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JOINT CENTER FOR ENERGY STORAGE RESEARCH

In-Situ Liquid-Phase (Electrochemical) TEM Towards Real Systems and Possible Mechanisms

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Telluride 2016: Ions in Solution: Biology, Energy, and Environment

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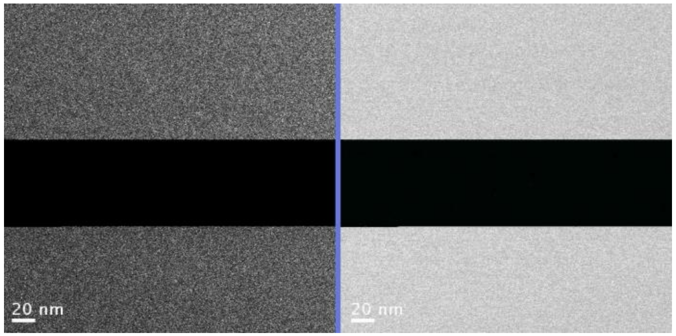
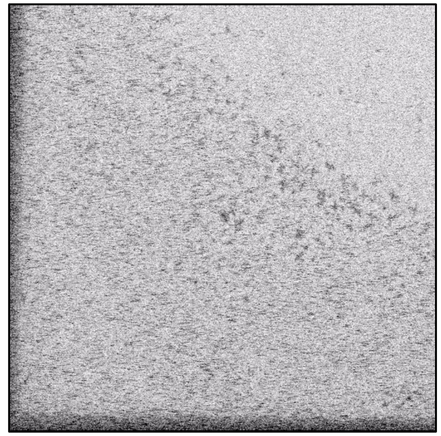
What systems can be studied using this technique?

Nanoparticle Nuc & Growth

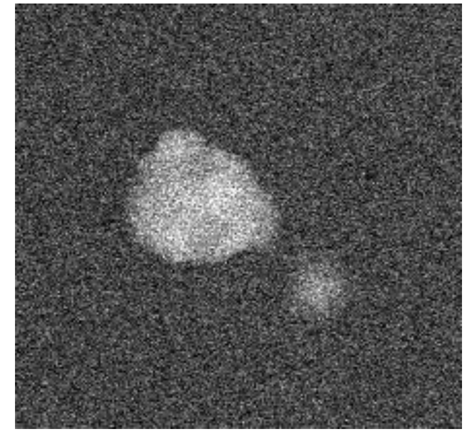


Evans et al. Nano Lett. **11**, pp 2809 (2011)

Assembly

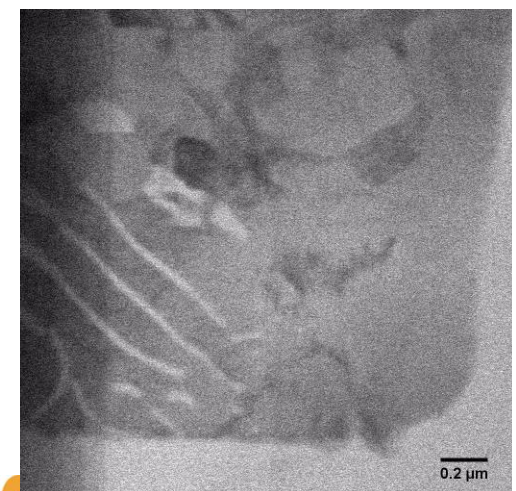


Galvanic Replacement

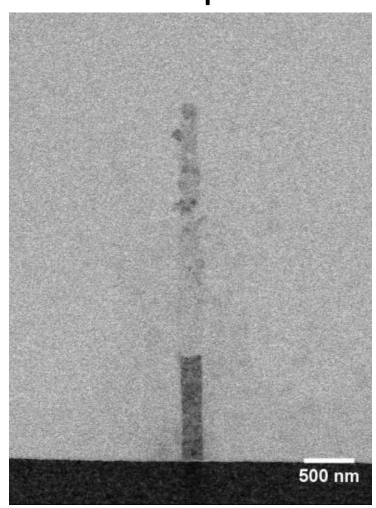


Sutter et al. Nat. Comm. **5**, pp 4946 (2014)

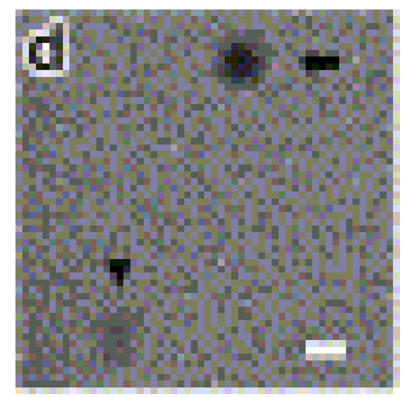
Corrosion



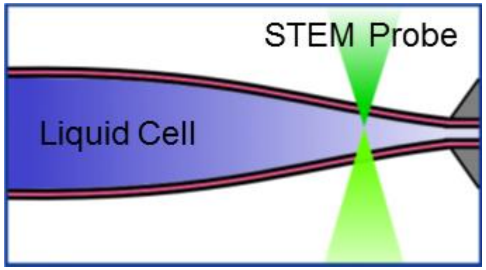
Electrodeposition



Structure/Dynamics of Biomaterials



Evans et al. Micron 43, pp 1085 (2012)



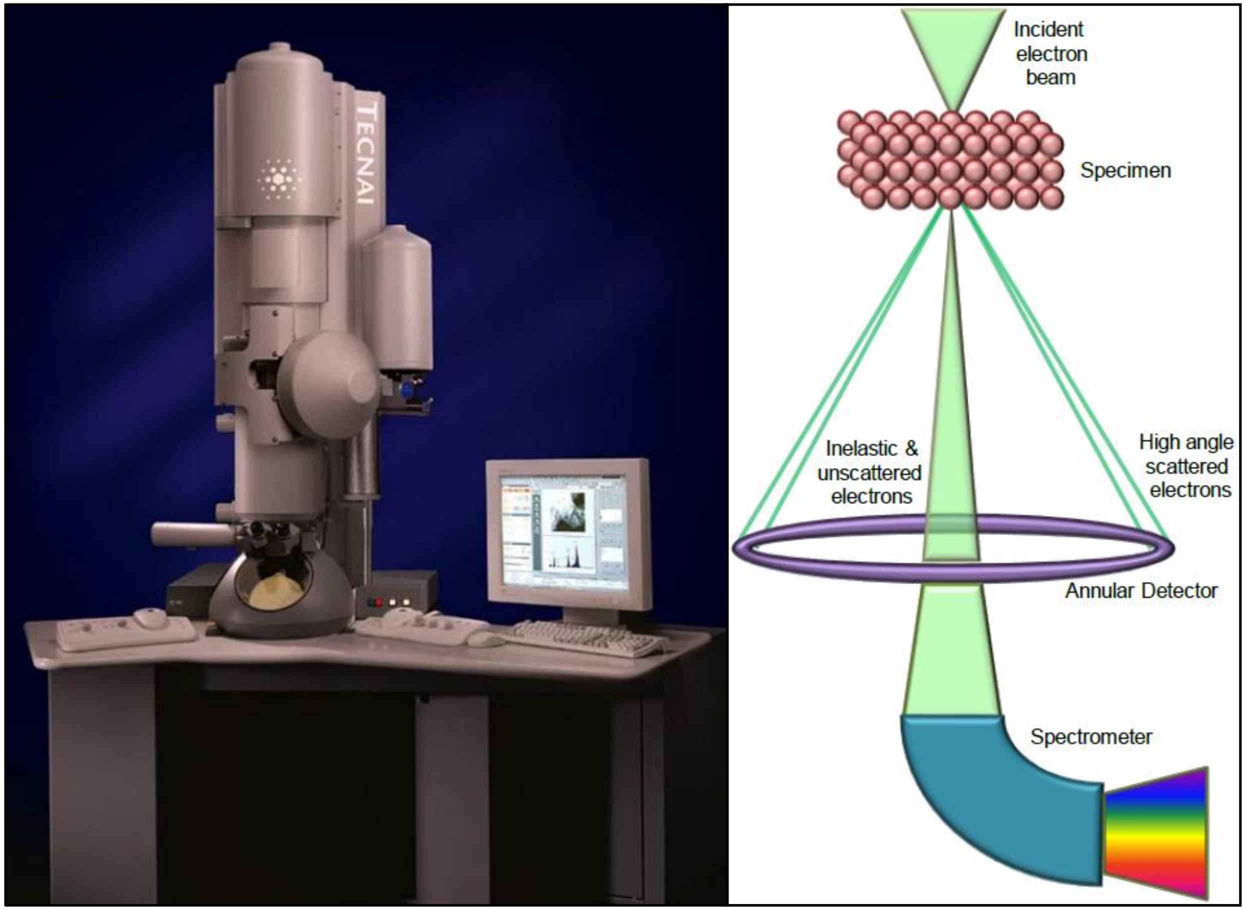
Capability of Experimental System:

- Real-time dynamic nanoscale imaging of materials in solution
- Site-specific information (grain boundaries, defects, interfaces…)
- Able to image almost any solution, except for very basic solutions will etch window
- Microfluidic control and possibly mixing
- Picoampere current control over ultramicroelectrodes, multiple electrodes
- Temperature control up to 175^{o}C (hexane)
- Chemical analysis and probing electronic states of materials/liquids

Complexity of Experimental System:

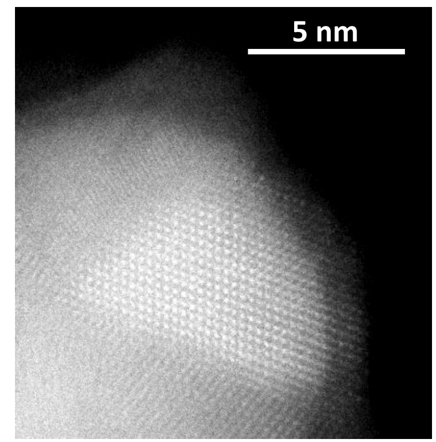
- Electron transparent samples require thicknesses below 1 um, generally 300 nm best
- Electron beam causes radiolysis damage to solution molecules
- Thin film membrane windows and solution create background noise in images
- Membrane window/solution interfaces, charge effects
- Radiolysis products create side reactions, change local chemistry in cell

Scanning 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

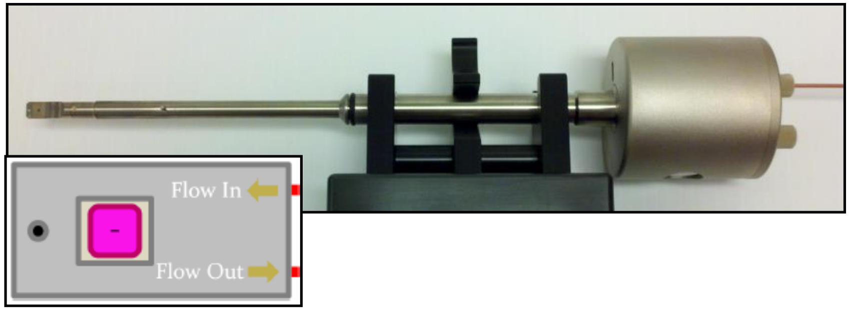
Column vacuum pressure: 10^{-7} Torr

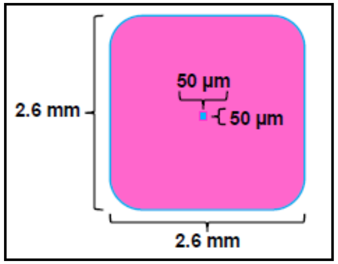


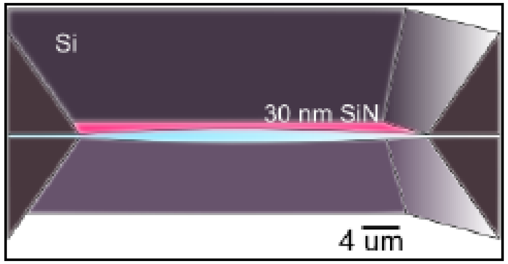
Atomic-resolution imaging and chemical analysis

Liquid Cell Transmission Electron Microscopy

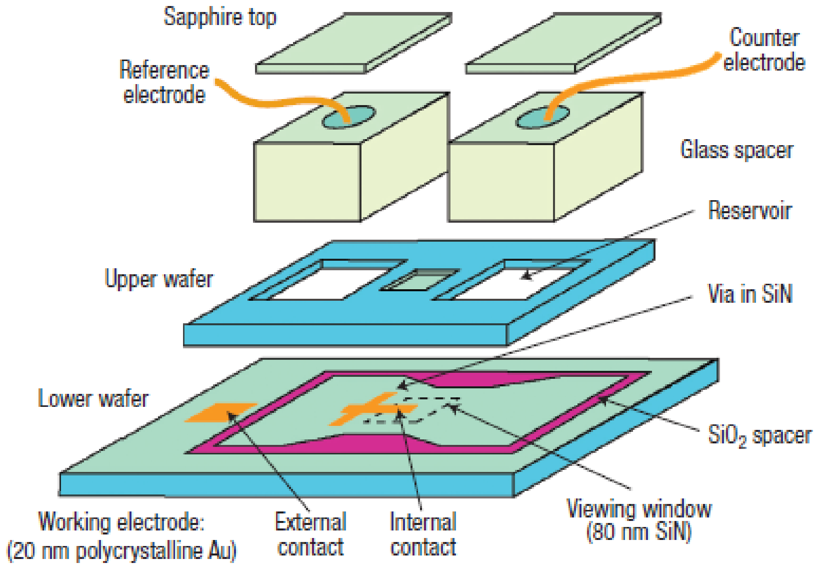
Commercial Microfluidic Liquid Cell TEM Holder



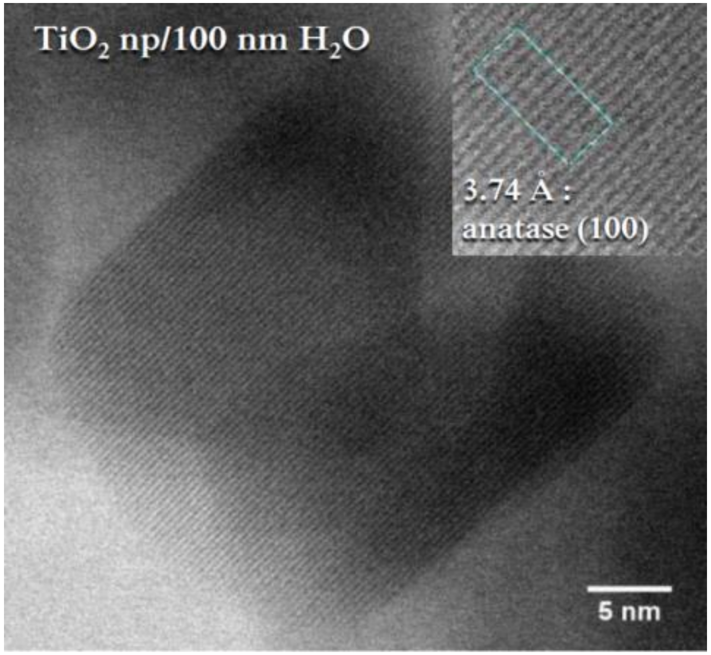




Custom MEMS-based Liquid Cell



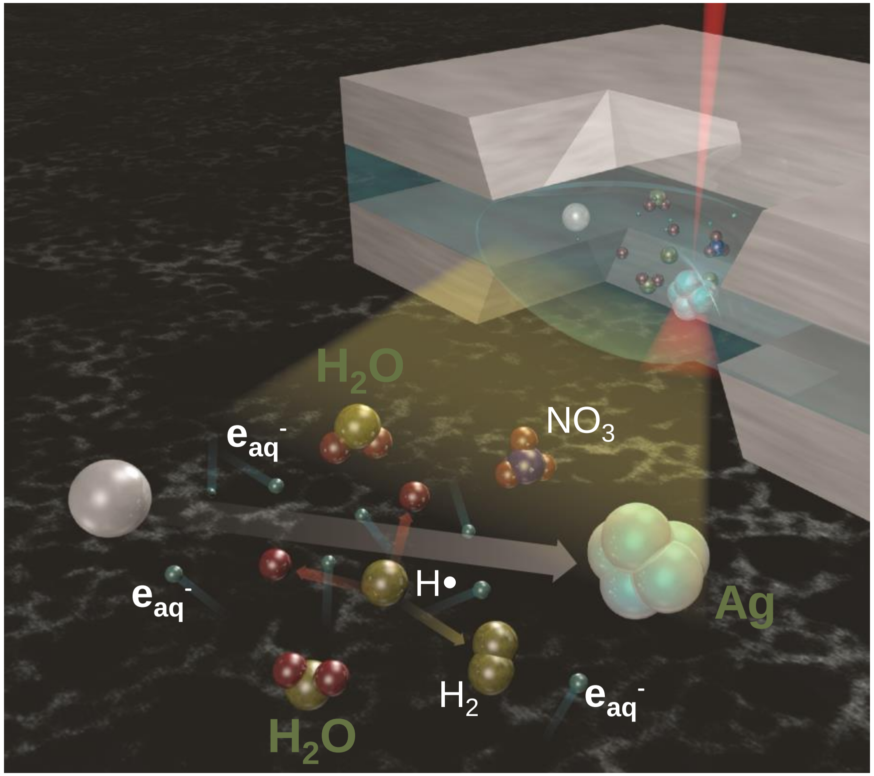
Williamson, M.J. et al. 2003. Nat. Mater. **2**, 532.

