SAND2015-3971C

Electrode Electrolyte Interfaces: Quantitative Electrochemistry during In Situ S/TEM Imaging

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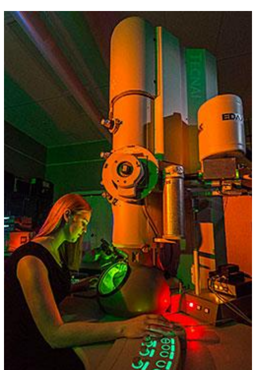
NMAVS May 19th 2015

Center for Integrated Nanotechnologies

CINT Core Facility: Albuquerque, NM

CINT Gateway Facility: Los Alamos, NM

Department of Energy, Basic Energy Sciences national user facility to provide expertise and instrumentation free of charge to support accepted peer-reviewed nanoscience research



***In Situ* Transmission Electron Microscopy Laboratory**

- Heating/Cryo
- Nanoindentation
- Electrical biasing
- *Liquid cell/electrochemistry*

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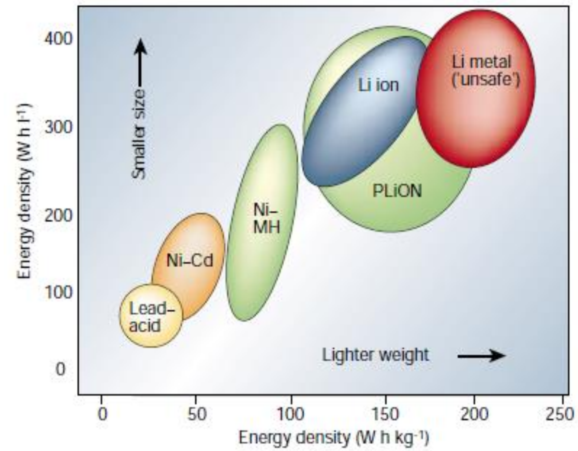
Lithium Ion Batteries: Improvement?

Why are we using Li-ion batteries?

- High volumetric (Wh/L) and gravimetric (Wh/kg) energy storage
- Rechargeable
- Highest discharge capacity
- High energy efficiency
- Good high rate capability



Tarascon J.-M. and Armand, M. (2001) Nature **414**, 359.

What can we do to improve Li-ion batteries?

- Increase charge density: new materials
- Increase reversibility for charging/discharging: solve <u>interfacial degradation</u>
- Decrease cost: battery design/materials

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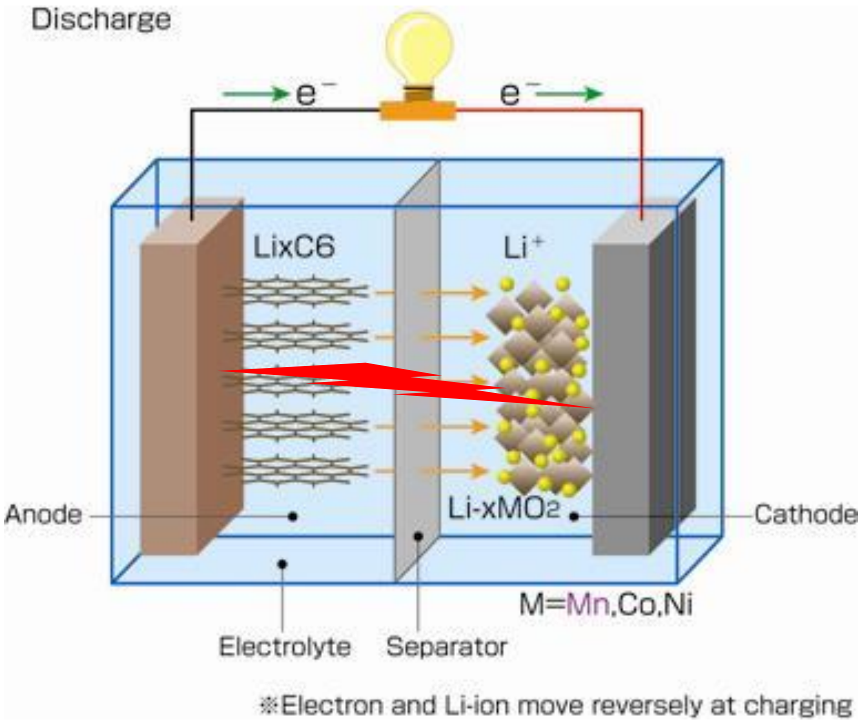
Li Metal Anodes for Lithium Ion Batteries

Li metal anodes could increase the energy density and reduce anode degradation?



Alloy Anode Material	Theoretical Capacity (mAh/g)
Li	3,860
Si	4,200
Graphite	~ 360
Sn	990
Al	990
Sb	650

Yoshio, M. et al., 2009 Lithium-Ion Batteries. Springer, New York, 11.

Why don't we use Li metal anodes?

Short circuit failure in Li-ion batteries from Li dendrite formation

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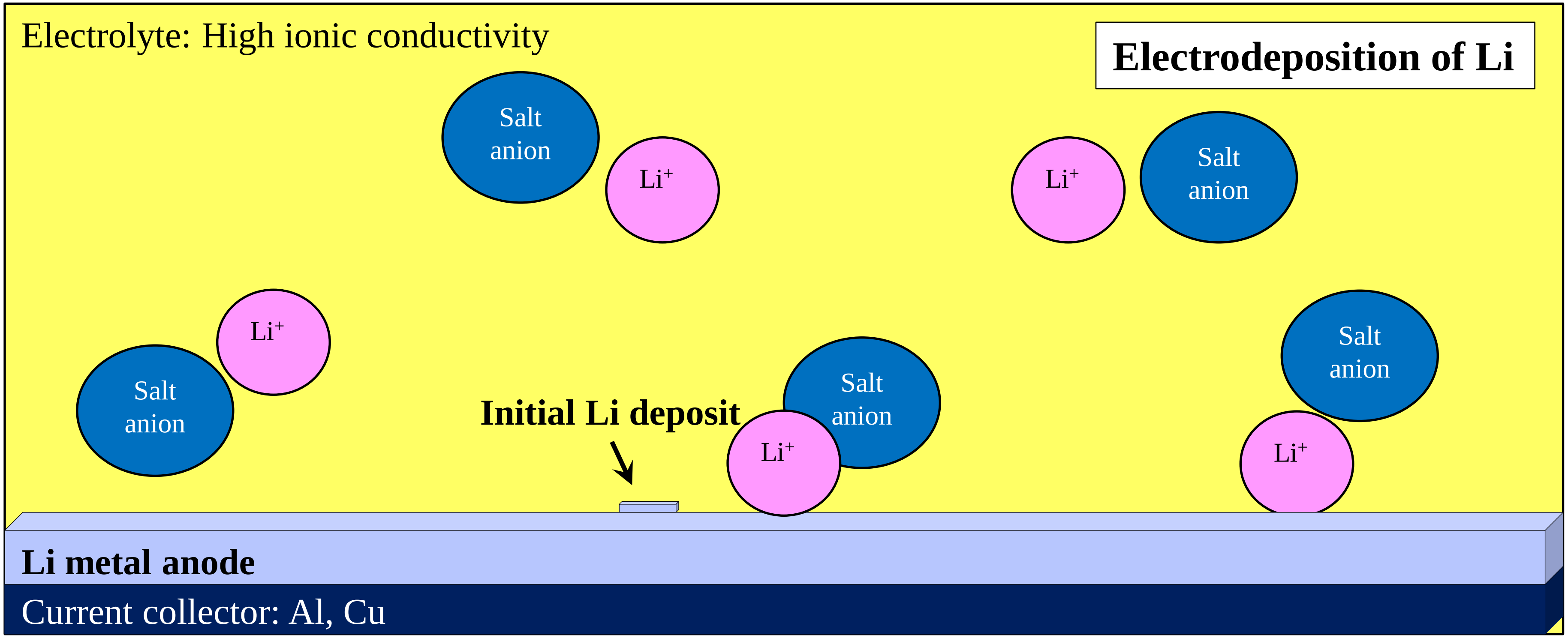
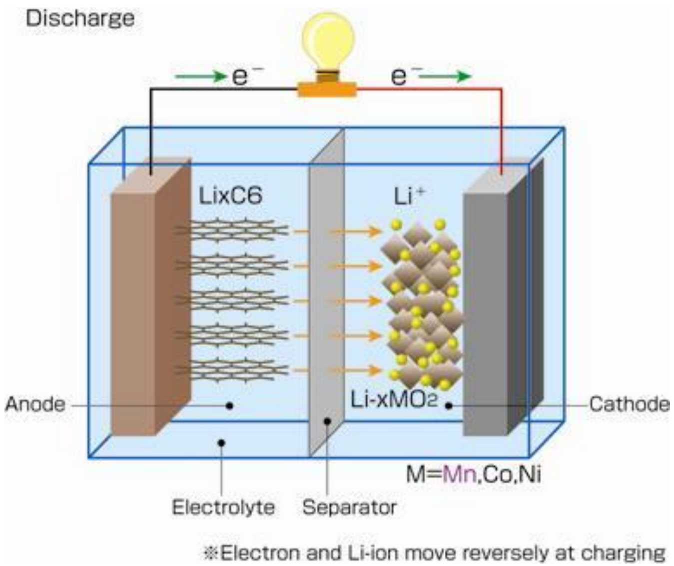
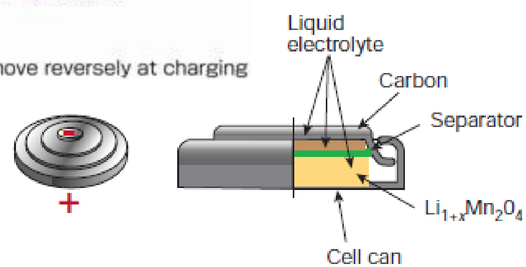
Li Metal – Electrolyte Interface



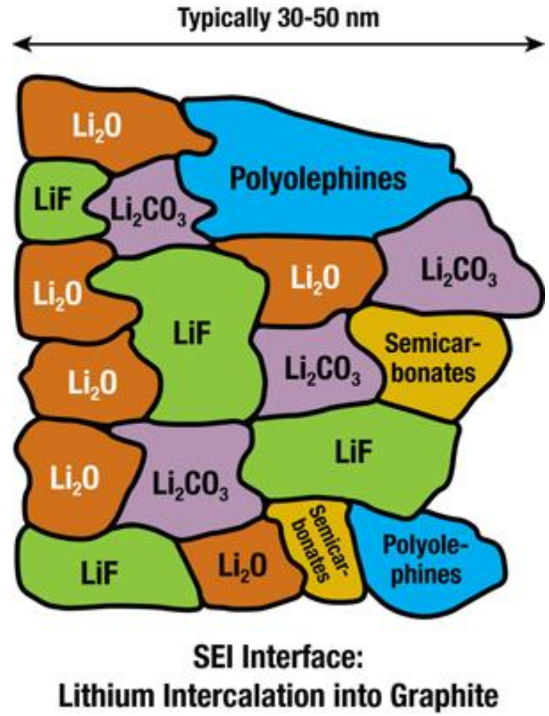
Known that a surface film forms at solid-electrolyte interface (SEI), what impact does this SEI film have on Li morphology for electrodeposition?

Solid Electrolyte Interface





Tarascon J.-M. and Armand, M. (2001) Nature **414**, 359.



Peled et al. (1997) J. Electrochem. Soc. **144**, L208.

SEI inorganic component composition is dependent on salt/electrolyte composition (water content) and the reaction with the anode material surface

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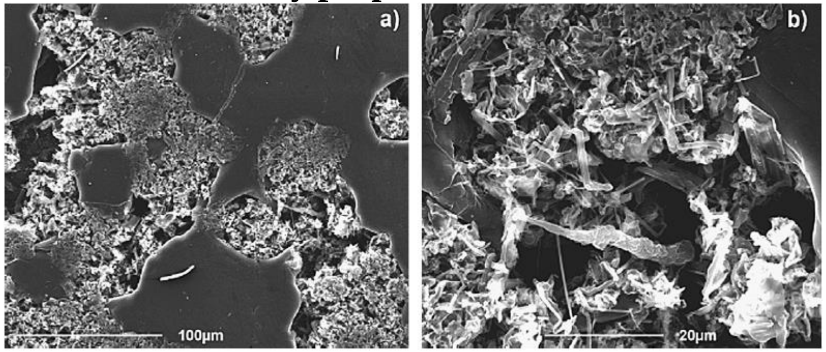
Characteristics of Li Dendrite Growth

Parameters determining Li morphology

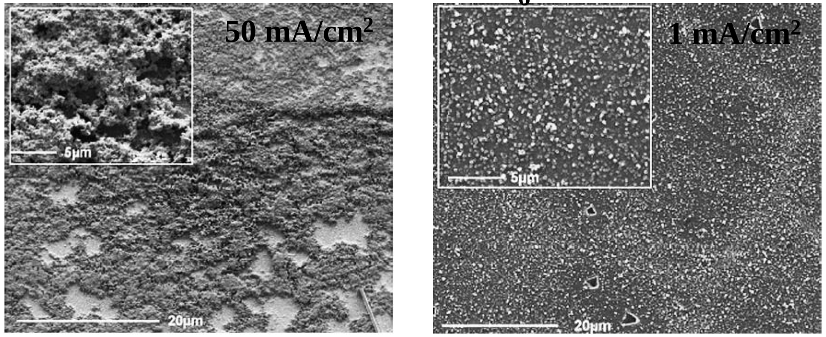
- Current density
- Temperature
- *Initial Li metal structure*
- Electrolyte (solute and solvent)
- Electrolyte additives
- Electrode Stack Pressure
- Environmental Considerations

Li dendrites preferentially grown on metal imperfections (higher surface energy states) and at high current densities. The local current density (current folcalization) is enhanced by surface imperfections. Preferential stripping at grain boundaries in defect Li metal.

Electrochemically prepared Li surfaces



Polished Li surfaces: 1 M $LiPF_6$ in EC/DMC



Gireaund, L. et al. 2006. Electrochem. Comm. **8**, 1639.

- Li dendrite tip morphology remains constant during growth (growth from base)
- Li growth under a protective film will undergo stress from non-uniform deposition
- Li electrode SA increases with the decrease in the discharge current & increase in cycles

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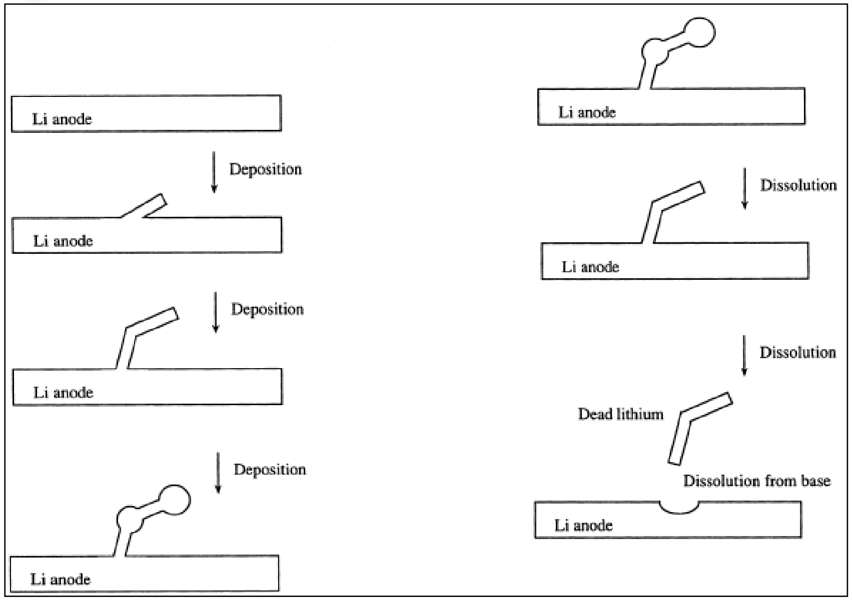
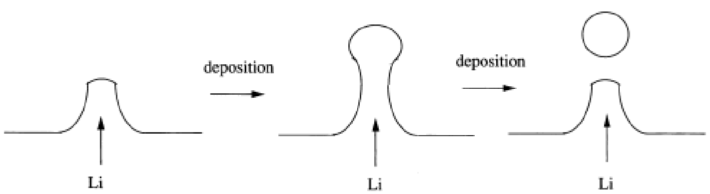
Models that Explain Li Deposition Morphology



Yamaki, J.-i. et al. 1998. J. Power Sources **74**, 219.

Observed dead Li dendrites: accumulates on anode decreasing capacity, and reduces thermal stability. Amount of dead Li is larger after low rate of discharge



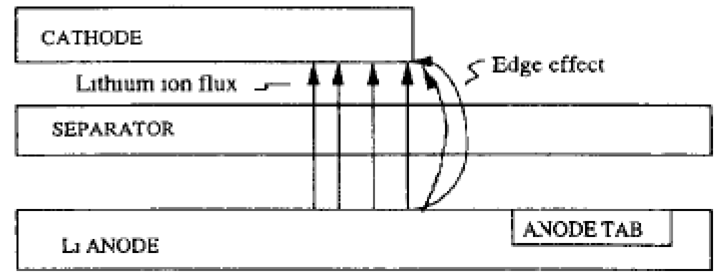
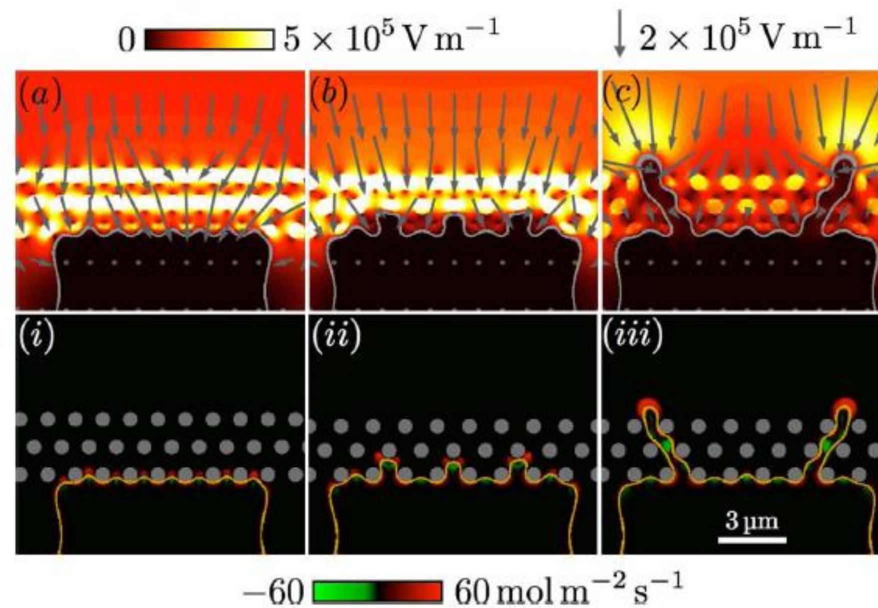


Fig 4 Lithium anode cut at the end of the cathode during cycling

Tobishima, S. et al. 1997. J. Power Sources **68**, 455.



Jana A. et al. 2015. J. Power Sources **275**, 912.

