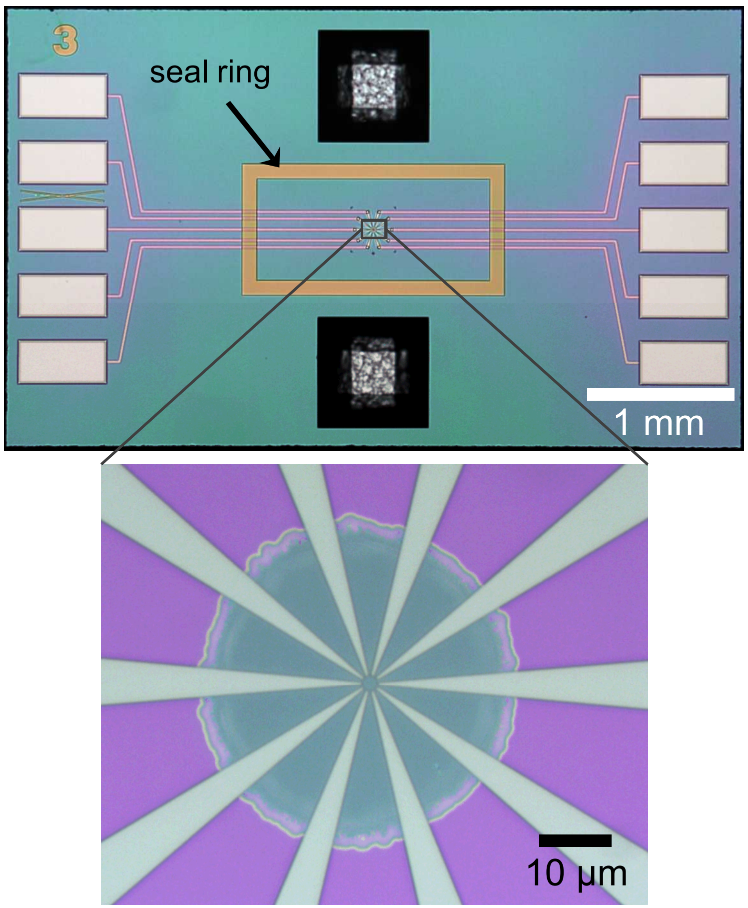


Abellan, P. *et al. Nano Lett.* (2014). doi:10.1021/nl404271k

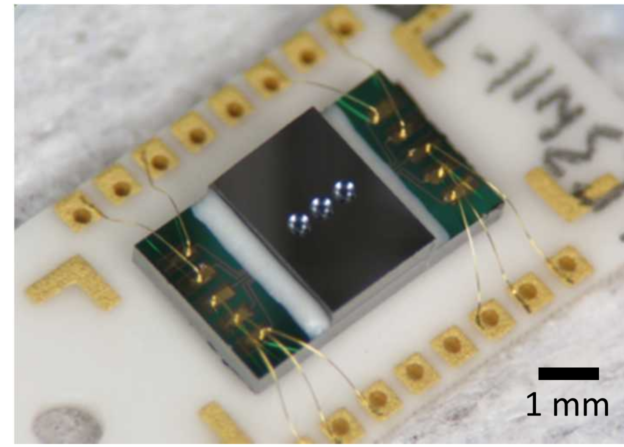
Microfabricated TEM Liquid Cell Design

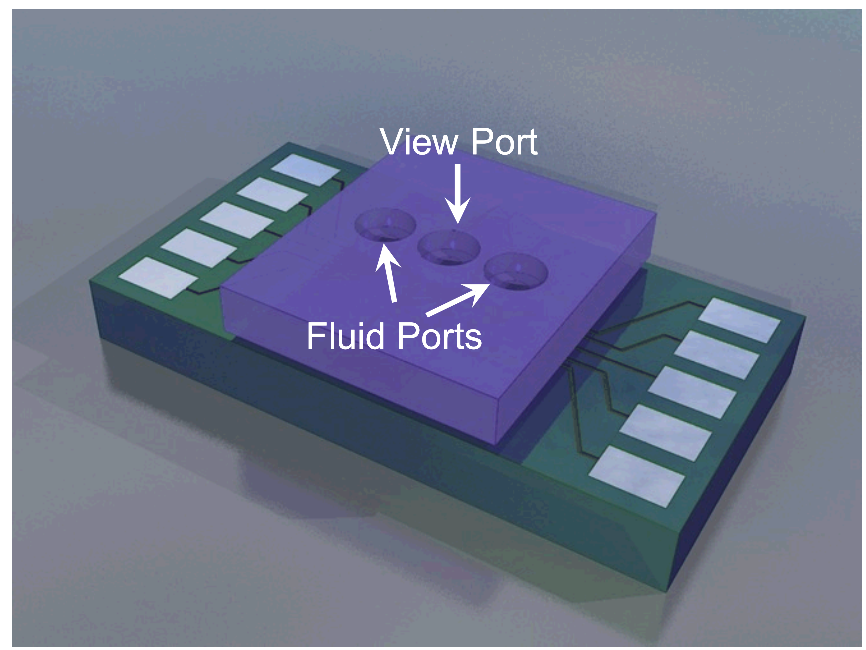
Advantages:

1. Multiple electrodes for multiple experiments
   - identical chemical environment
2. Insulated leads for quantitative electrochemistry
3. Auto-aligned windows using microspheres



Chip on TEM stub:

