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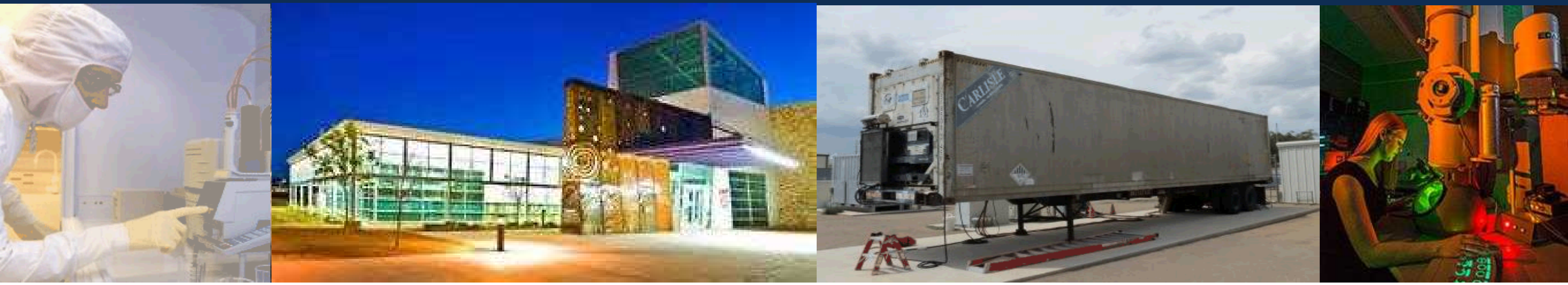

Energy Storage for the Electric Grid – NanoWatts to MegaWatts

Sean J. Hearne, Ph.D.

Manager, Center for Integrated Nano-Technologies

Sandia National Labs

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

Acknowledgements

The Team

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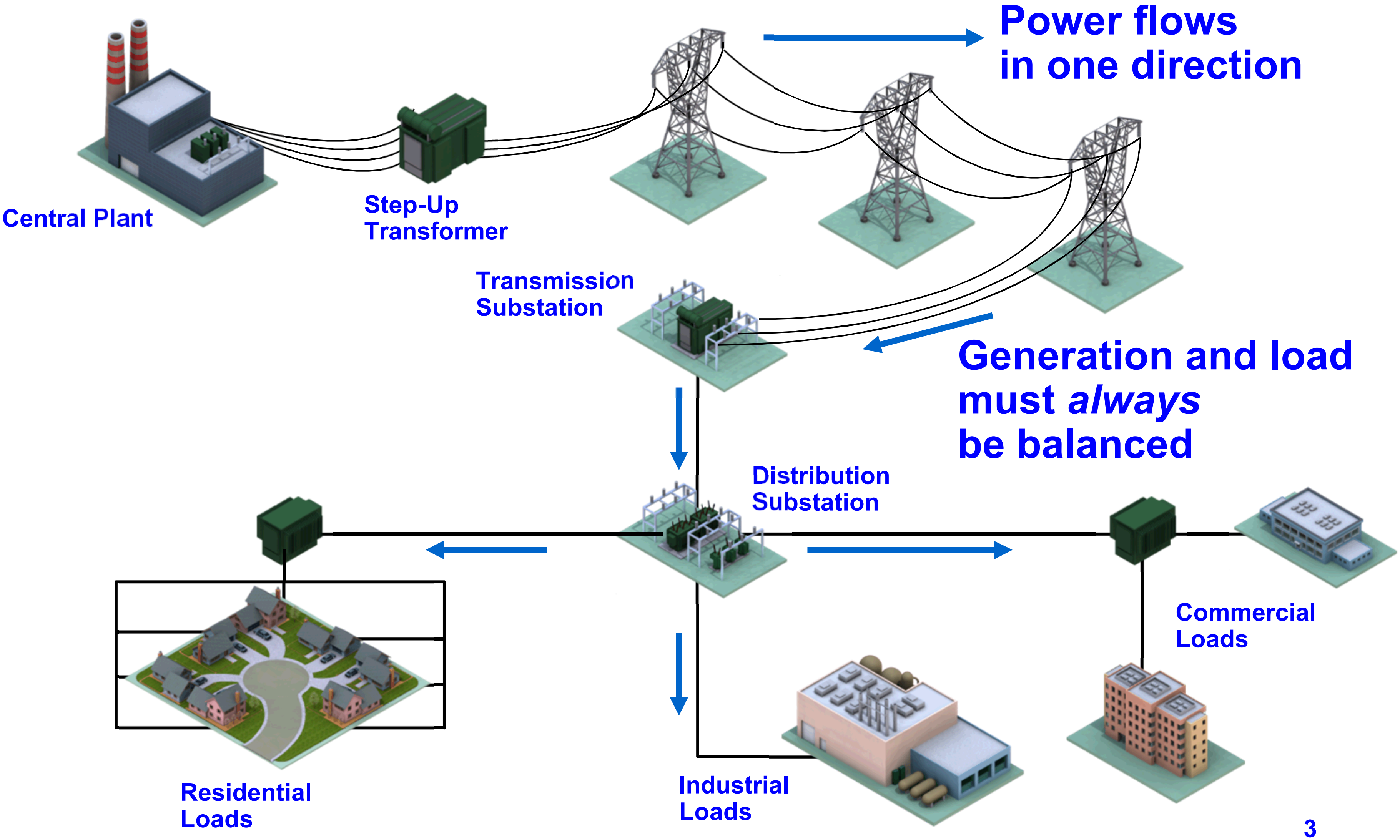
- Georgianne Huff
- Tom Drennen

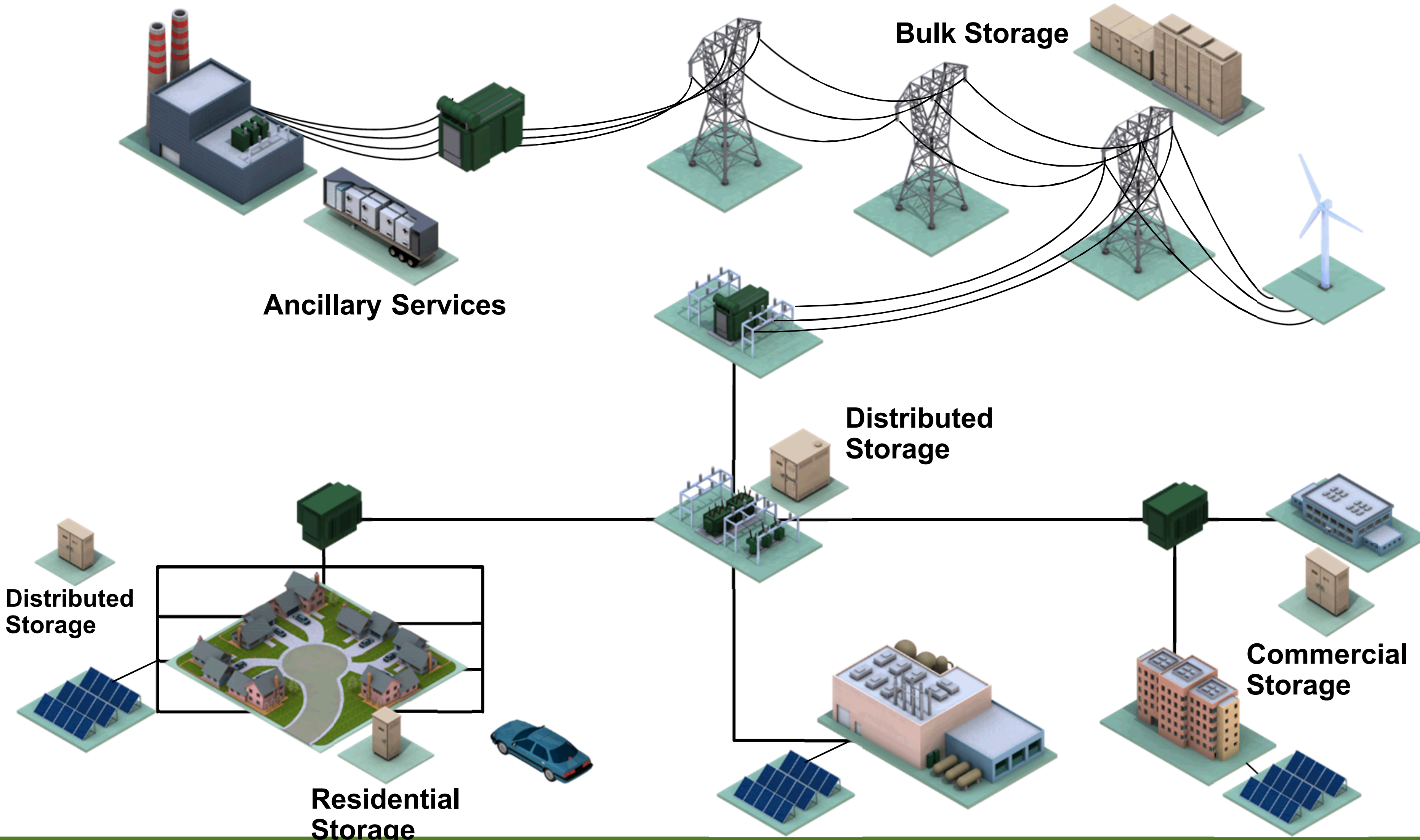
The Money

DOE - Office of Electricity Delivery & Energy Reliability

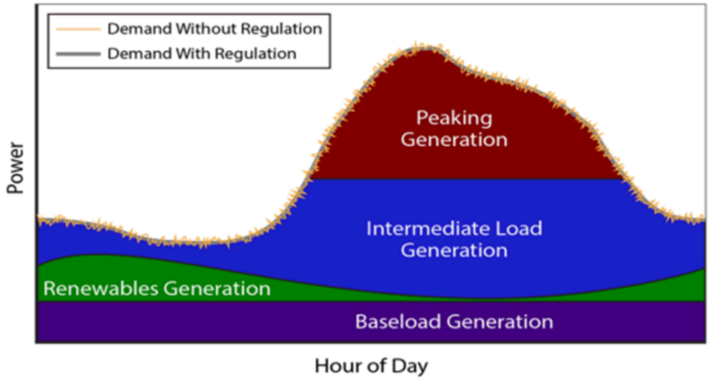
How the Electricity Grid Works Today



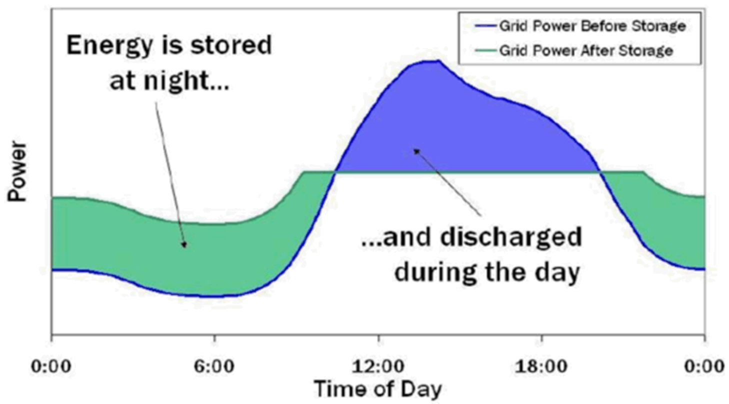
The Role of Storage



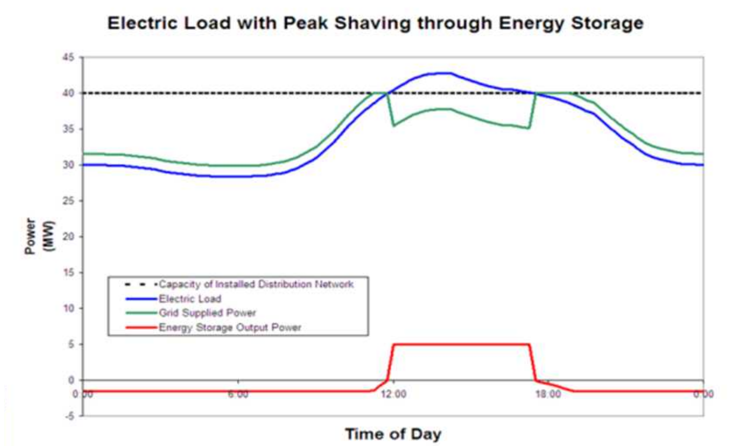
Uses of Energy Storage



Frequency Regulation: Method to maintain the grid frequency within an allowable bandwidth by sourcing or sinking real power to and from the grid in a dynamic way.



Arbitrage: Also known as “load-leveling”; buy energy at low prices at night, sell when demand for energy is high during the day



Peak Shaving: also known as “demand charge management”; energy storage allows utilities a less-expensive option to address growing peak demand without building additional substations

Energy Storage Technologies

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Energy

- Pumped Hydro
- Compressed Air Energy Storage (CAES)
- Batteries
  - Sodium Sulfur (NaS)
  - Flow Batteries
  - Lead Acid
  - Advanced Lead Carbon
  - Lithium Ion
- Flywheels
- Electrochemical Capacitors

Power

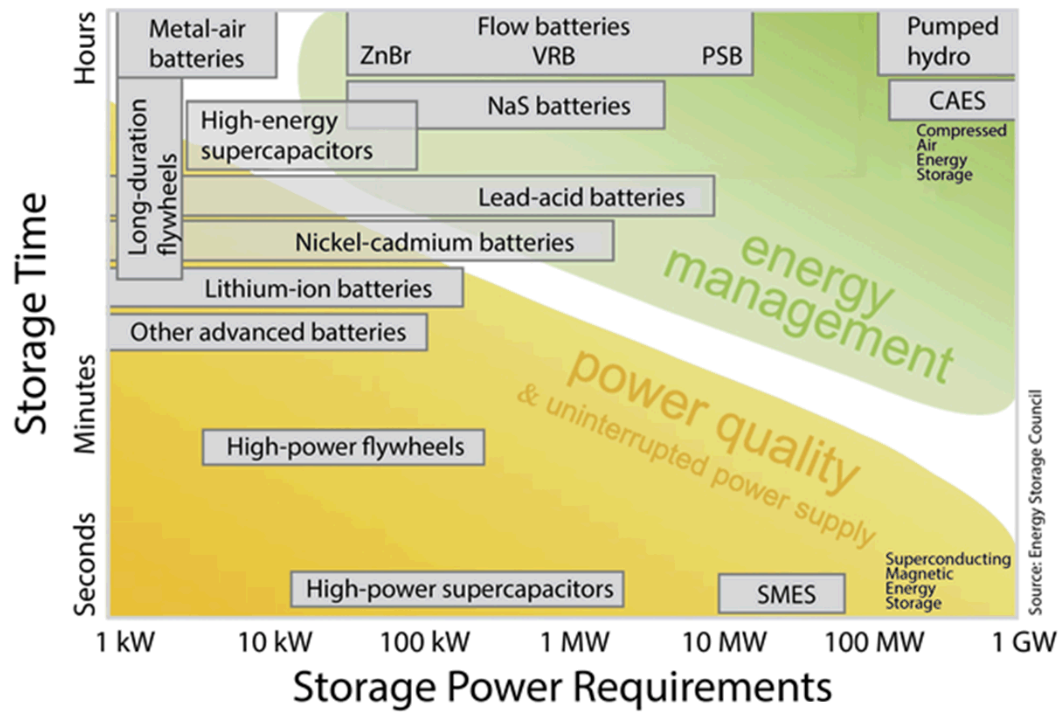
Two regimes, multiple technologies:

Power – short discharges (sec to min):

flywheels, capacitors, SMES, some batteries

Energy – long discharges (min to hr):

batteries, H_2 fuel cells, CAES, pumped hydro



Pacific Northwest NATIONAL LABORATORY

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Energy Storage Technologies

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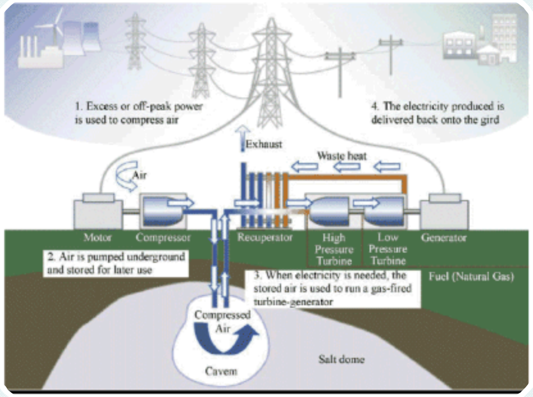

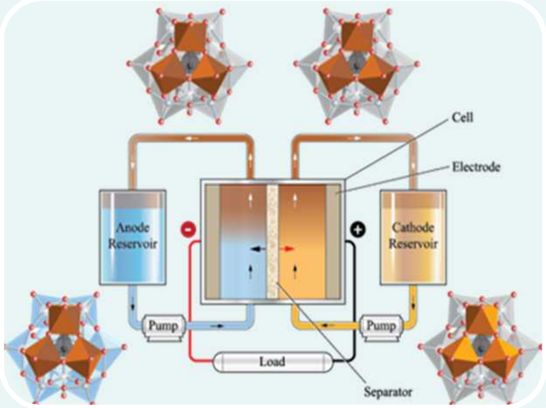

Pumped Hydro

- Nearly 99% of world-wide installed electrical storage capacity
- Advantage: Mature technology, large energy density
- Disadvantage: Large amount of space required for an installation, limited by geography, extremely slow response time

Compressed Air Energy Storage (CAES)

- When needed, the compressed air is mixed with natural gas, burned and expanded in a modified gas turbine.
- Advantage: large energy density/capacity
- Disadvantage: Results in low round-trip efficiencies of less than 50%, limited by geography

Redox Flow Batteries

- Advantage: Relatively safe, requires less space than pumped hydro or CAES
- Disadvantages: Low energy density, still researching optimal membrane/electrolyte pairing

Energy Storage Technologies continued

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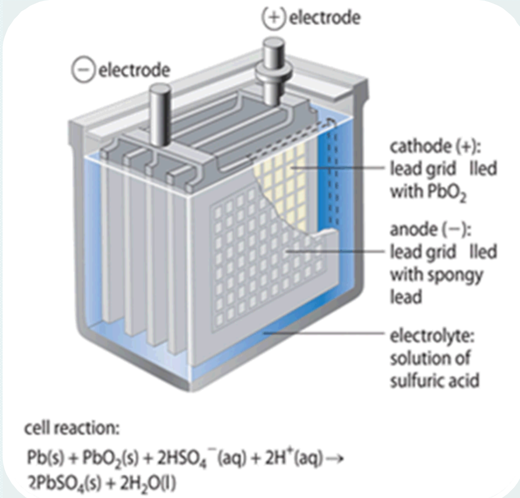
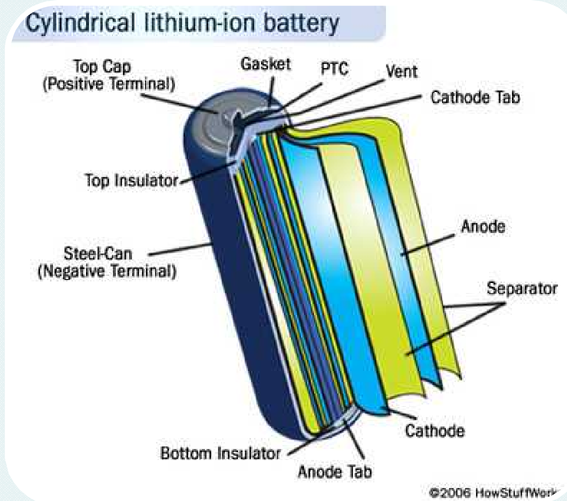
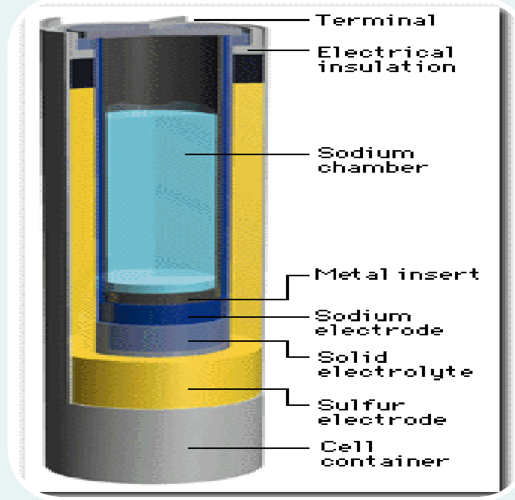






Lead Acid (Pb acid) Batteries

- Common applications in emergency power systems, stand-alone systems with PV, fluctuation mitigation for wind power
- Advantage: Mature technology, but not yet economically viable
- Disadvantage: Usable capacity decreases when high power is discharged

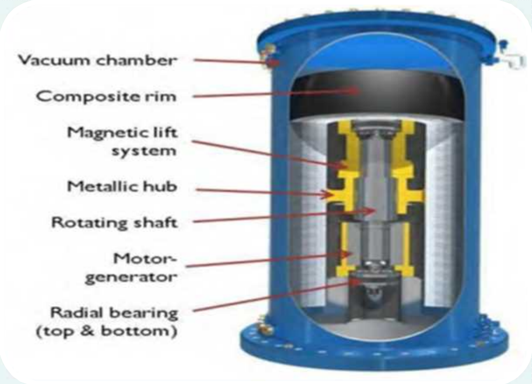
Lithium Ion (Li-ion) Batteries

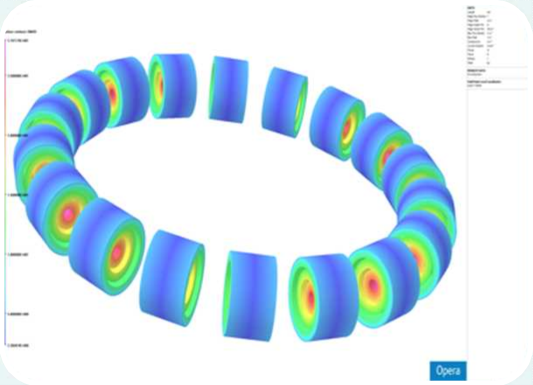
- Advantage: Very high efficiency, variable discharge time makes them flexible
- Advantage: High energy density lowers cost and increases mass production
- Disadvantage: High risk of thermal runaway

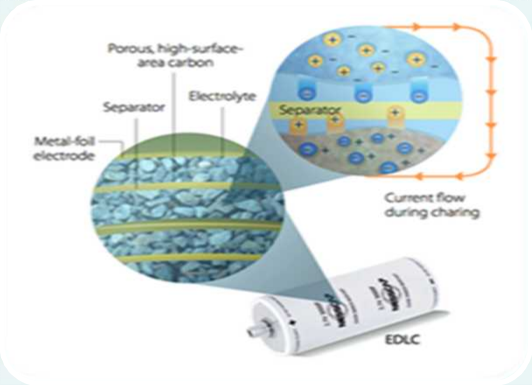
Sodium Sulfur (Na/S) Batteries

- Advantages: High energy efficiency, fast response time
- Disadvantage: Requires a heat source, which uses the battery's own stored energy

Energy Storage Technologies continued







Flywheels

- Advantages: Primary applications include frequency regulation, frequency response, solar PV and wind output smoothing, peak shaving, power quality
- Disadvantage: recent safety incident at Stephentown plant, concrete cover partially blown off
- Current safety mitigation: fire suppressant

Superconducting Magnetic Energy Storage (SMES)

- Energy is stored in the magnetic field created by the flow of direct current in a superconducting coil
- Advantages: Very high power capability, improving load leveling, no moving parts or loss of power
- Disadvantage: Cryogenics challenge (cold temperature technology)

Electrochemical Capacitors

- Advantages: High power capability, very fast charge/discharge, durability
- Disadvantages: Cannot be used to store energy over long periods

Why isn't storage everywhere?

Economics!

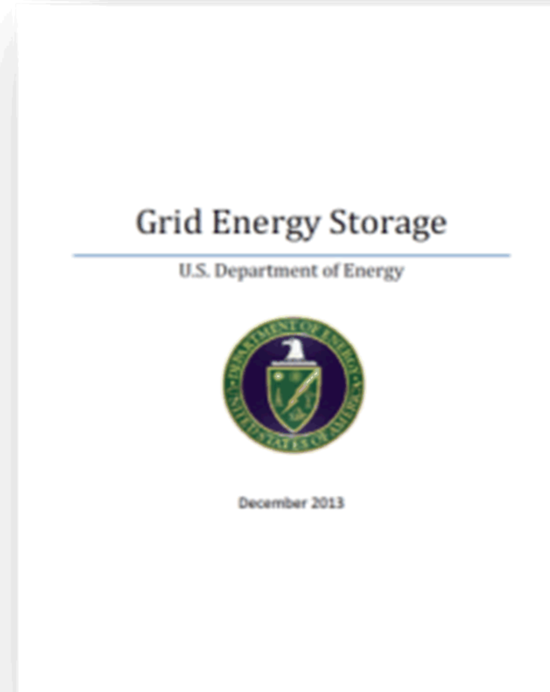
The cost is too high for the value of services provided

Energy Storage only makes money for the purchaser when electrons are flowing.

But Wait There is More

During the commissioning hearings of Dr. Moniz to head US DOE, Senator Wyden requested a strategic plan for grid energy storage.

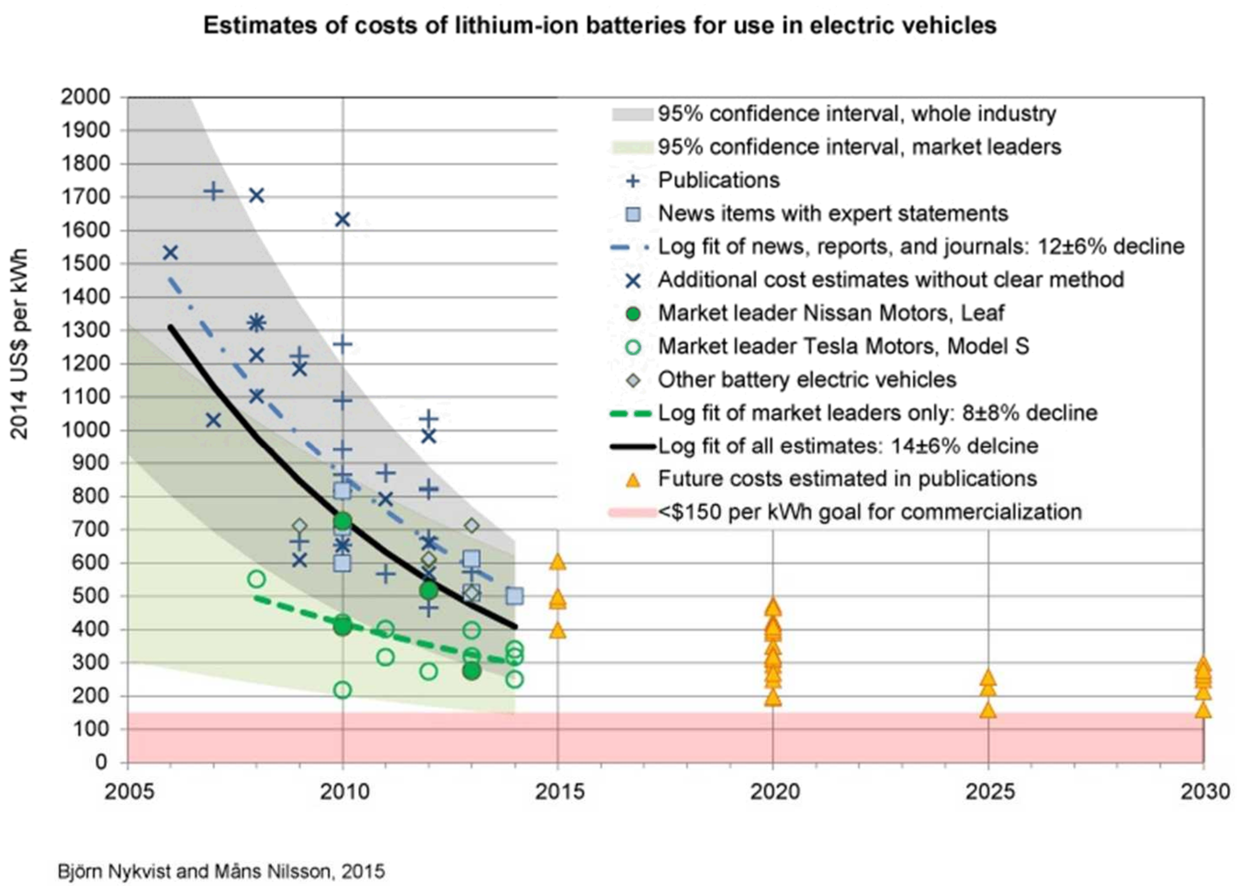
DOE Published the report in December 2013