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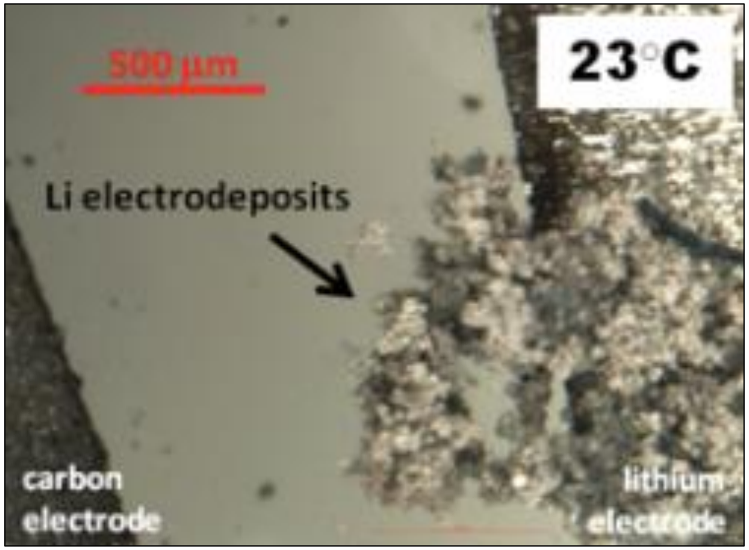
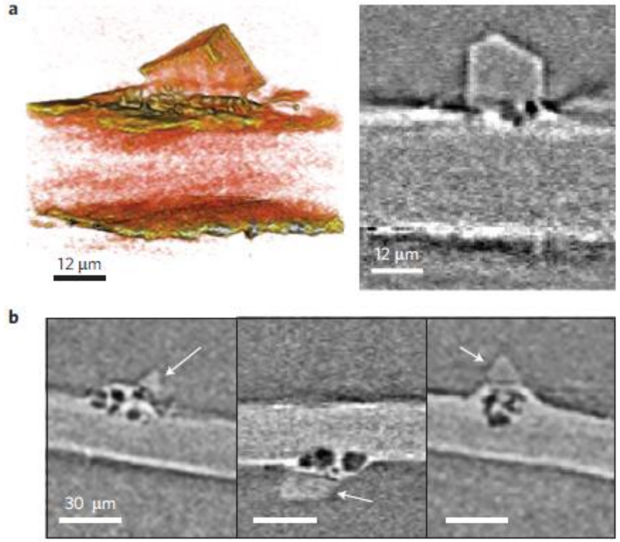
In Situ Techniques for Li Morphology Characterization

Optical Microscopy: 250 nm resolution



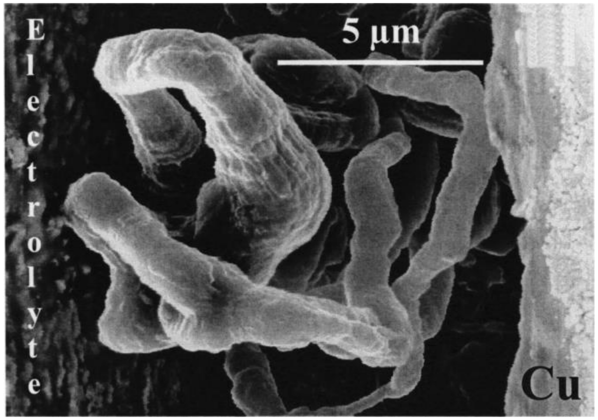
Love, C.T. et al. 2015. ECS Electrochem. Lett. **4**, A24.

X-ray microtomography: 1 µm resolution



Harry, K. et al. 2014. Nat. Mater. **13**, 69.

Scanning Electron Microscopy: 1 nm resolution



Dollé, M, et al. 2002. Electrochem. Solid St. **5**, A286.

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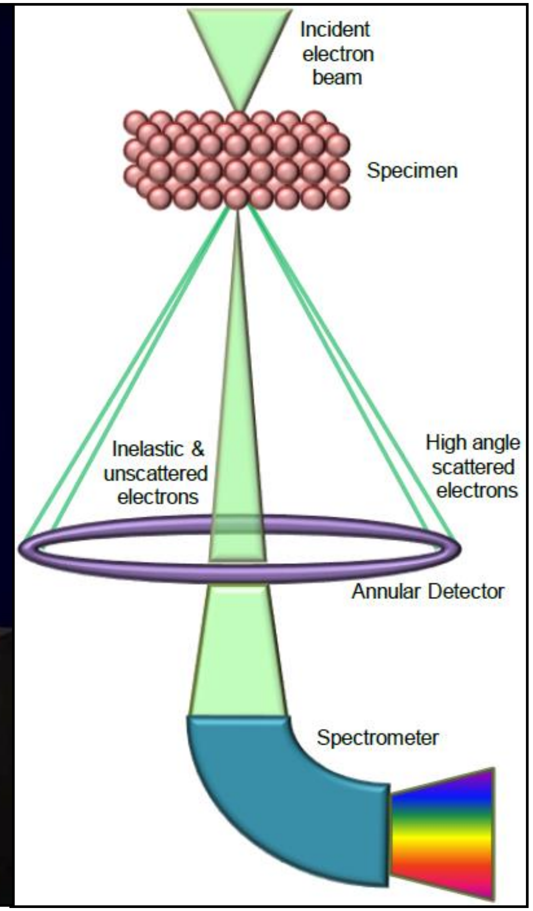
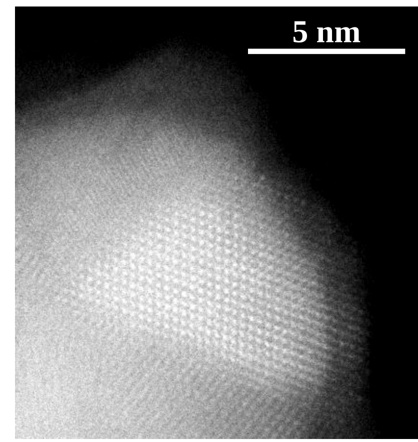
IN SITU TEM:
OBSERVE LI MORPHOLOGY

Transmission Electron Microscopy

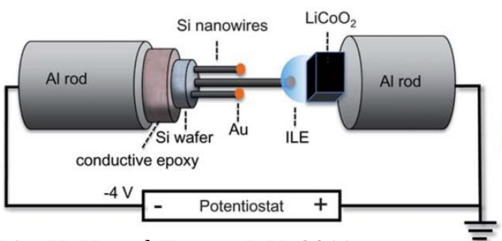


300 kV electron beam
Beam current 5 – 10 pA
Dark-field and Bright-field STEM
Generally: 5 sec 1k x 1k images

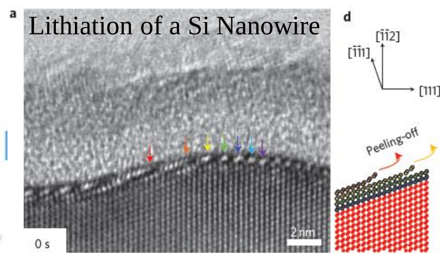
Column vacuum pressure: 10^{-7} Torr



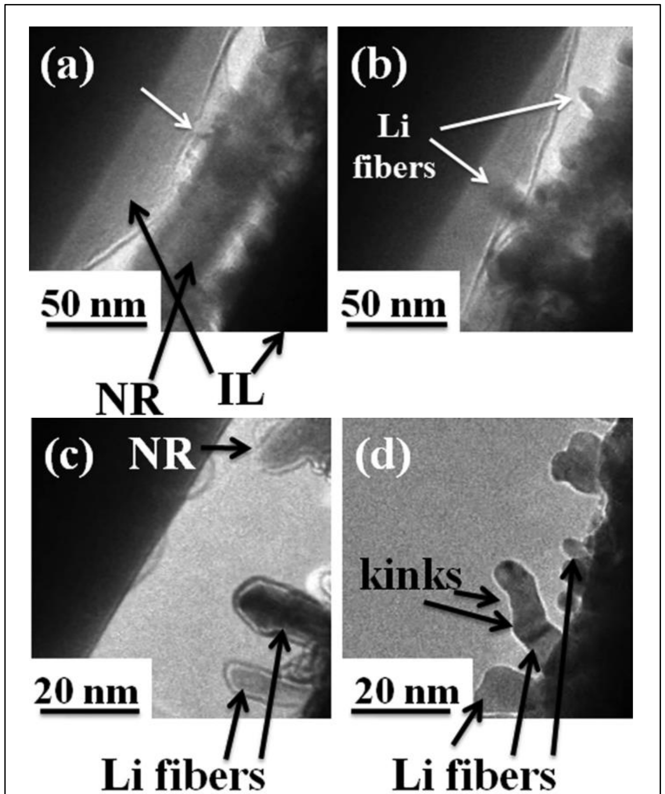
Vacuum Environment: Li Dendrite Formation



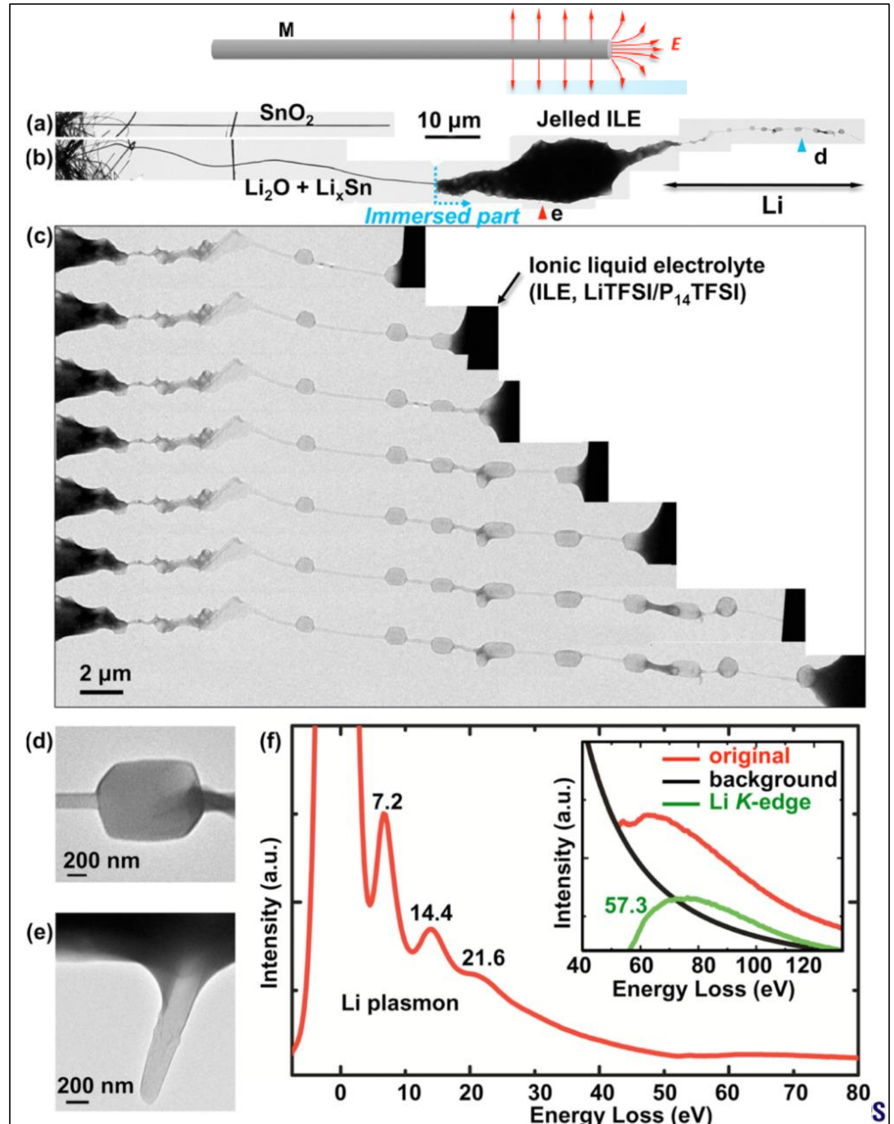
Liu, X. H. and Huang, J. Y. 2011. Energy Environ. Sci. **4**, 3844.



Liu, X. H. et al. 2011. Nature Nano. **7**, 3844.



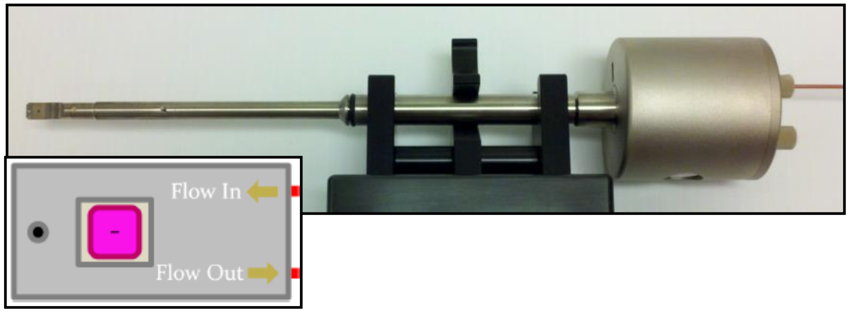
Ghassemi, H. et al. 2011. Appl. Phys. Lett. **99**, 123113.

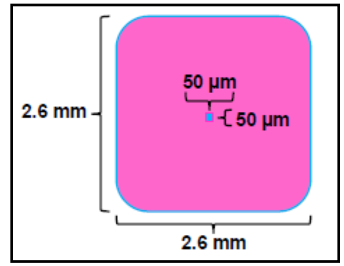


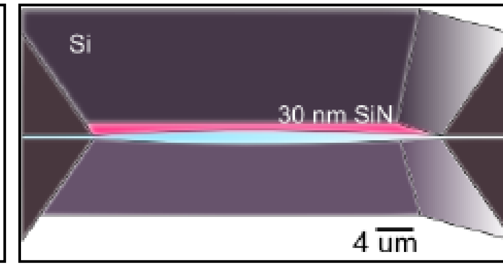
Liu, X. H. et al. 2011. Appl. Phys. Lett. **98**, 183107.

Liquid Cell Transmission Electron Microscopy

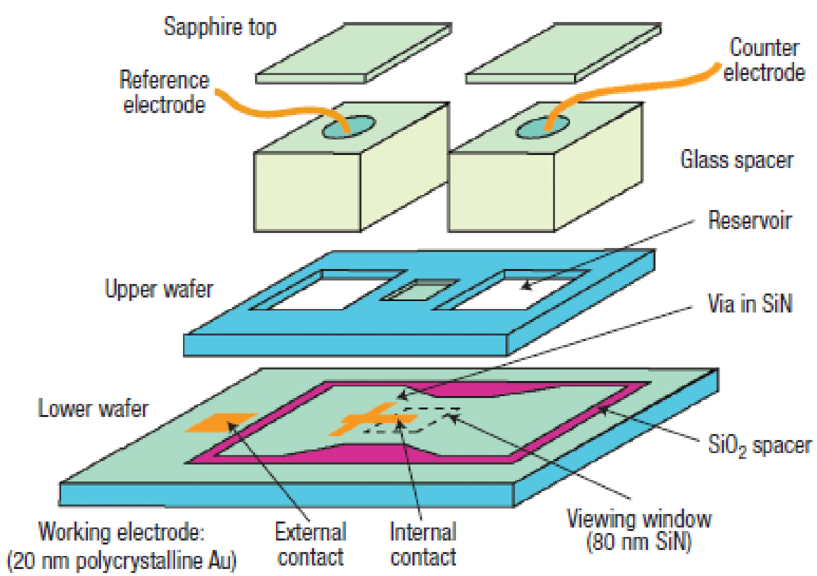
Commercial Microfluidic Liquid Cell TEM Holder



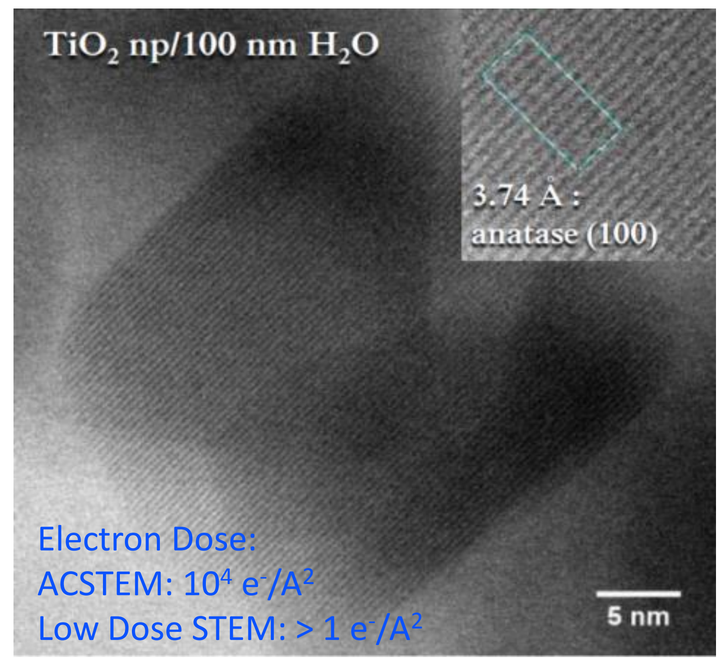




Custom MEMS-based Liquid Cell



Williamson, M.J. et al. 2003. Nat. Mater. **2**, 532.



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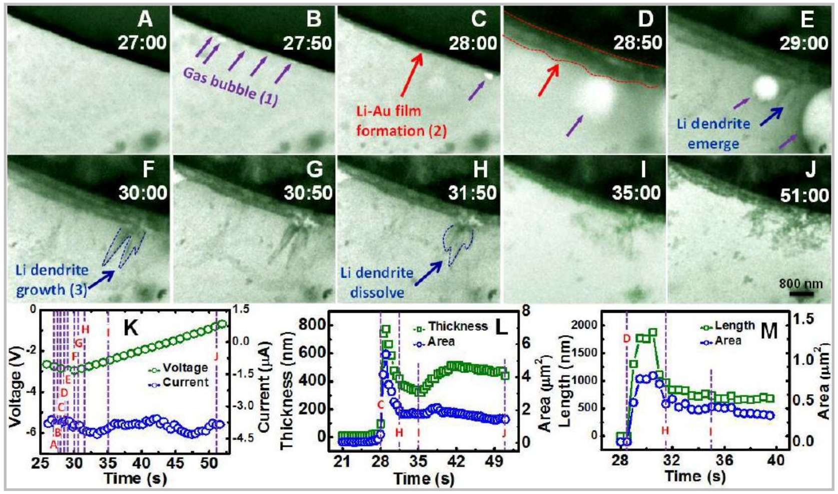
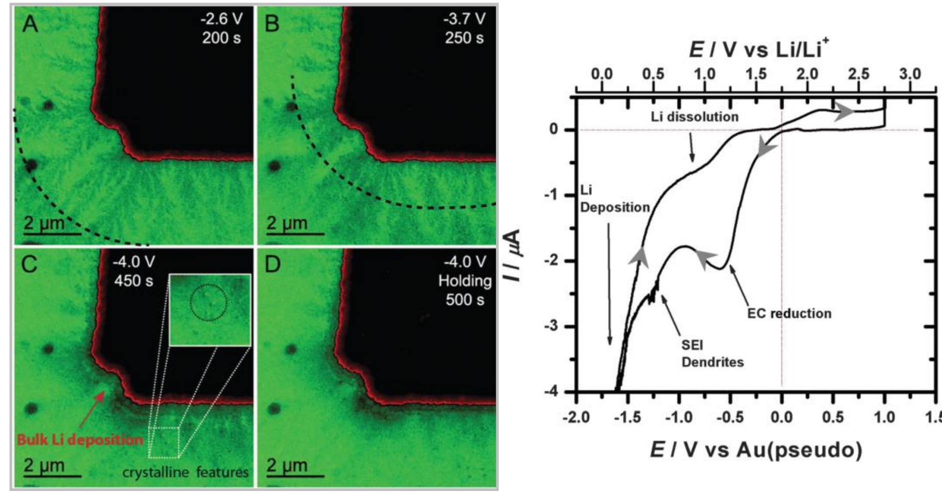
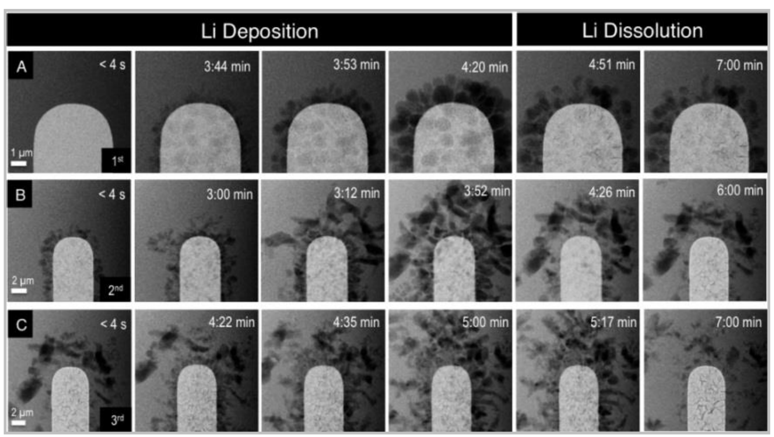
Li Deposition in Closed TEM Liquid Cell



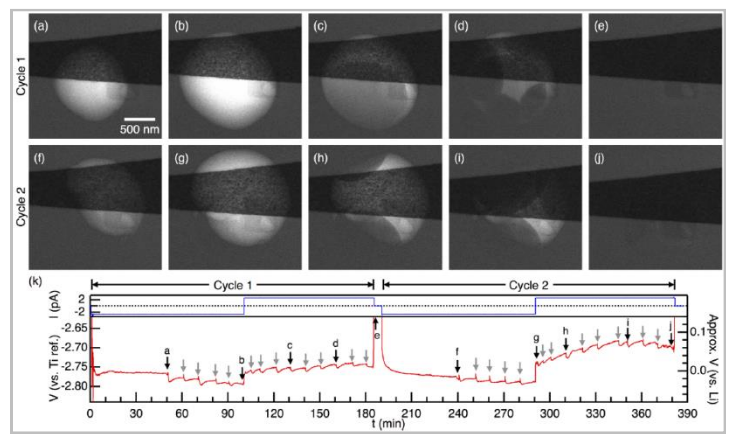
Zeng et al. (2014) Nano Letters **14**(4) 1745-1750.