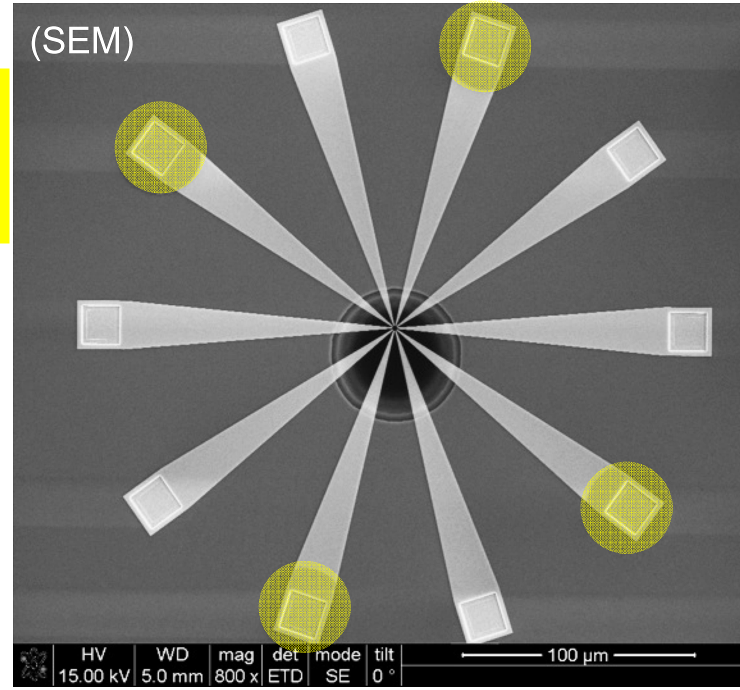


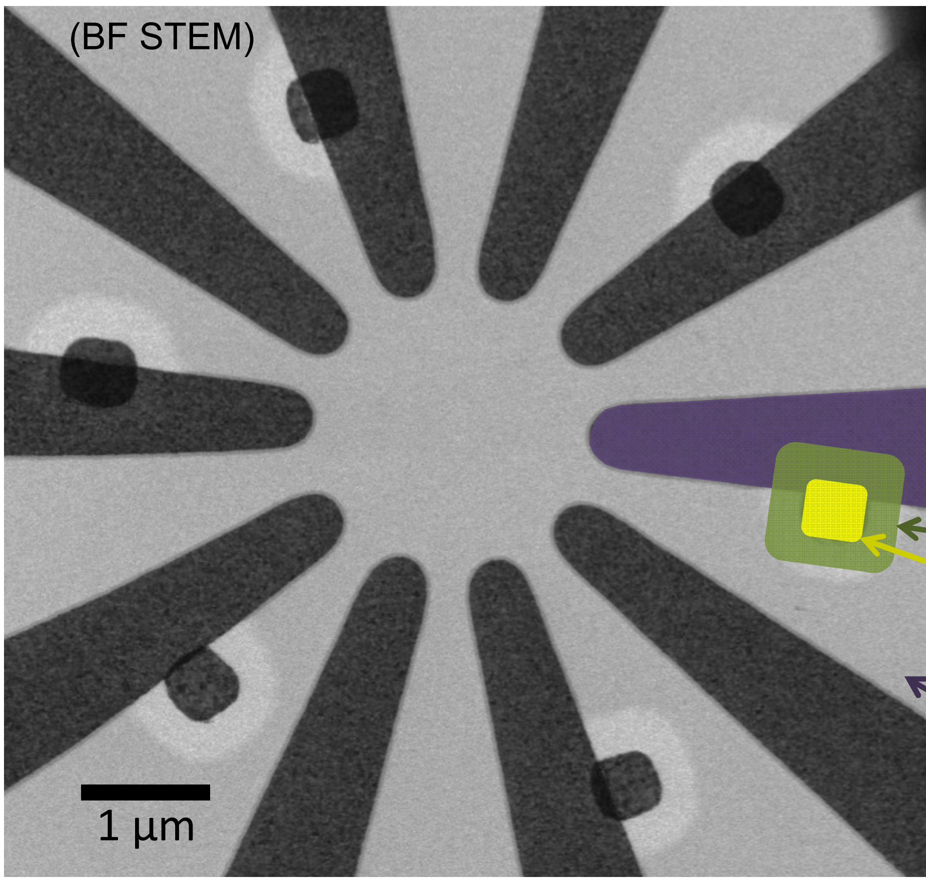


Sample design: Many tests, identical conditions

E-beam lithography used to define localized working electrode area:
All electrochemistry visible.

Large counter, reference electrodes





W masked with Al_2O_3

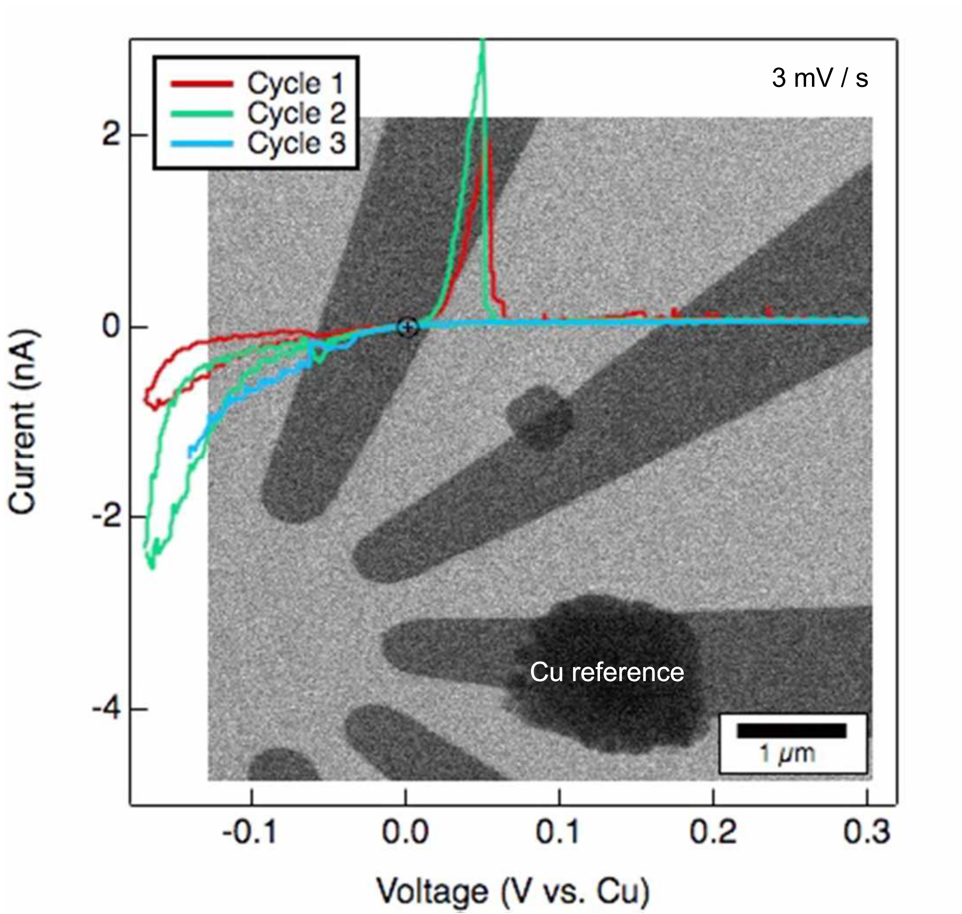
Al_2O_3 etched away

Small Ti or Au working electrode

SiN_x (+Al_2O_3) membrane

Cu electrodeposition: grains grow and shrink

Quantitative cyclic voltammetry possible while imaging in TEM:



Experiment details:
0.1 M H_2SO_4 + 0.1 M $CuSO_4$
0.25 μm^2 Au working
Cu reference deposited in-situ
Large-area Au counter

Imaging conditions:
FEI Tecnai F30
Brightfield STEM @ 300 kV
Beam blanked between images
Beam current ~10 pA
Image time: 5 sec
Dose per image: < 50 $e^- nm^{-2}$
Dose rate: < 10 $e^- nm^{-2} s^{-1}$