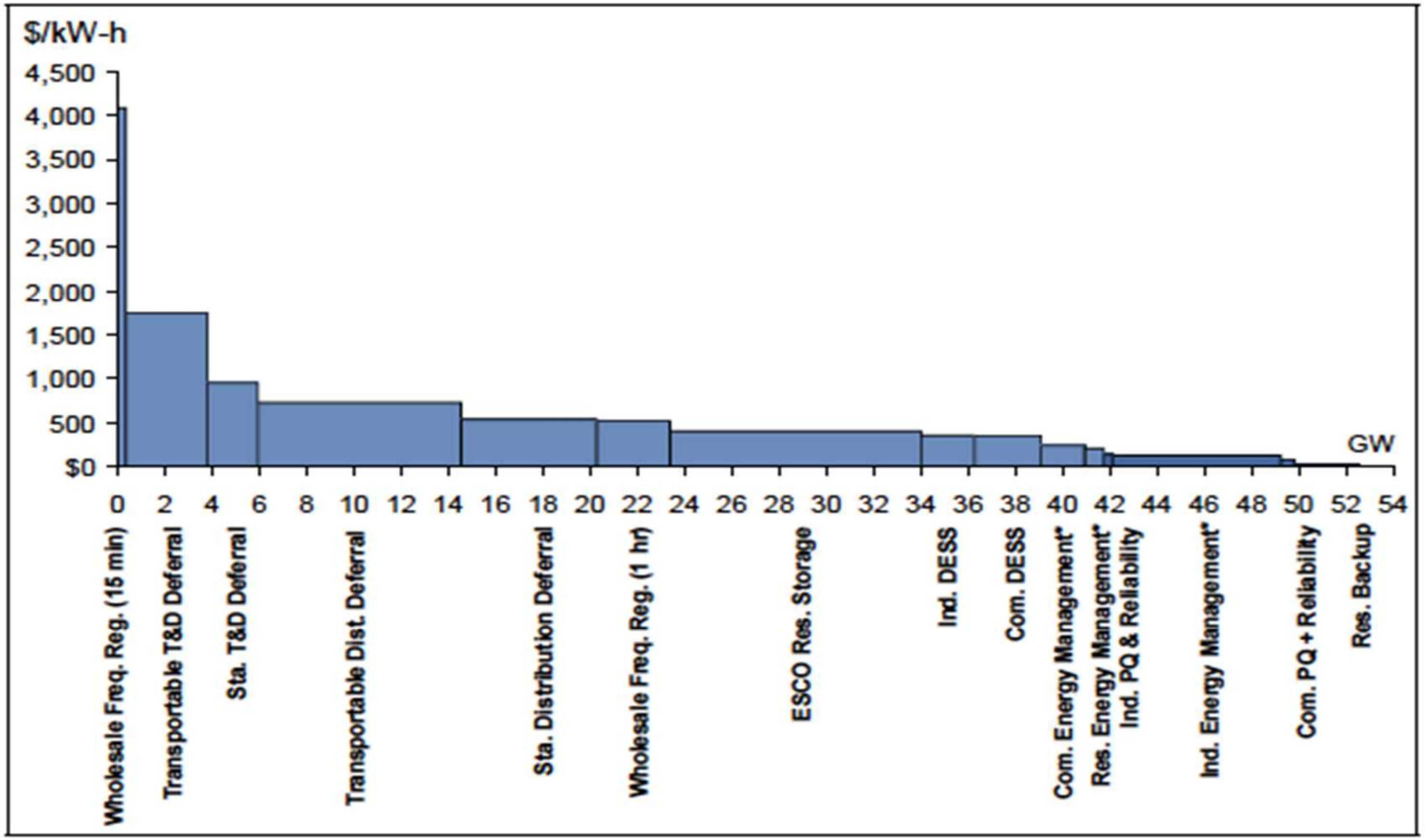
Four Critical Challenges were identified

1. Cost Competitive Energy Storage Technologies
2. Validated Reliability and Safety
3. Equitable Regulatory Environment
4. Industry Acceptance

Li-ion Battery Cost



Battery Value



Estimated value (bar height) and market size (bar width) for grid storage deployment.

Figure 13
Estimated Target Market Size and Target Value Analysis

Source: EPRI, 2010

- **Estimated to be $35.3B, ~19GWh market by 2020** (assuming $500kWh) - http://www.renewableenergyworld.com/articles/2010/08/pike-research-grid-energy-storage-a-35b-market-by-2020.html

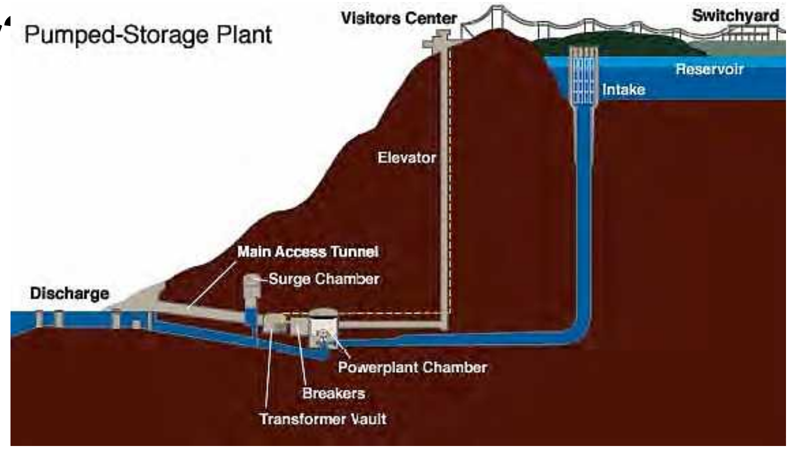
Is pumped hydro the answer?

How much energy is in displaced water?

1 cubic meter of water

100M height

=0.272 kWh

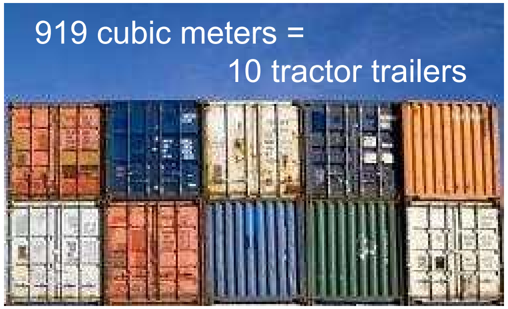


To get 0.5MWh of storage = 919 cubic meters

A tank 3 meters high will take up 306 sq. meters

Cost of real estate in New York City is **$5167 per sq. meter** [1]

The tank will cost $1.5M, but two tanks are needed. **The property costs $3M alone!**



[1] http://www.newyorkrealestateventures.com/manhattan-real-estate-information

What about Li-ion Batteries?

In NYC the space for a single tractor trailer is $170k.

The cost of the batteries $500 /kWh installed is $250k

Total cost = $420k (20x less than the space needs alone for pumped hydro.

For many applications, where space or environmental impact matters, batteries are a most desirable solution.

But…

Let's consider the degradation cost of Tesla batteries

60kWh battery costs $12,000 to replace when it reaches 80% of life. So, the degradation cost of Tesla batteries is $1000 /kWh [1]

Tesla batteries degrade at 0.03% per cycle [2] = $0.30 per cycle per kWh

Current average electricity cost in Kentucky = $0.09 kWh

So, using Tesla batteries to store energy for the grid is a loosing proposition even if the power was free!

Better analysis: G. Freeman " Estimating the Microeconomic Benefits of Vehicle-to-Grid Services in New York City" *Proceedings US Association for Energy Economics* (2015).

[1] https://en.wikipedia.org/wiki/Tesla_Model_S
[2] http://my.teslamotors.com/fr_CA/forum/forums/battery-degradation-finally-some-data

Using Nanoscience to understand degradation in Li batteries

Li Metal Anodes for Lithium Ion Batteries

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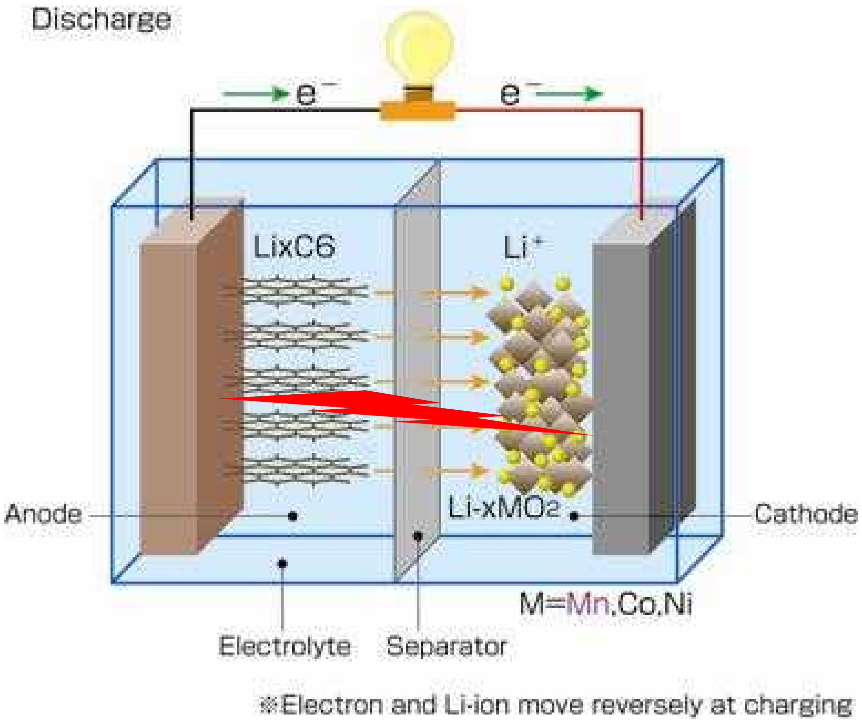
Li metal anodes can increase the capacity by a factor of 10!



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

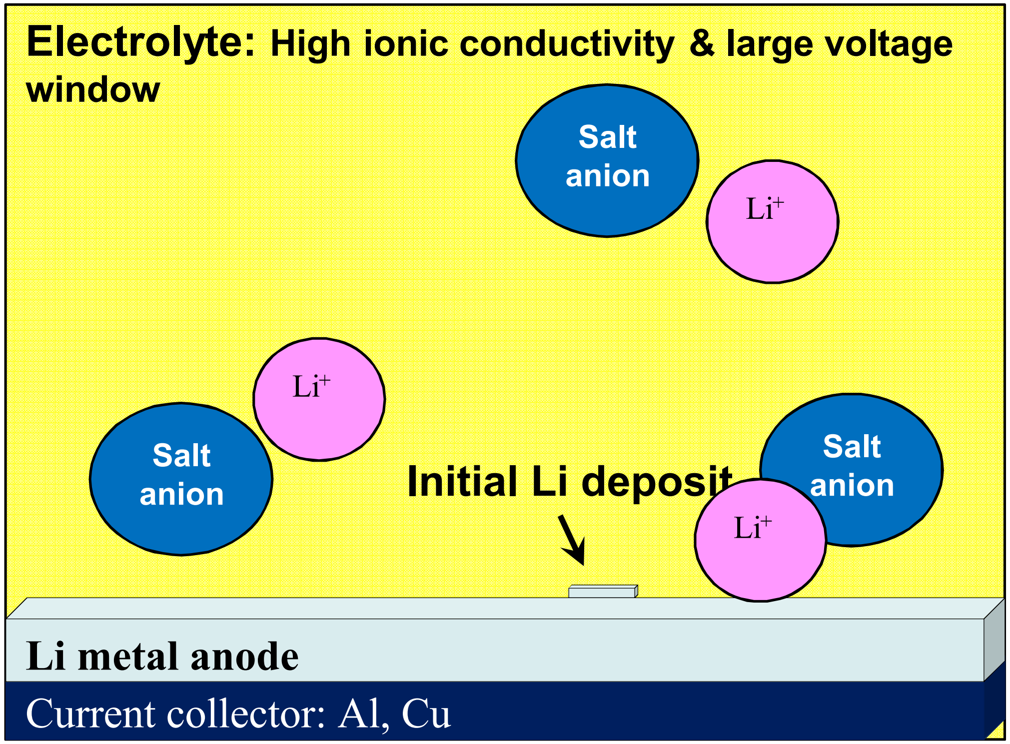
Yoshio, M. et al., 2009 Lithium-Ion Batteries. Springer, New York, 11

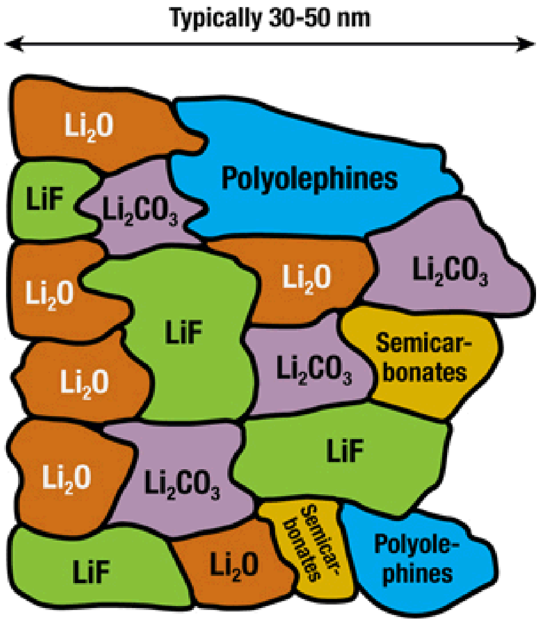
Why don't we use Li metal anodes?

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

Li Metal – Electrolyte Interface

Electrodeposition of Li





SEI Interface:
Lithium Intercalation into Graphite

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

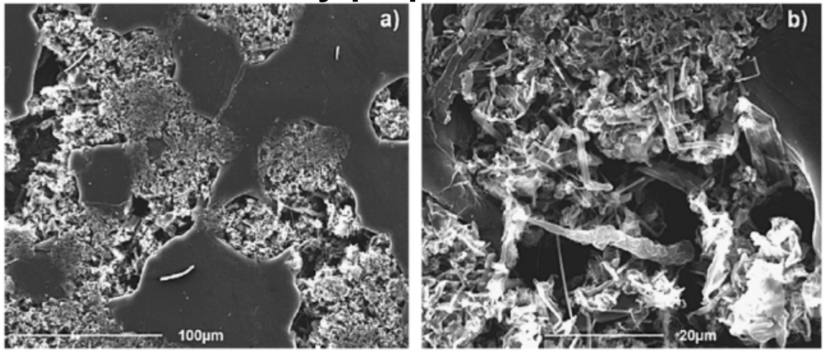
Known that a surface film forms at solid-electrolyte interface (SEI), what impact does this SEI film have on Li morphology for electrodeposition?