Sacci et al. (2014) Chem. Commun. **50**, 2104-2107.



Medhi et al. (2015) Nano Letters **15**, 2168-2173.



Leenheer et al. (2015) ACS Nano. DOI: 10.1021/acsnano.5b00876.

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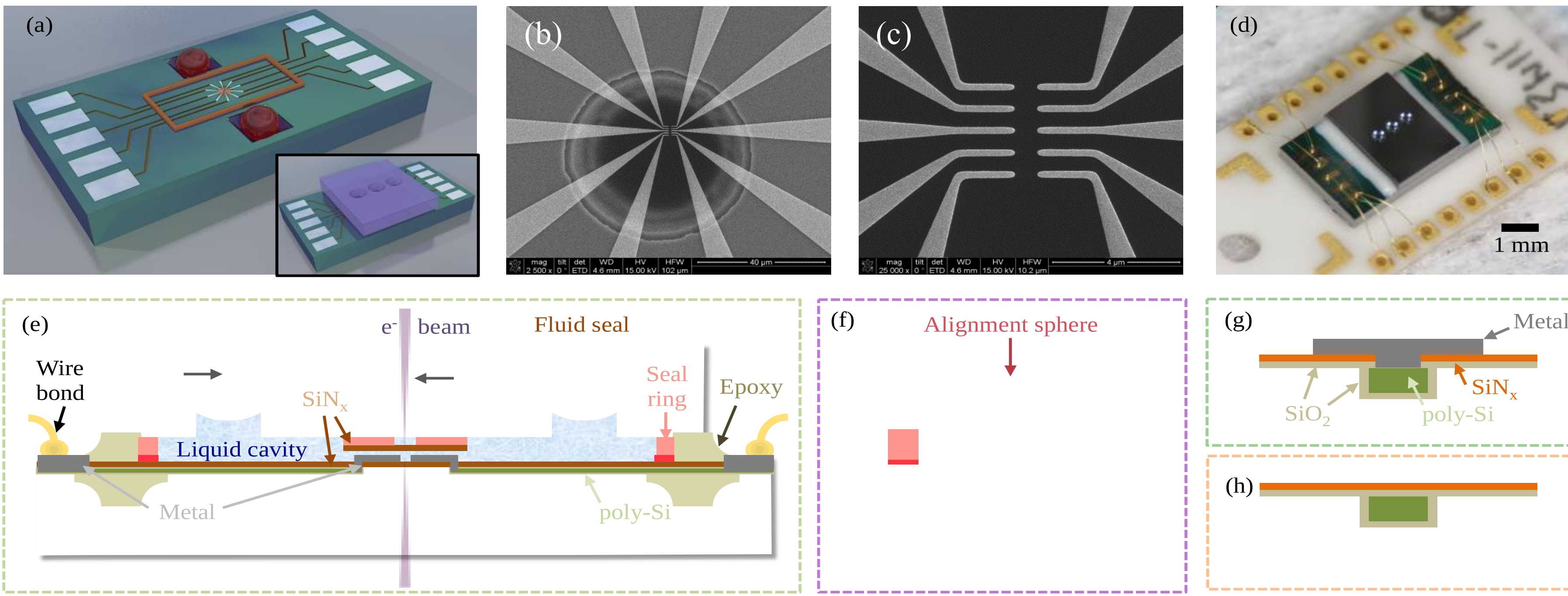
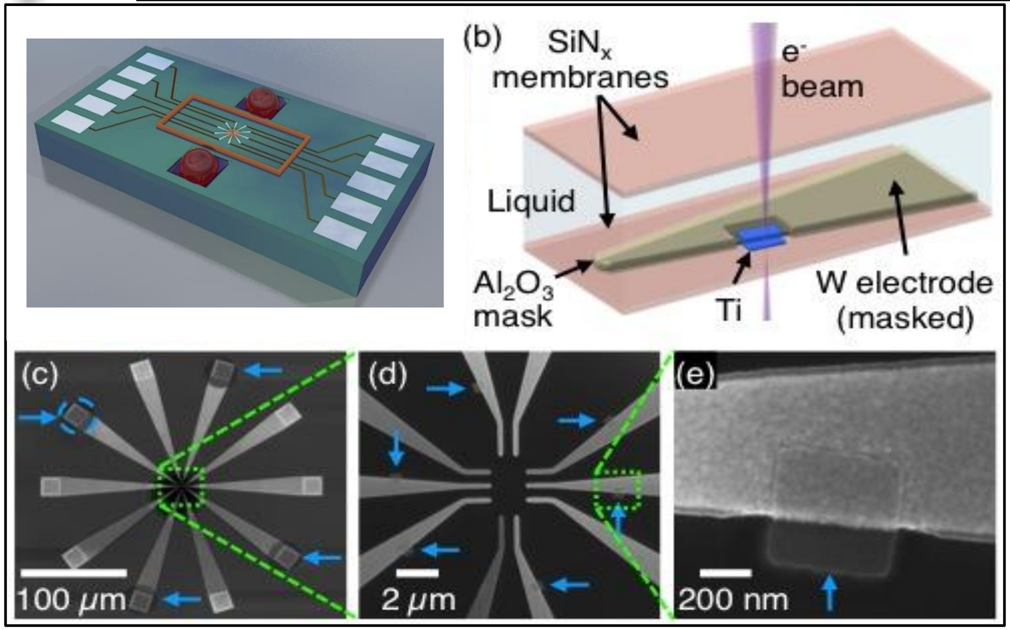
Electrochemical TEM Discovery Platform

- Electrically isolated electrodes allow for defined current control down to femptoampere levels
- Ultramicroelectrodes are at technologically relevant current densities
- Active electrode areas are confined to viewable region in the 30 nm thick SiN window



Leenheer et al., (2015) JMEMS. DOI:10.1109/JMEMS.2014.2380771.

Customization of EChem TEM Discovery Platform

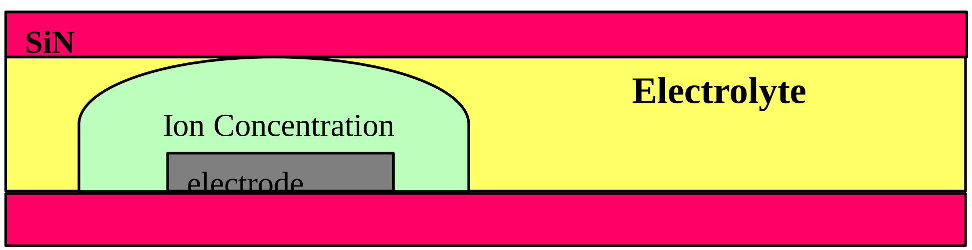


Leenheer et al., (2015) JMEMS. DOI:10.1109/JMEMS.2014.2380771.

- 10 Custom Designed Electrodes
- Multiple Experiments on Same Platform
- Beads Simplify Window Alignment
- Liquid Thickness > 120 nm
- Passivated Leads to localize electrochemistry
- Picoampere Current Control
- Chemical compatibility with cell
- Conduct in situ & ex situ testing

Consideration to Depletion of Li in Electrolyte

$$\mathbf{i_{max} = \mathit{n}F\Delta cV/t}$$



N : # e$^-$ transferred
F: 96485 C/mol
V: ~ 2.8 nL
T: 1 hr
i_{max} (10% of 1 mM): 7.5 pA

Diffusion limited reaction at 400 nm cell thickness: >75 pA (1 um^2)
Absolute limiting current for 0.26 μm^2 electrode is 4,000 mA/cm^2

Use ~ 1 μm^2 electrode area

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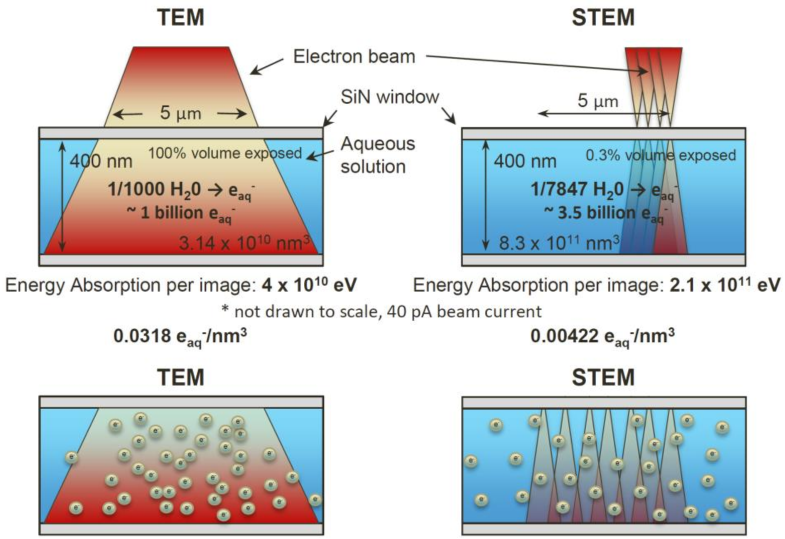
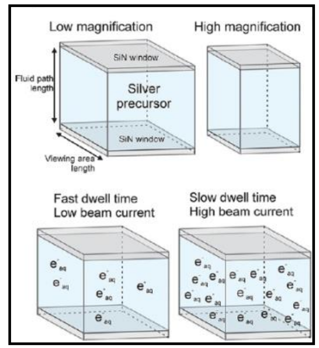
Electron Beam Damage on Liquids

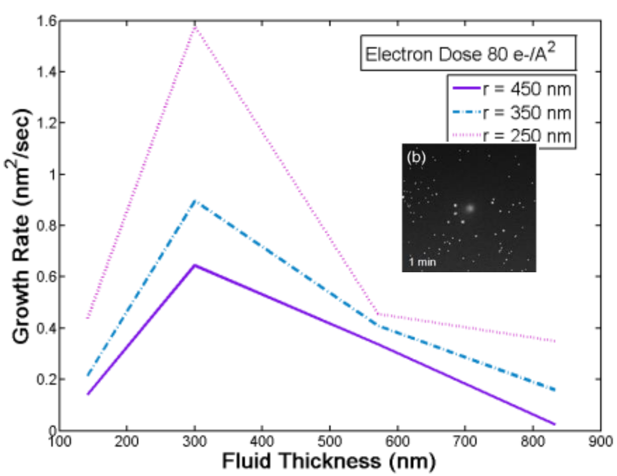
$$H_2O \rightarrow 2.7\ e_{aq}^- + 2.7\ H^+ + 0.61\ H + 0.43H_2 + 2.87OH + 0.61\ H_2O_2 + 0.026HO_2$$





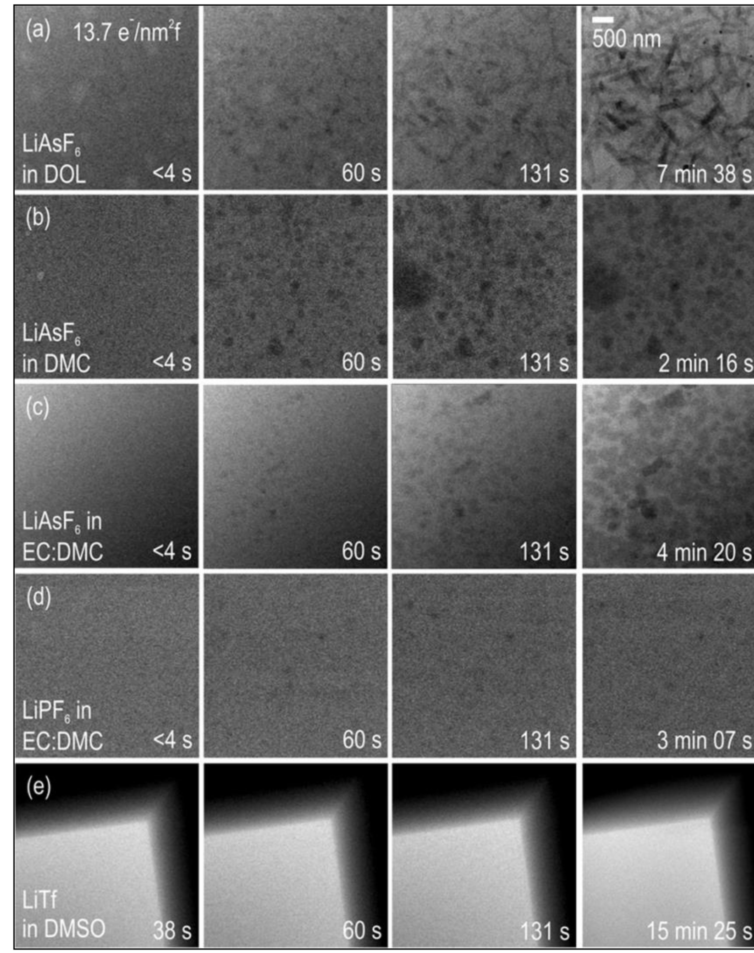
Woehl et al. ACS Nano **6**, 8599 (2012).

Thickness dependence on Beam Induced Radical Formation



- Maximum solvated electrons were produced at ~ 300 nm thick liquid layers

- Liquid thickness has dramatic effect on beam induced degradation of electrolyte



Abellan et al. Nano Lett. **14**, 1293 (2014).

1 M LIPF$_6$ IN EC/DMC (>10 PPM H_2O)

Galvanostatic Control of Working Electrode

Electric current is kept at a defined set point

We are using a femptoammeter to control currents below picoampere level

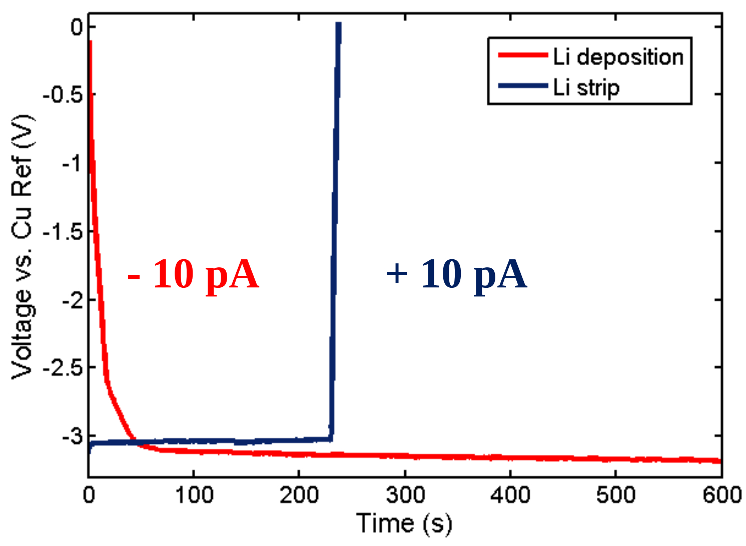
The voltage applied is dependent on the resistance during the measurement, value plotted vs. time

Voltage plateau's define electrochemical processes

The electron beam can produce currents to be read during the measurement

Pseudo-reference electrodes were used, where potential values vary with changes in the conditions

Galvanostatic experiments allow us to directly measure the Coulombic efficiency at each of the deposition/stripping cycles



Coulombic Efficiency: 39.47%

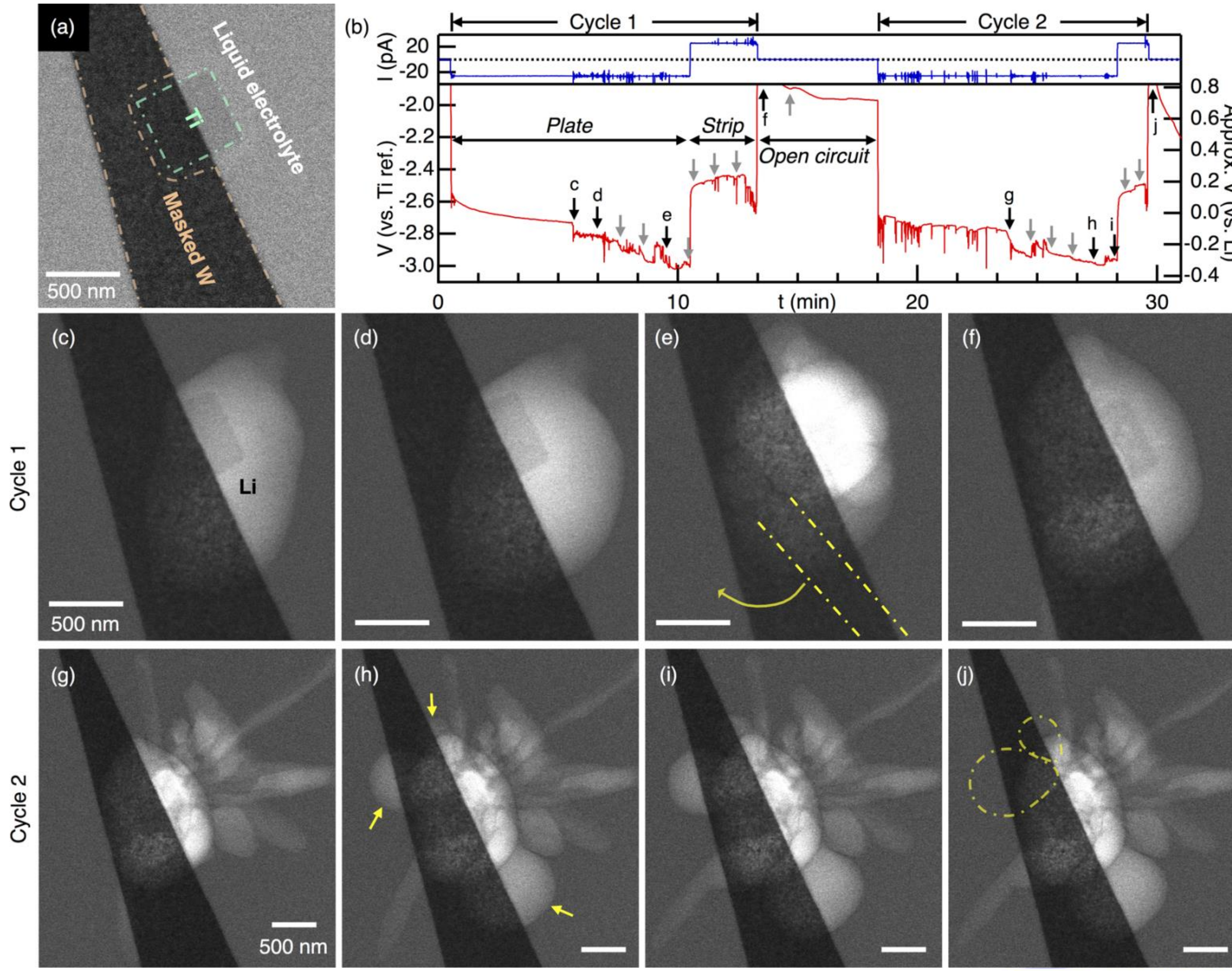
Li Morphology during Cycling

WE: 0.26 µm^2 Ti electrode
CE: 750 µm^2 Ti electrode
Coated with ALD Al_2O_3
Liquid thickness: >1 µm
Galvanostatic control: +/- 10 mA/cm^2
Electron dose per image: 25-50 e$^-$/Å^2