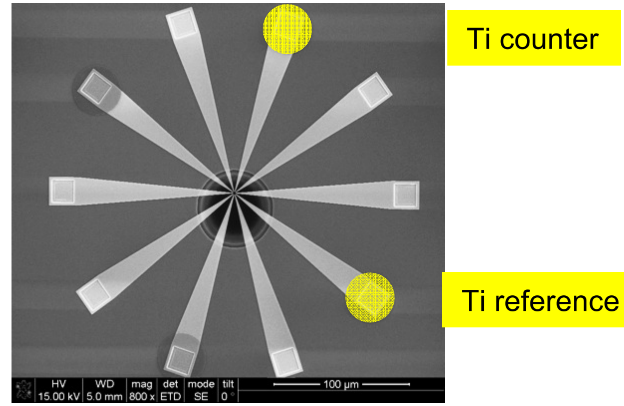
Chronopotentiometry for Li in aprotic electrolyte

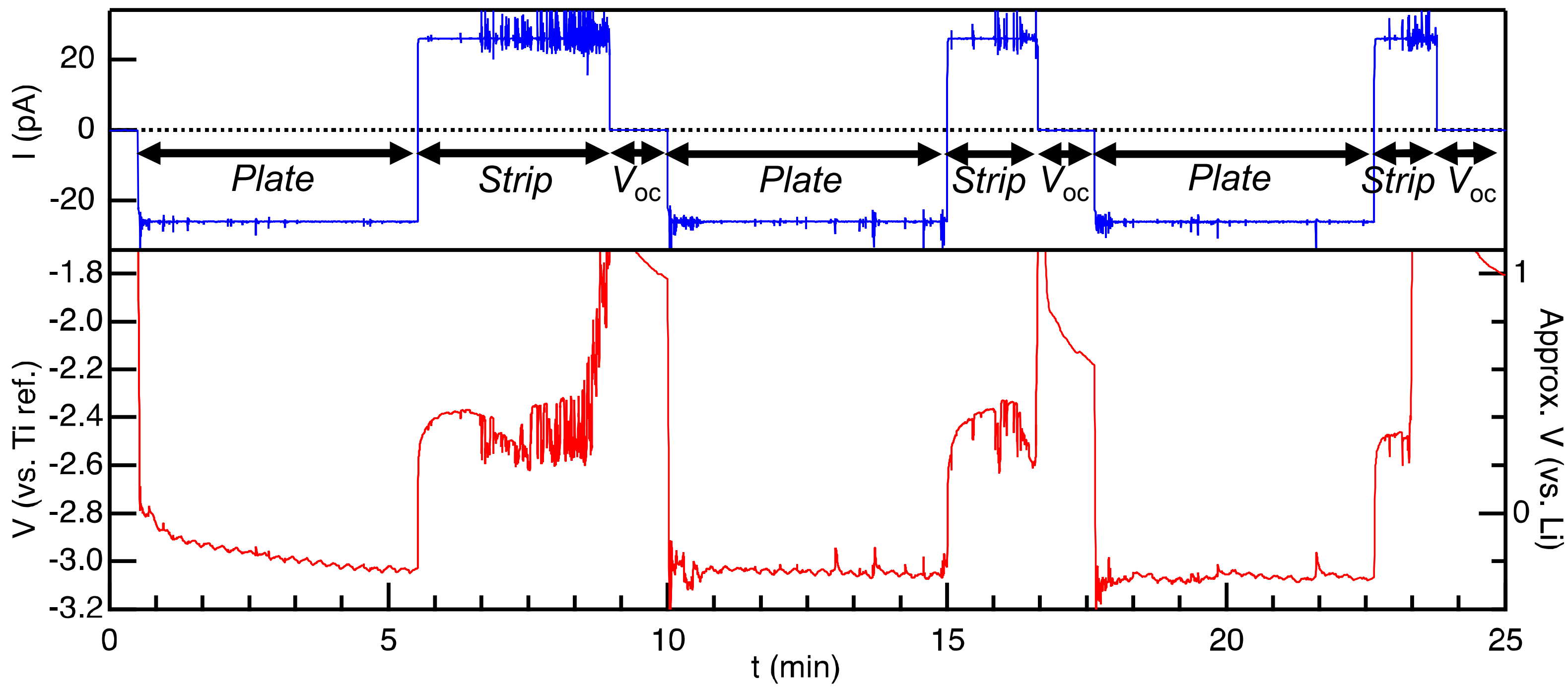
Experiment details:

1:1 ethylene carbonate : dimethyl carbonate (EC:DMC) + 1 M $LiPF_6$

0.25 µm² Ti working, Large Ti counter/reference electrodes

±25 pA galvanostatic (10 mA/cm²)





Li cycling during imaging shows rounded grains

Experiment details:

1:1 ethylene carbonate : dimethyl carbonate (EC:DMC) + 1 M $LiPF_6$

0.25 μm^2 Ti working, Large Ti counter/reference electrodes

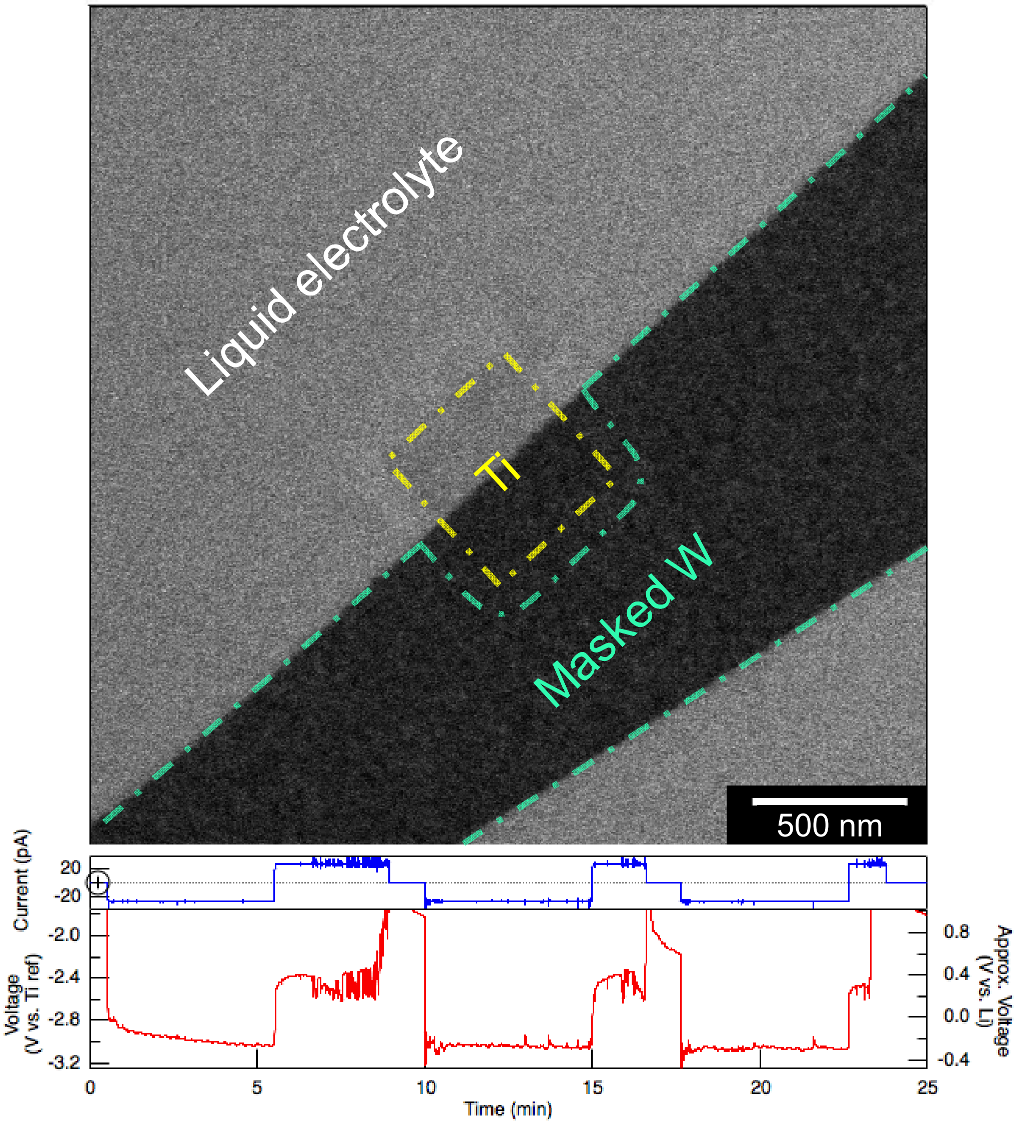
±25 pA galvanostatic (10 mA/cm^2)

Low-density Li appears **lighter** than surroundings in BF STEM.

Multiple, rounded grains grow while imaging.

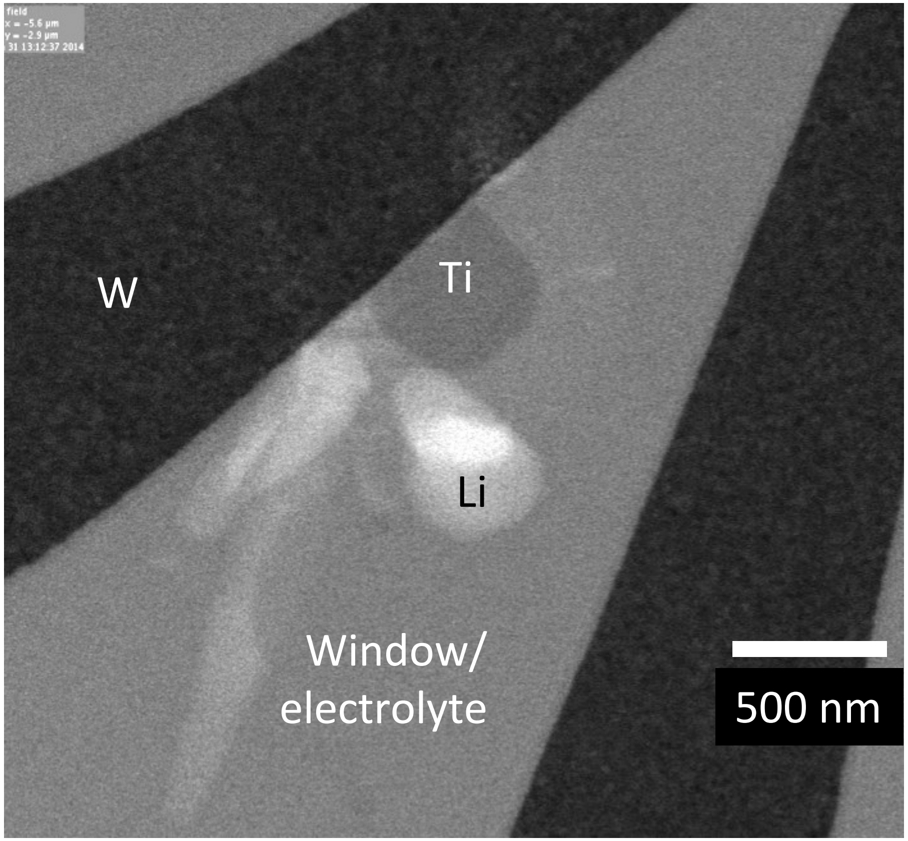
Disconnected Li evident after stripping.

Where are the dendrites?



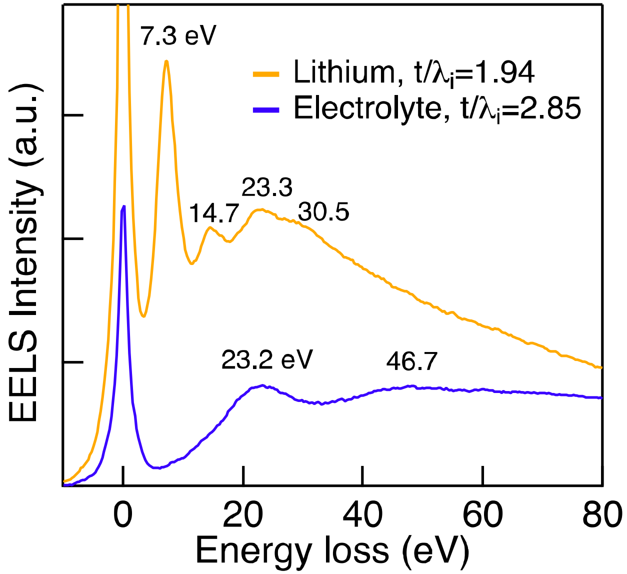
Needle “dendrites” form without beam exposure

10 minutes plating at 2 mA/cm^2



Crystalline, dendritic Li deposition.