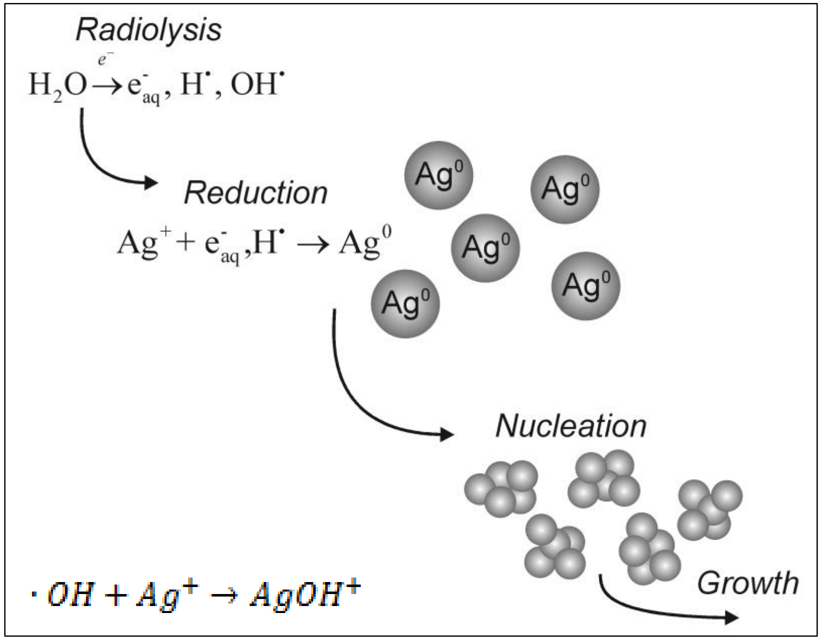


Electron Dose:
ACSTEM: >10^4 e^-/A^2
Low Dose STEM: <10 e^-/A^2

Radiolysis of Water by the Electron Beam

Radiolysis of water and Ag reduction from $AgNO_3$





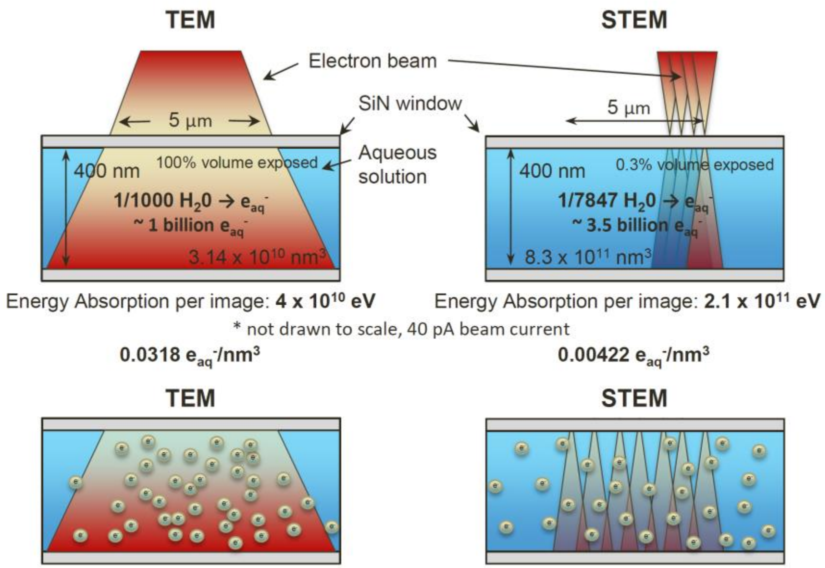
Woehl *et al.*, ACS Nano (2012)
Abellan et al., ChemComm. (2014)

Amount of products formed depends on the electron dose

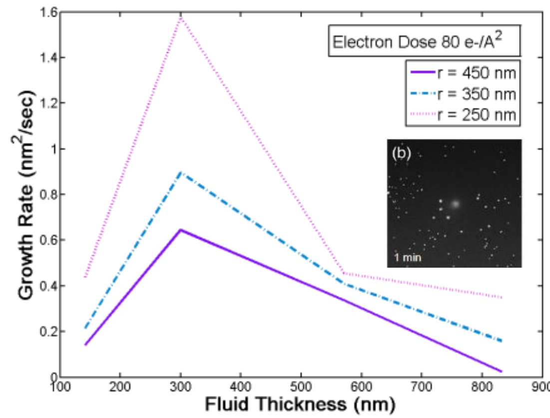
$$H_2O \rightsquigarrow 0.28\ e^-_{aq}, 0.062\ H^\bullet, 0.28\ {}^\bullet OH, 0.047\ H_2, 0.073\ H_2O_2, 0.28\ \mu mol\ J^{-1}$$

Buxton, VCH Weinheim (1987)

STEM Imaging for Controlled Electron Doses

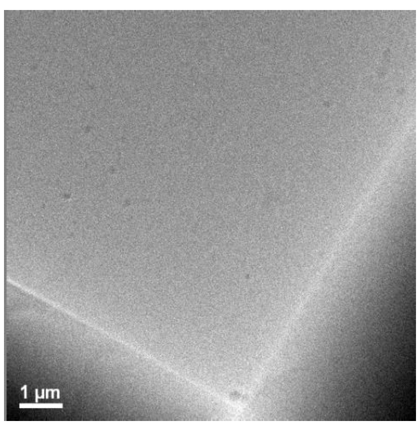


Thickness dependence on Beam Induced Radical Formation

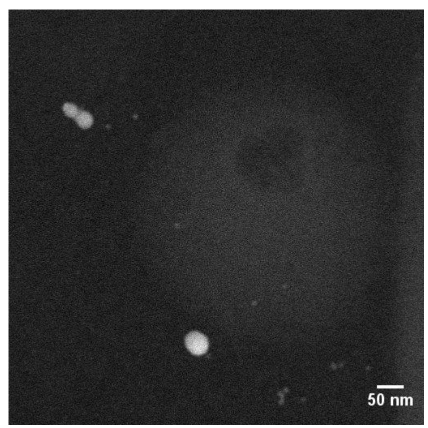


- Maximum solvated electrons were produced at ~ 300 nm thick liquid layers
- Liquid thickness has dramatic effect on beam induced degradation of electrolyte

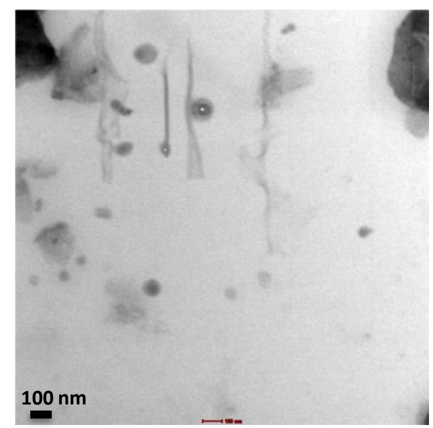
Polymerized Carbon Chains formed in 1 M $LiPF_6$ EC:DMC (0.22 $e^-/Å^2$)



Bubble Formation in Dimethoxyethane (1.46 $e^-/Å^2$)



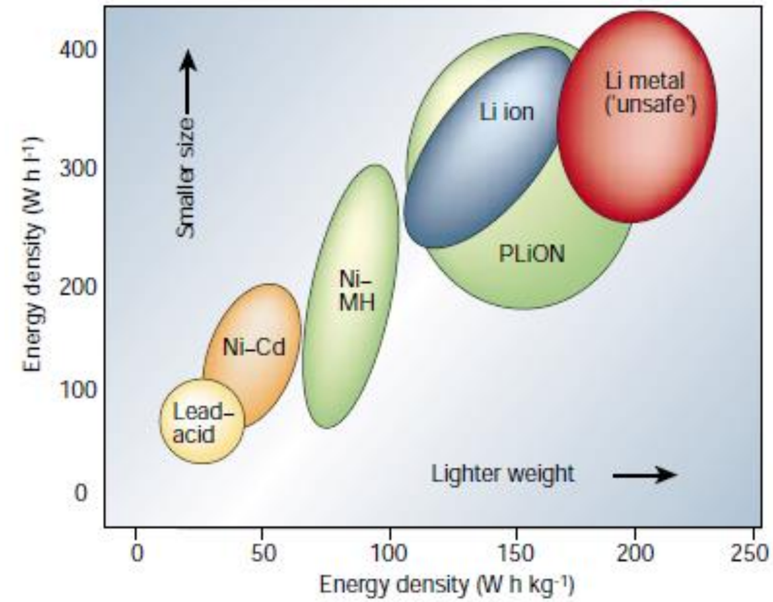
Precipitation in 0.1 M $MgBH_4$ in DME (23.5 $e^-/Å^2$)



Dramatic difference in electrolyte breakdown with air exposure

Li Ion Batteries

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



Why are we using Li-ion batteries?

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

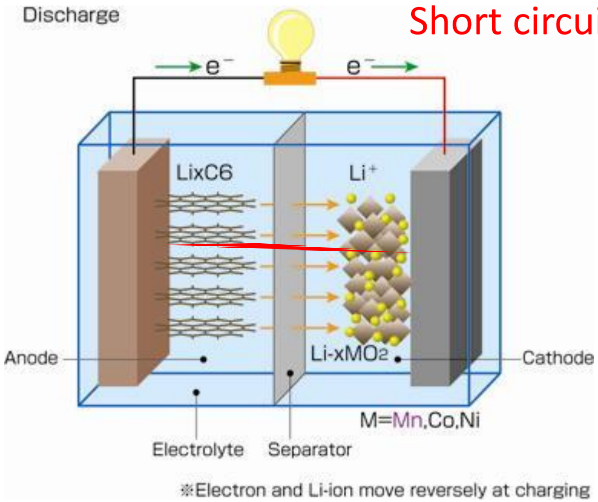
What can we do to improve Li-ion batteries?

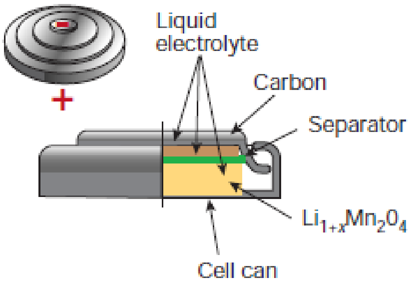
- Increase charge density: new materials
- Increase reversibility for charging/discharging: solve <u>interfacial degradation</u>
- Decrease cost: battery design/materials

Li Metal Anodes for Lithium Ion Batteries

Why don't we use Li metal anodes?

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





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

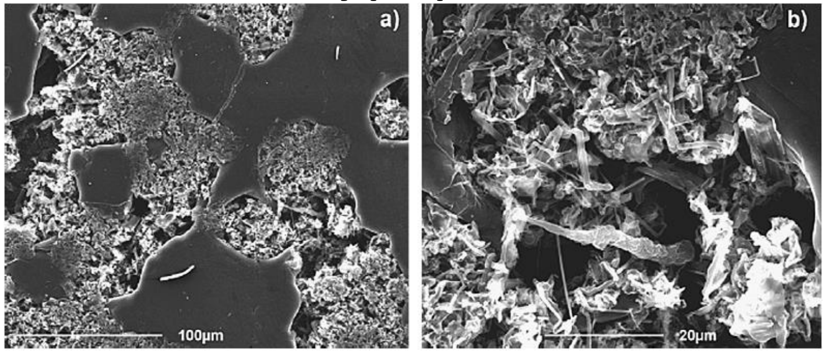
Parameters determining Li morphology

- *Current density*
- Temperature
- *Initial Li metal structure*
- *Electrolyte (solute and solvent)*
- Electrolyte additives
- Electrode stack pressure
- *Environmental considerations*

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

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

Electrochemically prepared Li surfaces



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

Models that Explain Li Deposition Morphology

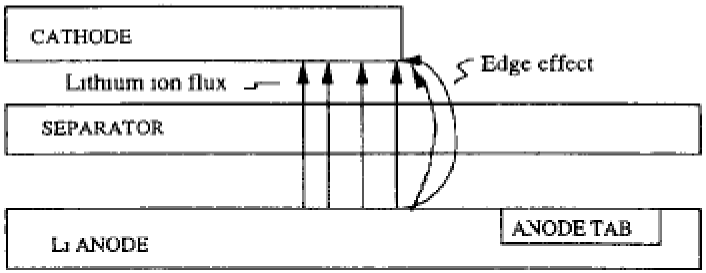
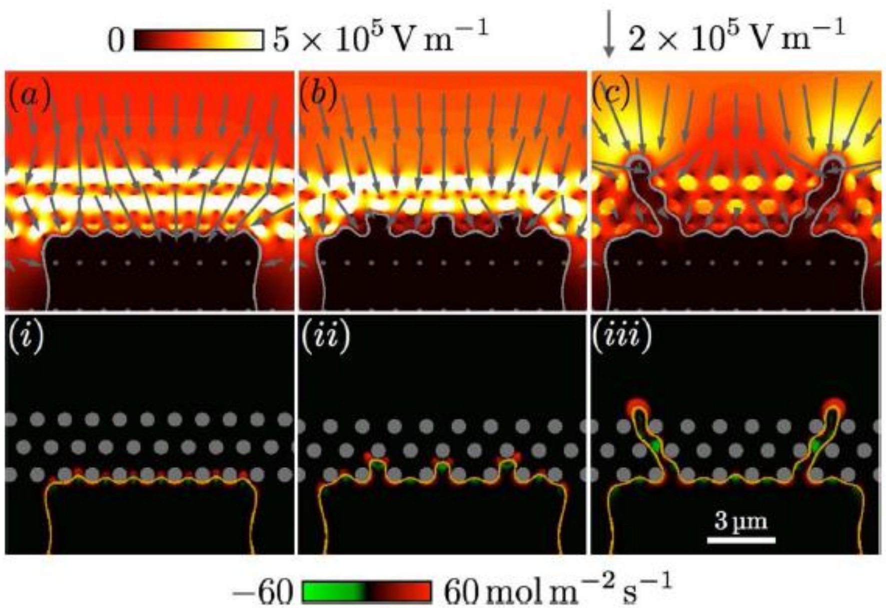
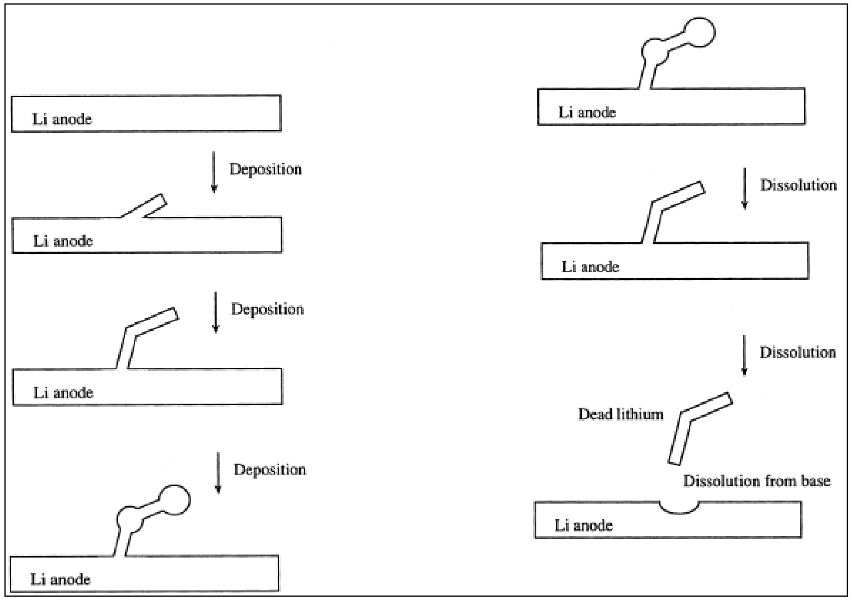


Fig 4 Lithium anode cut at the end of the cathode during cycling

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

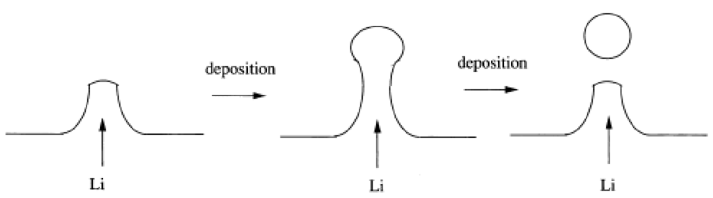


Jana A. et al. 2015. J. Power Sources **275**, 912.