Characteristics of Li Dendrite Growth

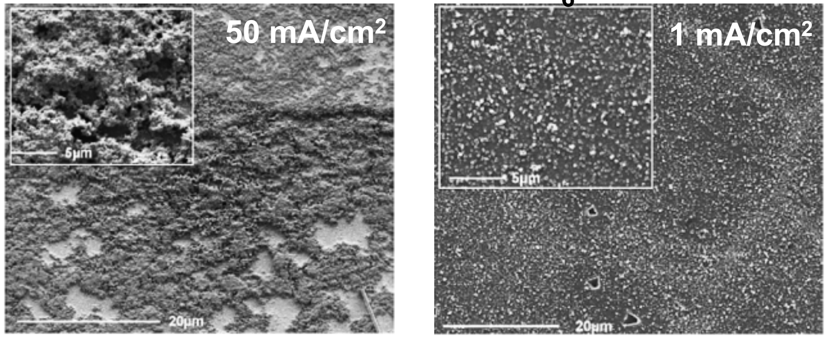
Parameters determining Li morphology

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

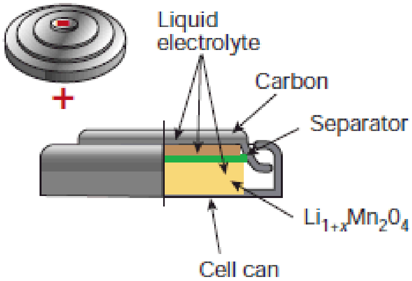
Electrochemically prepared Li surfaces



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



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

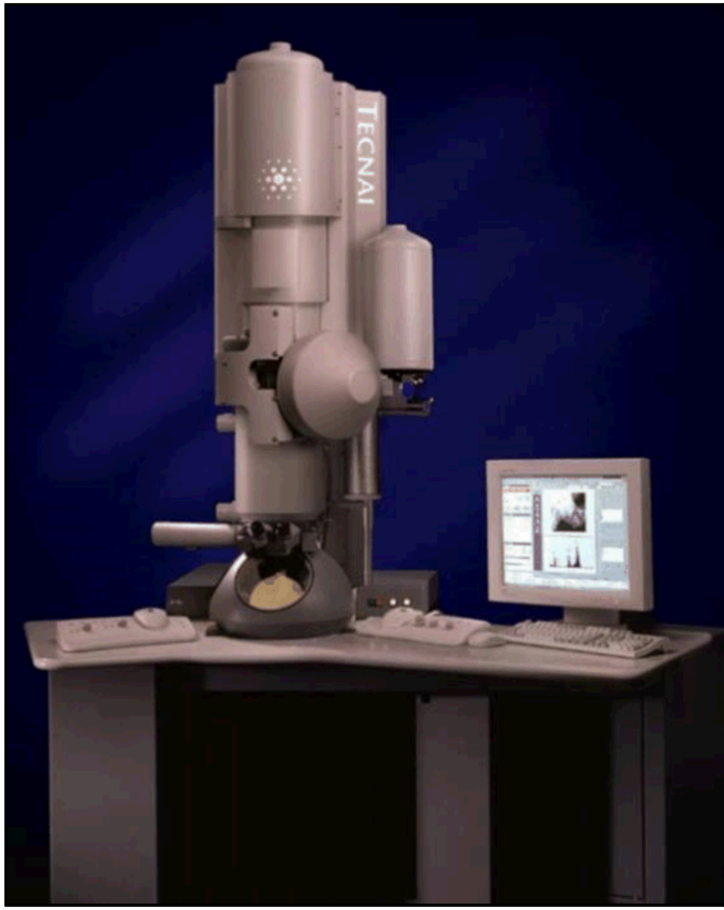


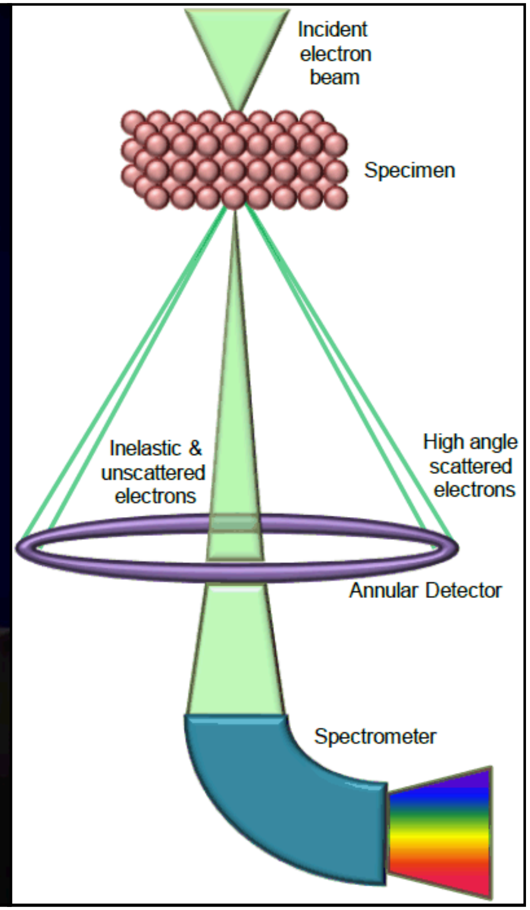
Tarascon J.-M. and Armand, M. (2001) Nature 414, 359.

Li dendrites preferentially grown on metal imperfections (higher surface energy states) and at high current densities. The local current density (current focalization) is enhanced by surface imperfections.

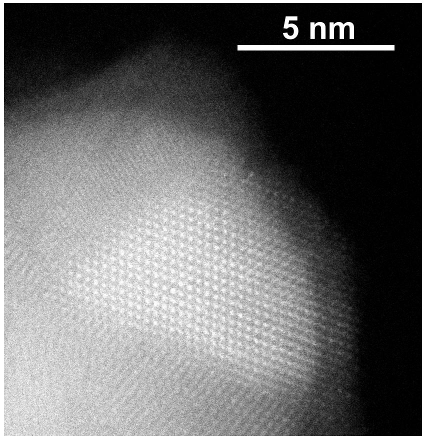
Li dendrite tip morphology remains constant during growth (growth from base)

Transmission Electron Microscopy



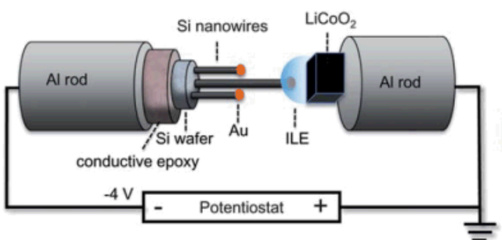


300 kV electron beam
Beam current 5 – 10 pA
Dark-field and Bright-field STEM
Generally: 5 sec 1k x 1k images

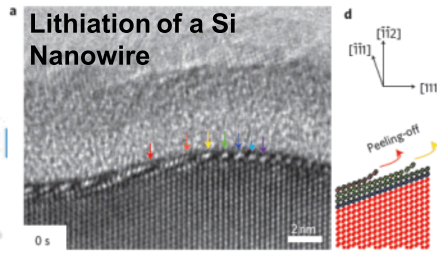


Atomic-resolution imaging and chemical analysis

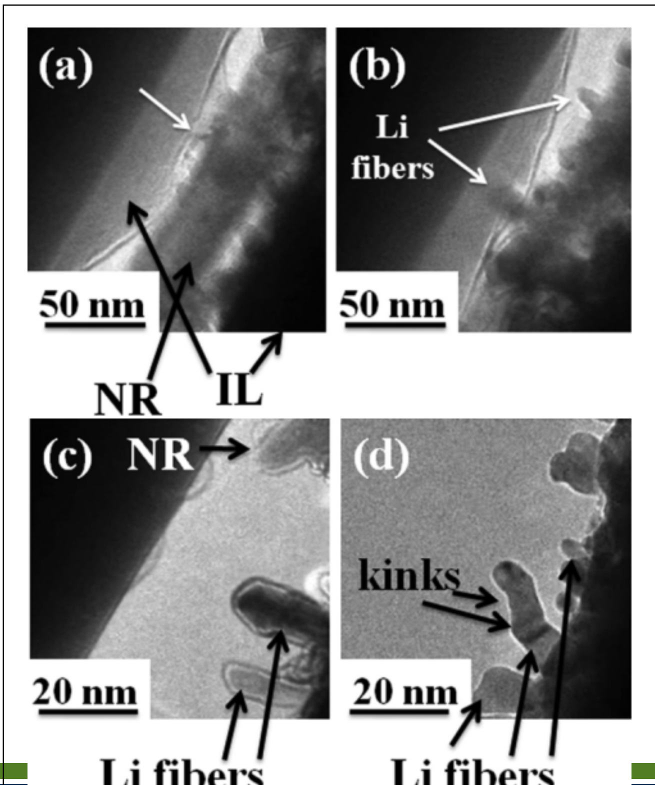
Vacuum Environment: Li Dendrite Formation



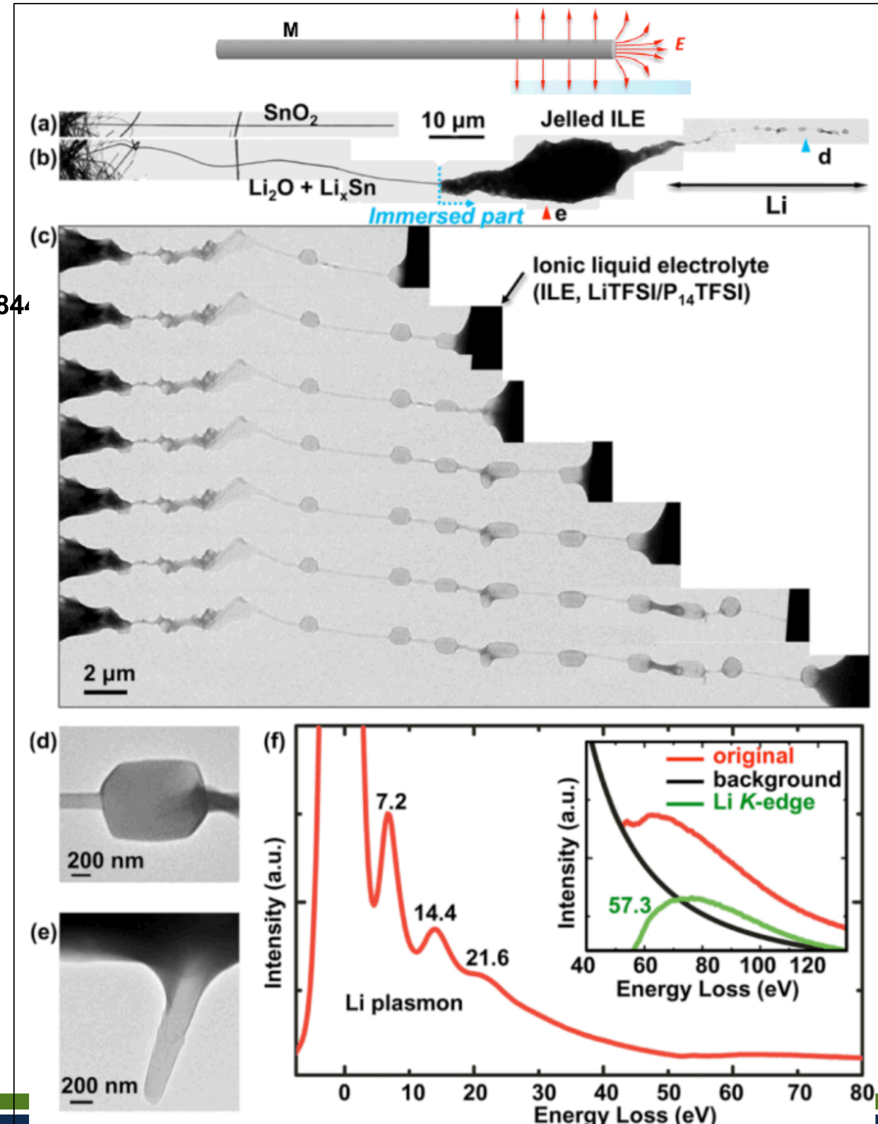
Liu, X. H. and Huang, J. Y. 2011. Energy Environ. Sci. 4, 3844.



Liu, X. H. et al. 2011. Nature Nano. 7, 384



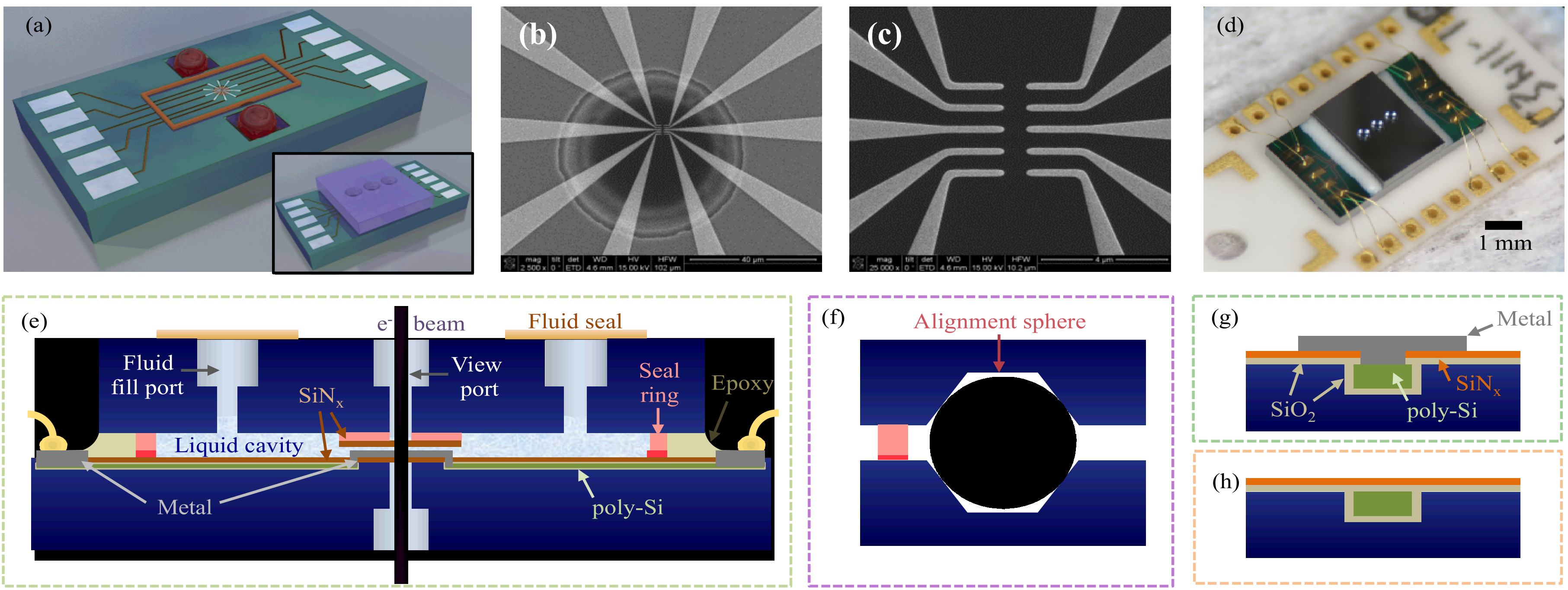
Ghassemi, H. et al. 2011. Appl. Phys. Lett. 99, 123113.