The electron beam impacted the initial Li plating, shown in voltage plateau as increase in noise and drop to more negative potential value

Correlate spikes in electrochemical data with nucleation of new Li grains

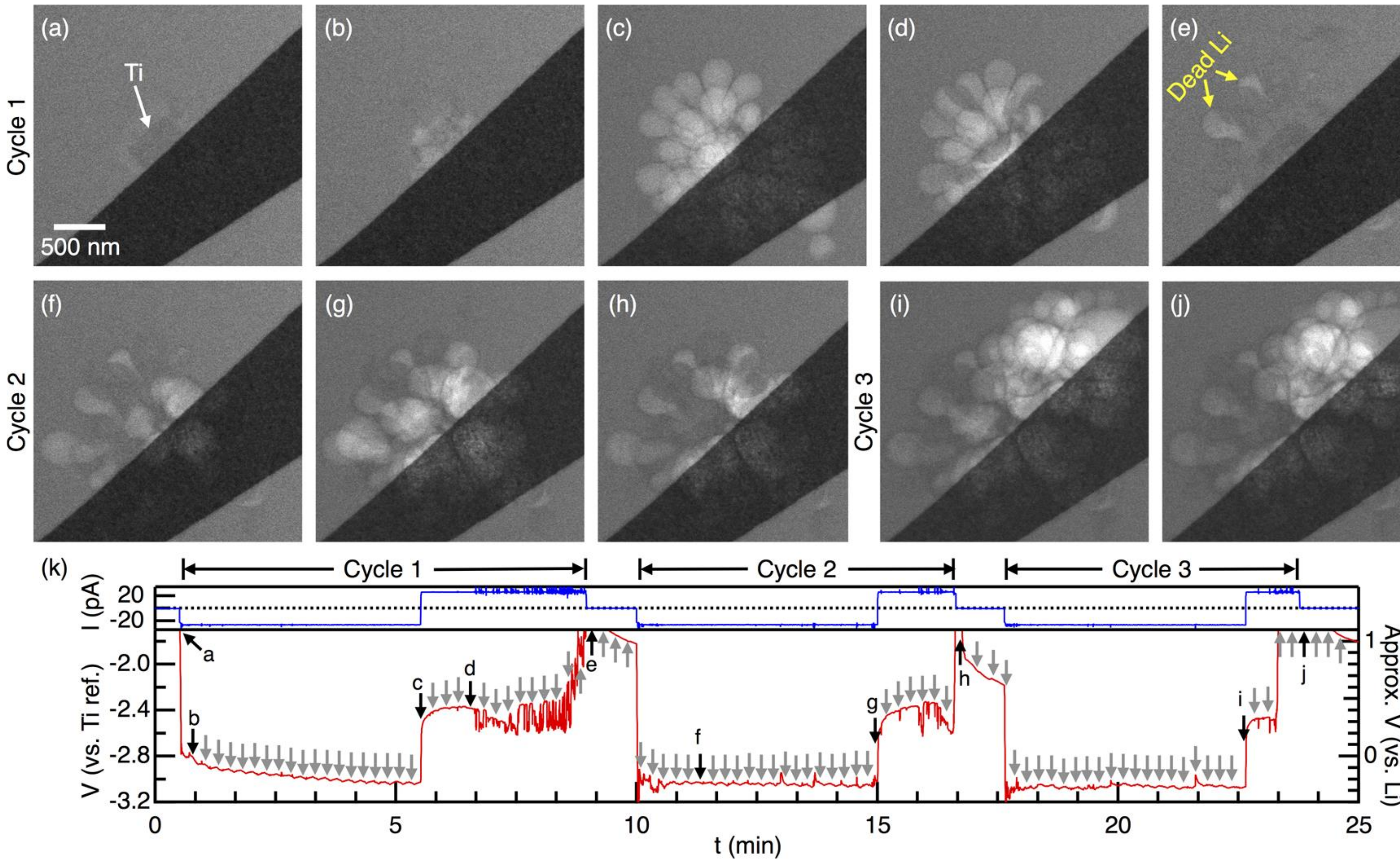
Unable to distinguish electrochemically the nucleation of a rounded grain vs. a dendrite



Leenheer et al., (2015) Nano Lett. (In Press).

Li Morphology: High E⁻ Beam Dose

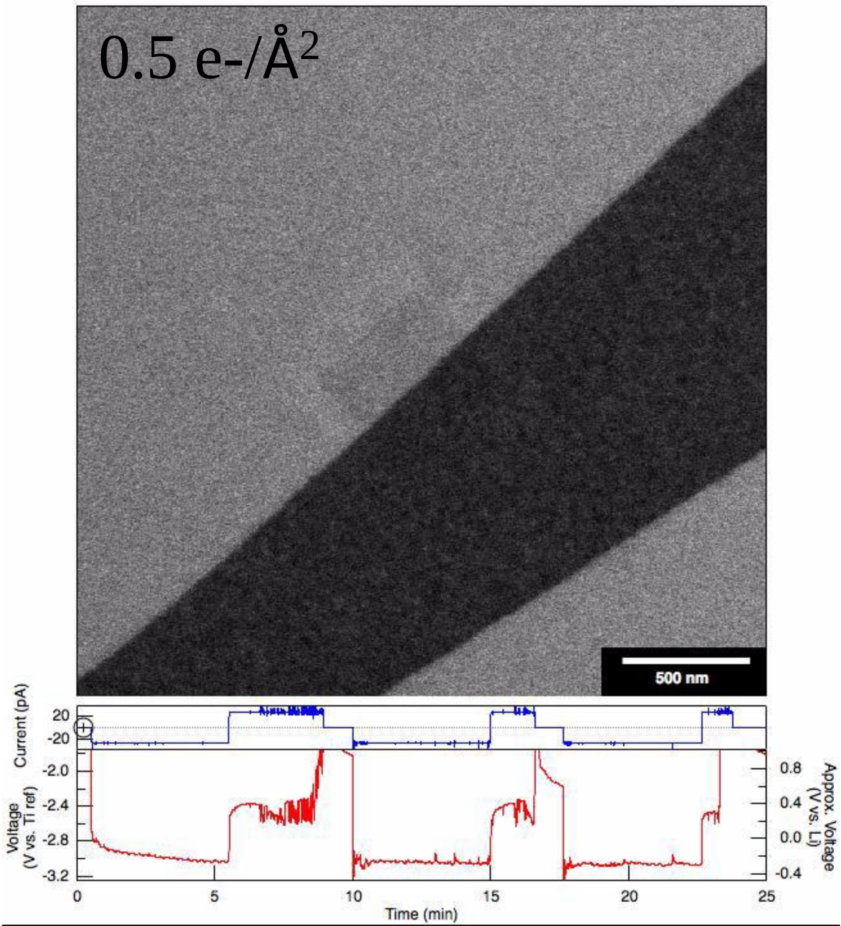
Galvanostatic control at +/- 10 mA/cm^2, Electron dose per image: 25 - 50 e$^-$/Å^2, Imaging every 15 seconds



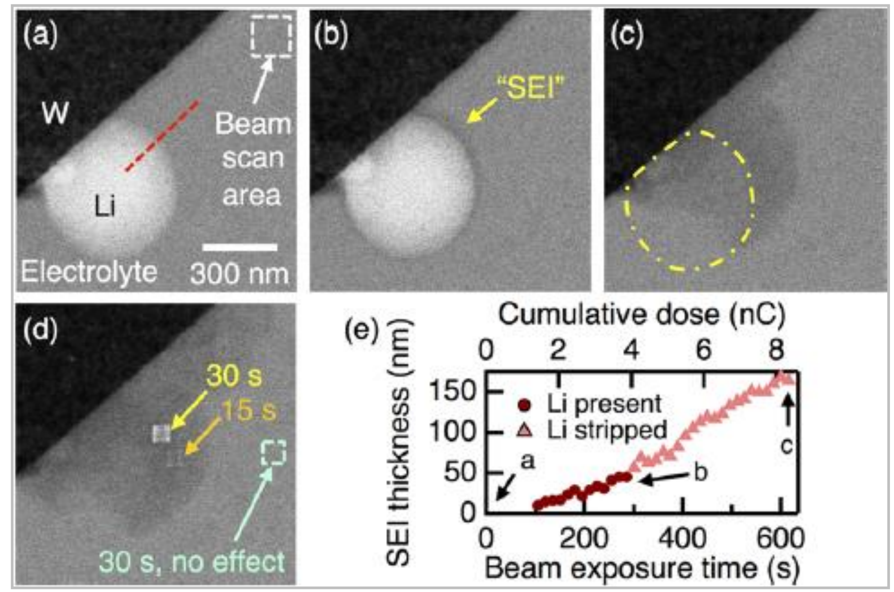
Electron beam increases nucleation and creates rounded Li deposits

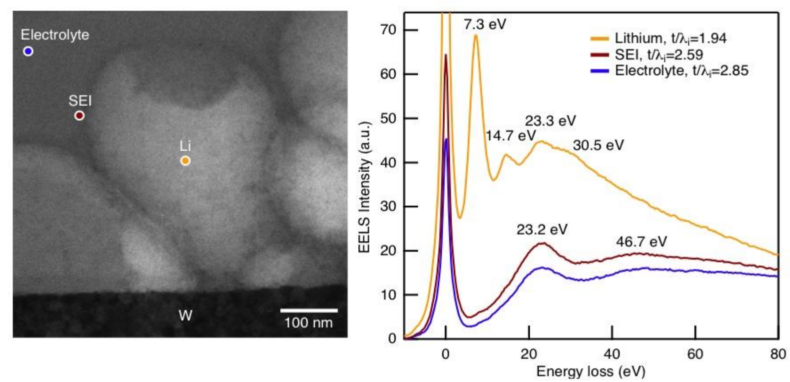
Leenheer et al., (2015) Nano Lett. (In Press).

How Does SEI Evolve with Cycling?



Leenheer et al. (2015) ACS Nano. DOI: 10.1021/acsnano.5b00876.





- Increased contrast is observed about Li deposits from electron beam degradation products
- Native SEI characterization is very difficult using an electron beam for imaging/spectroscopy

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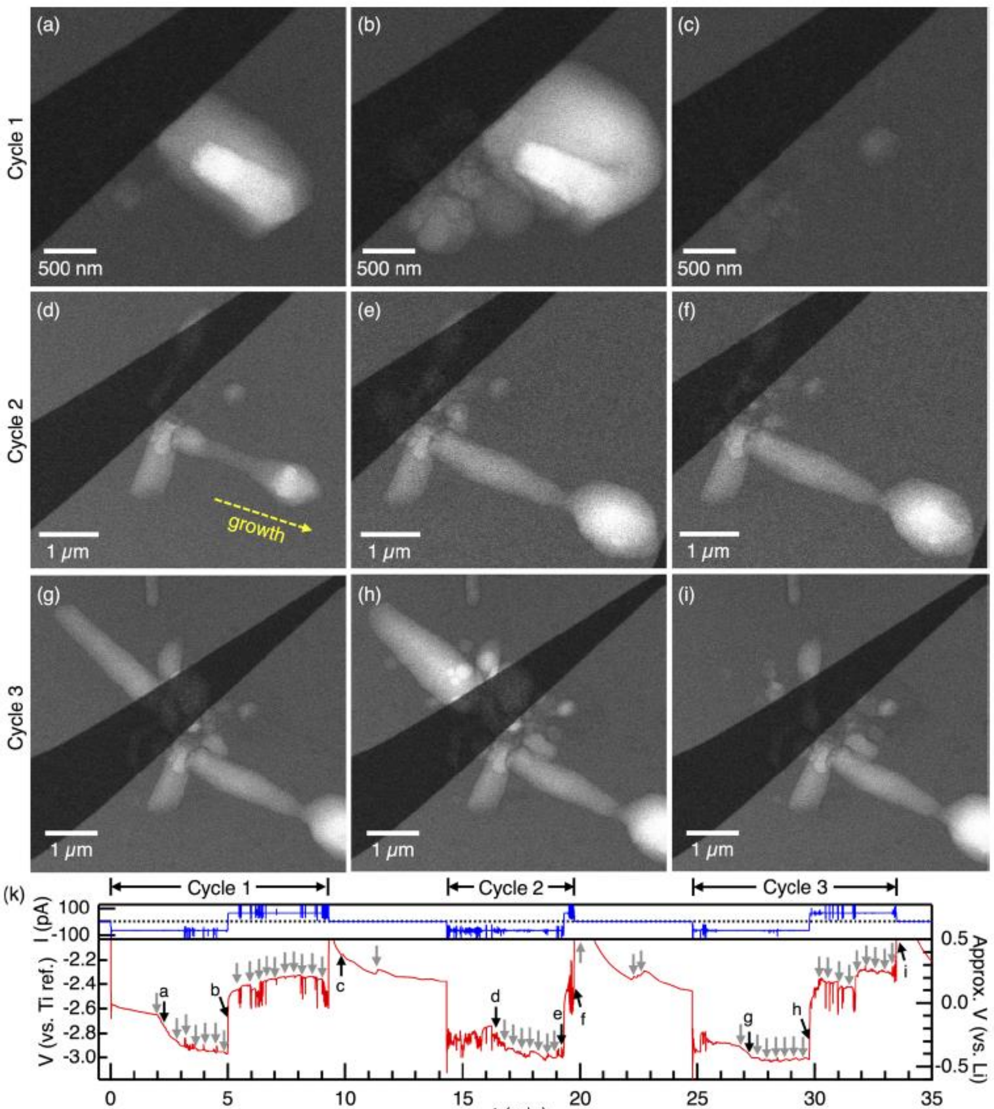
Li Deposition: High Current Density



Leenheer et al. (2015) ACS Nano. DOI: 10.1021/acsnano.5b00876.

Galvanostatic control at +/- 25 mA/cm^2
Electron dose per image: 12.5 - 25 $e^-/Å^2$
Imaging every 15 seconds

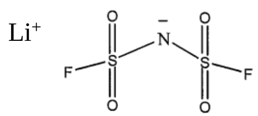
- Li dendrites observed more readily at higher current densities
- Li dendrites were observed more frequently at later cycles
- Since the current densities used were well below the diffusion limited regime for these 0.26 μm^2 electrodes, the diffusion-limited model for Li dendrites must be applicable to propagation rather than initiation
- TEM observation creates enhanced Li dendrite growth?
    - Large electrolyte volume to electrode area, ratio, radial diffusion, lack of separator pressure and beam-induced SEI

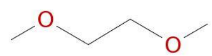
4 M LIFSI IN DME (4 PPM H_2O)

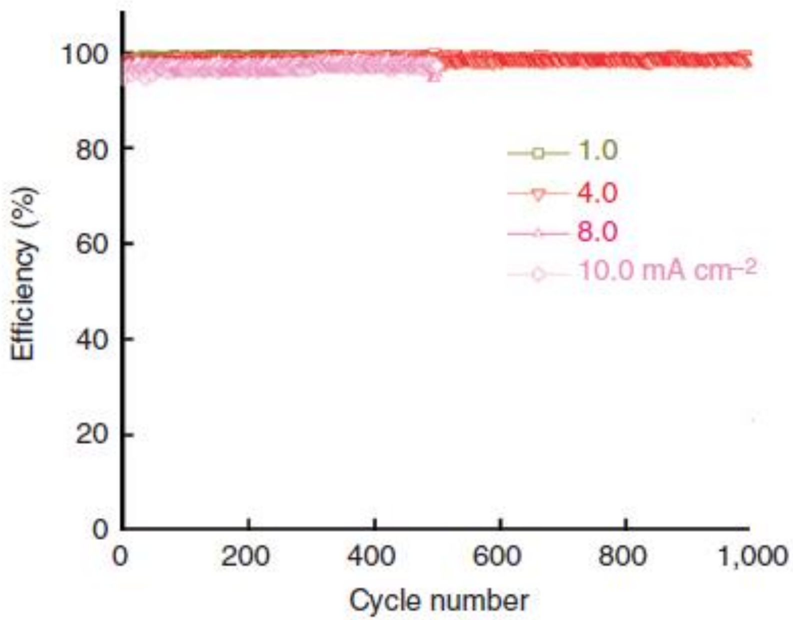
Electrolyte Suppresses Li Dendrites?

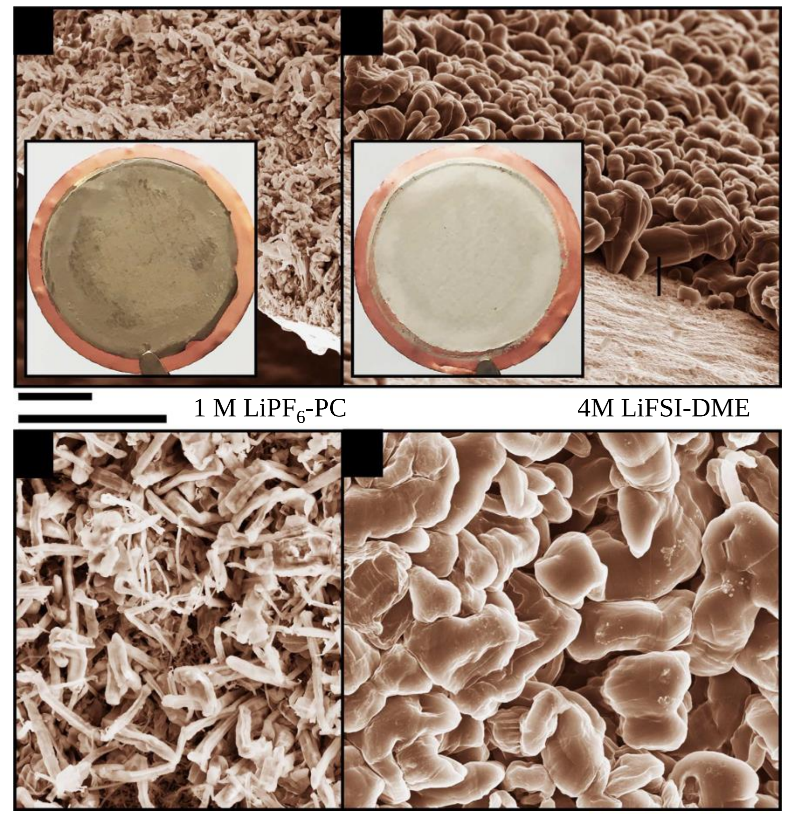
Technical challenge

- Tailoring the electrolyte to suppress Li dendrite formation may solve this issue, allowing for Li metal anodes to be used for increased capacity
- 4 M Lithium bis(fluorosulfonyl)imide (LiFSI) in 1,2-dimethoxyethane (DME) (< 1 ppm H_2O), increased solvent coordination





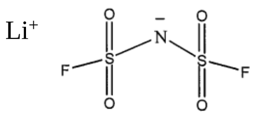




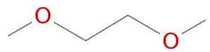
Qian et al., Nature Comm. 6, 6362 (2015).

Measuring Electrolyte Thickness and Damage

LiTFSI



DME



$\lambda_{i\ (DME)} = 195$ nm

$\lambda_{i\ (4M\ LiFSI\ in\ DME)} = 210$ nm

Jungjohann et al. 2012, Microsc. Microanal. **18**(3), 621.