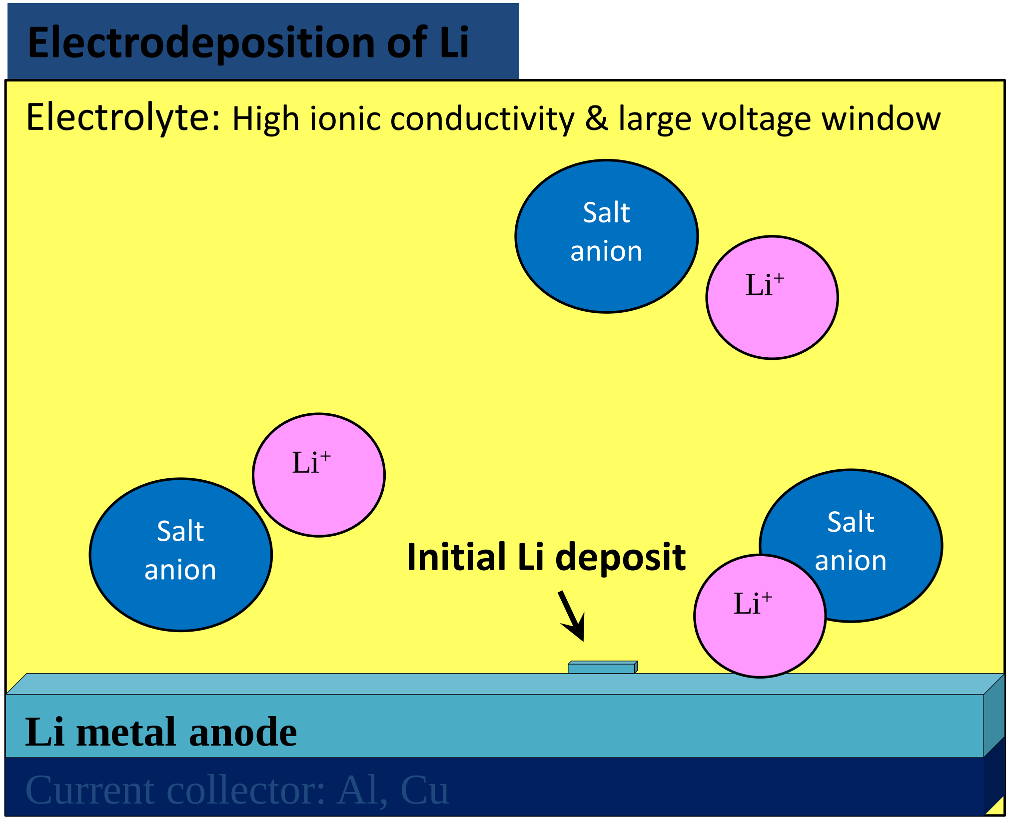


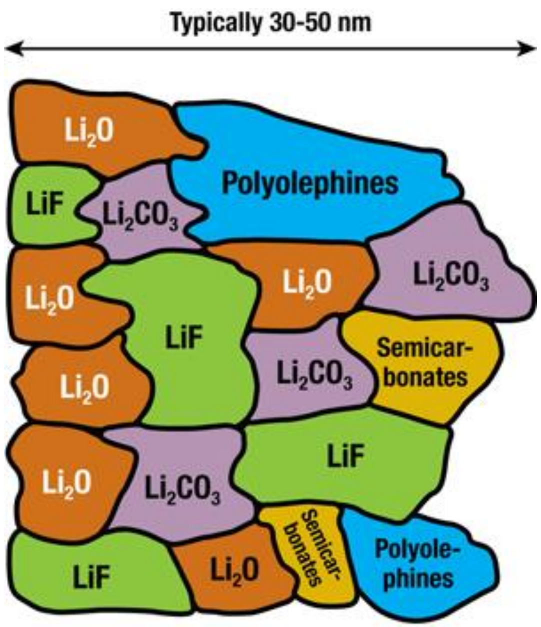
Yamaki, J.-i. et al. 1998. J. Power Sources **74**, 219.

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



Li Metal – Electrolyte Interface





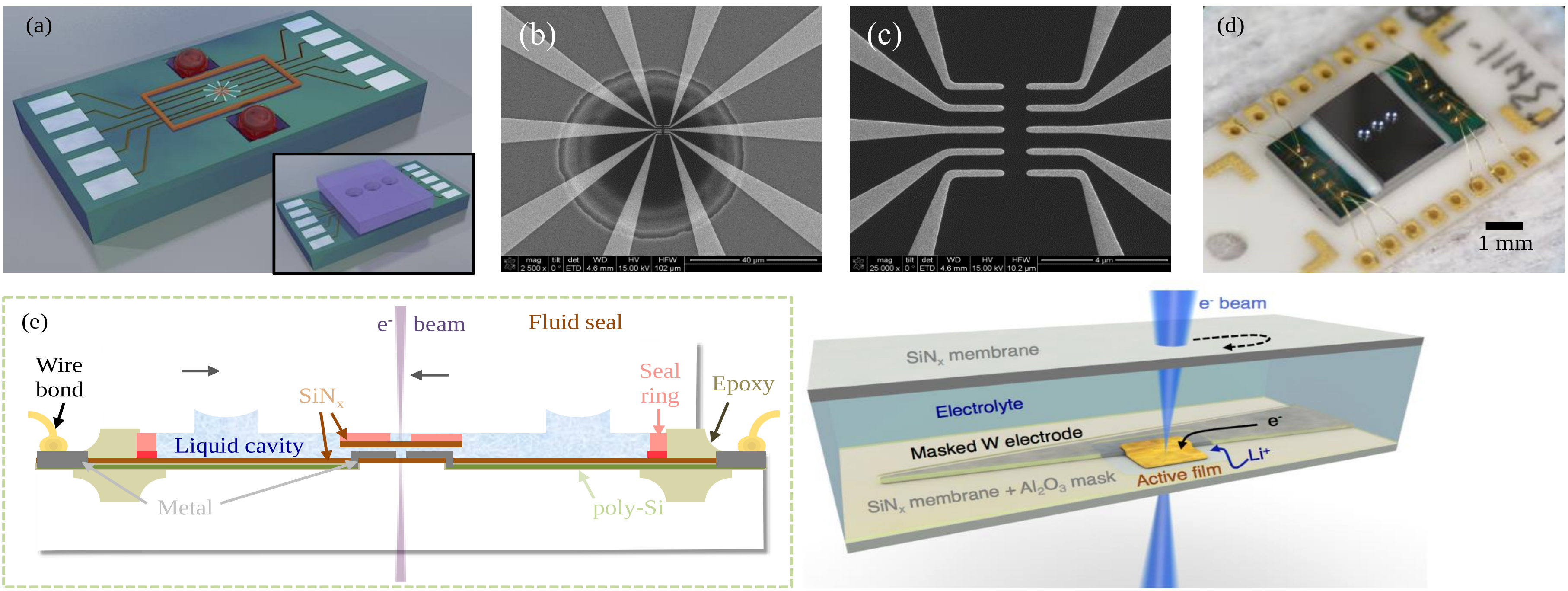
SEI Interface:
Lithium Intercalation into Graphite

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

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

CINT's Electrochemical TEM Discovery Platform

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



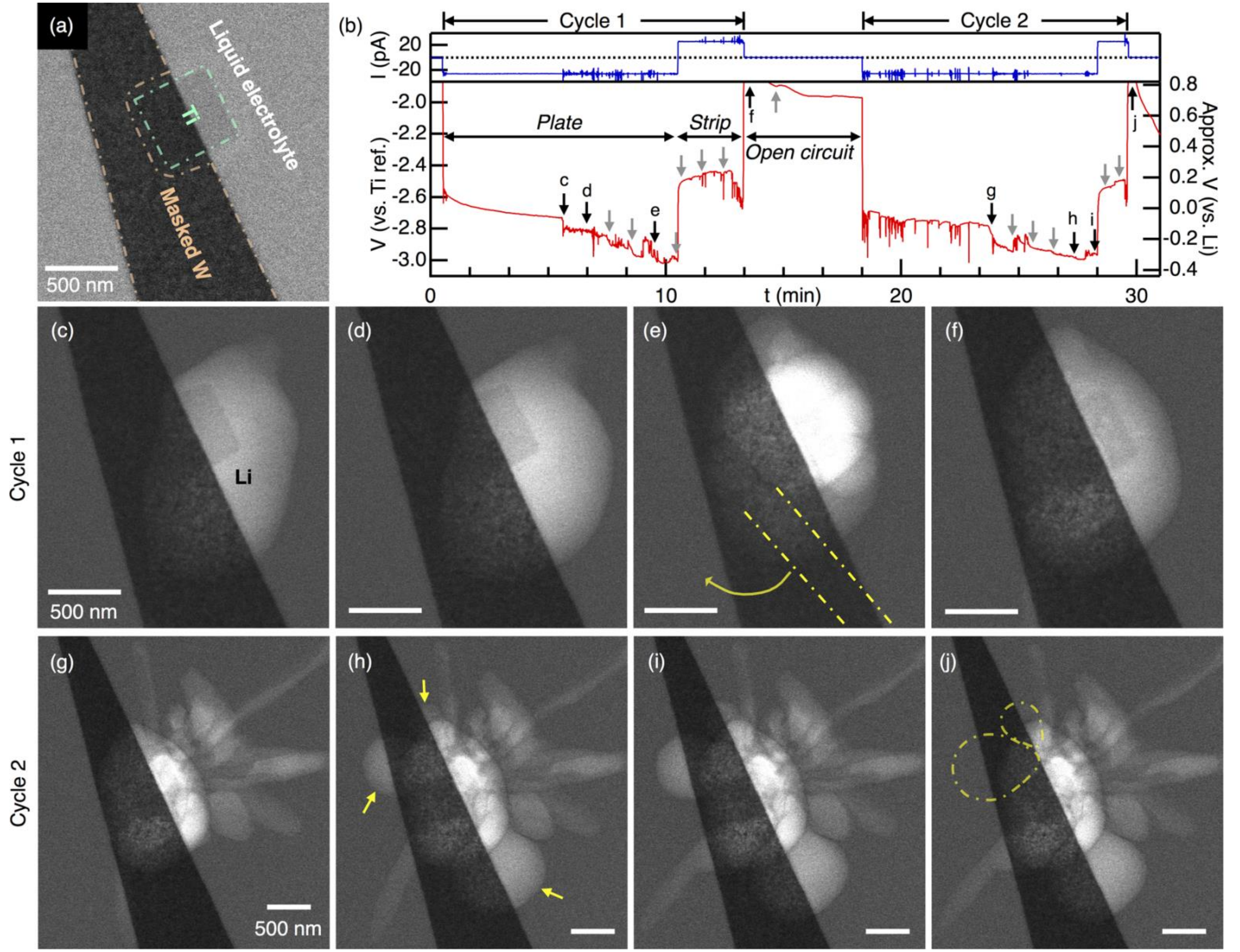
Leenheer et al., (2015) JMEMS. DOI:10.1109/JMEMS.2014.2380771.

Reproducible electrochemical control during imaging

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 $e^-/Å^2$

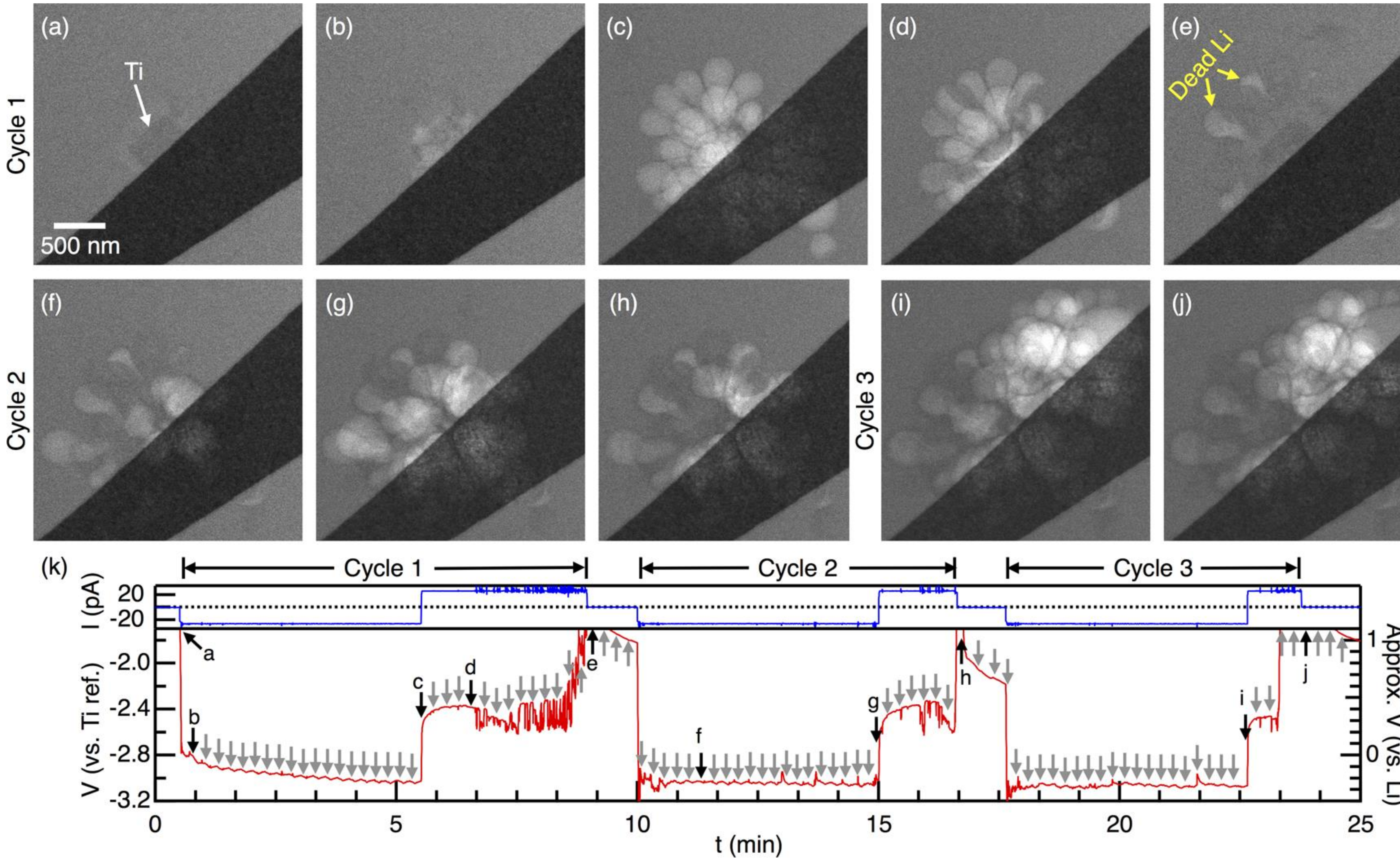
- The electron beam impacted initial Li plating
- Correlate spikes in electrochemical data with nucleation of new Li grains
- Unable to distinguish electrochemically the nucleation of a rounded grain vs. a dendrite



Leenheer et al. (2015) ACS Nano **9**(4), 4379-4389.