Liu, X. H. et al. 2011. Appl. Phys. Lett. 98, 18310

Electrochemical TEM Discovery Platform

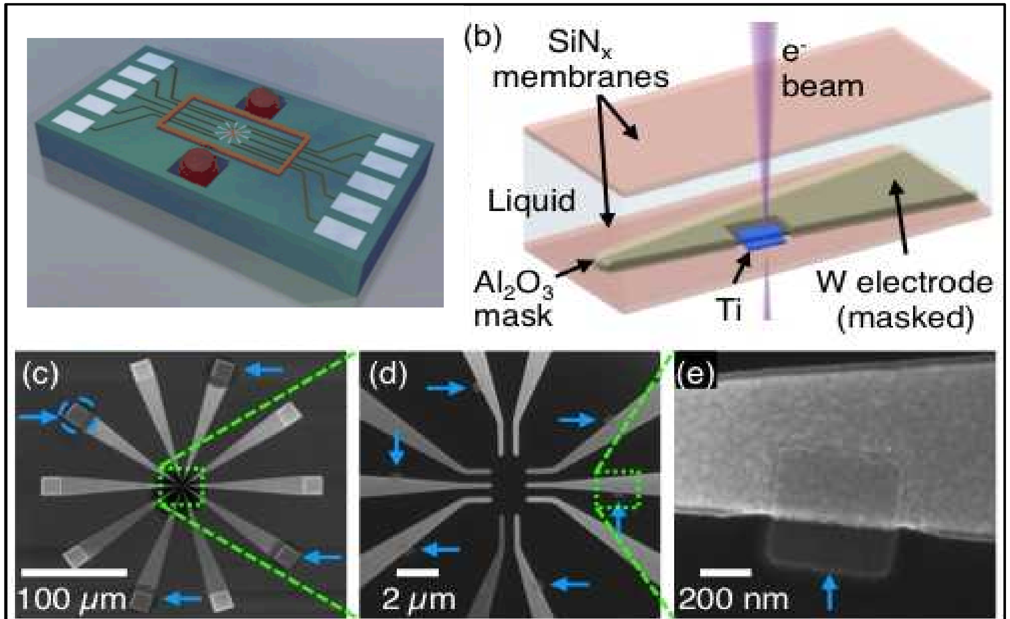
- Electrically isolated electrodes allow for defined current control down to femptoampere levels
- 10 ultramicroelectrodes can be controlled at technologically relevant current densities
- Active electrode areas are confined to viewable region in the 30 nm thick SiN window



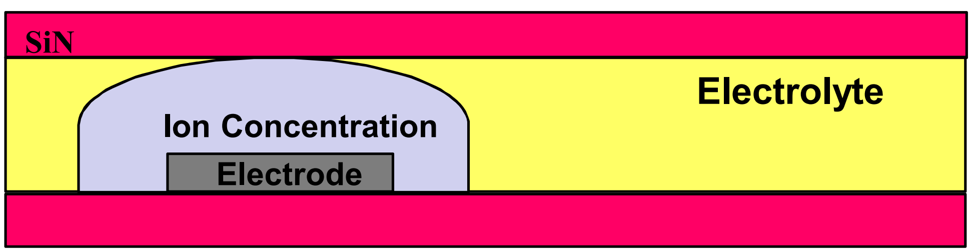
Leenheer et al., (2015) JMEMS. DOI:10.1109/JMEMS.2014.2380771

Reproducible electrochemical control during imaging

Customization of EChem TEM Discovery Platform



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



- 10 Custom Designed Electrodes
- Multiple Experiments on Same Platform
- Passivated Leads to Localize Electrochemistry
- Picoampere Current Control
- Liquid Thickness > 120 nm
- Beads Simplify Window Alignment
- Chemical Compatibility with Cell
- Conduct in-situ & ex-situ Testing

Consideration to Depletion of Li in Electrolyte

$$i_{max} = nF\Delta cV/t$$

N : # e^- transferred
F: 96485 C/mol
V: ~ 2.8 nL
T: 1 hr
i_{max} (10% of 1 mM): 7.5 pA
Use ~ 1 µm^2 electrode area

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

1 M $LiPF_6$ IN EC/DMC (>10 PPM H_2O)

Galvanostatic Control of Working Electrode

Sandia National Laboratories

Electric current is kept at a defined set point

We are able to control currents below pA level

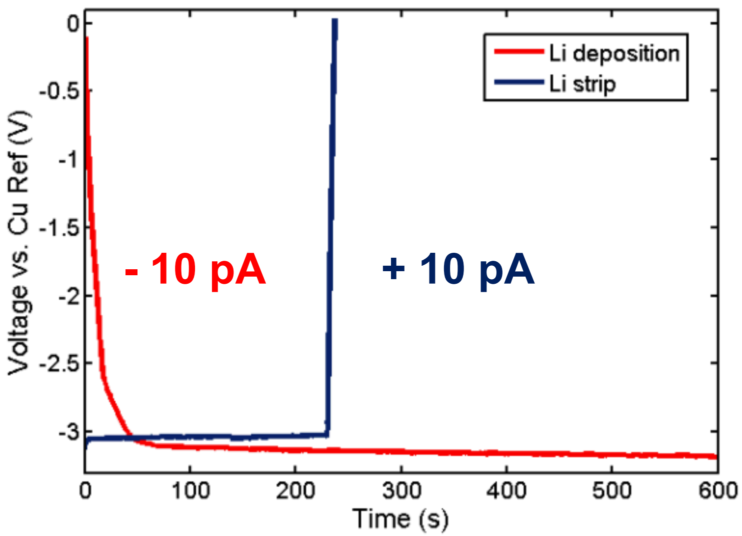
The voltage applied is dependent on the resistance during the measurement, value plotted vs. time

Voltage plateau defines the 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



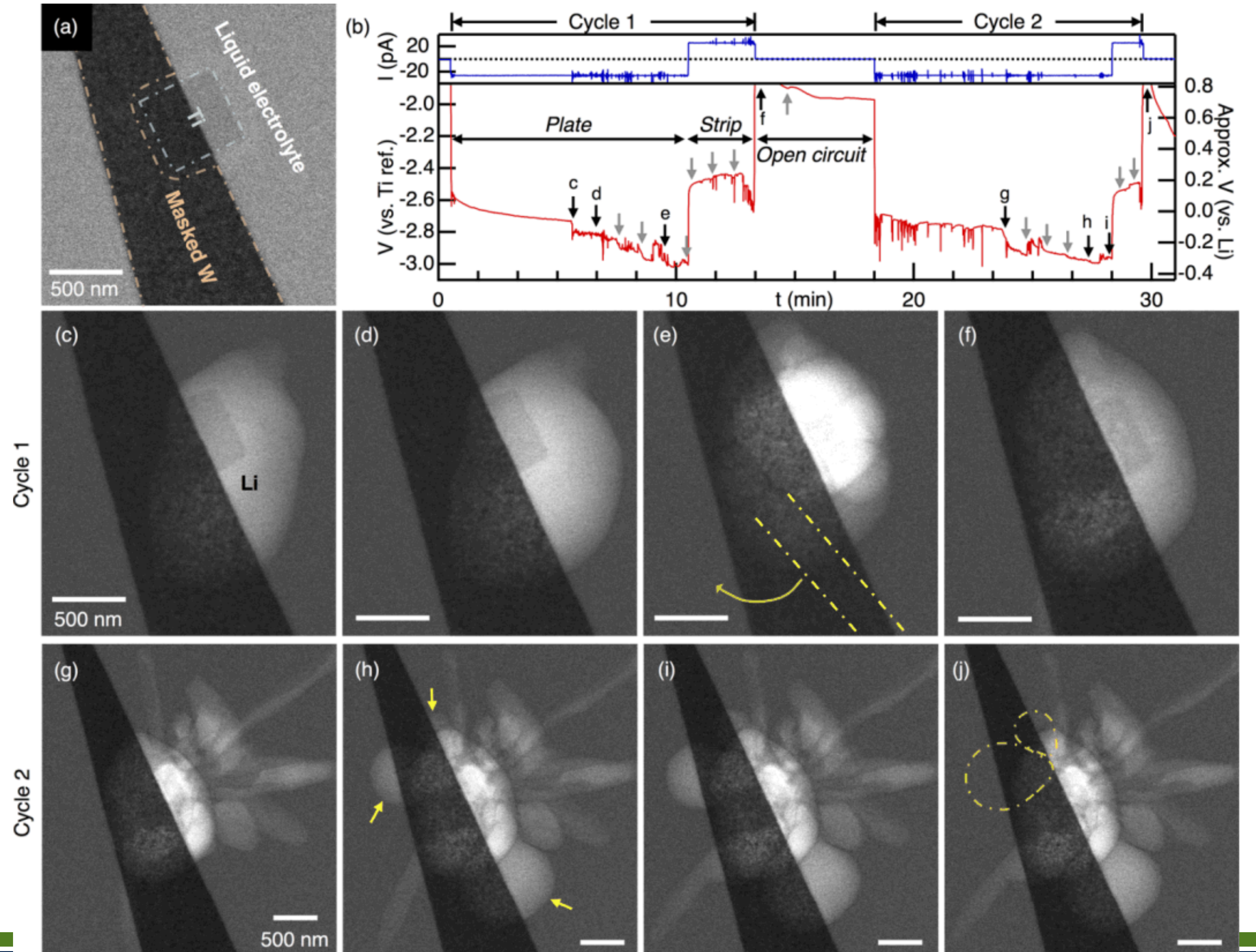
Coulombic Efficiency: 39.47%

NANOSTRUCTURES for ELECTRICAL ENERGY STORAGE

Li Morphology during Cycling

WE: 0.26 µm² Ti electrode
CE: 750 µm² Ti electrode
Coated with ALD Al_2O_3
Liquid thickness: >1 µm
Galvanostatic control: +/- 10 mA/cm²
Electron dose per image: 25-50 $e^-/Å^2$

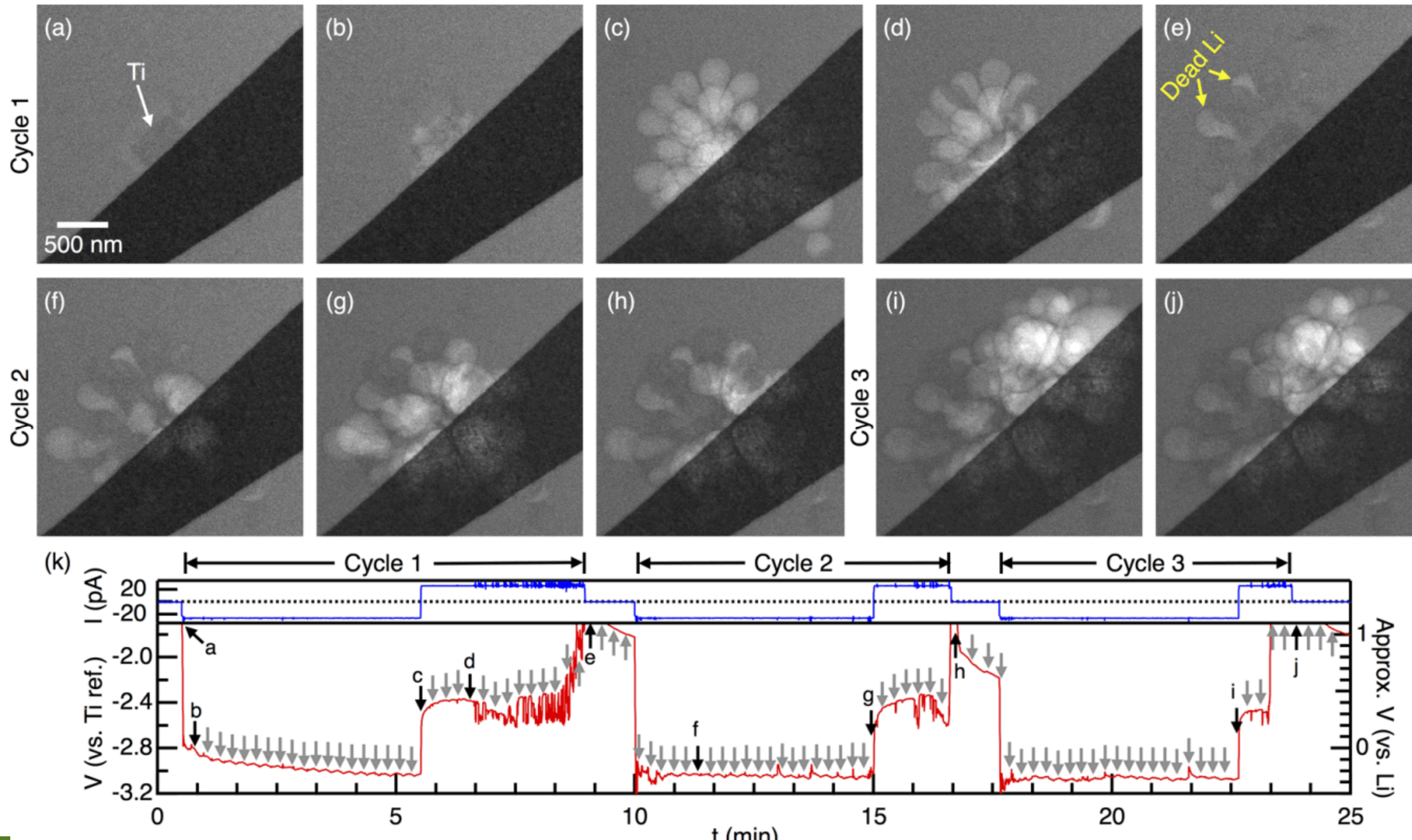
- **The electron beam impacted initial Li plating**
- **Correlate spikes in electrochemical data with nucleation of new Li grains**
- **Unable to distinguish electrochemically the nucleation of a rounded grain vs. a dendrite**



Leenheer et al. (2015) ACS Nano. DOI: 10.1021/acsnano.5b0

Li Morphology: High E$^-$ Beam Dose

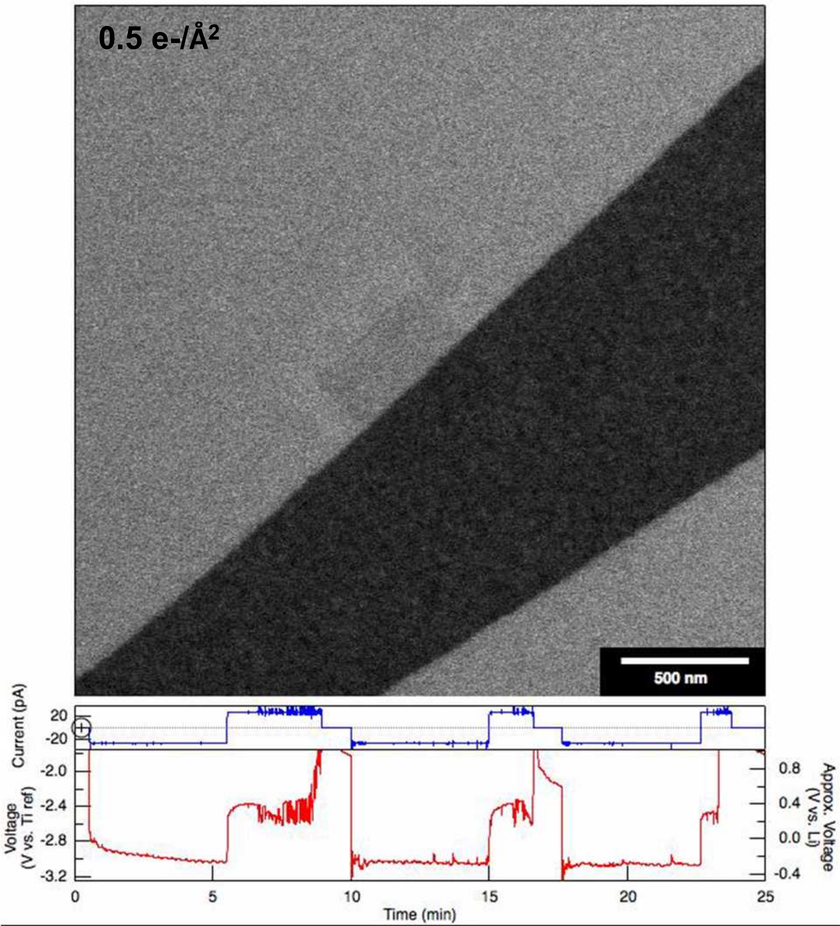
Galvanostatic control at +/- 10 mA/cm^2, Electron dose per image: 25 - 50 e$^-$/Å^2, Imaging every 15 seconds