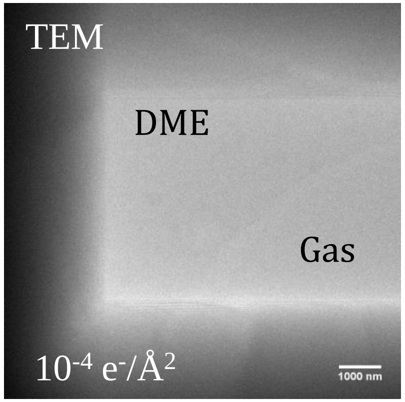
$$Z_{eff} = \frac{\sum f_n Z_n^{1.3}}{\sum f_n Z_n^{0.3}}$$

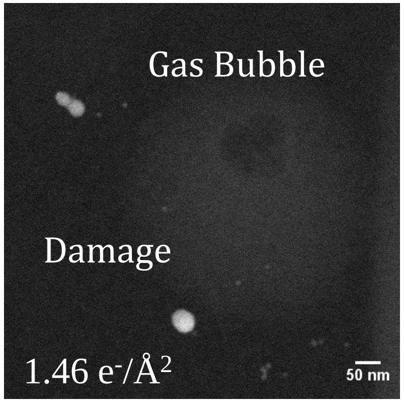
$$E_M = 7.6Z^{0.36}$$

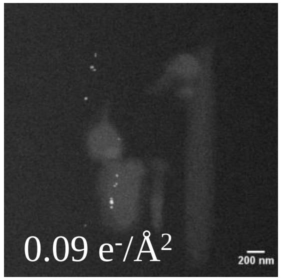
$$\lambda_i = \frac{106FE_0}{E_M \ln((2\beta E_0)/E_M)}$$

- Z_{eff}: *Effective atomic number*
- f_n: *Atomic fraction of element n*
- Z_n: *Atomic number of element n*
- E_M: *Average energy loss (eV)*
- Z: *Average atomic number*
- λ_i: *Inelastic mean free path length*
- E_o: *Accelerating voltage*
- β: *Collection angle (mrad)*
- F: *Relativistic correction factor*

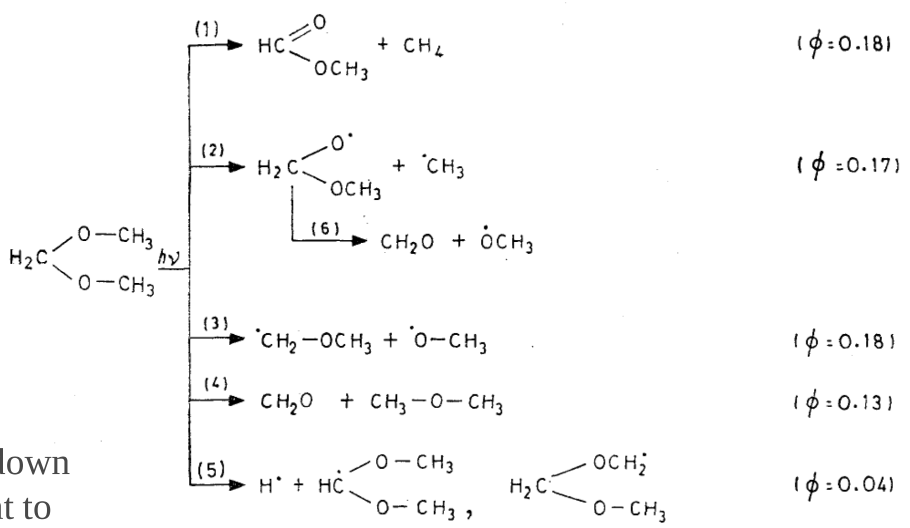
Malis, T.; Cheng, S. C. ; Egerton, R.F. J. of Elec. Micro. Tech.. 1988, **18,** 193.







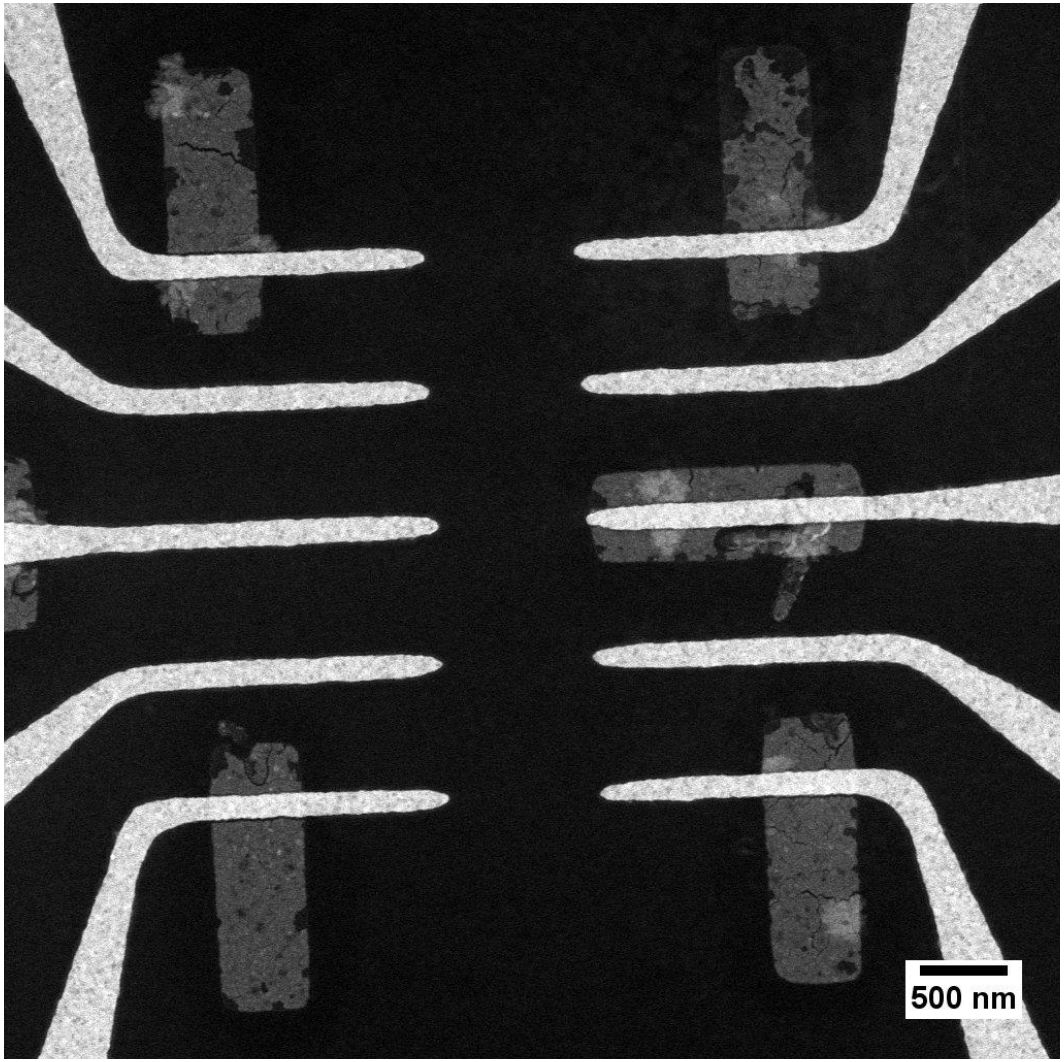
Dramatic difference in electrolyte breakdown with air exposure, DME is more tolerant to electron beam with air exposure

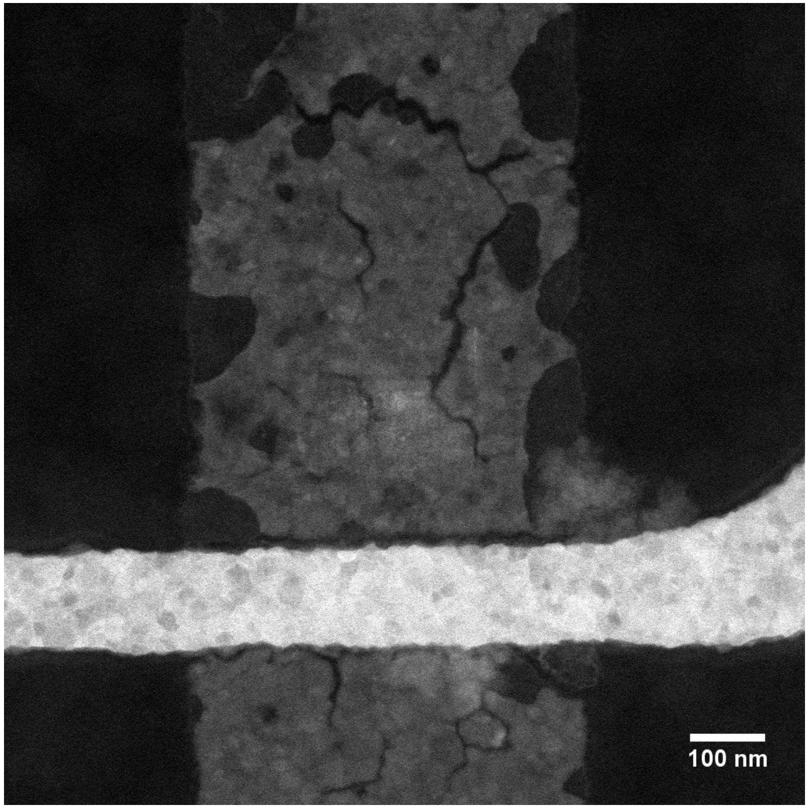


Schuchmann, H.-P. and von Sonntag, C.. 1976, J.C.S. Perkin II **12**, 1408.

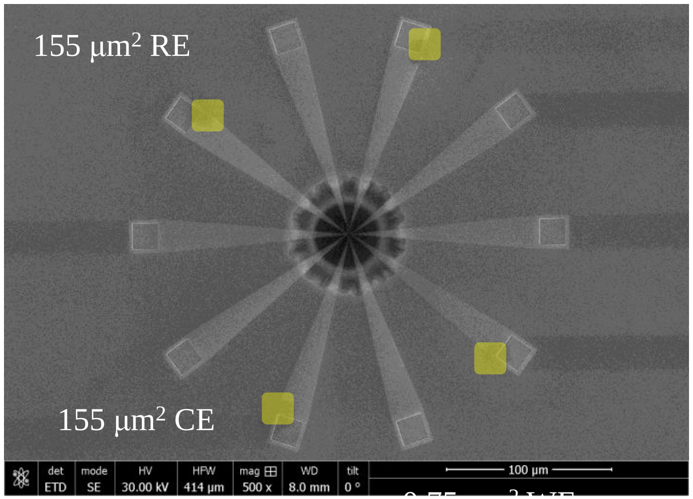
Metal Electrode Surface Structure?

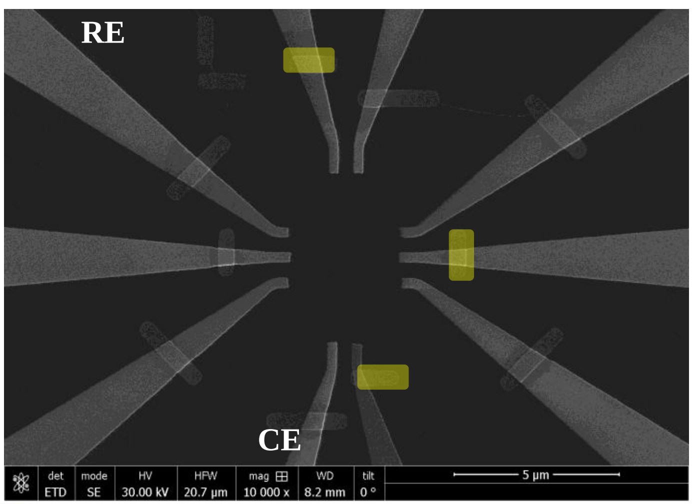
E-beam evaporated 40 nm Cu with no adhesion layer



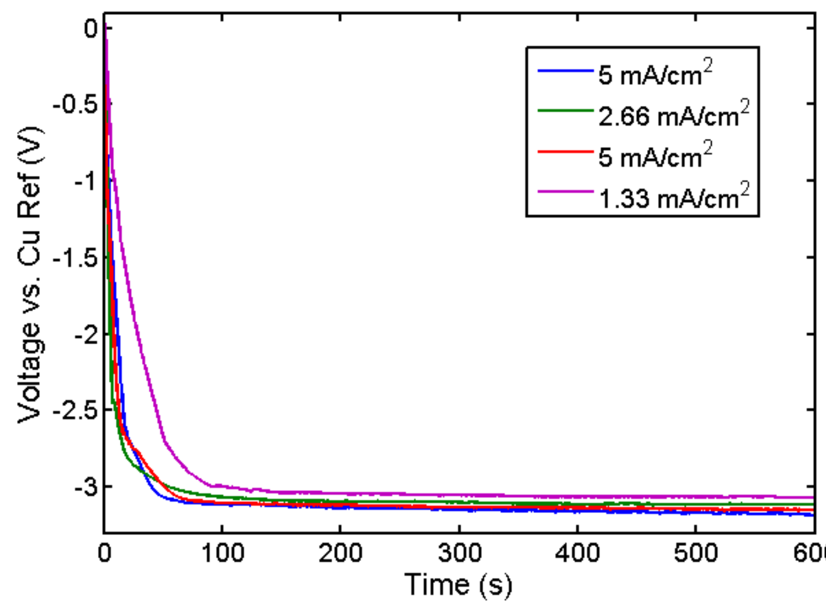


Current Density Dependence on Li Morphology





- 40 nm Cu electrodes (5 nm Ti adhesion layer)
- W electrodes coated with Al_2O_3/SiO_2 (40 nm) passivation layer
- Cu WE Area: 0.75 μm^2
- Cu RE & CE Areas : 155 μm^2
- 4M LiFSI in DME (3 ppm H_2O)
- Dose per frame: 0.03 – 0.28 e^-/Å^2
- Electrolyte Thickness: > 1.5 μm

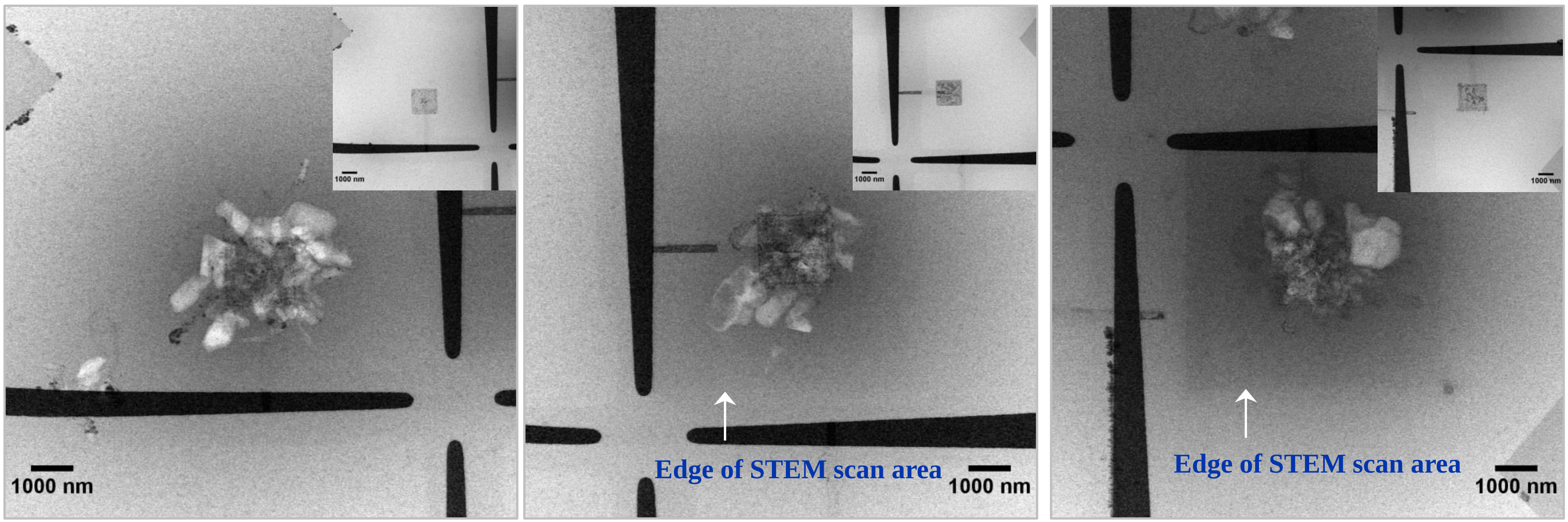


WHAT IS THE EFFECT OF THE ELECTRON BEAM?

Electron Beam Induced Degradation and SEI

- Compare beam effects in identical electrochemical environments, same closed cell with 4 Si electrodes and 4 Cu working electrodes
- Galvanostatic control at 2.25 mA/cm^2 for 2 min deposition/stripping steps for 10 cycles

WE#3 : No Beam | WE#1 : < 3.84 e-/Å^2 | WE#4 : < 20.16 e-/Å^2



- Li deposits push membrane windows apart, increasing scattering in the background
- Electron beam adds background scattering by electrolyte breakdown forming polymerized carbon chains

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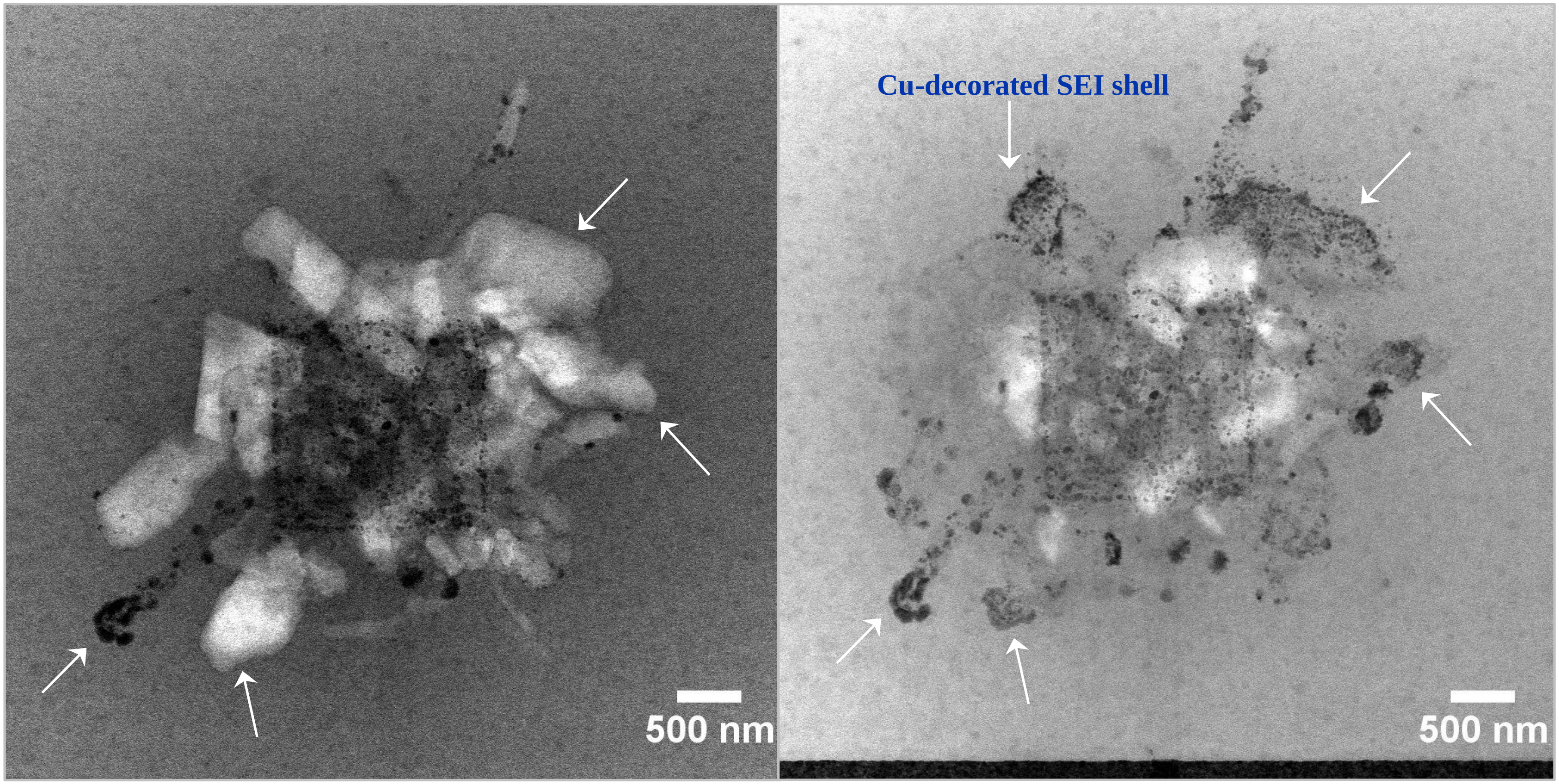
Native Electrode Electrolyte Interfaces