Li Morphology: High Electron Beam Dose

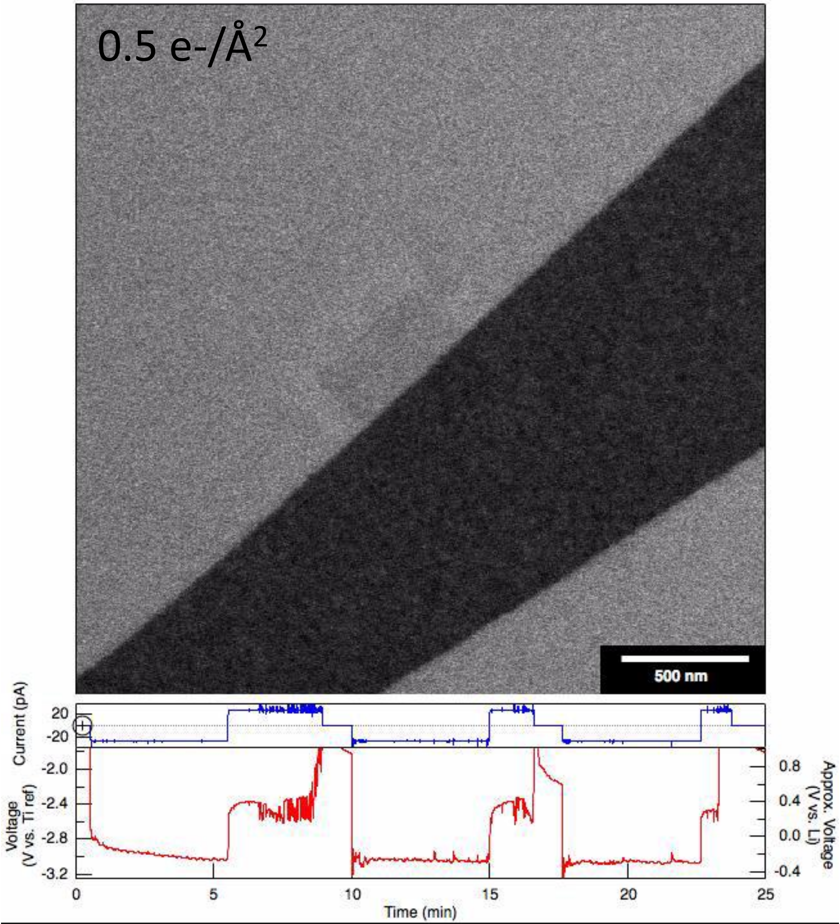
Galvanostatic control at +/- 10 mA/cm^2, Electron dose per image: 25 - 50 e$^-$/Å^2, Imaging every 15 seconds



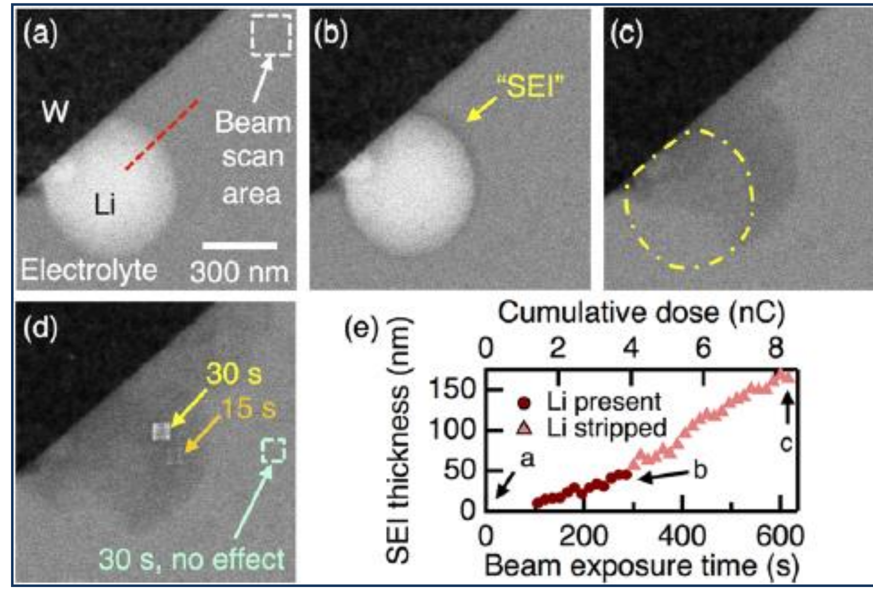
Leenheer et al. (2015) ACS Nano **9**(4), 4379-4389.

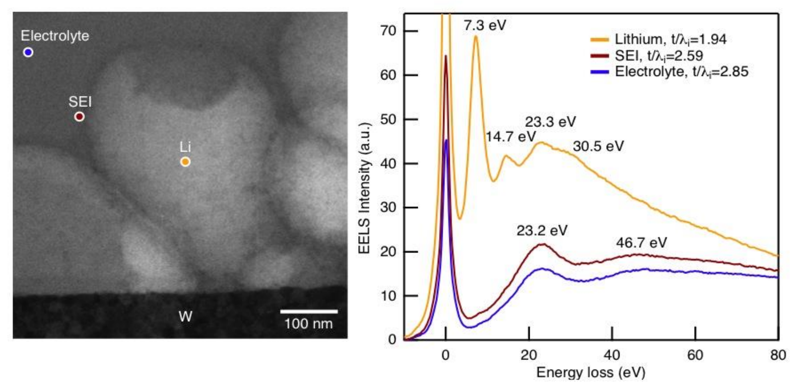
Electron beam increases nucleation and creates rounded Li deposits

How Does SEI Evolve with Cycling?



Leenheer et al. (2015) ACS Nano **9**(4), 4379-4389.





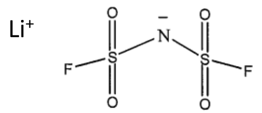
Increased contrast is observed about Li deposits from electron beam induced electrolyte degradation

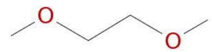
Native SEI characterization is very difficult using an electron beam for imaging/spectroscopy

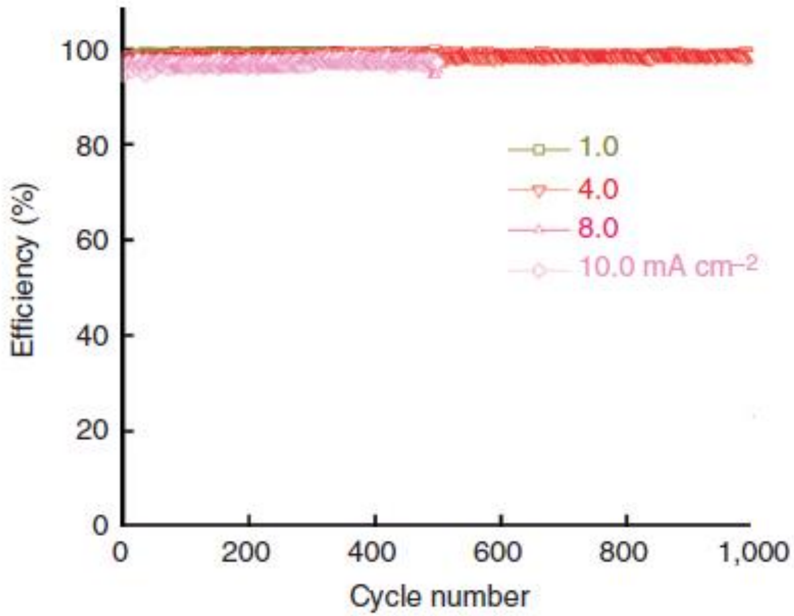
Different Electrolyte Suppresses Li Dendrites?

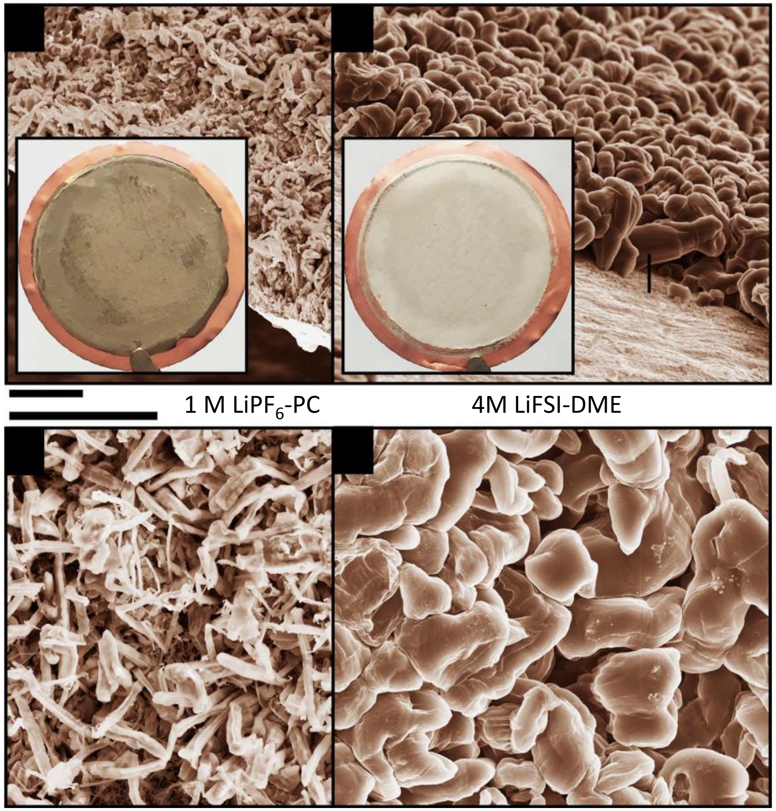
Technical challenge

- 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





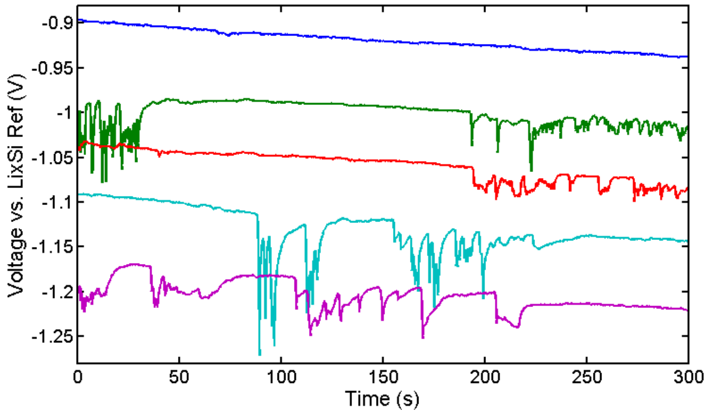


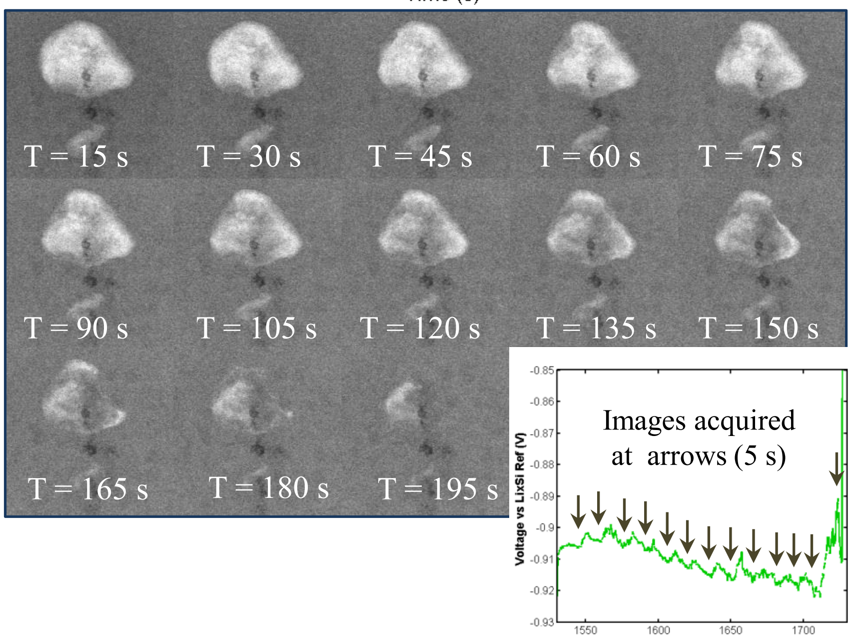


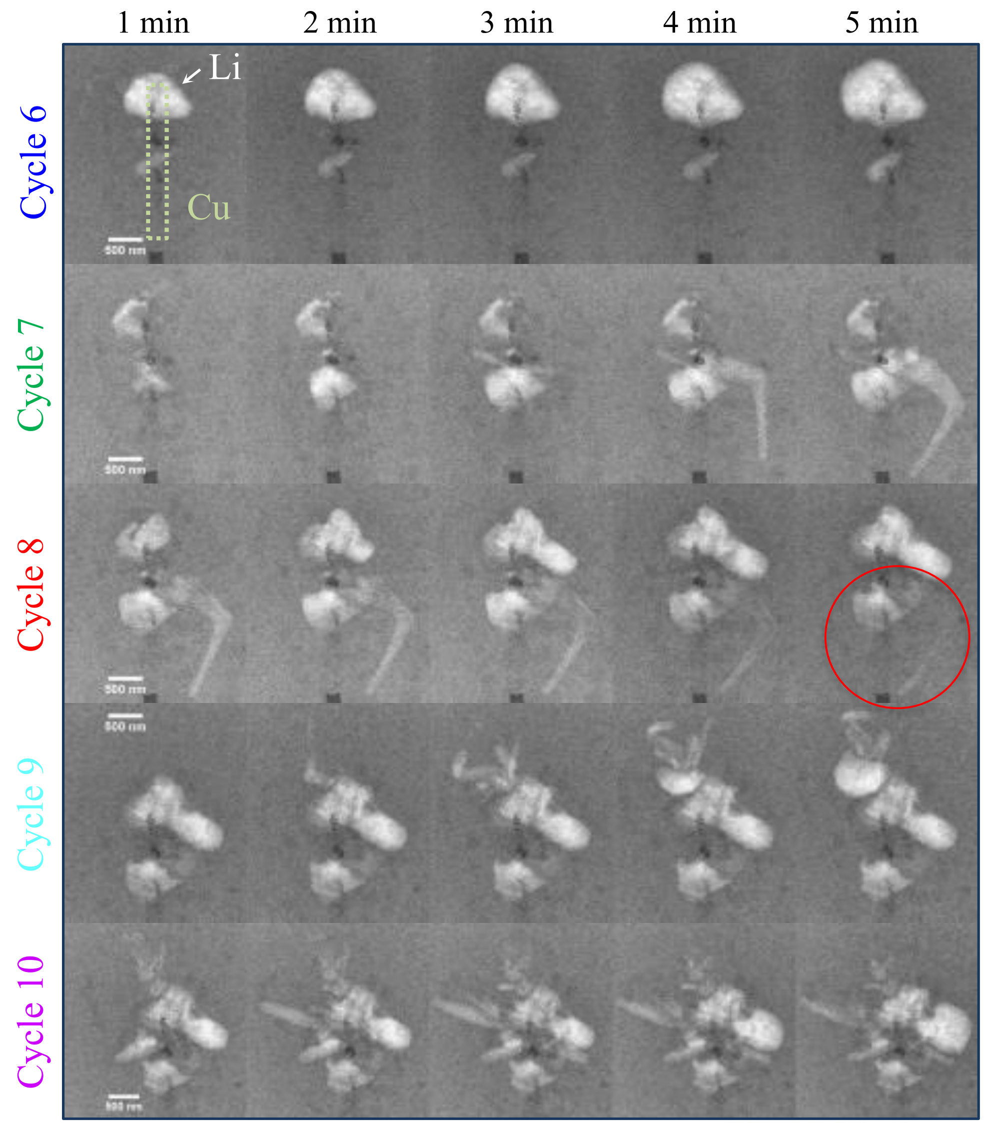
Qian et al., Nature Comm. 6, 6362 (2015).