EELS confirms Li bulk plasmon peak:



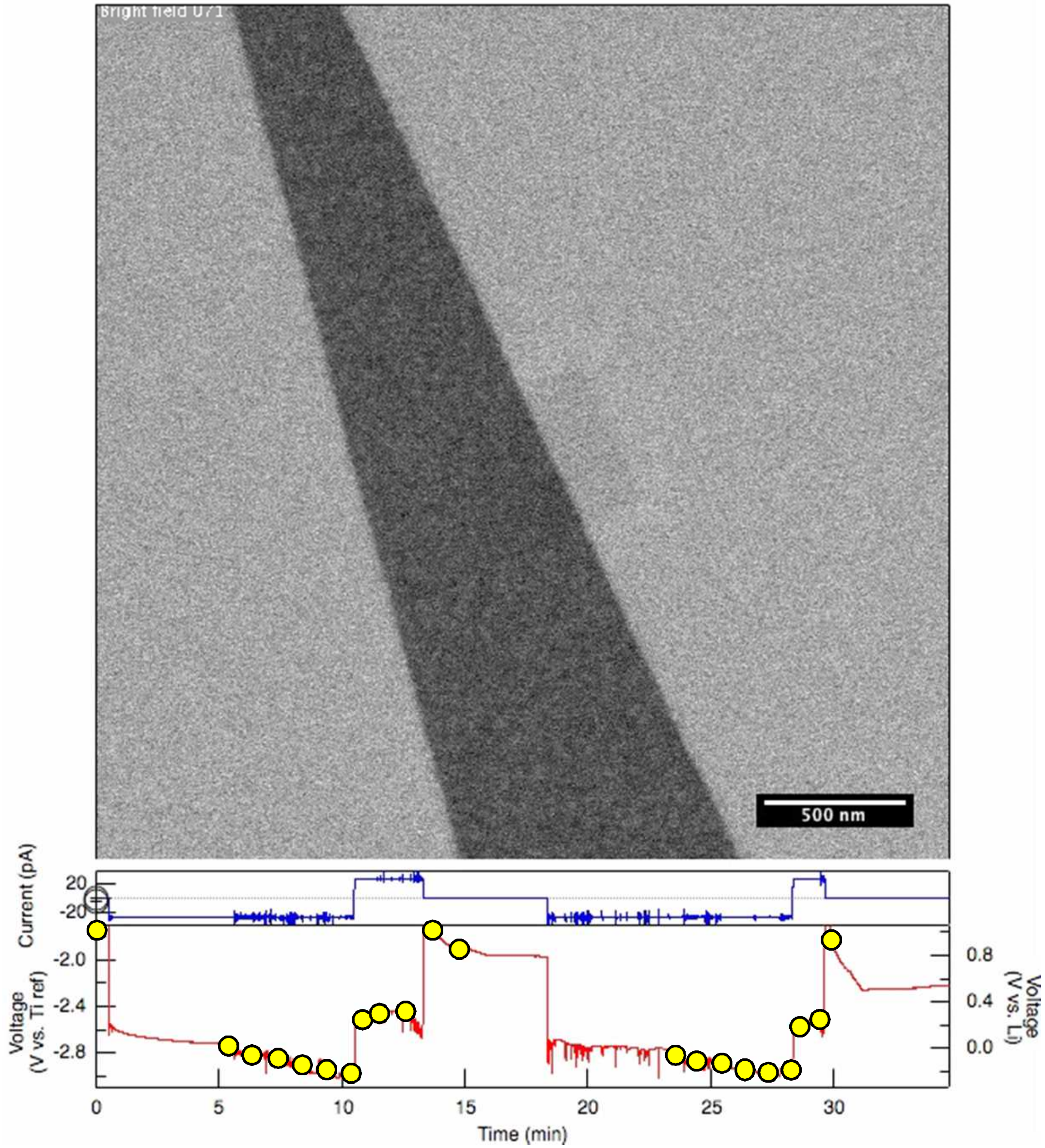
Science questions:

1. **What is the effect of the electron beam?**
2. **What is the dynamic morphology of deposited Li and SEI?**

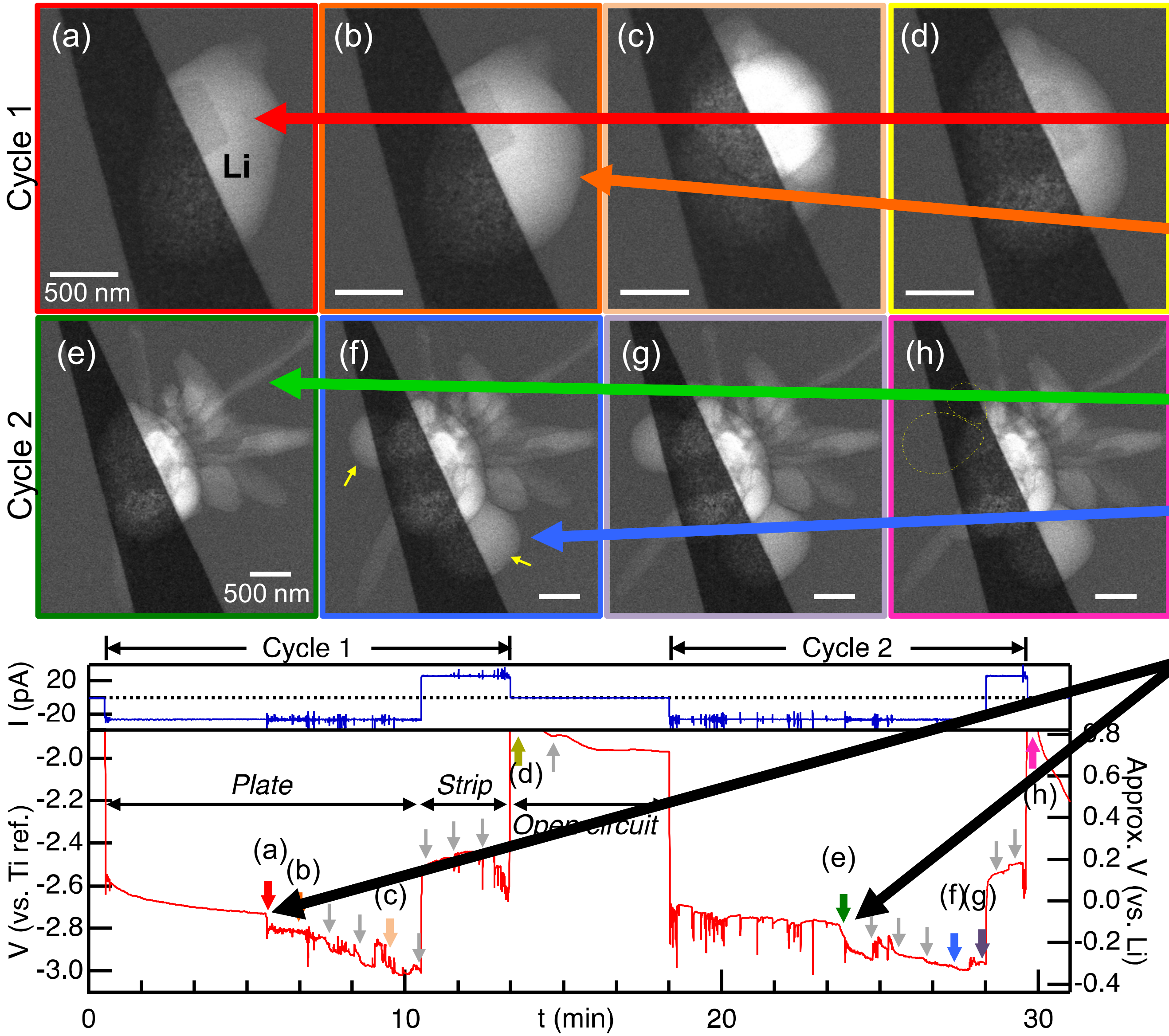
Li growth with little imaging reveals beam effects