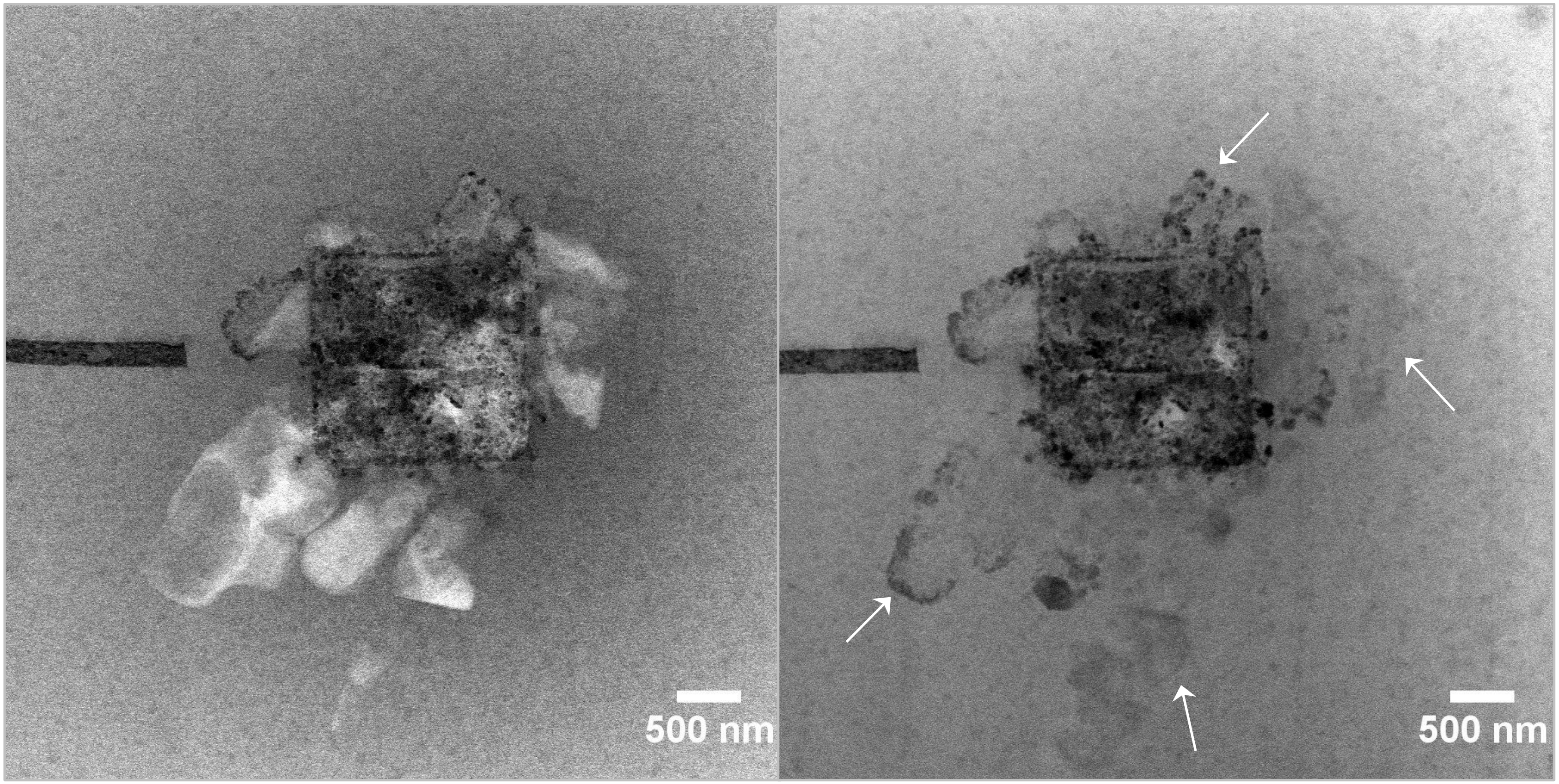
WE#3 : No Beam



- Cu deposited along the Li deposits, after self-discharge of 'dead' Li, the Cu decorating the solid-electrolyte interface provides increased contrast which retains structure even after Li dissolution

Native Electrode Electrolyte Interfaces

WE#1 : < 3.84 e-/Å^2 Total Dose During Electrochemistry

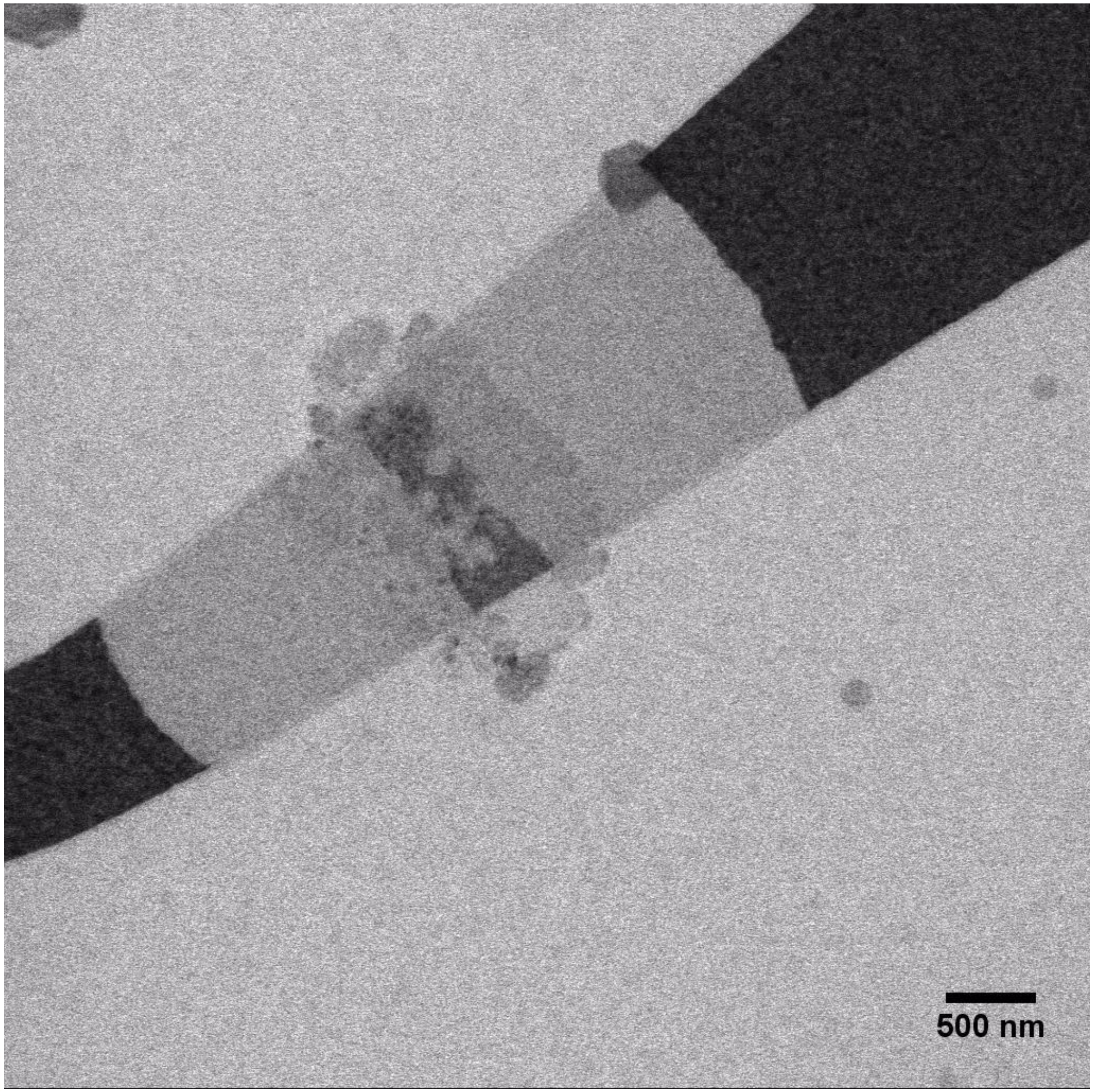


WHERE IS LI INITIALLY DEPOSITING?

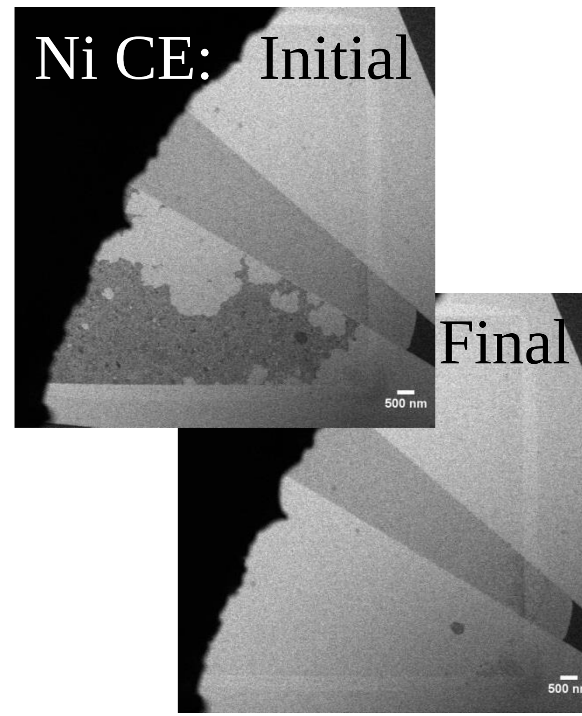
MORPHOLOGY?

Where is Li depositing? Δ Beam Dose

Katharine Harrison, Nathan Hahn, and Kevin Zavadil



- Ni WE Area: ~1 μm^2
- Ni RE & CE Areas : 100 μm^2
- Electron Beam Dose: < 2.53 $e^-/Å^2$
- Dose per frame: 0.03 $e^-/Å^2$
- Electrolyte Thickness:
- **Coulombic Efficiency:**



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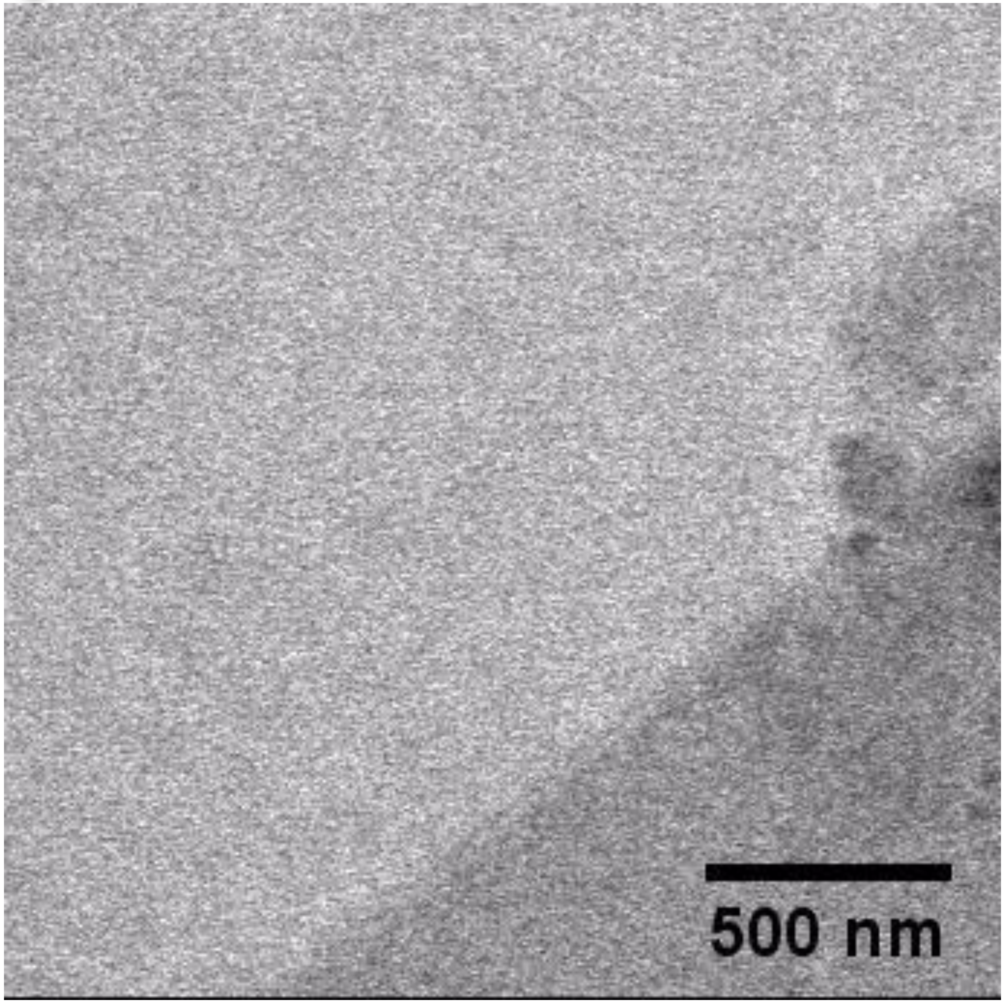
SEI Cracking to Allow for New Growth



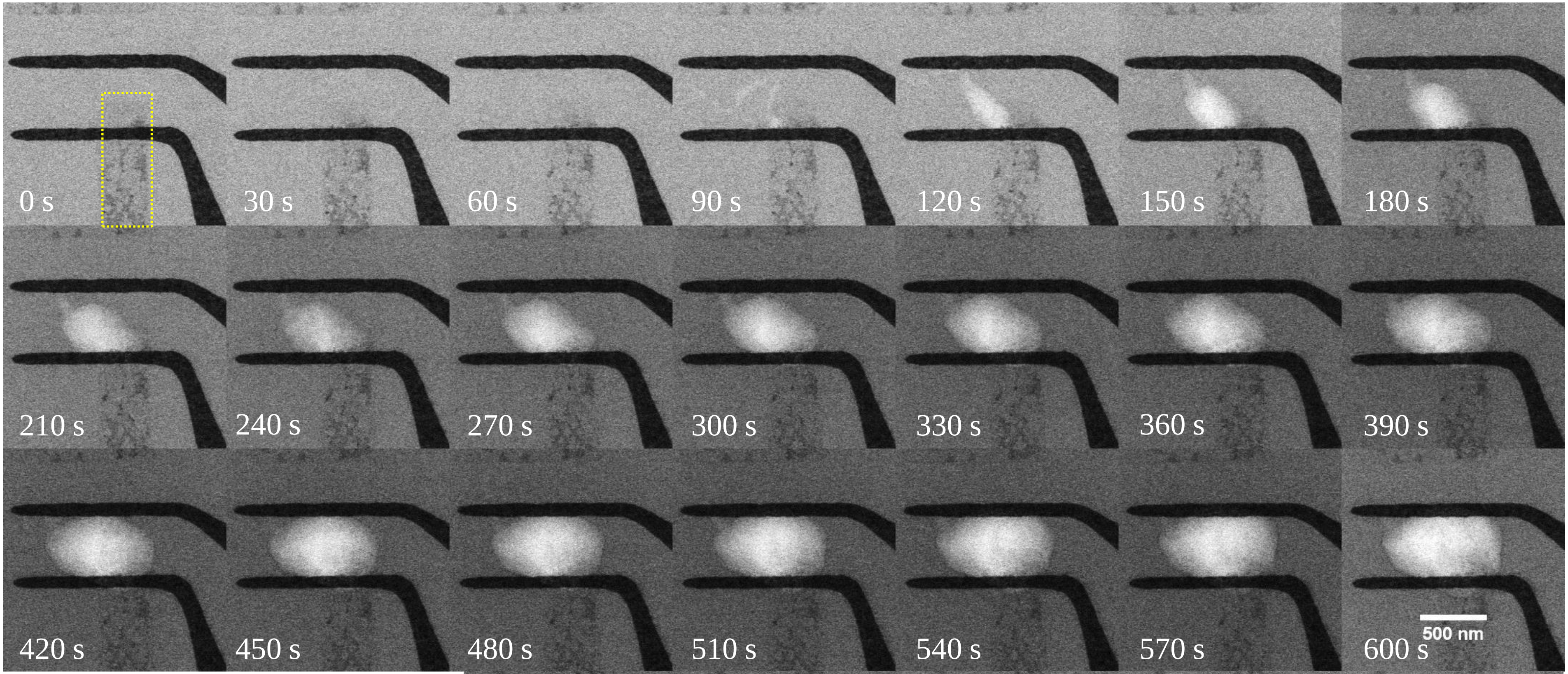
- Ni WE Area: ~1 μm^2
- Ni RE & CE Areas : 100 μm^2
- Electron Beam Dose: < 2.53 $e^-/Å^2$
- Dose per frame: 0.03 $e^-/Å^2$
- Electrolyte Thickness:

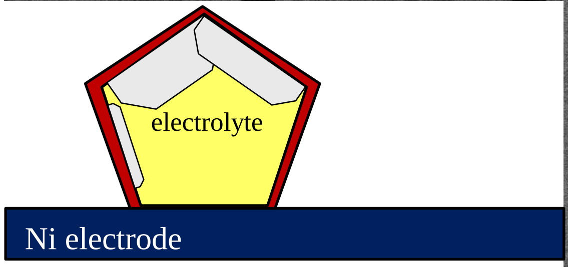
Although SEI cracks and Li grain grows, it quickly is impeded by rapid SEI formation over the grain and closure of the Li ion transport. Ni concentration may have been too high and additionally impeded deposition of Li.