Effects of Multiple Cycles on Li Nucleation

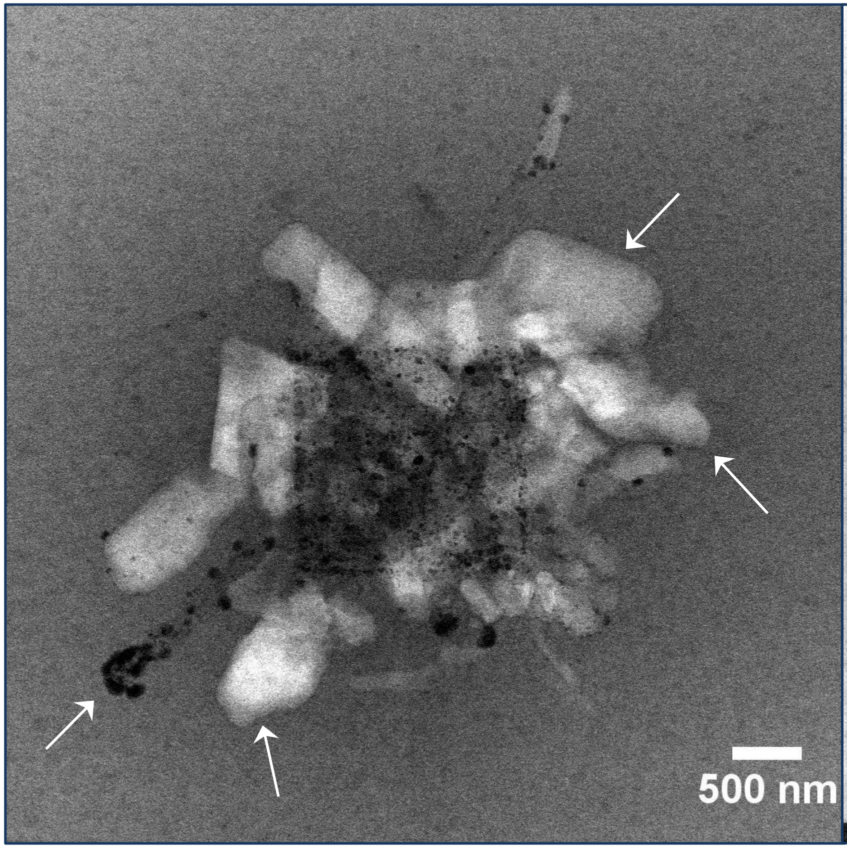
WE #2 Cu: **2.25 mA/cm²** for 5 min deposition

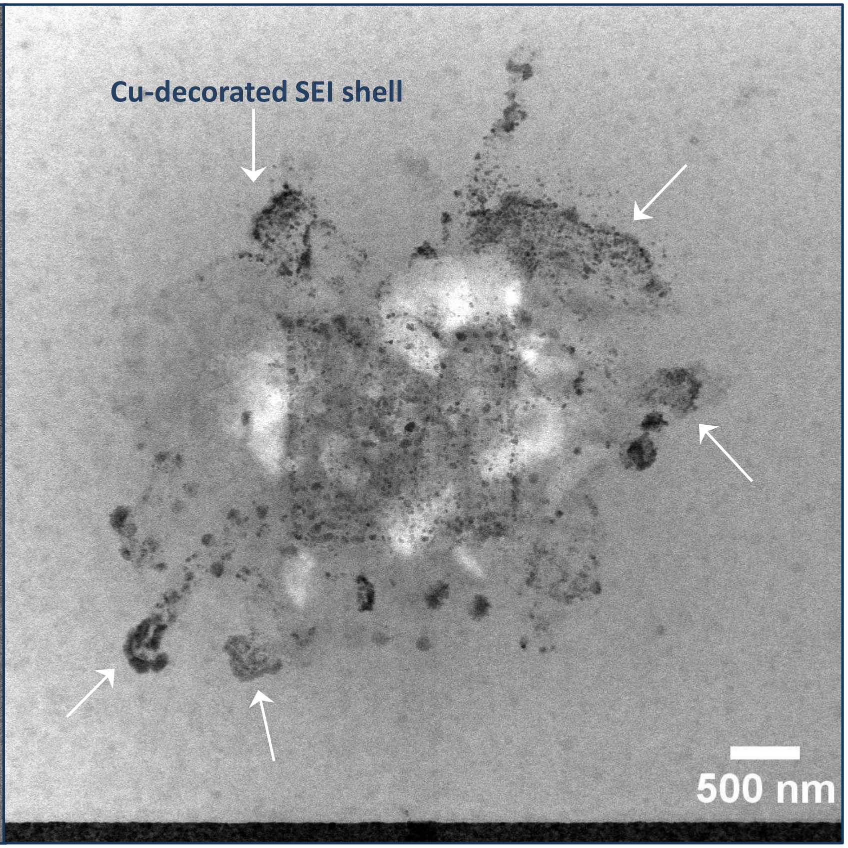






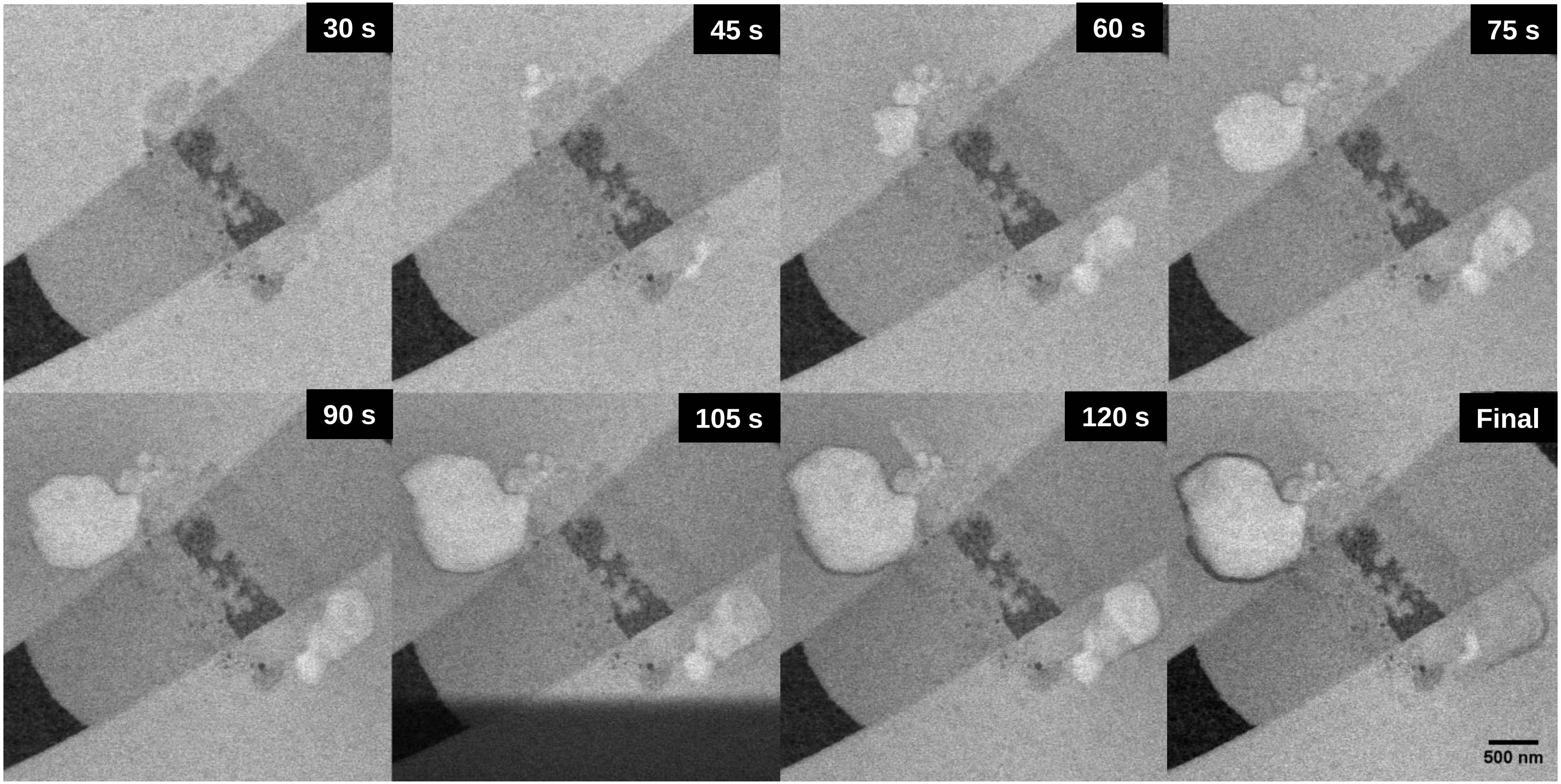
Self-Discharge During Li Plating on Working Electrode





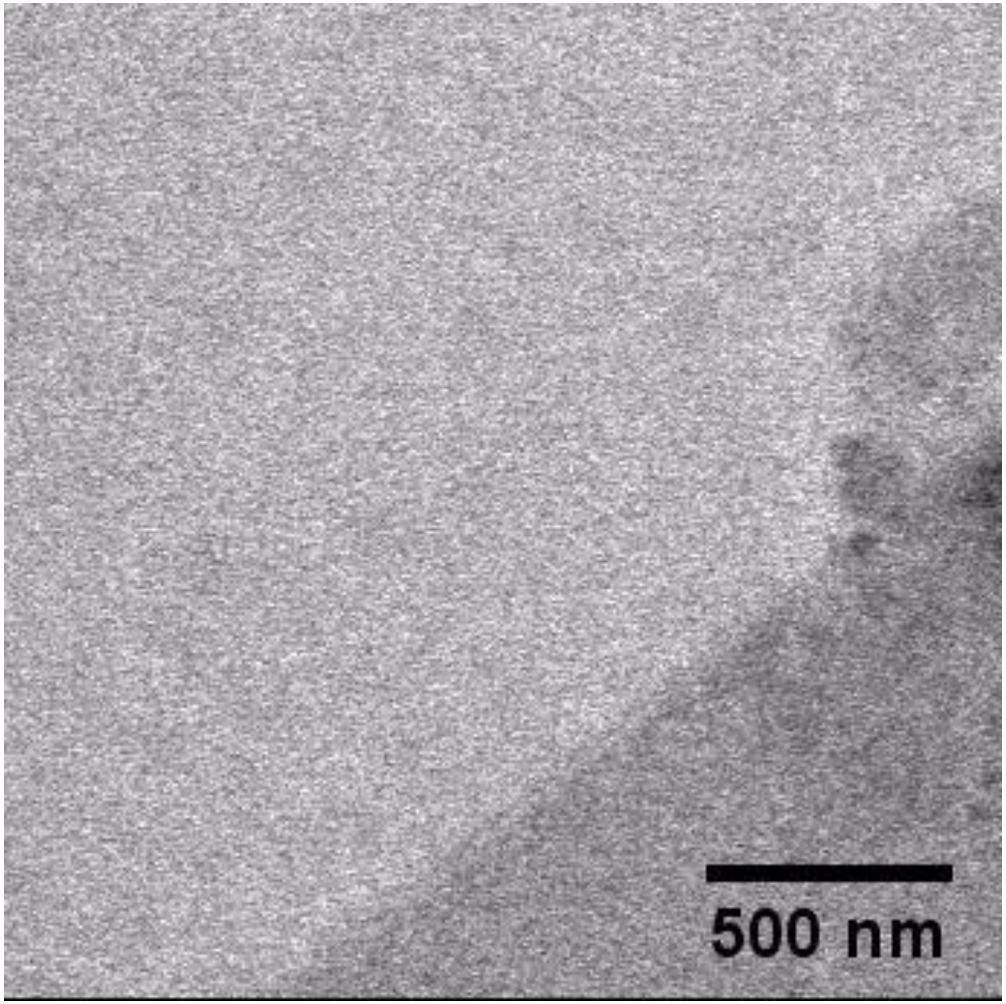
Li Deposition on Surface of Metal-Infused SEI

(Degradation and dissolution of the Ni metal counter electrode produced mobile metal ions that deposited along with the SEI to form a e- conducting SEI on the metal electrode surface)



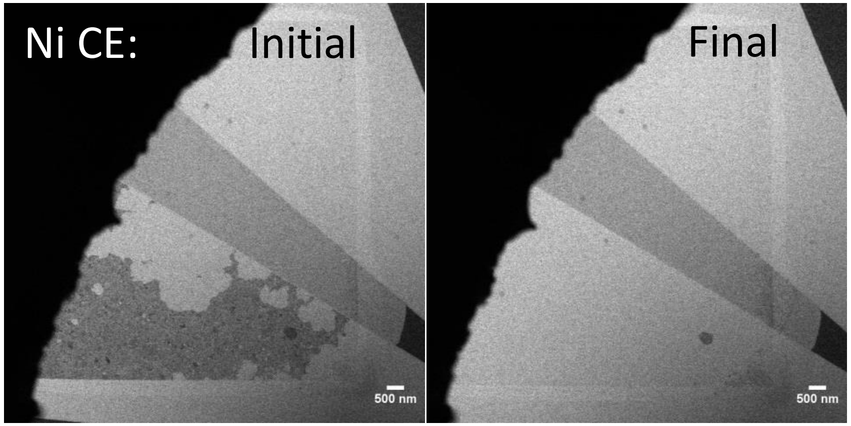
Li Transport Pathways

(Deposition and stripping typically occur from the triple-point where the Li grain/electrode/electrolyte or SEI meet)



- 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 $e^-/Å^2$
- Current Density: 6 mA/cm^2
- Electrolyte Thickness: 500 nm

Although SEI cracks and Li grain grows, it is quickly impeded by rapid SEI formation over the grain and closure of the Li ion transport.