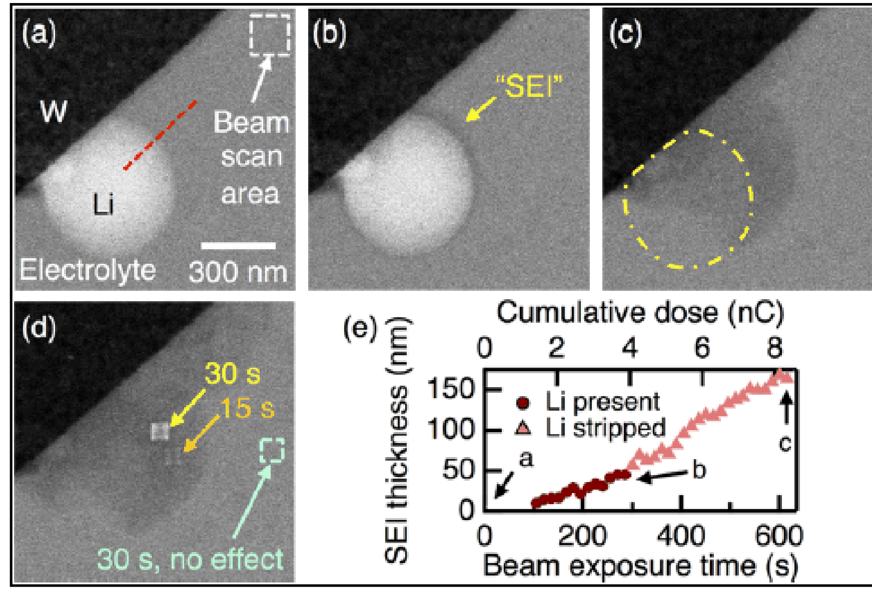


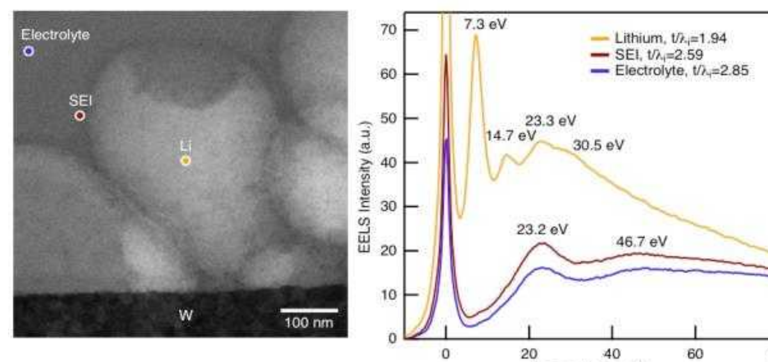
Electron beam increases nucleation and creates rounded Li deposits

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

How Does SEI Evolve with Cycling?





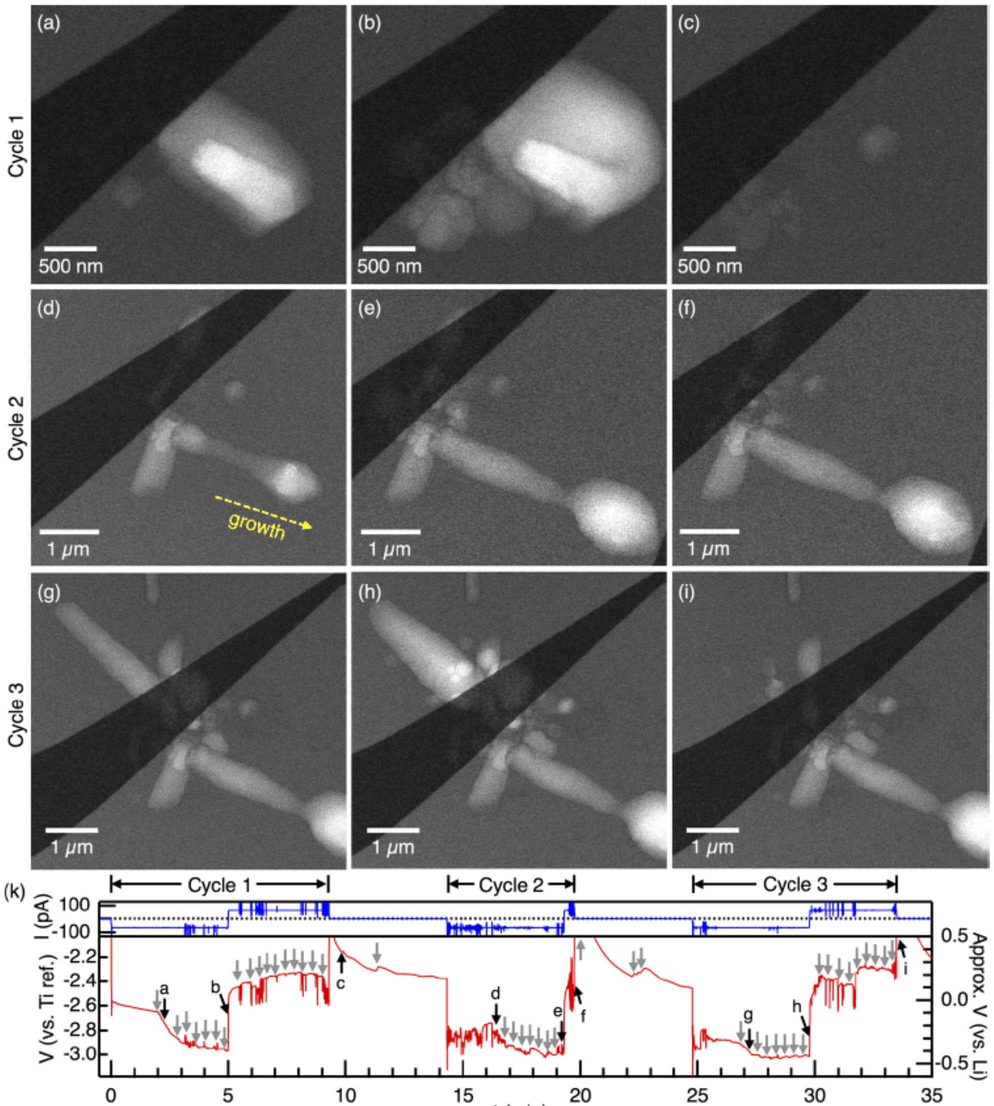


Leenheer et al. (2015) ACS Nano. DOI: 10.1021/acsnano.5b00876.

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

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

Li Deposition: High Current Density



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

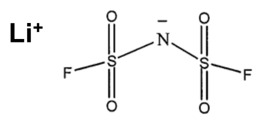
Leenheer et al. (2015) ACS Nano. DOI: 10.1021/acsnano.5b00876.

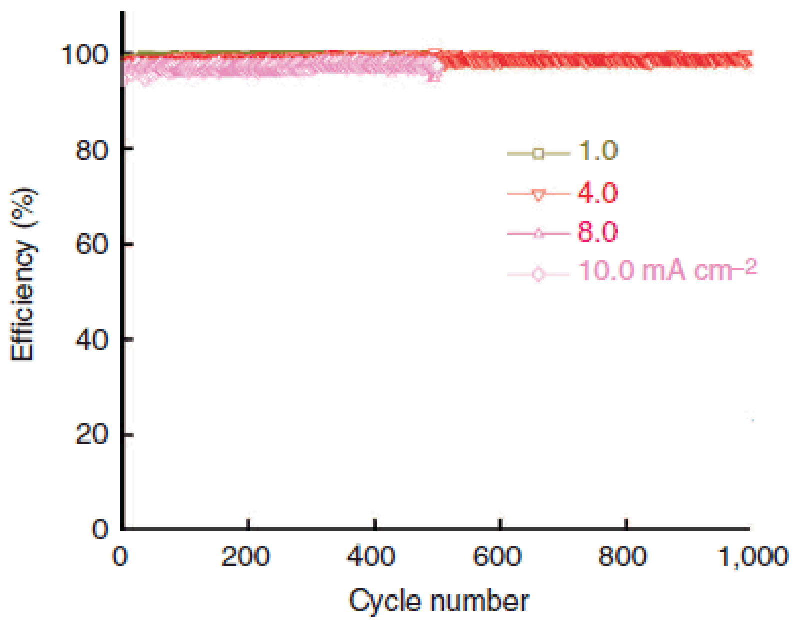
4 M LiFSI IN DME (4 PPM H_2O)

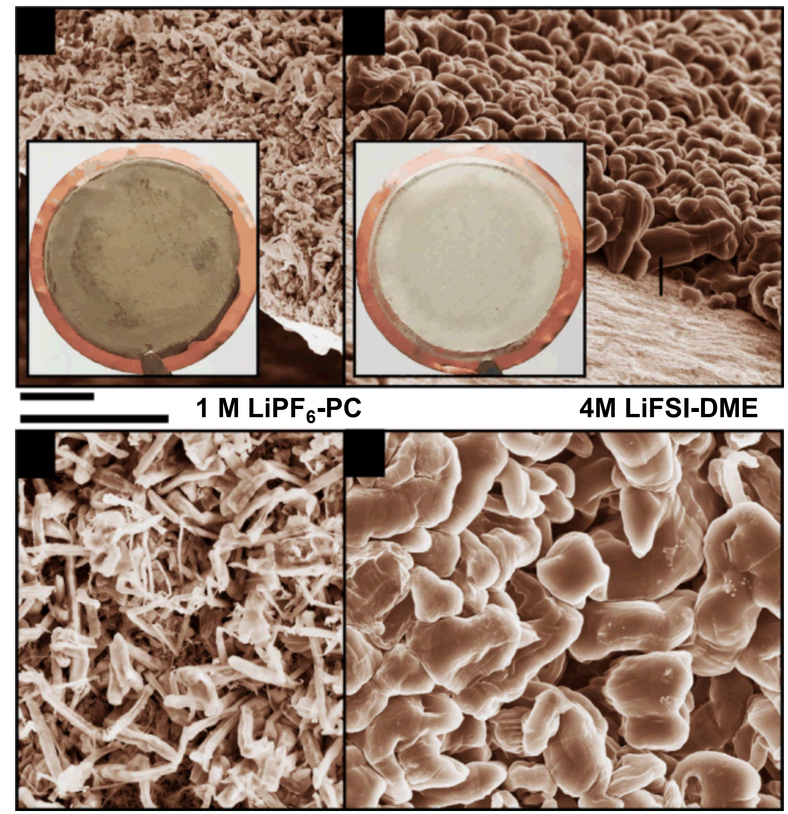
Electrolyte Suppresses Li Dendrites?

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**







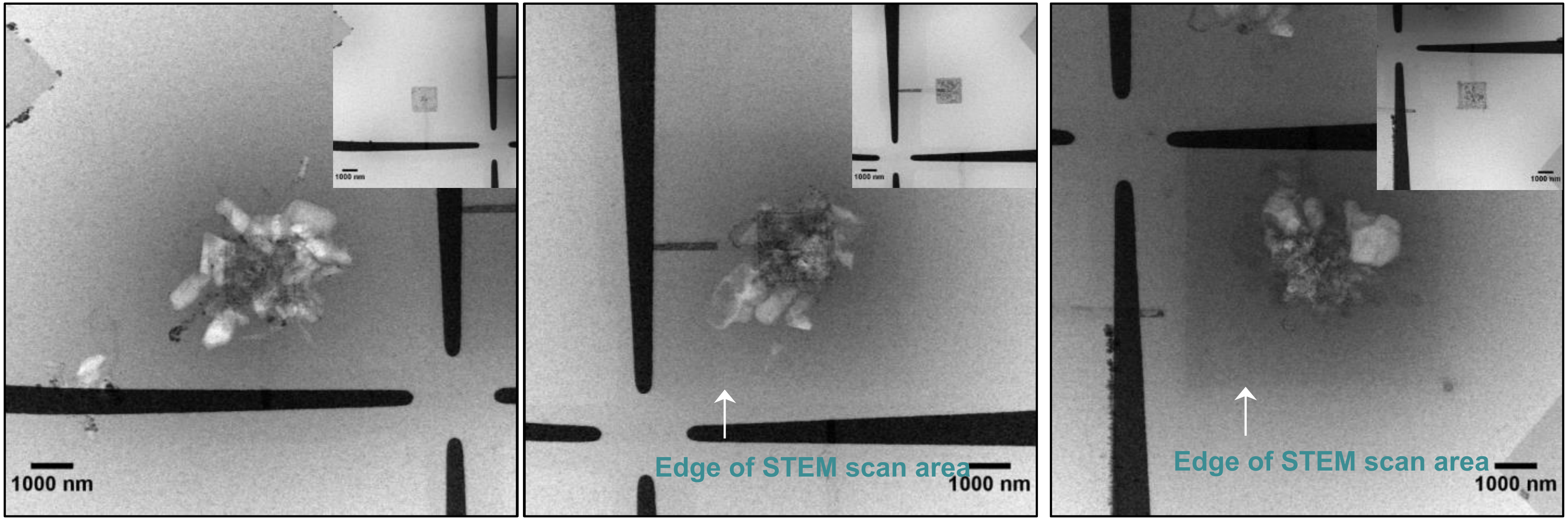
Qian et al., Nature Comm. 6, 6362 (2015).