"Snapshot" imaging strategy:

- No beam exposure for 1st half of deposition
- Image periodically for 2nd half of deposition and during stripping



Beam exposure changes Li/electrolyte interface



Observations:

1. Faceted grain deposited with beam off.
2. After imaging, grain becomes rounded.
3. 2nd cycle: initially needle-like dendrites.
4. 2nd cycle after imaging: only new round grains.
5. Voltage drops upon imaging.
6. Noise in voltage associated with grain nucleation or stripping.

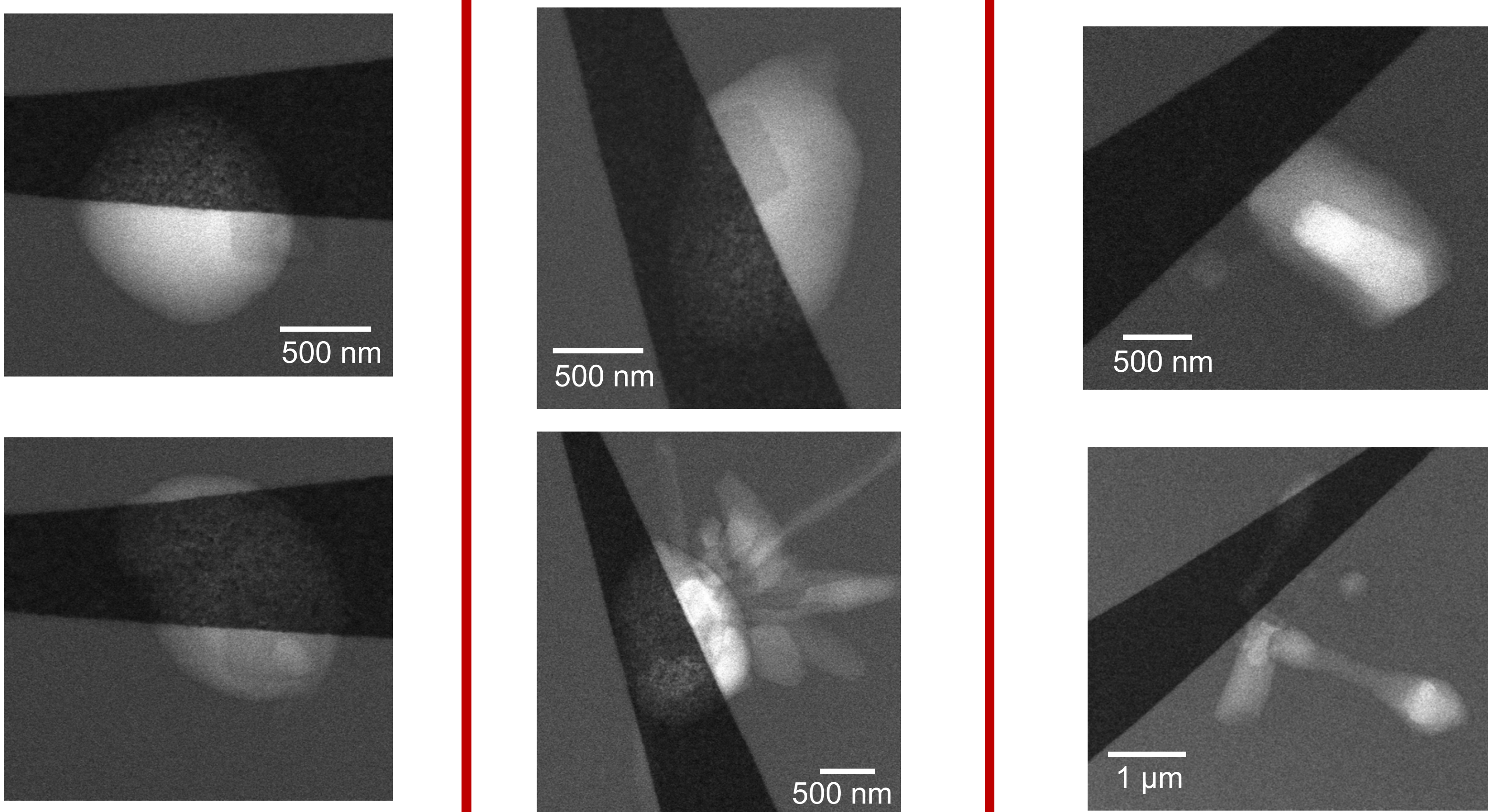
Higher current density results in more dendrites

Plate equivalent amount of Li on separate electrodes; no imaging during deposition.