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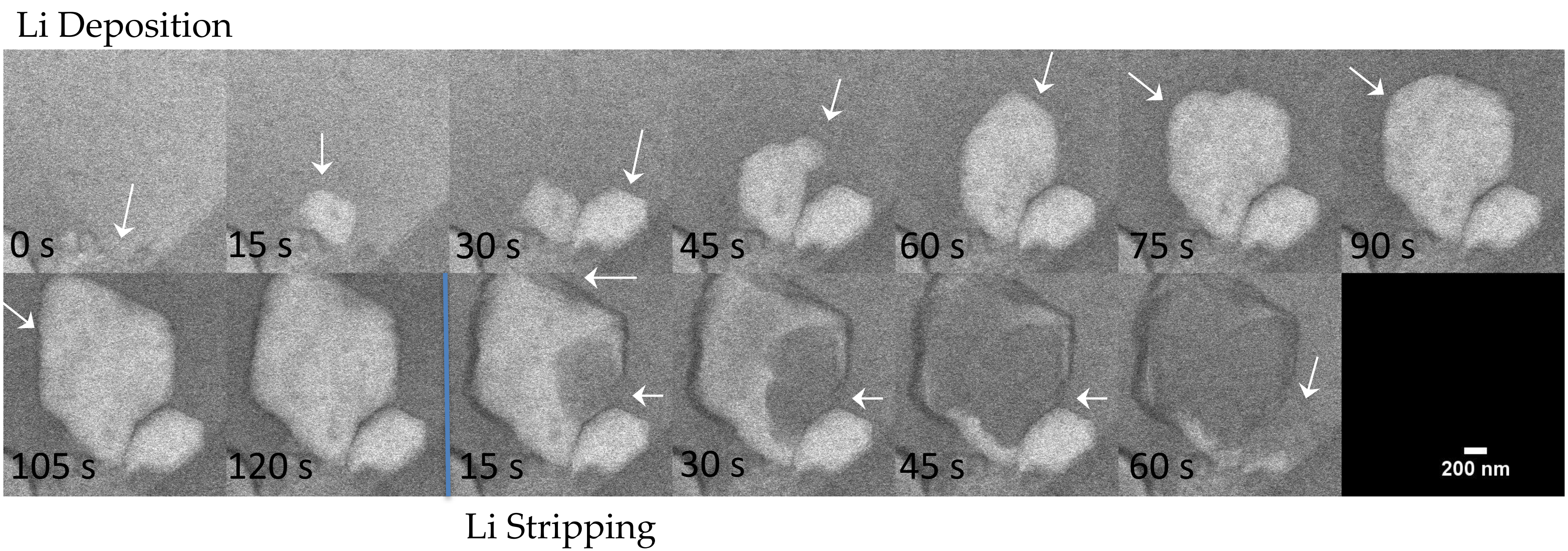

- Ni WE Area: ~1 µm^2
- Ni RE & CE Areas : 100 µm^2
- Electron Beam Dose: < 2.53 e$^-$/Å^2
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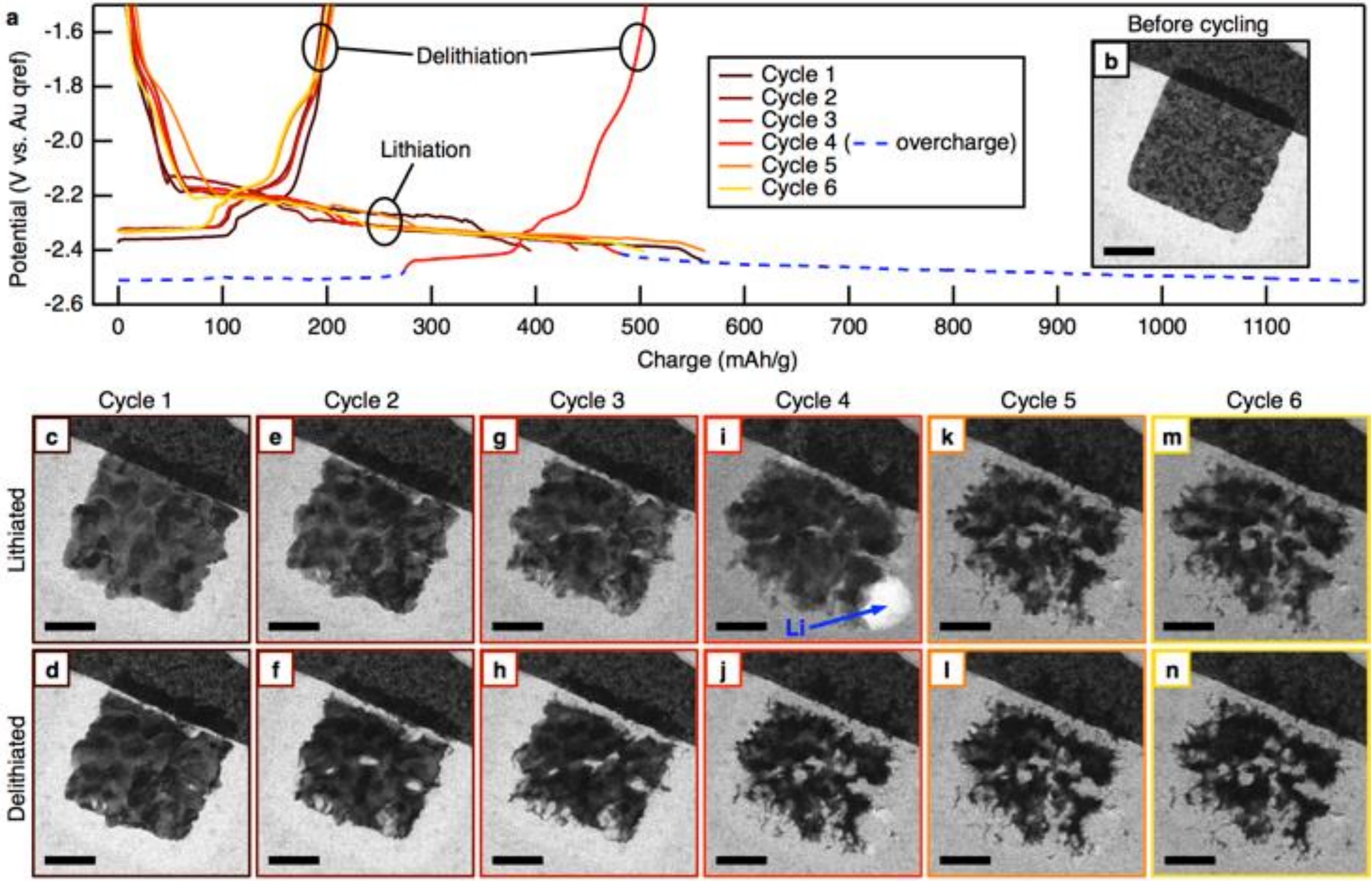
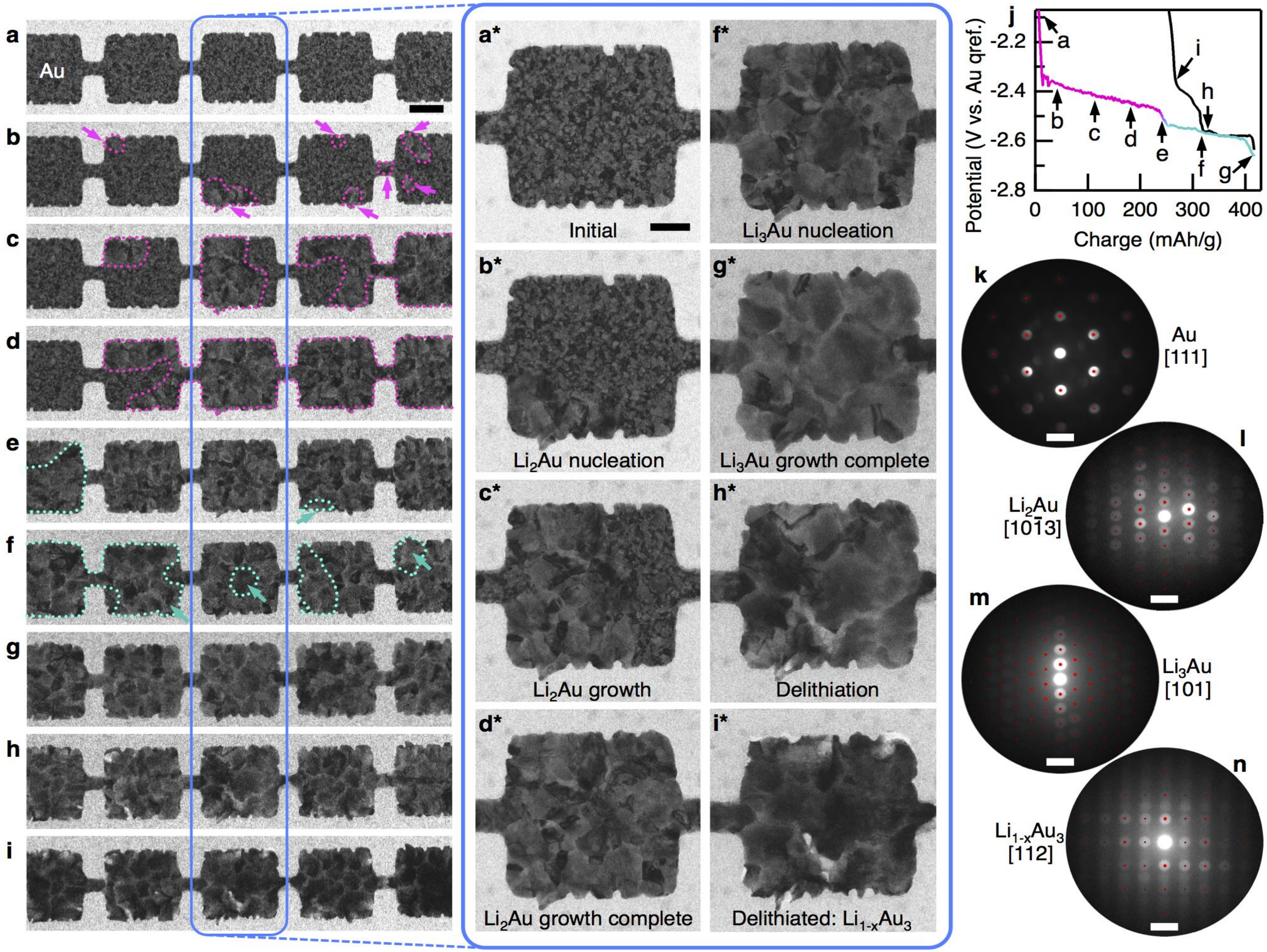
- Current Density: 6 mA/cm^2
- Electrolyte Thickness: 500 nm

Li Alloying of Au: 1M $LiPF_6$ in EC/DMC



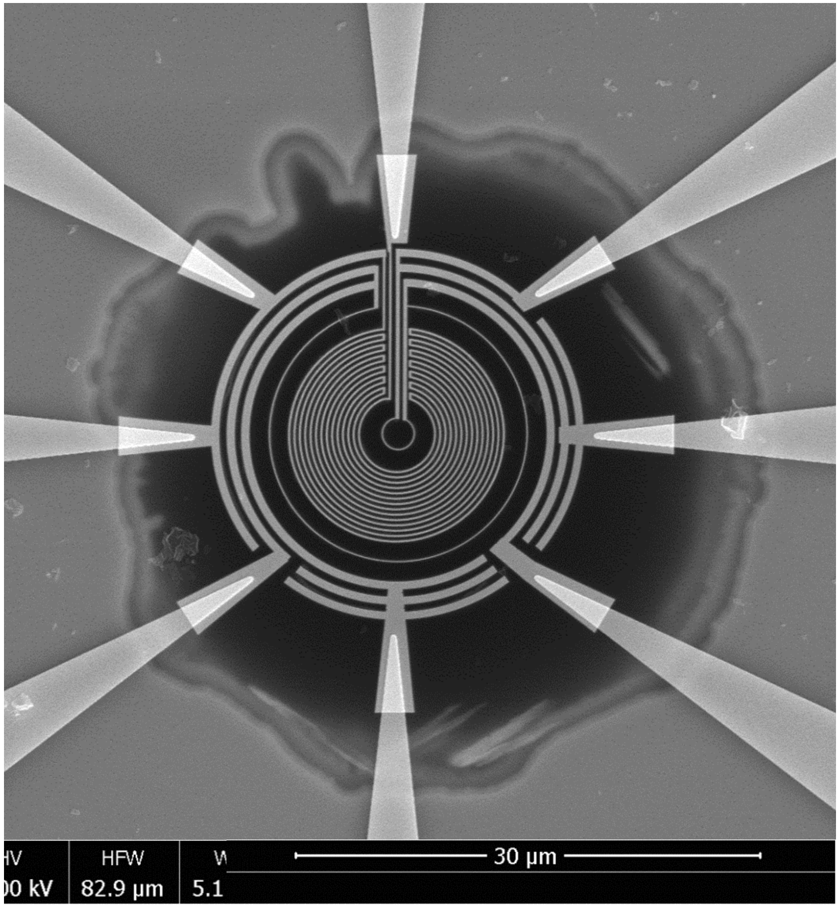
Leenheer et al., ACS Nano **10**(6), 5670 (2016)

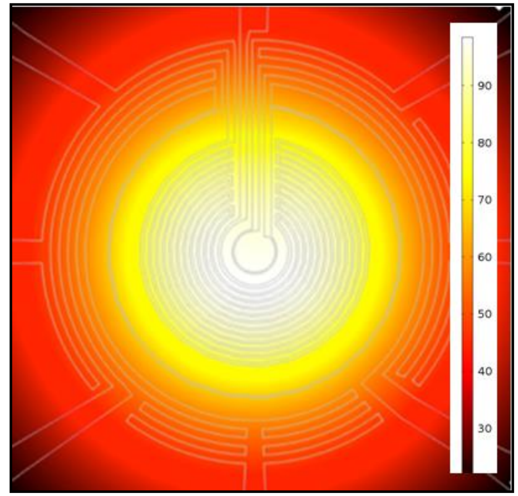
Li Alloying of Au: Discrete Initiation Sites for Alloying

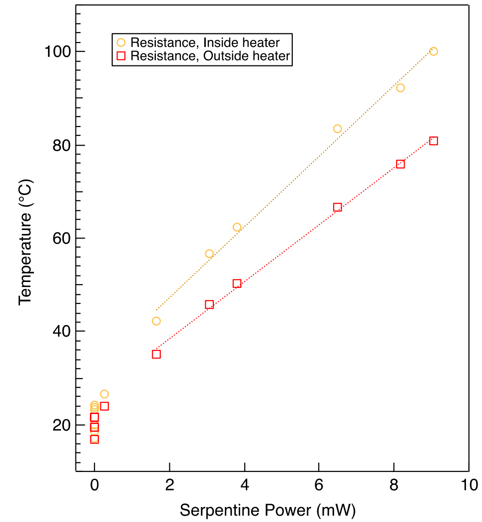


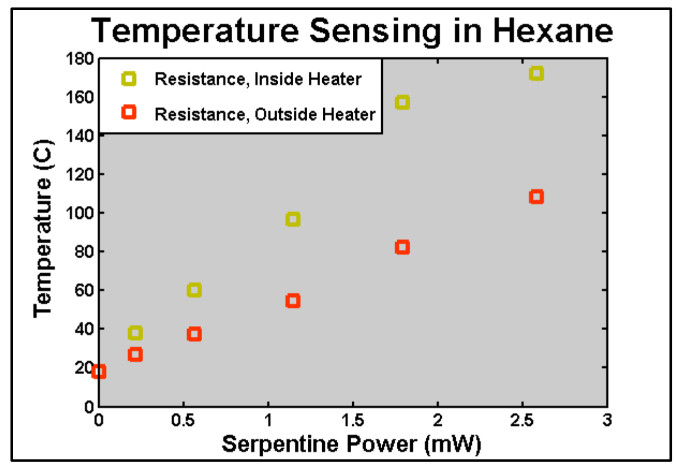
Leenheer et al., ACS Nano **10**(6), 5670 (2016)