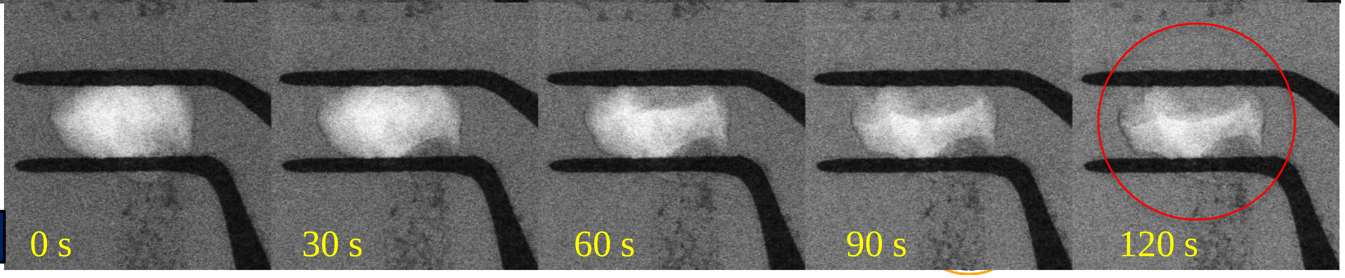
Incomplete Stripping at Li-SEI Interface

Cu WE: **1.33 mA/cm²** for 10 min deposition

Electrolyte thickness: ~ 300 nm

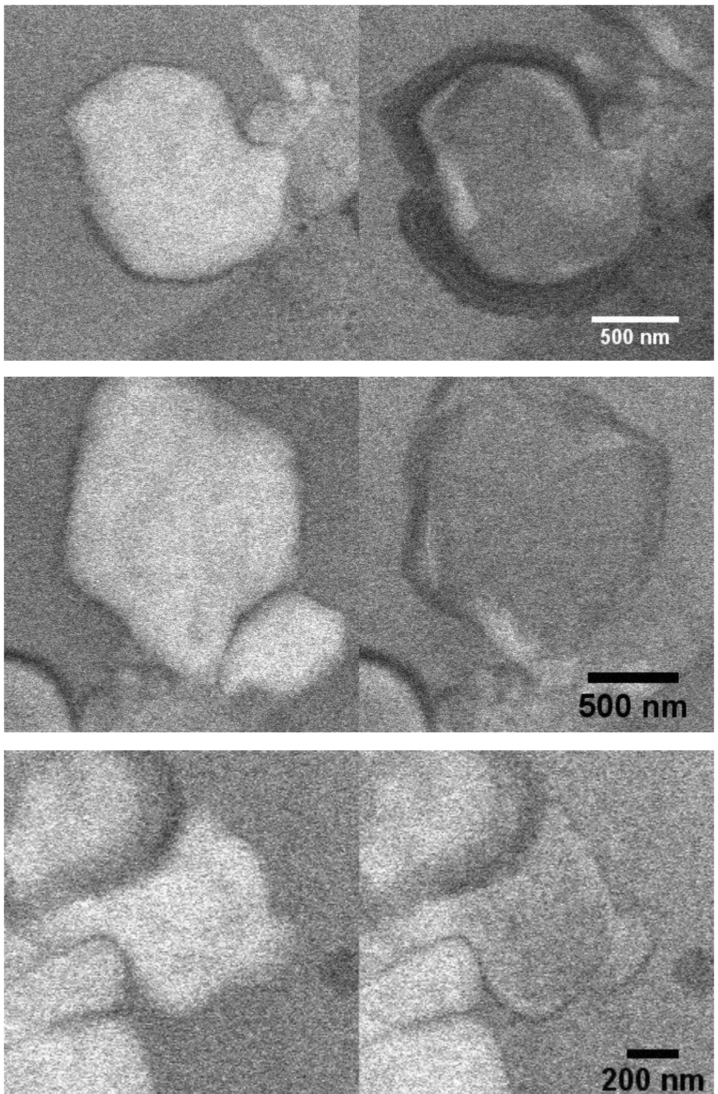


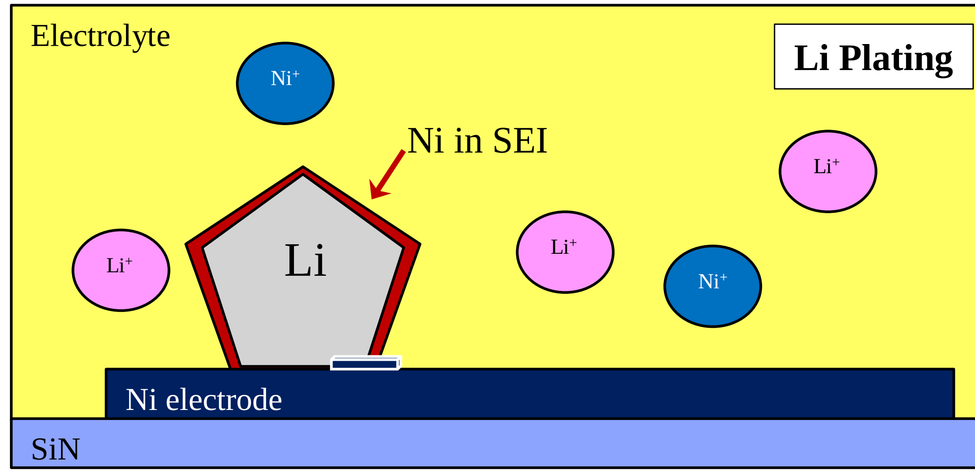


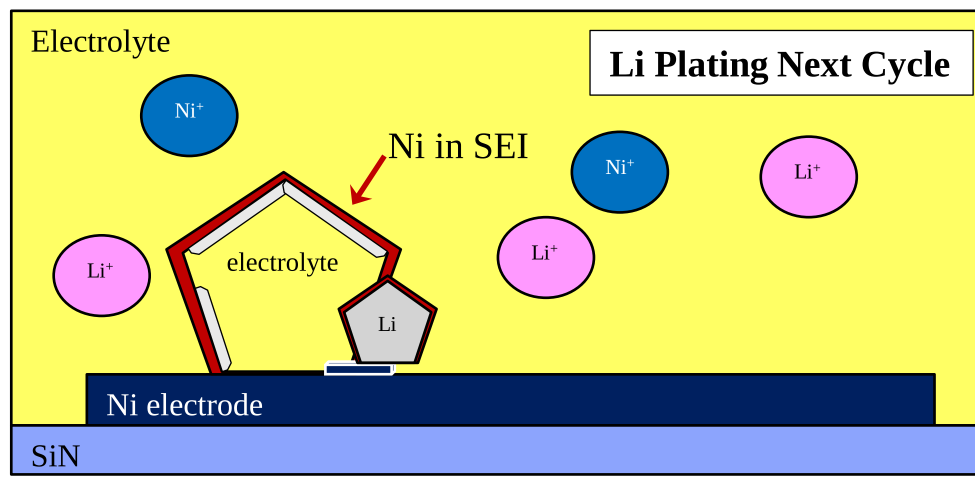


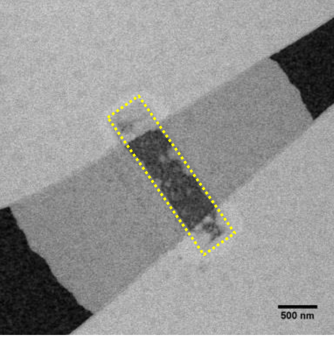
Incomplete Stripping at Li-SEI Interface

Ni WE: 10 mA/cm^2









Where is Li nucleating during cycling?

Katharine Harrison, Nathan Hahn, and Kevin Zavadil

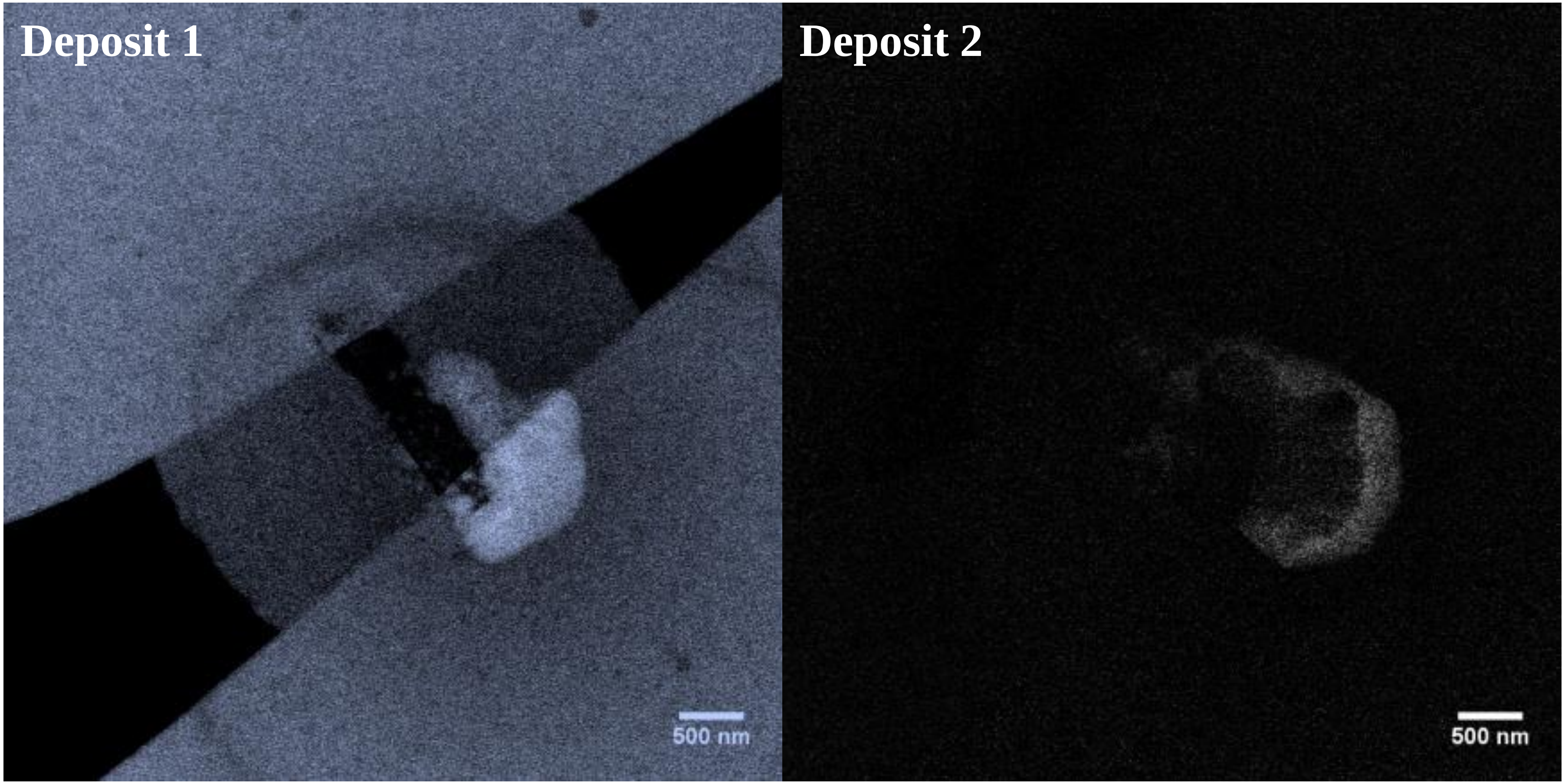
Ni WE & CE : 10 cycles at 10 mA/cm^2 (50 pA), beam current: 0.12 nA

Ni integration into SEI adds conductivity? See Li deposit on top of SEI

Li deposits do not strip and reform, nucleation in new areas

Incomplete Stripping at Li-SEI Interface

Conformal Li coating on initial Li deposit!

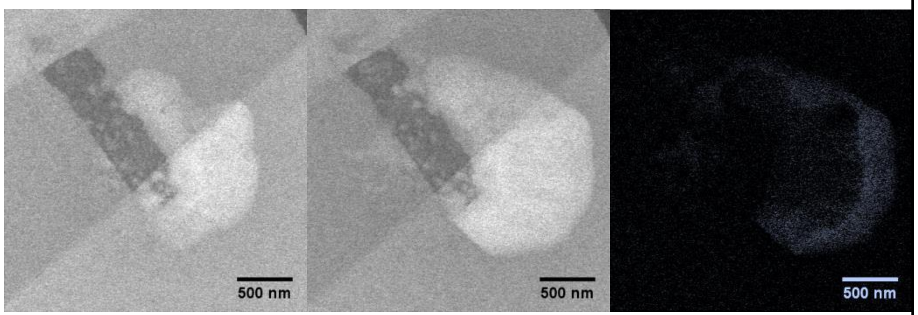


10 mA/cm^2

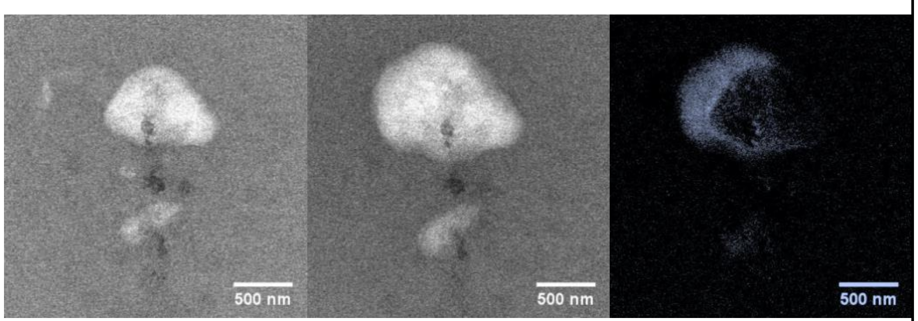
Li Coating on Li Grain only during Cycle 1 to 2

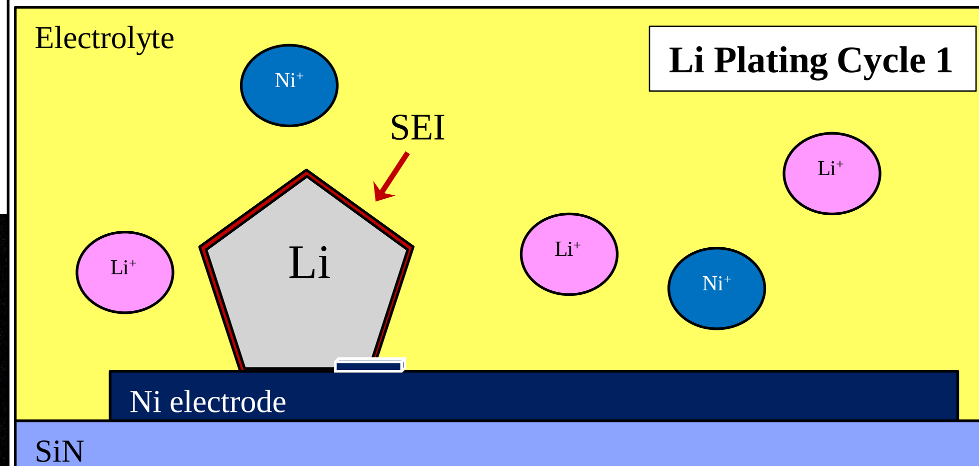
What characteristic's about the SEI after the initial cycle promote the formation of this conformal deposition?

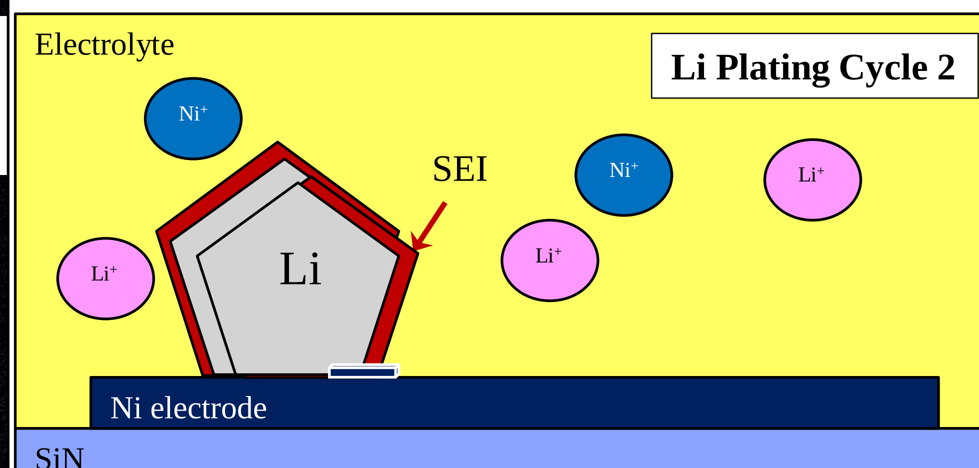
Ni WE: 10 mA/cm^2



Cu WE: 2.25 mA/cm^2







SEI's role in modifying interfacial energies and Li$^+$ transport ?

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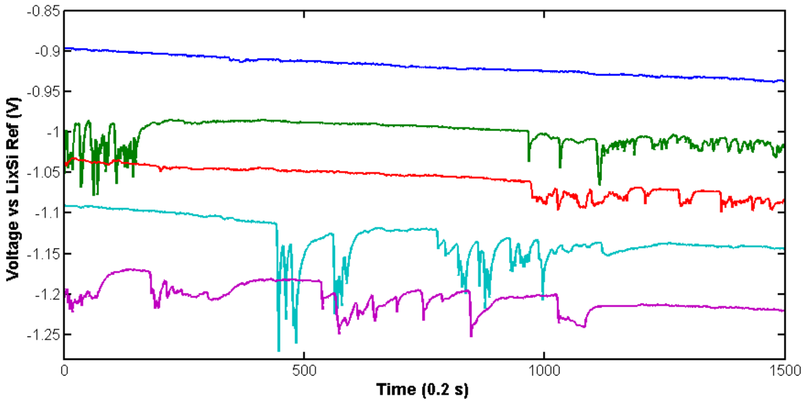
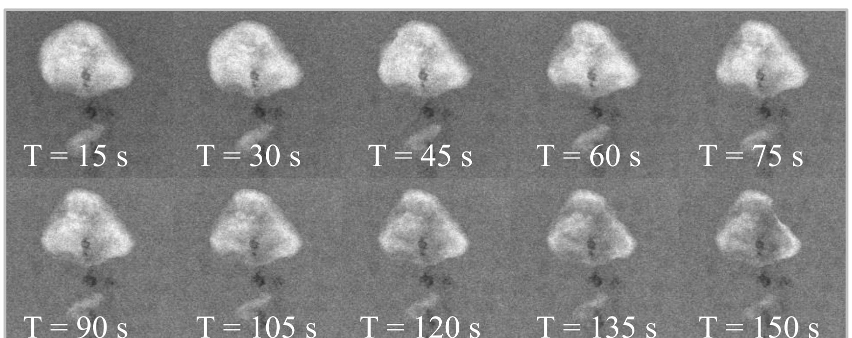
WHERE AND WHEN ARE LI DENDRITES DEPOSITING?

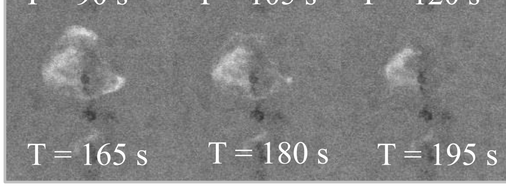
DENDRITE SUPPRESSION?