Electron Beam Induced Degradation and SEI

Compare beam effects in identical electrochemical environments, same closed cell

Galvanostatic control at 2.25 mA/cm² for 2 min deposition/stripping steps for 10 cycles

WE#3 : No Beam | **WE#1 : < 3.84 e-/Å²** | **WE#4 : < 20.16 e-/Å²**



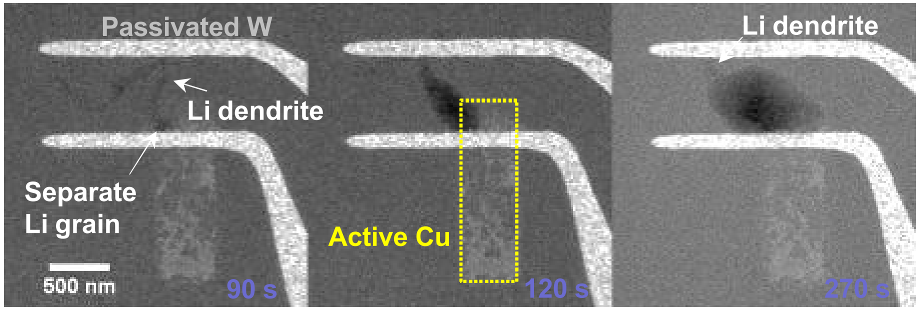
Li deposits push membrane windows apart, increasing scattering in the background

Electron beam adds background scattering by electrolyte breakdown forming polymerized carbon chains

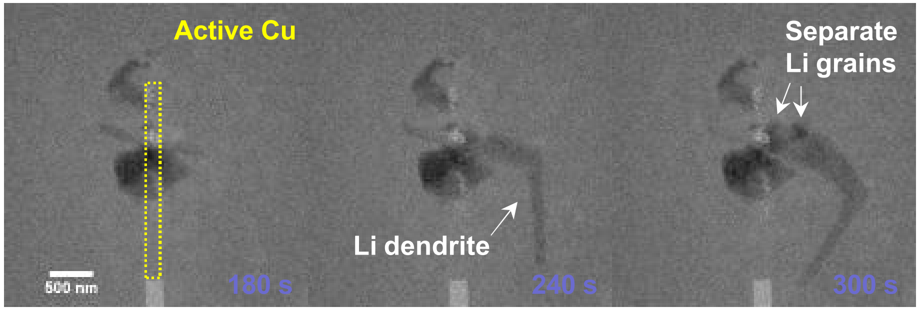
Li Dendrite Disconnection

- **D**uring 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***
- **S**elf-discharge mechanism or corrosion?
- **How is the electron beam impacting ion diffusivity?**

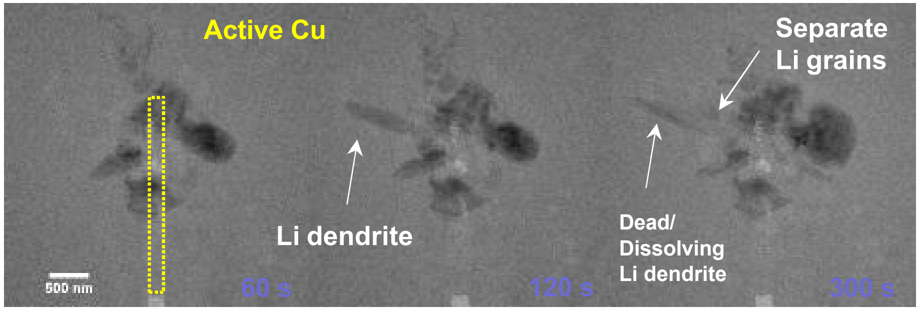
EC-Scanning TEM: -1.33 mA/cm^2 on 1 µm^2 Cu: *Cycle 1*



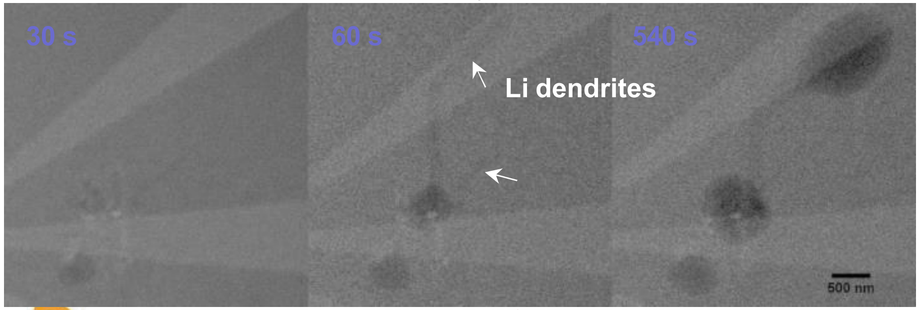
-2.25 mA/cm^2 on 0.44 µm^2 Cu: *Cycle 7*



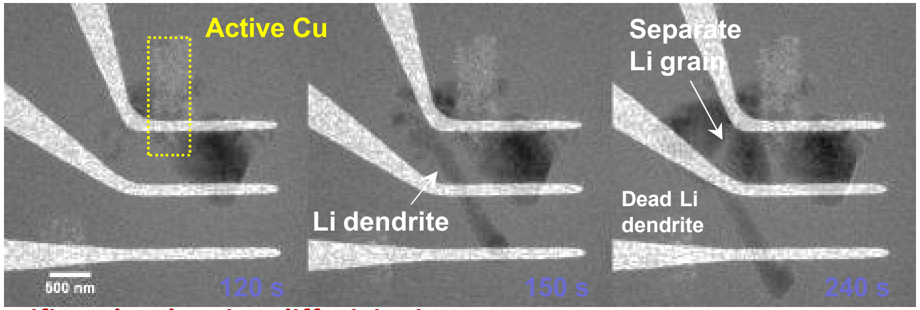
-2.25 mA/cm^2 on 0.44 µm^2 Cu: *Cycle 10*



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



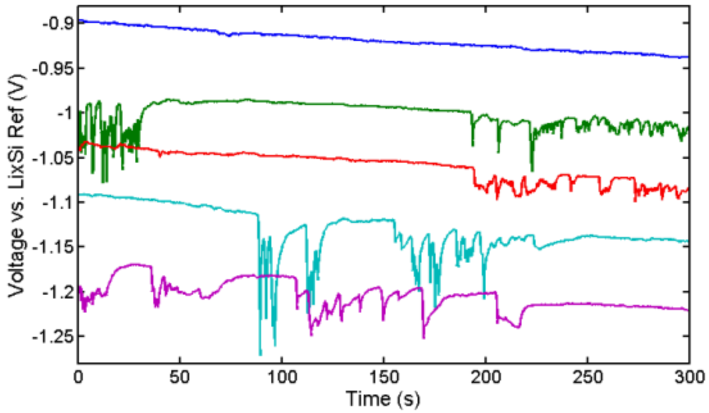
-5 mA/cm^2 on 1 µm^2 Cu : *Cycle 1*

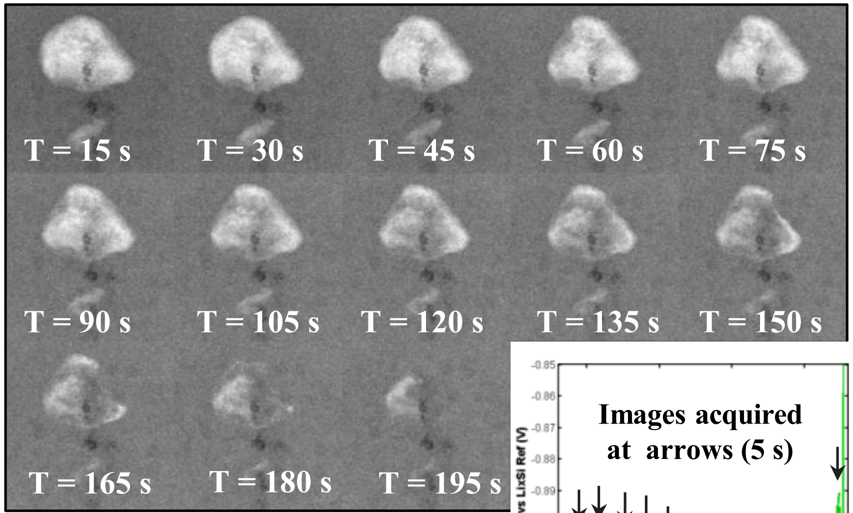


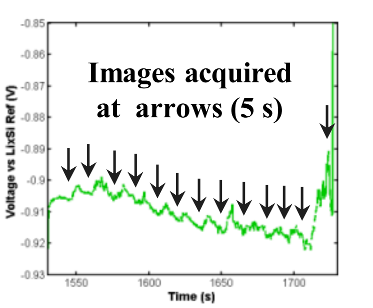
The velocity of the dendrite growth decreases significantly when ion diffusivity increases

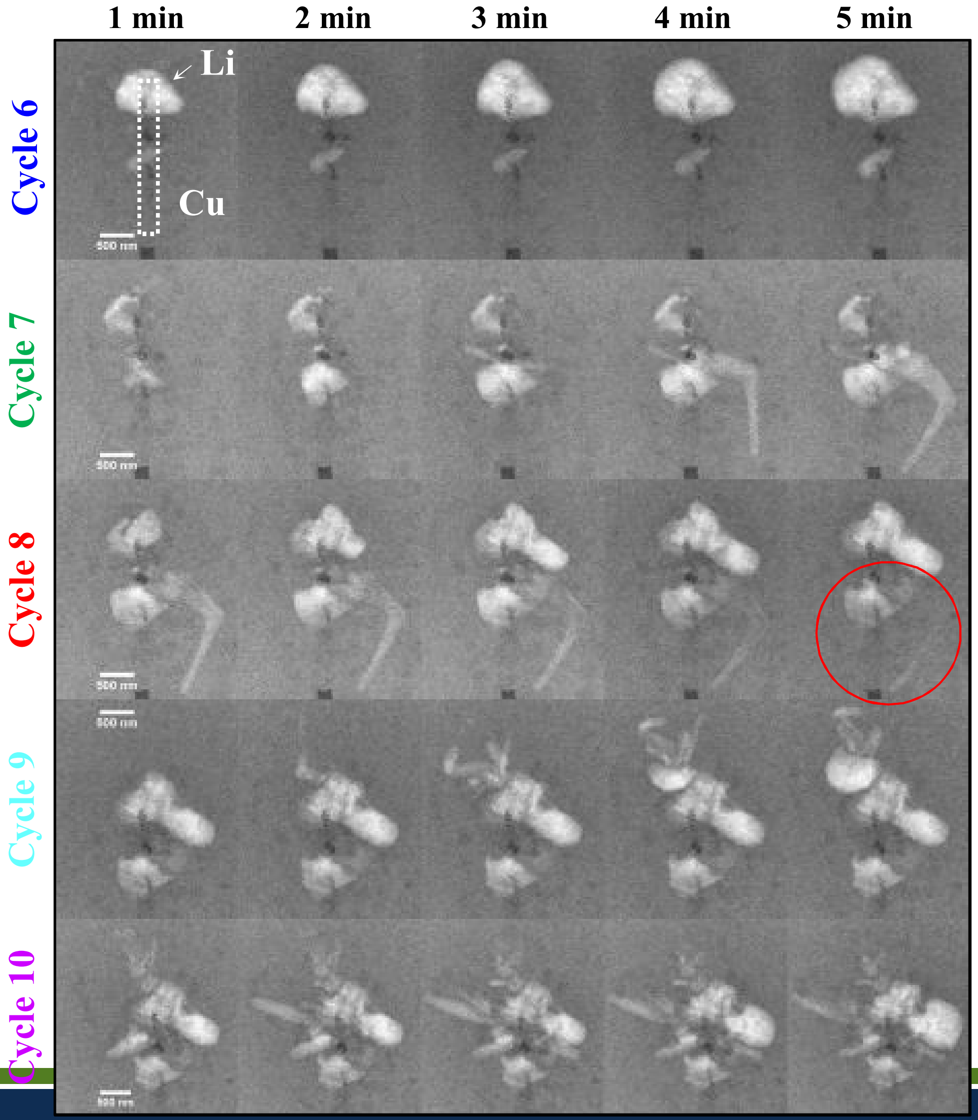
Effects of Multiple Cycles on Li Nucleation

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



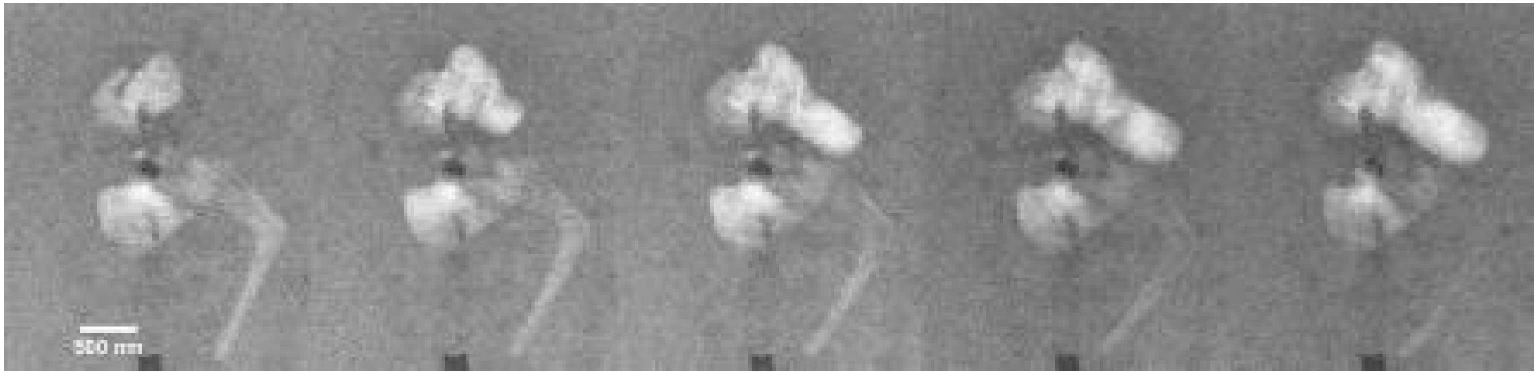


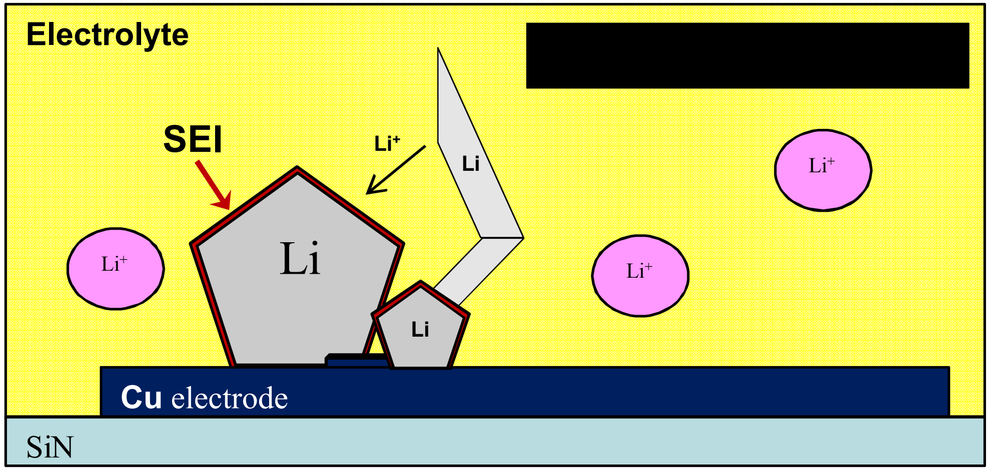




Self Discharge Mechanism or Conservation?