Temperature Control up to 175°C





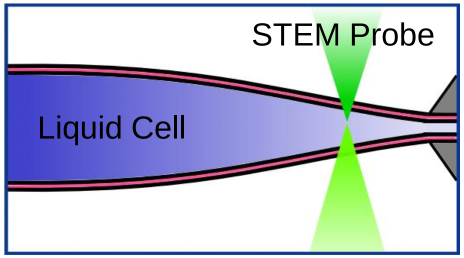


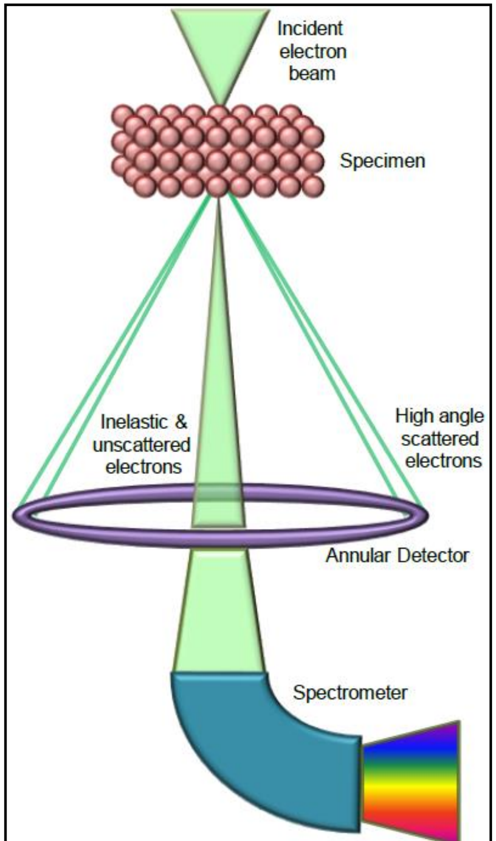


445 K

Liquid thickness plays a larger role in heating calibration than the liquid thermal conductivity, therefore measurement of the temperature changes on column is preferable

Measuring Water Thickness using Electron Energy Loss Spectroscopy





t/λ_i values : measured using EELS
t : thickness of material (nm)
λ_i : inelastic mean free path of e^- through the material

Atomic Number Formula

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

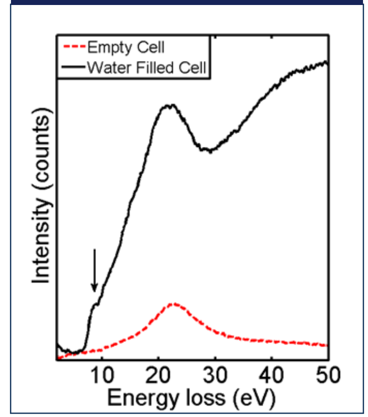
$$E_M = 7.6 Z^{0.36}$$

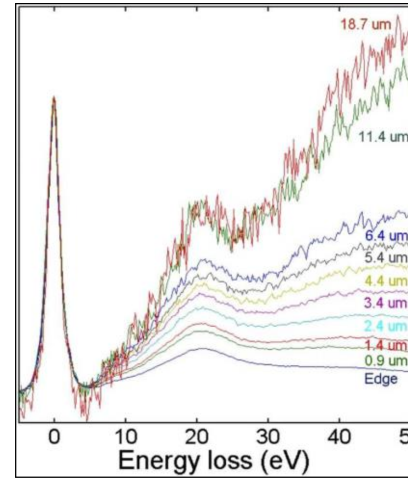
$$\lambda_i = \frac{106 F E_0}{E_M \ln((2\beta E_0)/E_M)}$$

- 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*

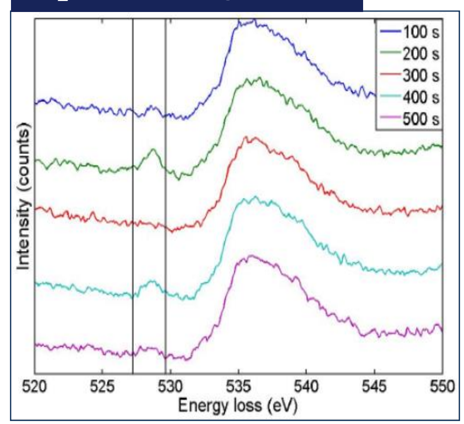
Malis et al. *J. of Elec. Micro. Tech.* **8**, 193-200 (1988).

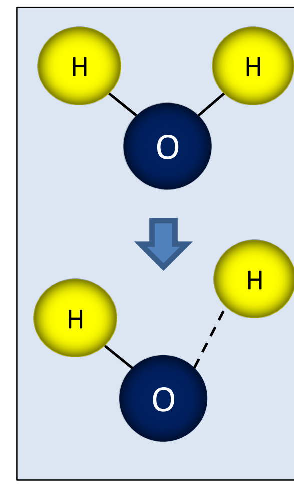
Low Energy Loss





H_2O: O k-edge





Jungjohann et al., Micro. Microanal. **2012**, 18, 621.

Conclusions

- Imaging at atomic to nanoscale in solution
- Temporal resolution is limited to seconds
- Not imaging ions, though seeing structural changes in solids
- Radiation damage limits our electron dose, and high-magnification imaging of native processes
- Able to relate the structural changes in electrodes to electrochemical data
- Future work:
  - larger and more sensitive detectors (same electron dose more information)
  - Imaging Li metal working electrodes instead of metal (Cu, Ni, Ti)
  - Mapping electrode initial structure to identify ‘deposition initiation regions’

Center for Integrated Nanotechnologies

CINT Core Facility: Albuquerque, NM

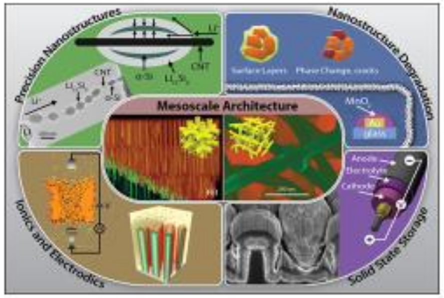
CINT Gateway Facility: Los Alamos, NM

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

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

John Sullivan, SNL

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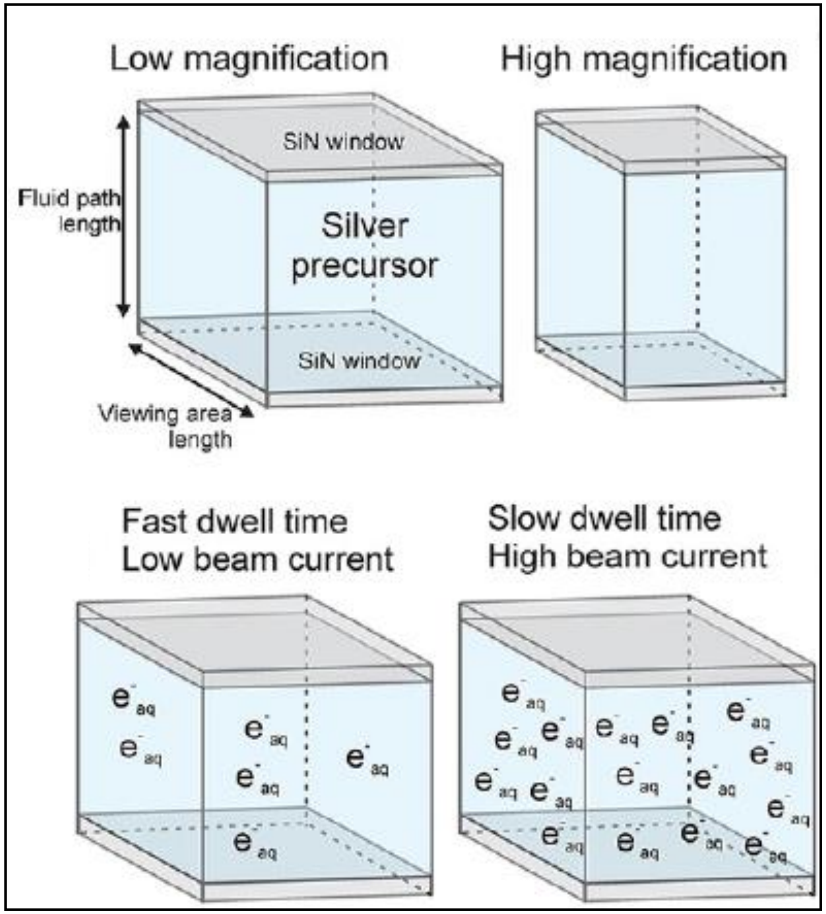
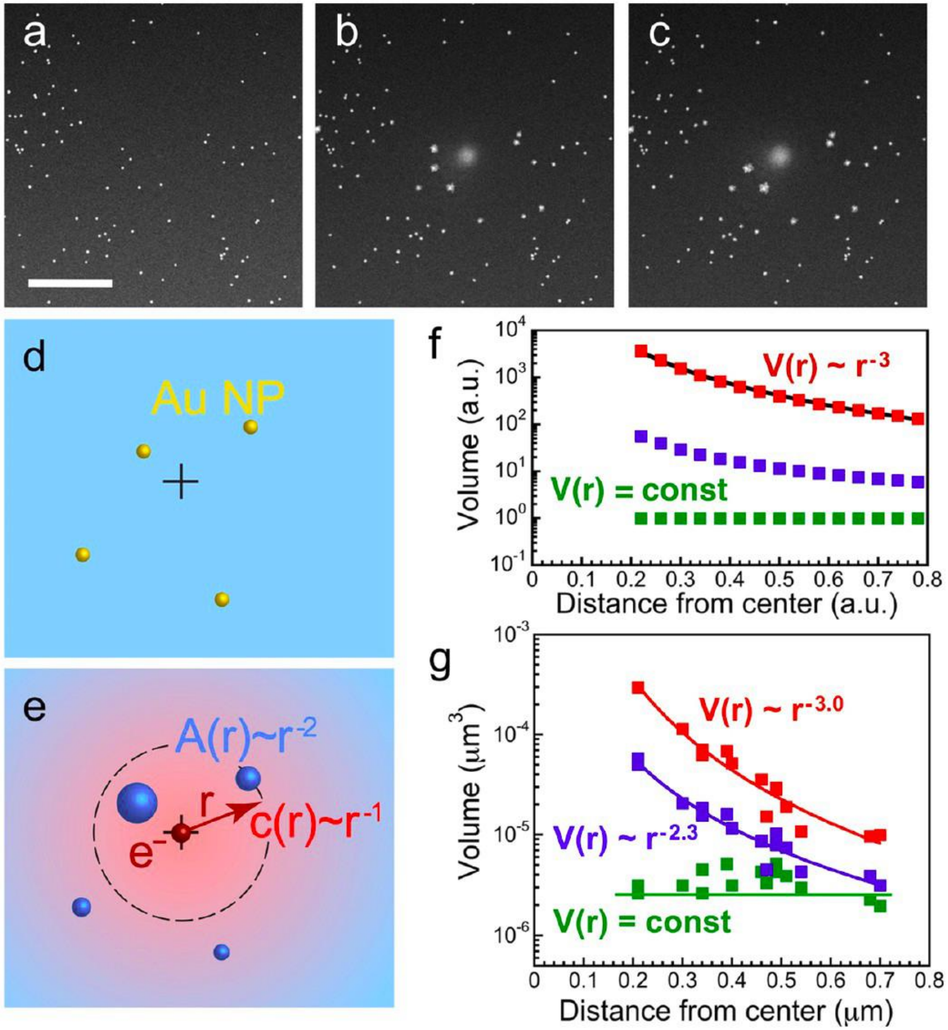
Scanning TEM to Control Radiolysis Product Production



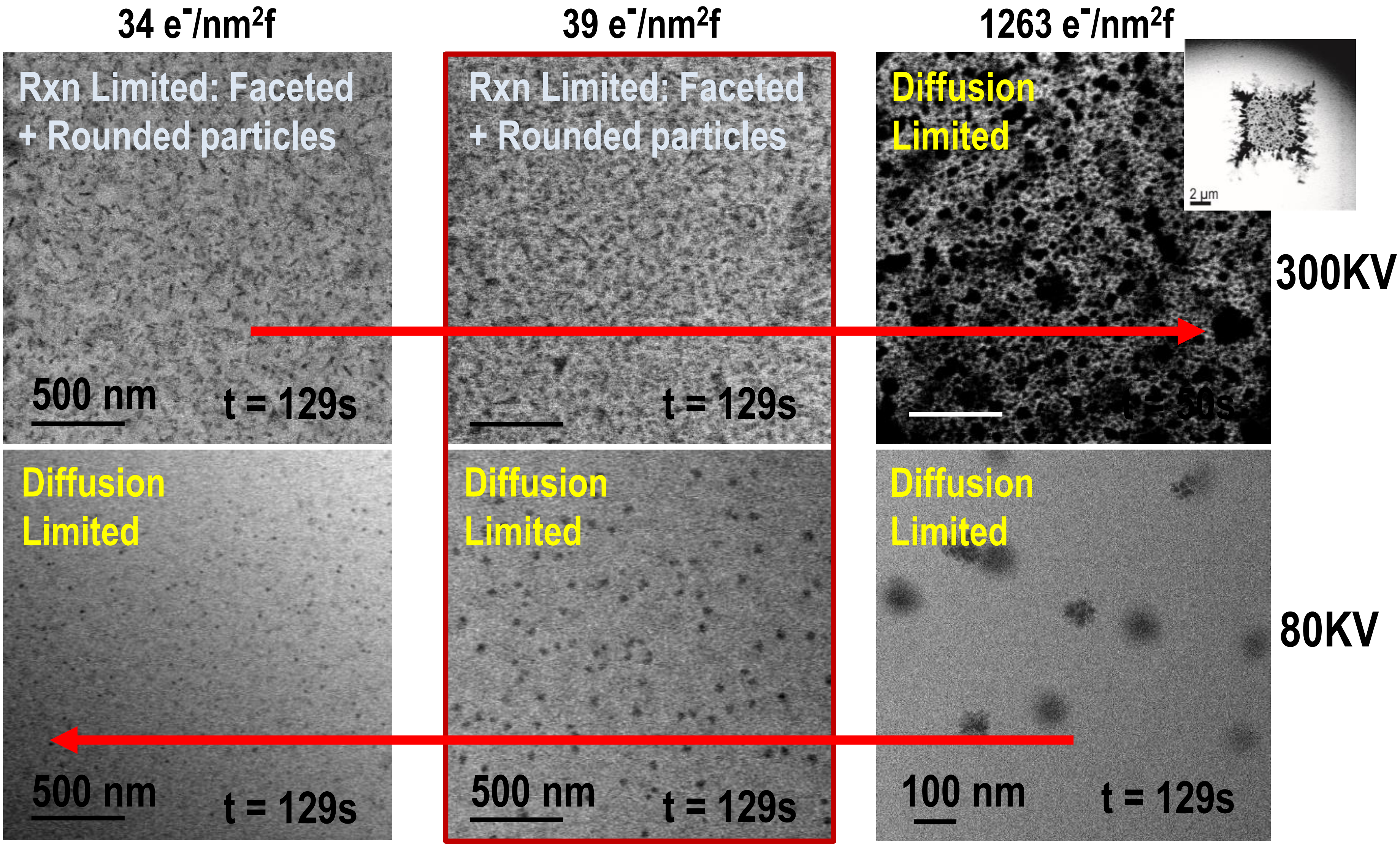
Woehl et al. ACS Nano **6**, 8599 (2012).