1 mA/cm^2 | 10 mA/cm^2 | 25 mA/cm^2

Cycle 1

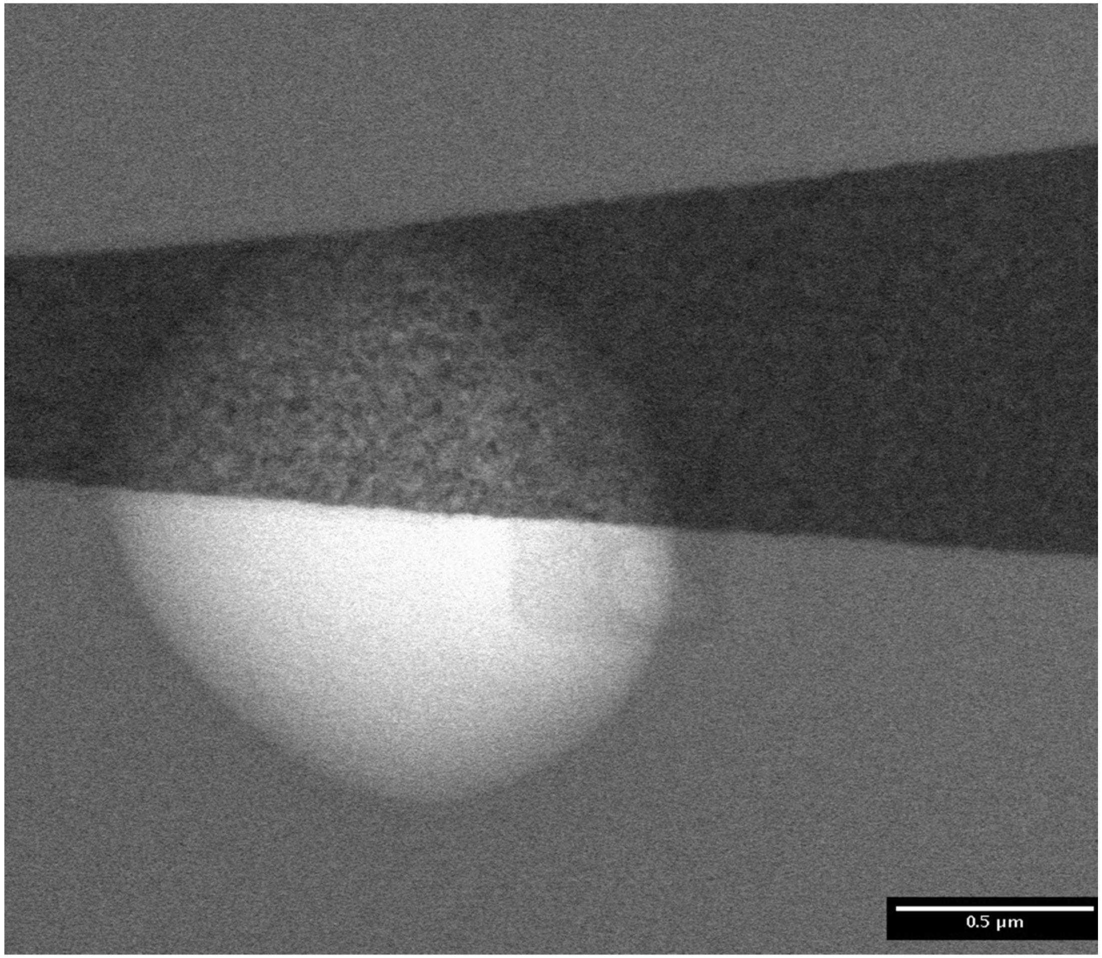
Cycle 2



Higher current density leads to more rodlike, dendritic growth.

Stripping initiates from discrete, weak SEI points

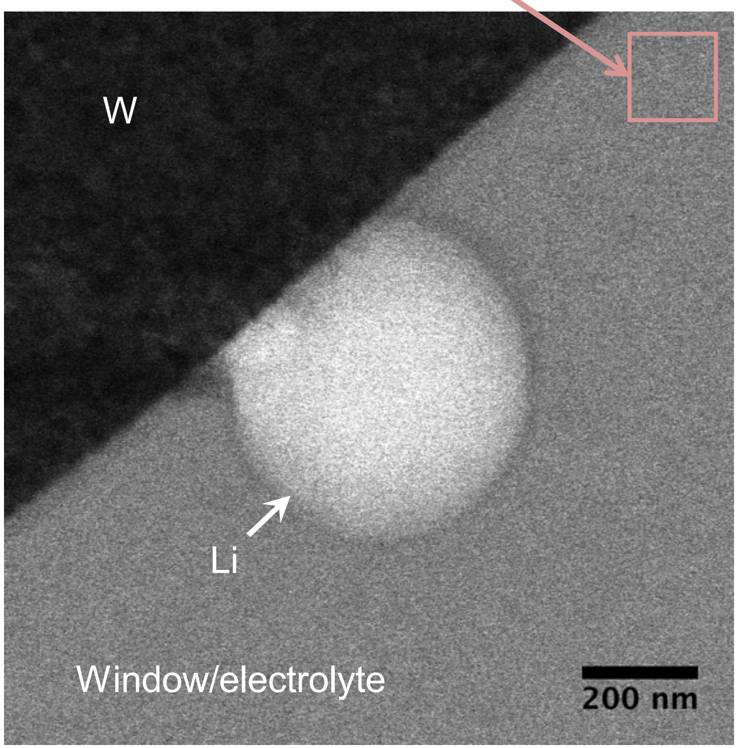
SEI forms protective shell around Li grains. Very different from Cu stripping.



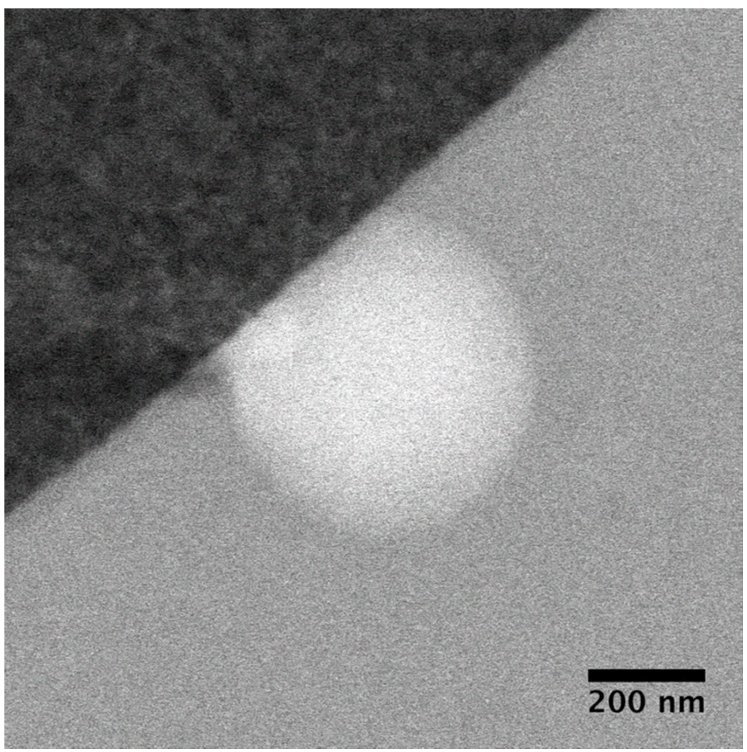
Beam creates intermediates that diffuse to SEI

During Li plating, surface layer forms with nearby beam scanning:

Scan beam 15 s between images in square while plating.