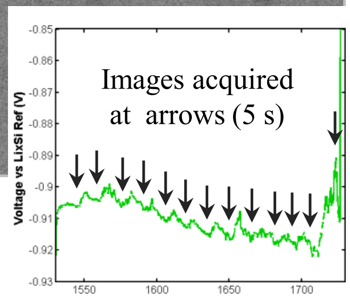
Effects of Multiple Cycles on Li Nucleation

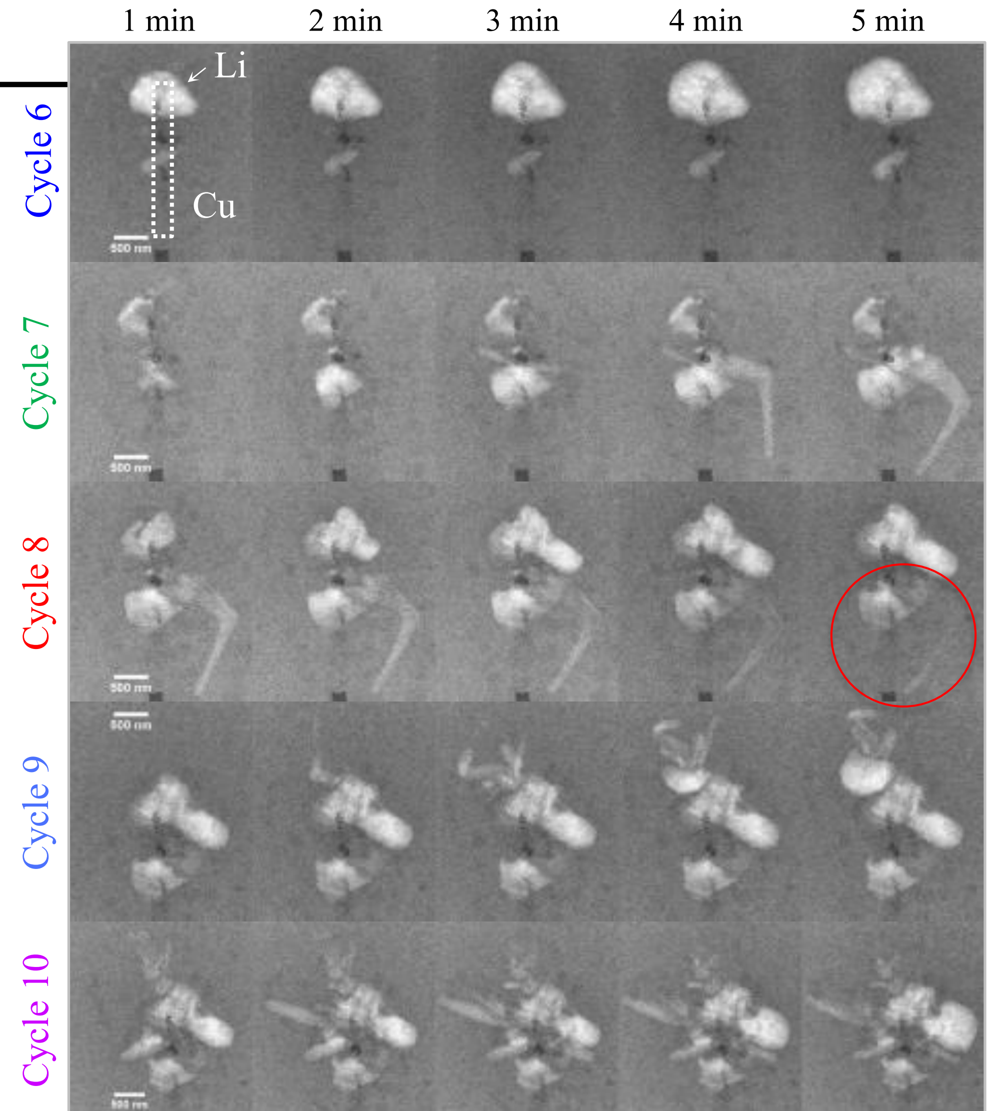
WE #2 Cu: **2.25 mA/cm²** for 5 min deposition











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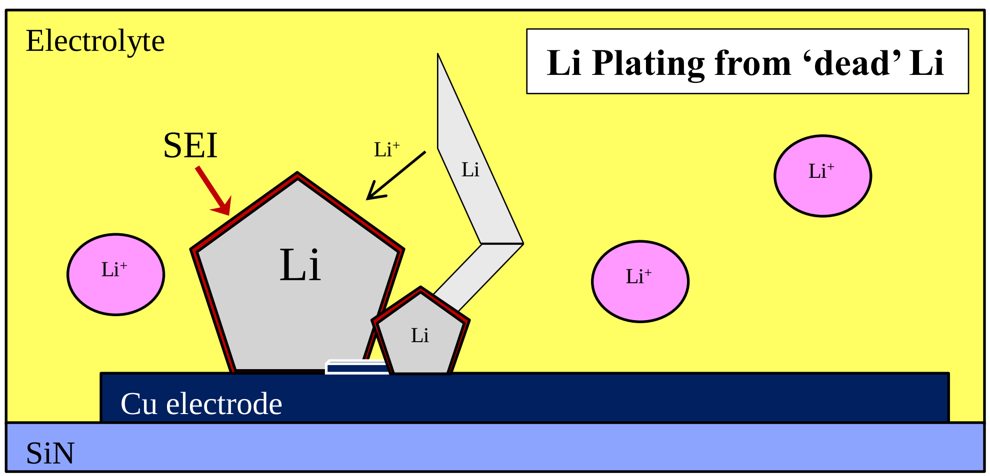
Self Discharge Mechanism or Conservation?

Li dendrite disconnected from electrode by neighboring grain, will dissolve during next deposition step

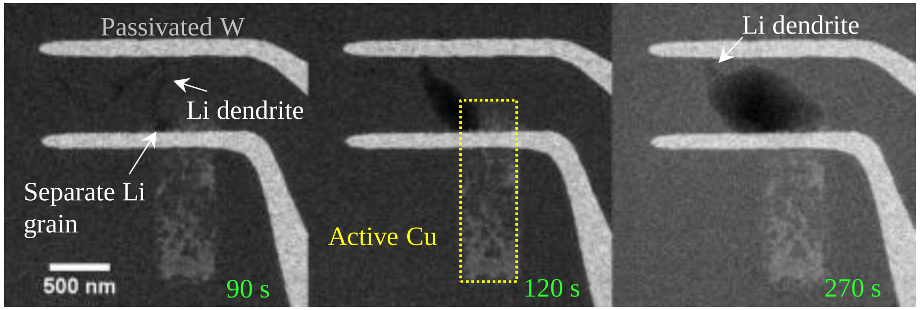


Need comparison to results when using a Li metal CE

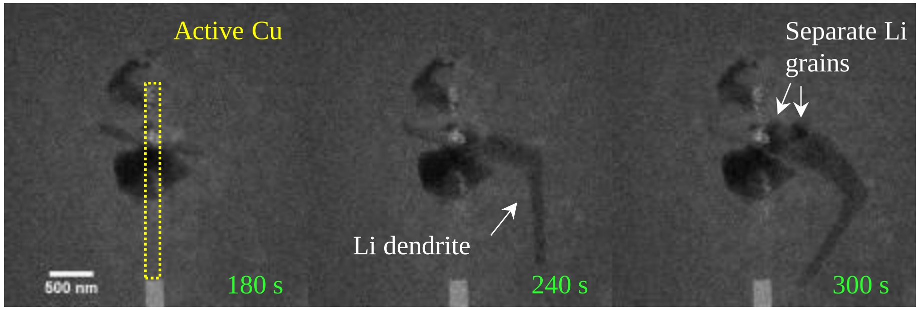
Li Dendrite Disconnection

- During deposition the *Li dendrites become electrochemically inactive at the metal electrode by being disconnected during the growth of a neighboring low-aspect-ratio grain.*
- ***Not current density or cycle # dependent***
- Self-discharge mechanism
- How is the electron beam impacting ion diffusivity?

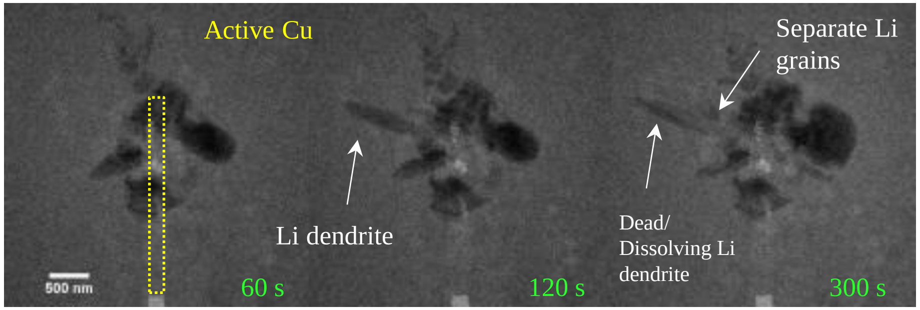
EC-Scanning TEM: -1.33 mA/cm^2 on 1 μm^2 Cu: ***Cycle 1***



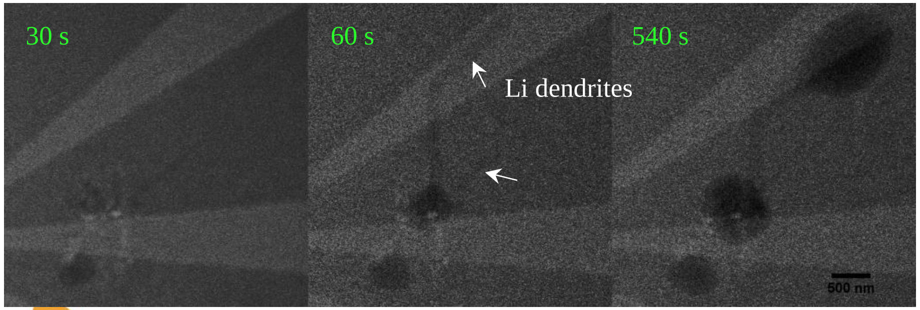
-2.25 mA/cm^2 on 0.44 μm^2 Cu: ***Cycle 7***



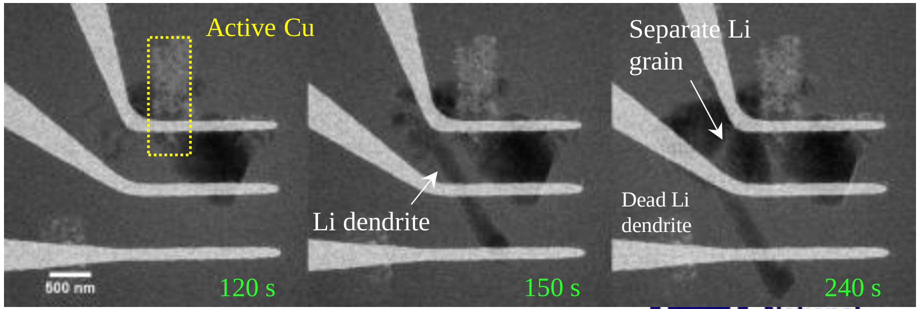
-2.25 mA/cm^2 on 0.44 μm^2 Cu: ***Cycle 10***



-5 mA/cm^2 on 0.75 μm^2 Cu : ***Cycle 1***



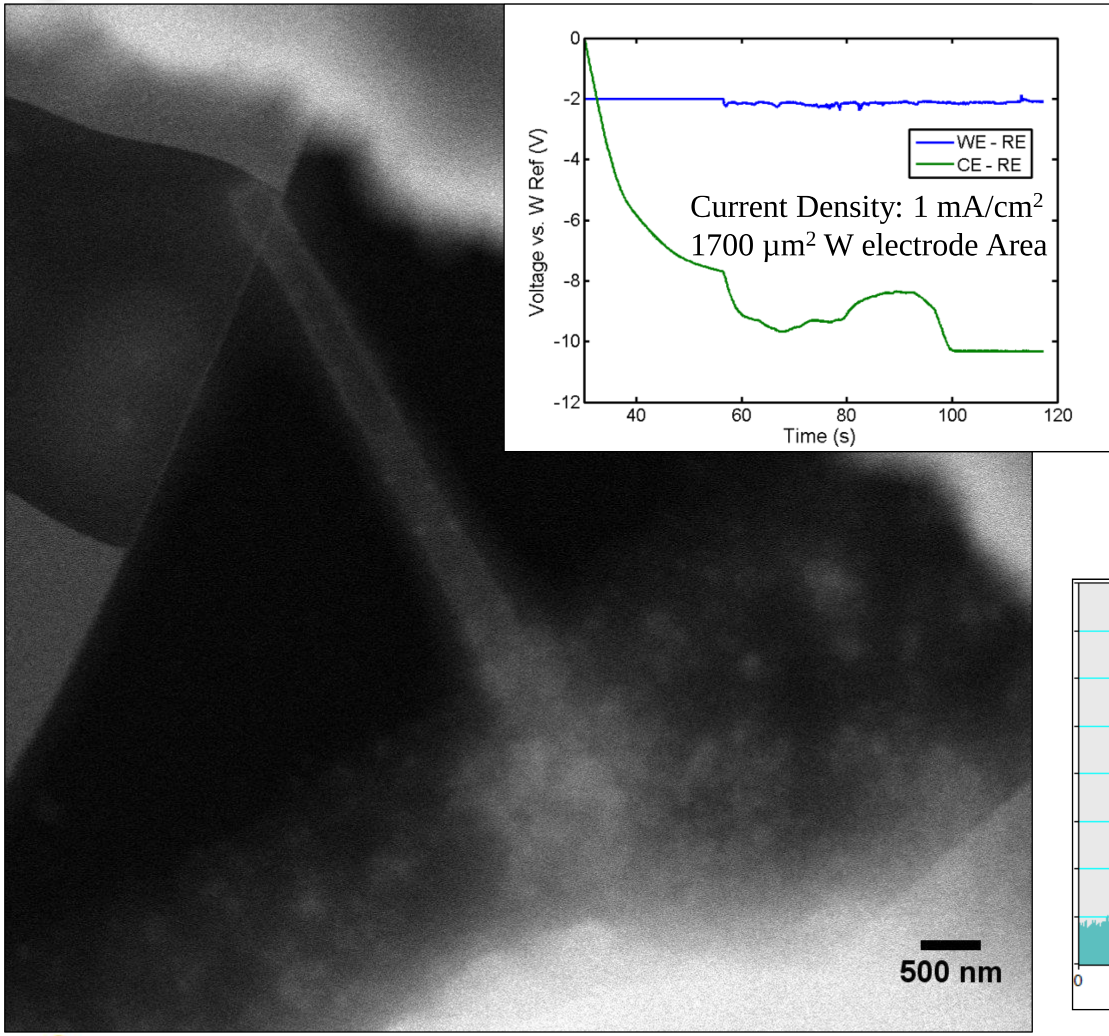
-5 mA/cm^2 on 1 μm^2 Cu : ***Cycle 1***

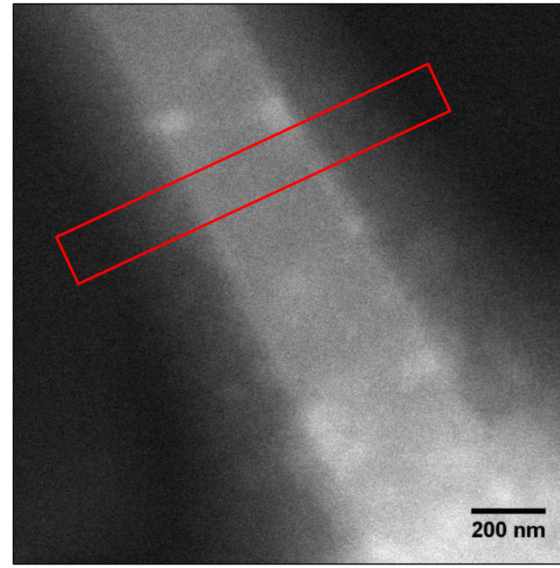


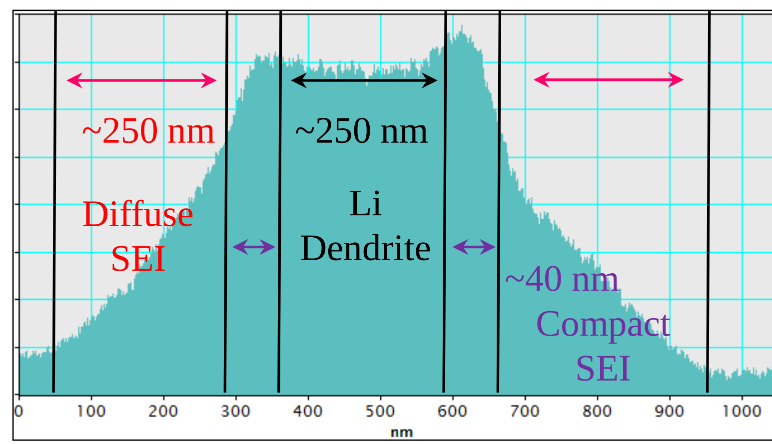
The velocity of the dendrite growth decreases significantly when ion diffusivity increases

J. Tan & E. Ryan (2013) 223[rd] ESC Meeting Abstract #433.

Li Dendrites formed at High Current Densities







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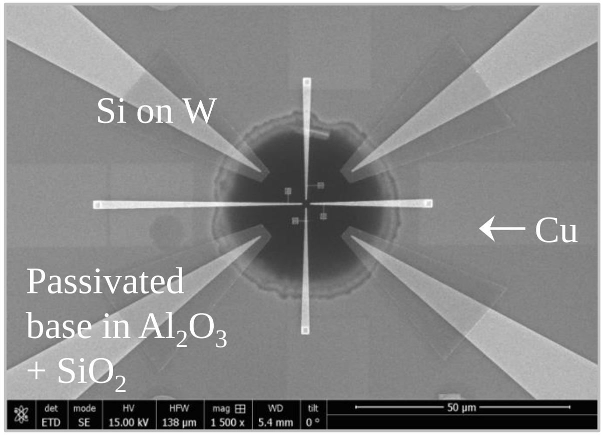
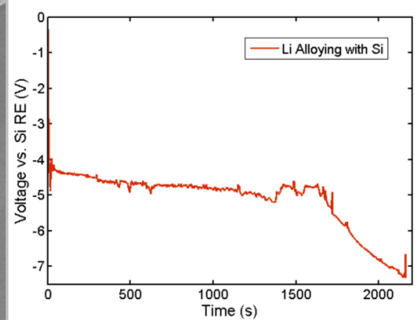
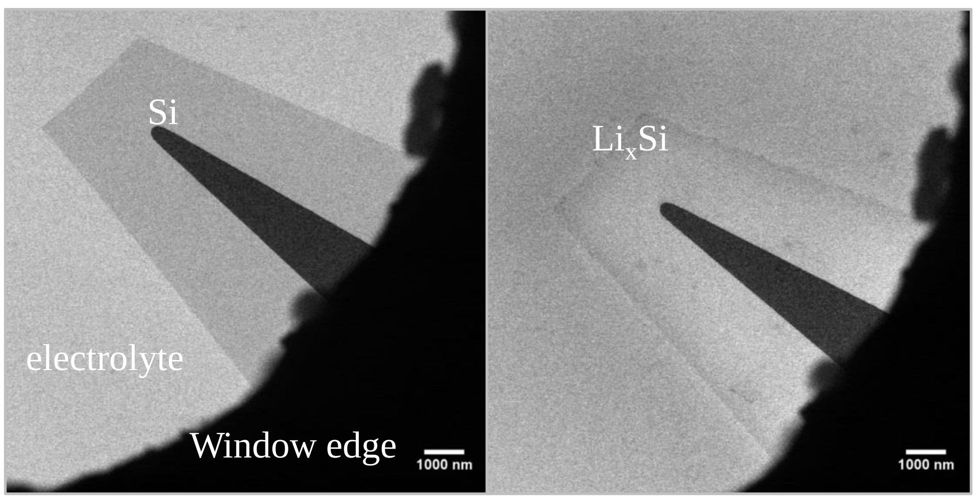
Li Containing Counter and Reference Electrodes

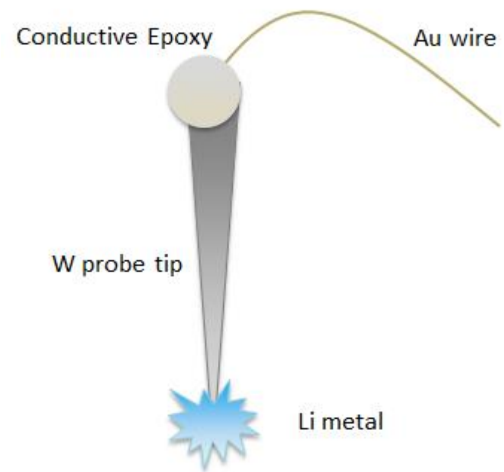
Lithiation of 500 µm² Si electrode from 4 M LiFSI in DME







Li scraped on W probe



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Conclusions

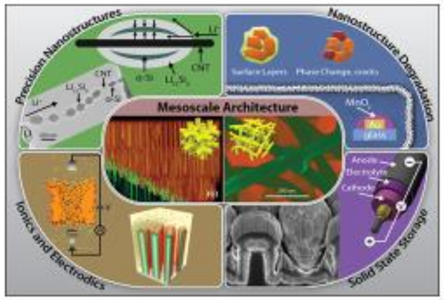
- Able to electrochemically control the deposition/stripping of Li in TEM
- Observe similar morphology as previous imaging techniques, but with higher spatial resolution
- Li morphology is dependent on many factors: electrolyte/salt, electrode surface, SEI, current density, *pressure and temperature*
- Li dendrites observed at higher current densities and during later cycles
- Nucleation activation barrier decreased at higher current densities

- Is electrolyte breakdown (no Li metal CE) affecting Li morphology & Coulombic efficiency?
- Effect of electron beam on ion diffusivity to affect dendrite growth?

Acknowledgements

Nanostructures for Electrical Energy Storage
A DOE Energy Frontier Research Center

NEES major research areas
- Nanostructure Interface Science
- Mesoscale Architectures & Ionics
- Nanostructure Degradation Science
- Solid State Energy Storage



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Electrochemical Platform Design and Production:

Michael Shaw, SNL