- Electron beam current
- Pixel dwell time
- Magnification



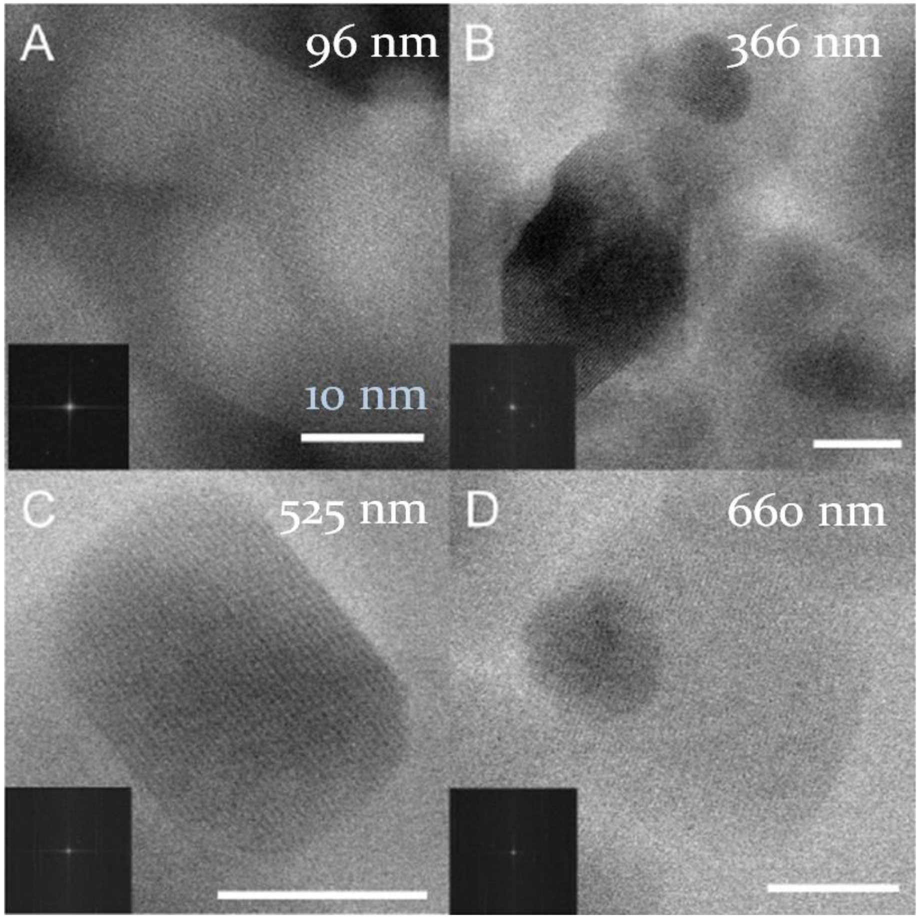
Jungjohann et al. Nano Lett **13**, 2964 (2013).

Aqueous Electrons Concentration can Control Nanoparticle Growth Mode



Abellan et al. CISCEM 2014 & AIEP 2015

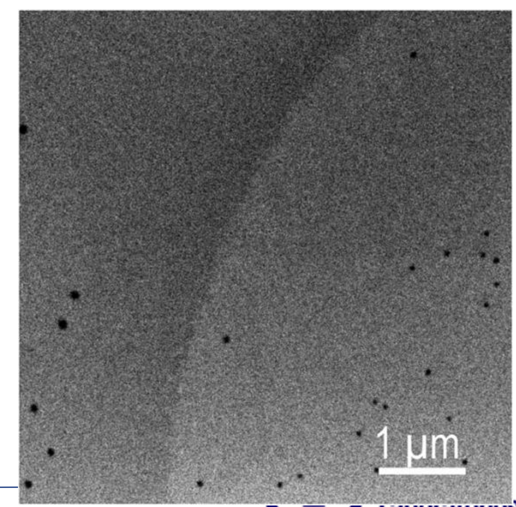
Liquid TEM Resolution and Limitation of HRTEM Imaging



<u>TiO_2 nanoparticles in water</u>

- 30 nm SiN membrane windows
- Water thickness increased
  - 96 nm
  - 366 nm
  - 525 nm
  - 660 nm
- Contrast from fringes decreases with increased background scattering from water

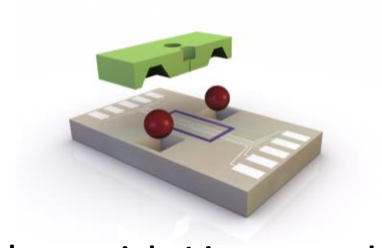
E-beam radiolysis damage produces hydrogen gas bubbles



Abellan et al. ChemComm 2014

Pristine Li Working Electrodes within EChem Platform

(previous attempts have been hindered by epoxy poisoning during curing and increased liquid layers due to scraping thick smudge of Li metal on electrodes)

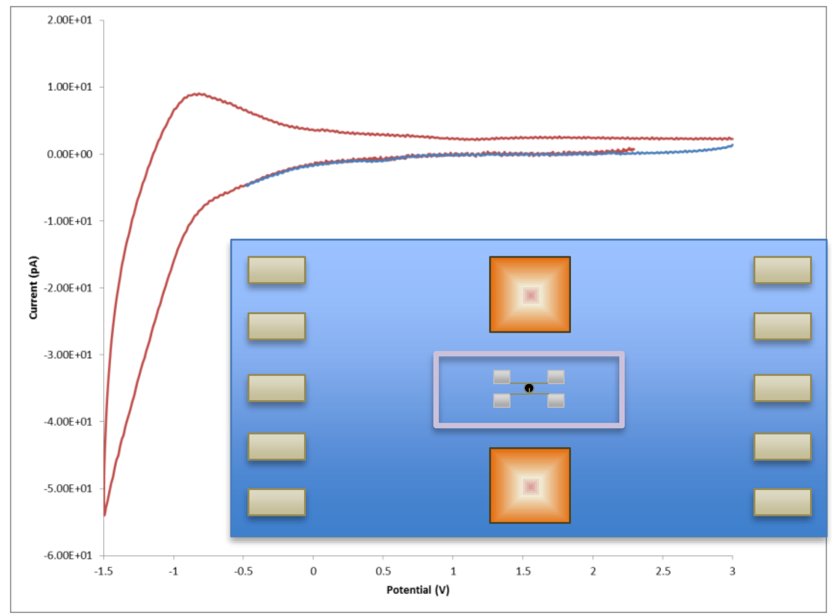


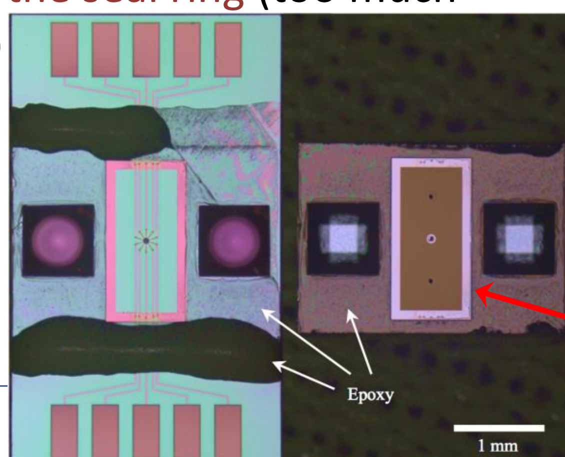
Epoxies Tested:

- Loctite LV Hysol 1C – outgassing
  - blocking layer with tape, metal
- Torr seal – outgassing during curing
- Crystal Bond w/DP100 for liquid sealing – not mechanically strong enough
- M Bond 610 – THF reacts with Li
- Chlorinated polyolefin thermoplast – toluene evaporation effected the Li metal, also tested with pentane
- UV Cured Masterbond
  - Low (UV15TK) and high viscosity wicked into the seal ring (too much Li scraped?)
- Silicone

Other Methods Tested:

- Inserting W metal probes with Li scraped on tips in through the fill ports, not at Li potential due to contact with Si?
- Formation of a AuIn alloy on seal ring

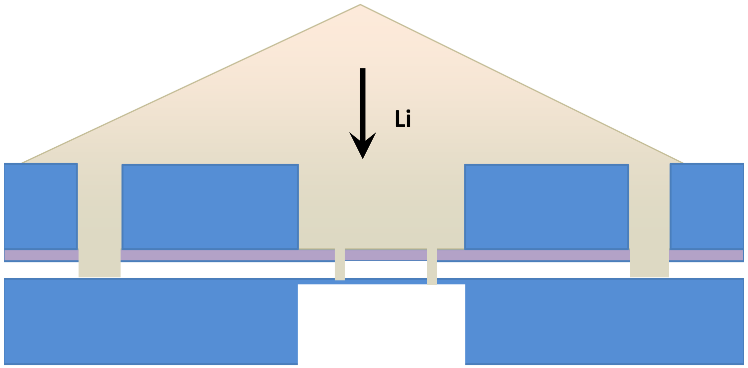


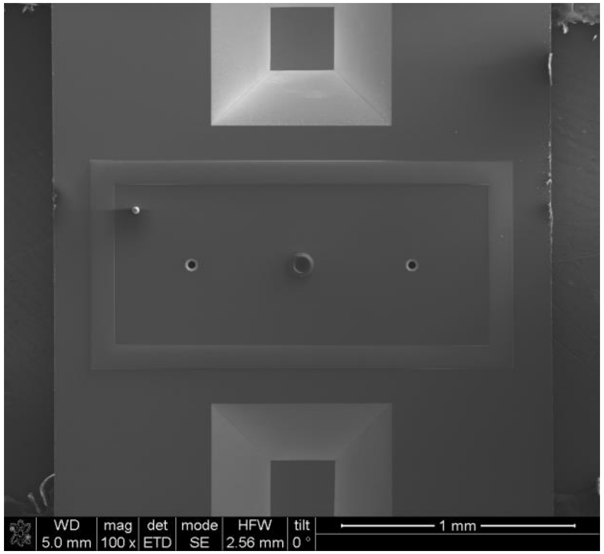


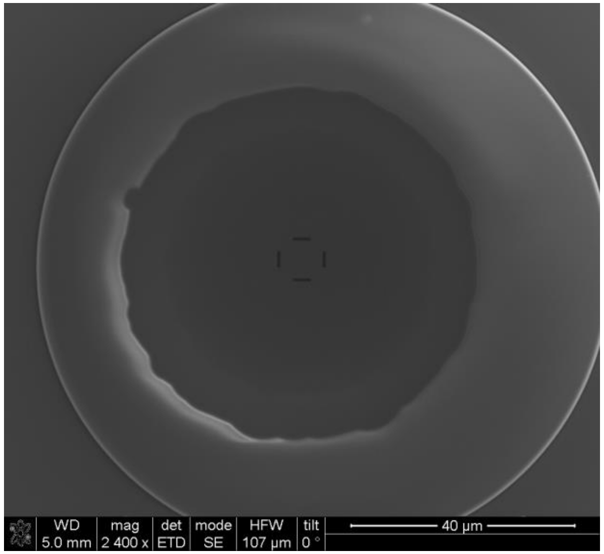
seal ring

E-beam Evaporation of Li Metal Electrodes Using a Shadow Mask

(This will provide pristine working electrodes on the membrane windows and larger electrodes off of the window)





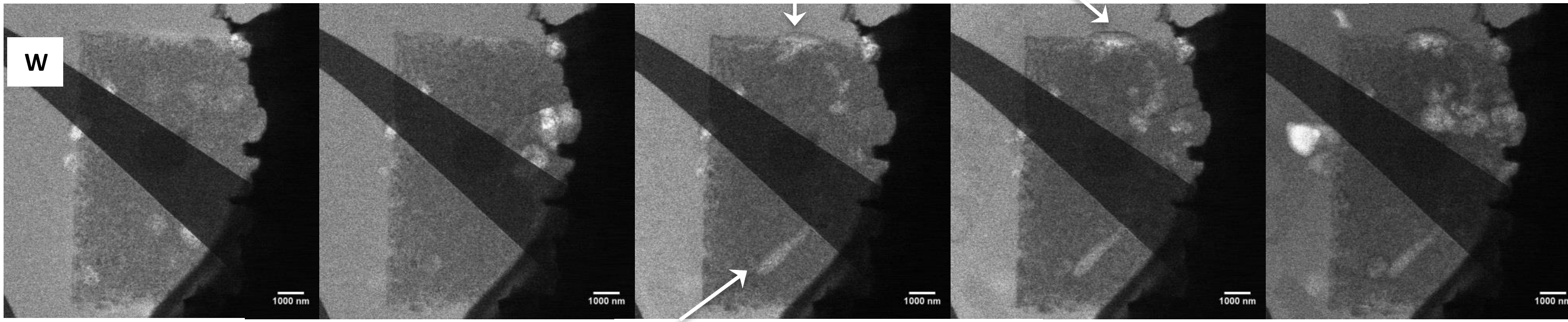


4 M LiFSI in DME system with an ALD deposited 50 nm LiAlS layer on Ni Electrode

50 nm LiAlS on Ni

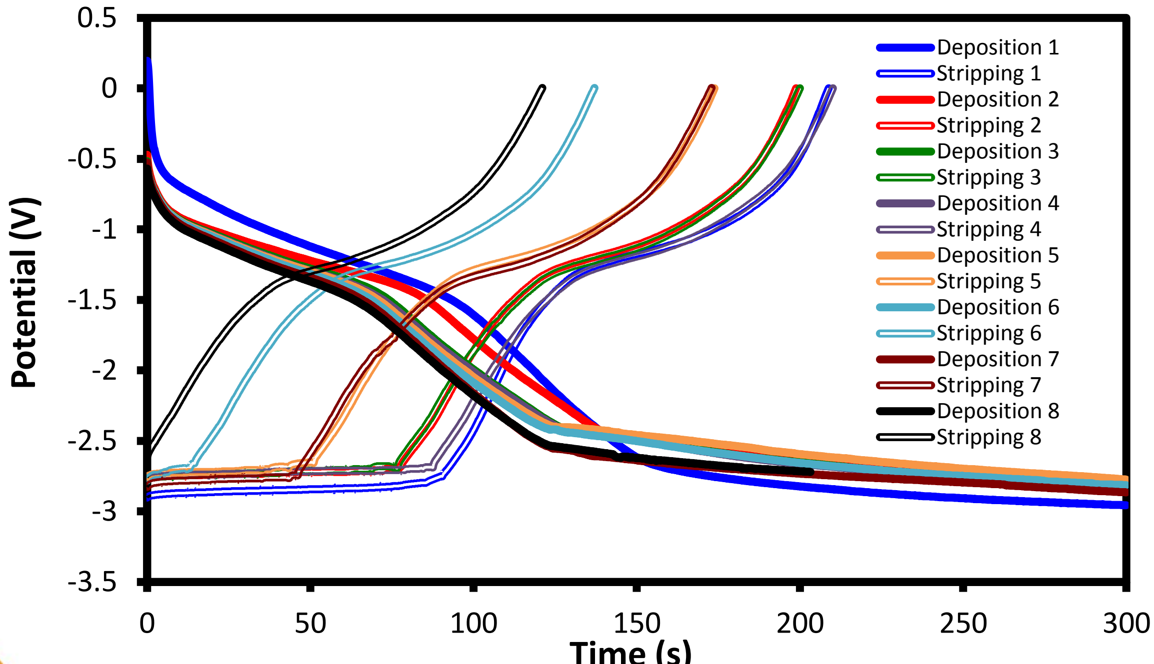
Cracking of inorganic film

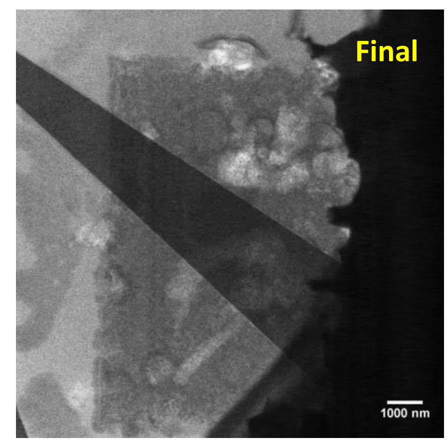
Li deposition through cracked film



4 M LiFSI in DME

Li deposition below film





- Stripping more consistent with ALD film
- Li depositing below ALD film
- Li stable in cell
- Failure of CE at cycle 8