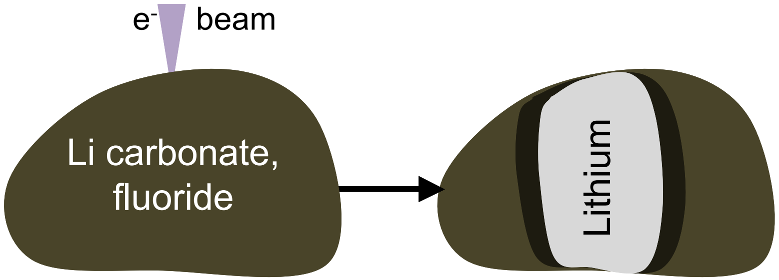
(Electrochemically strip Li halfway through experiment, SEI growth continues)



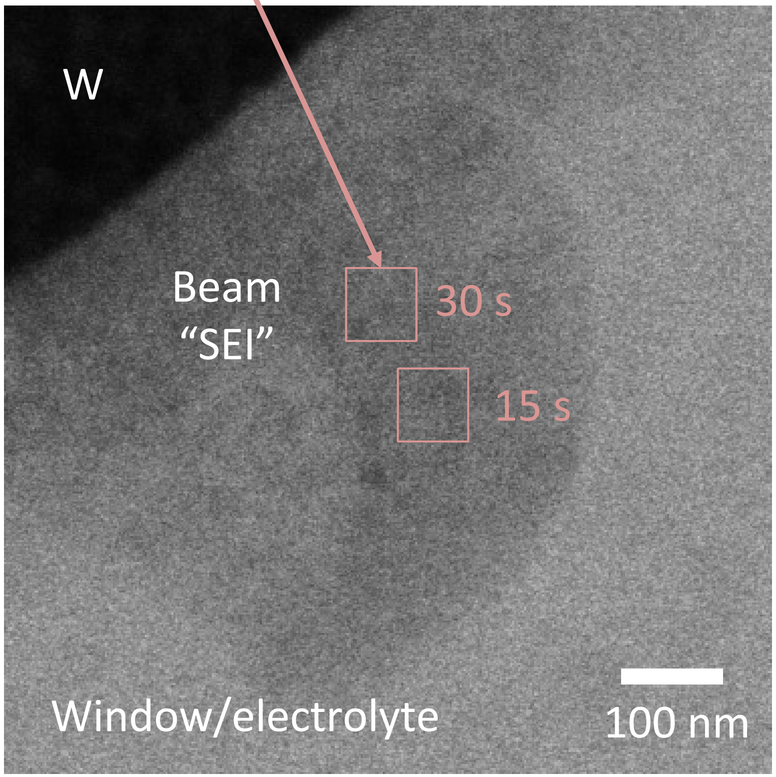
(30 s between frames)

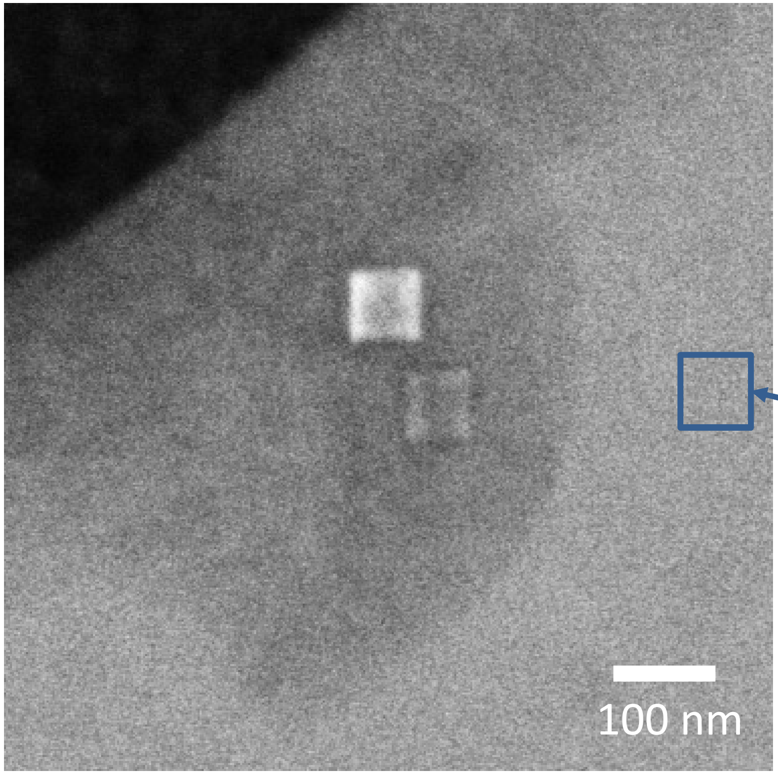
Electron beam can probe SEI properties

Scanning in surface layer possibly reduces it back to Li?



Scan beam in squares within "SEI."

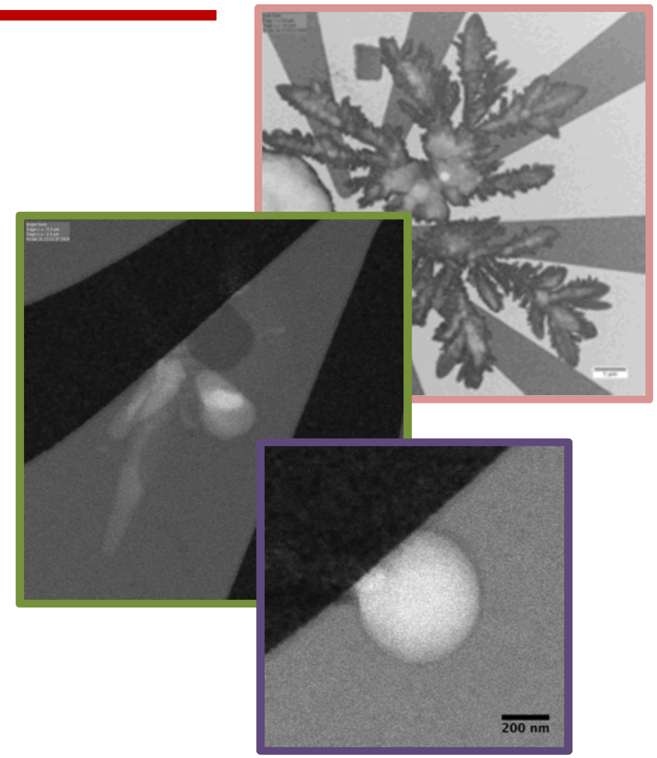




No visible change

Conclusion: Quantitative electrochemistry, Li cycling electrochemistry possible in CINT TEM Liquid Cell.

- SEI (beam-induced or natural) determines Li plating and stripping behavior.
- Li morphology varies with beam exposure and current density.
- Electron beam affects aprotic electrolytes; minimize exposure!



Liquid cell platforms available through CINT user proposals: cint.lanl.gov

Thanks to:
Tom Harris, Mike Shaw and John Nogan (fabrication), Yang Liu and Katie Jungjohann (TEM)
Kevin Zavadil, Kevin Leung, Nick Hudak, Kyle Fenton, Mani Nagasubramanian (echem)