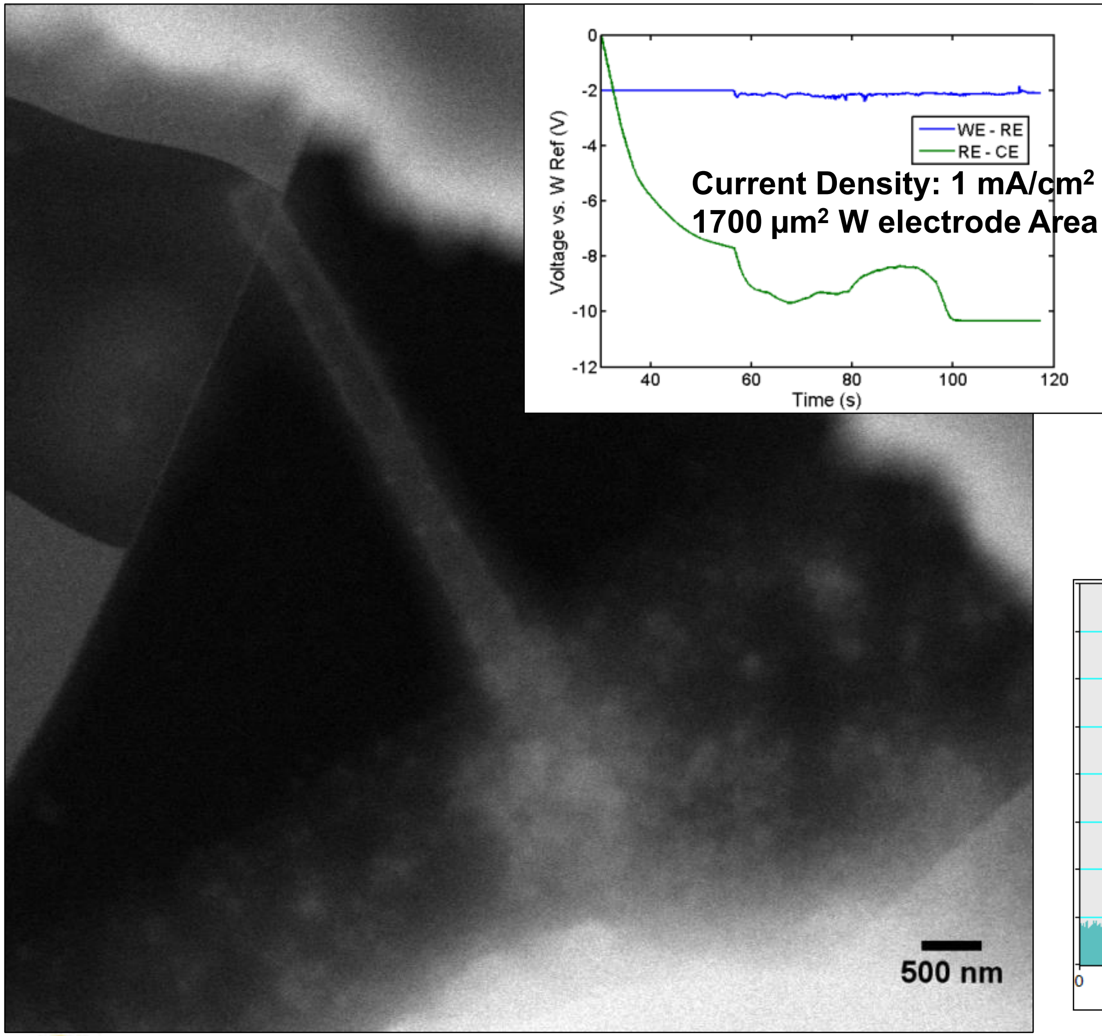
Li dendrite disconnected from electrode by neighboring grain, will dissolve during next deposition step

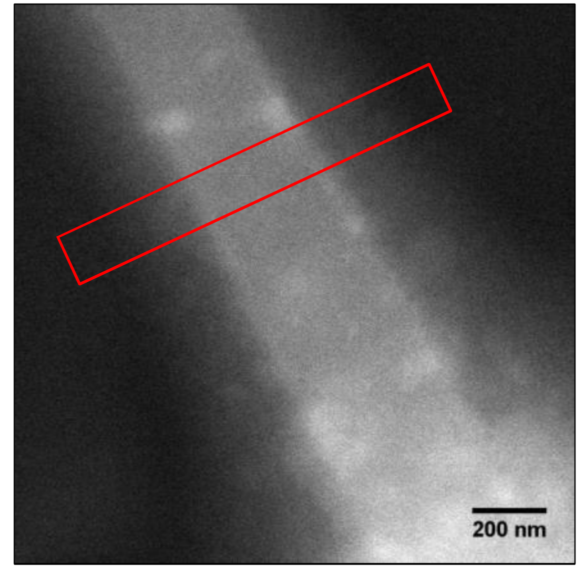


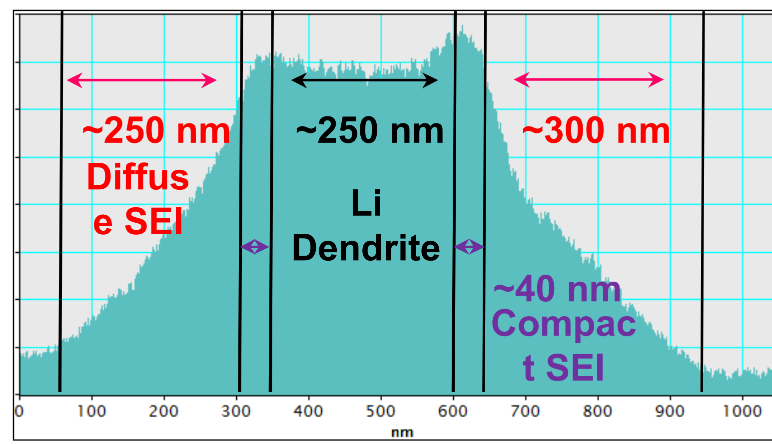


Need comparison to deposition results when using a Li metal CE

Li Dendrites formed at High Current Densities



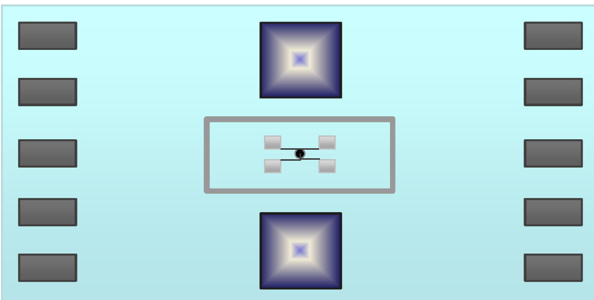


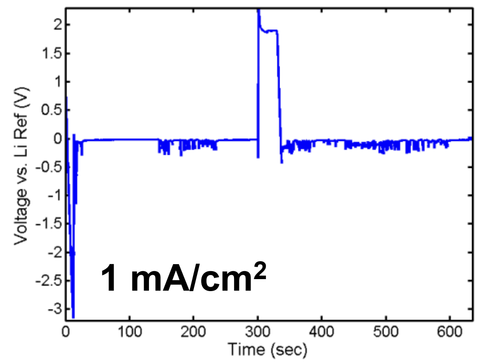


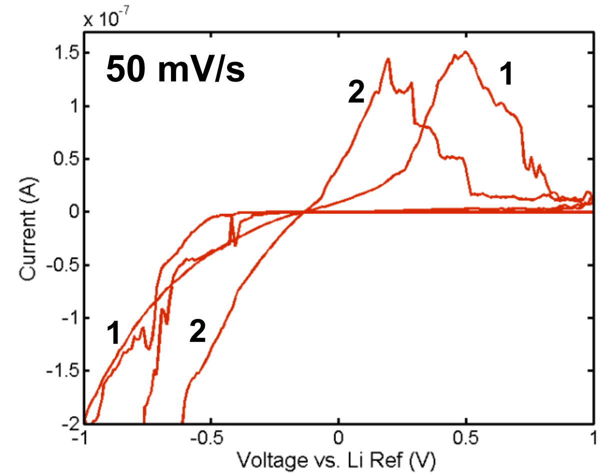
Remove electrolyte to observe structural details in SEI

Technical challenge

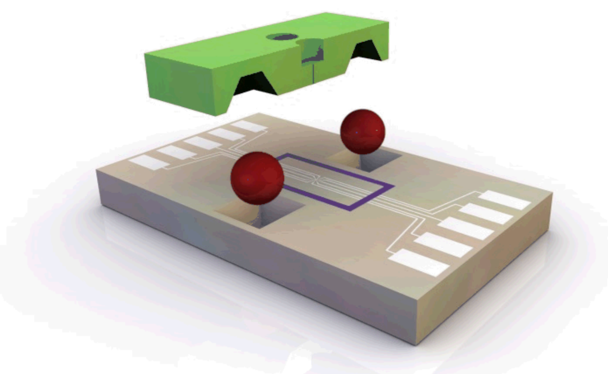
- **Using the 4 M LiFSI in DME system, determine the effect of using a Li metal counter and reference electrodes on the cycling efficiency and Li morphology.**

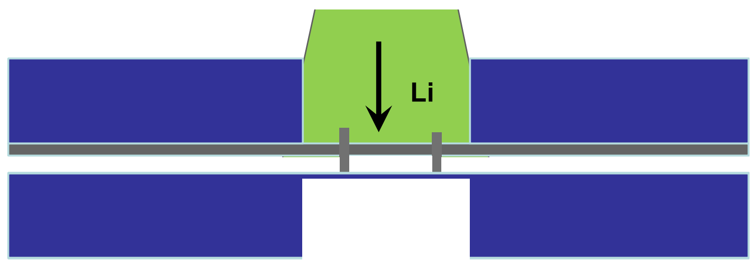




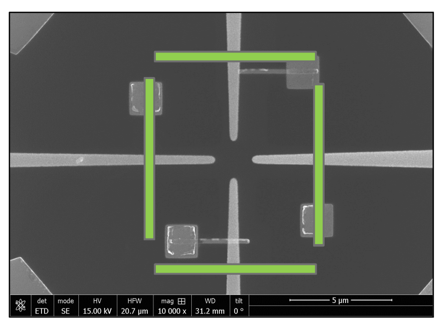


Shadow mask to evaporate conformal Li WEs onto the cell





- **Conformal Li metal electrodes will enable testing of Li morphology with protective films**
- **Li metal electrode vs. Li CE & RE**



- **What is the interfacial structure between Li metal electrode with protective layer?**
- **Chemical composition at the interface?**

- **Deposit 300 nm SiO_2 on SiN membrane**
- **Wet etch to open center port**
- **FIB electrode shadow mask design**
- **Beads align shadow mask to base**

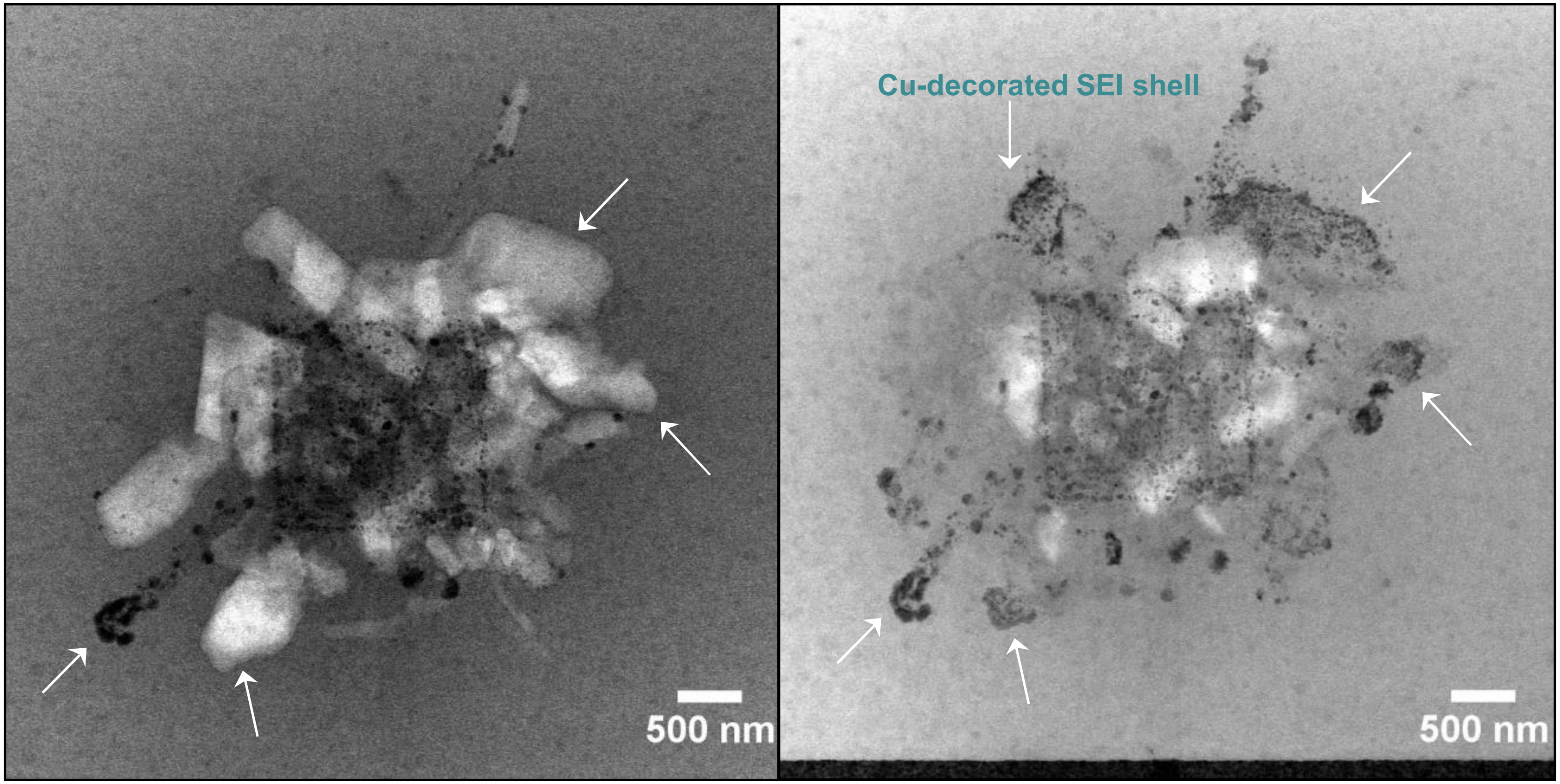
Conclusions

- Able to electrochemically control the deposition/stripping of Li in TEM
- 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 for both salt/electrolyte systems
- Comparison between salt/electrolytes identifies similarities in effects due to cell design and differences due to salt/electrolyte (dead Li dissolution)
- Is electrolyte breakdown (no Li metal CE) affecting Li morphology & Coulombic efficiency?
- The electron beam can influence the electrochemical data and surface film properties on ultramicroelectrodes, even at low dose imaging
- Effect of electron beam on ion diffusivity to affect dendrite growth?

Backup slides

Li Morphology: No Electron Beam Influence

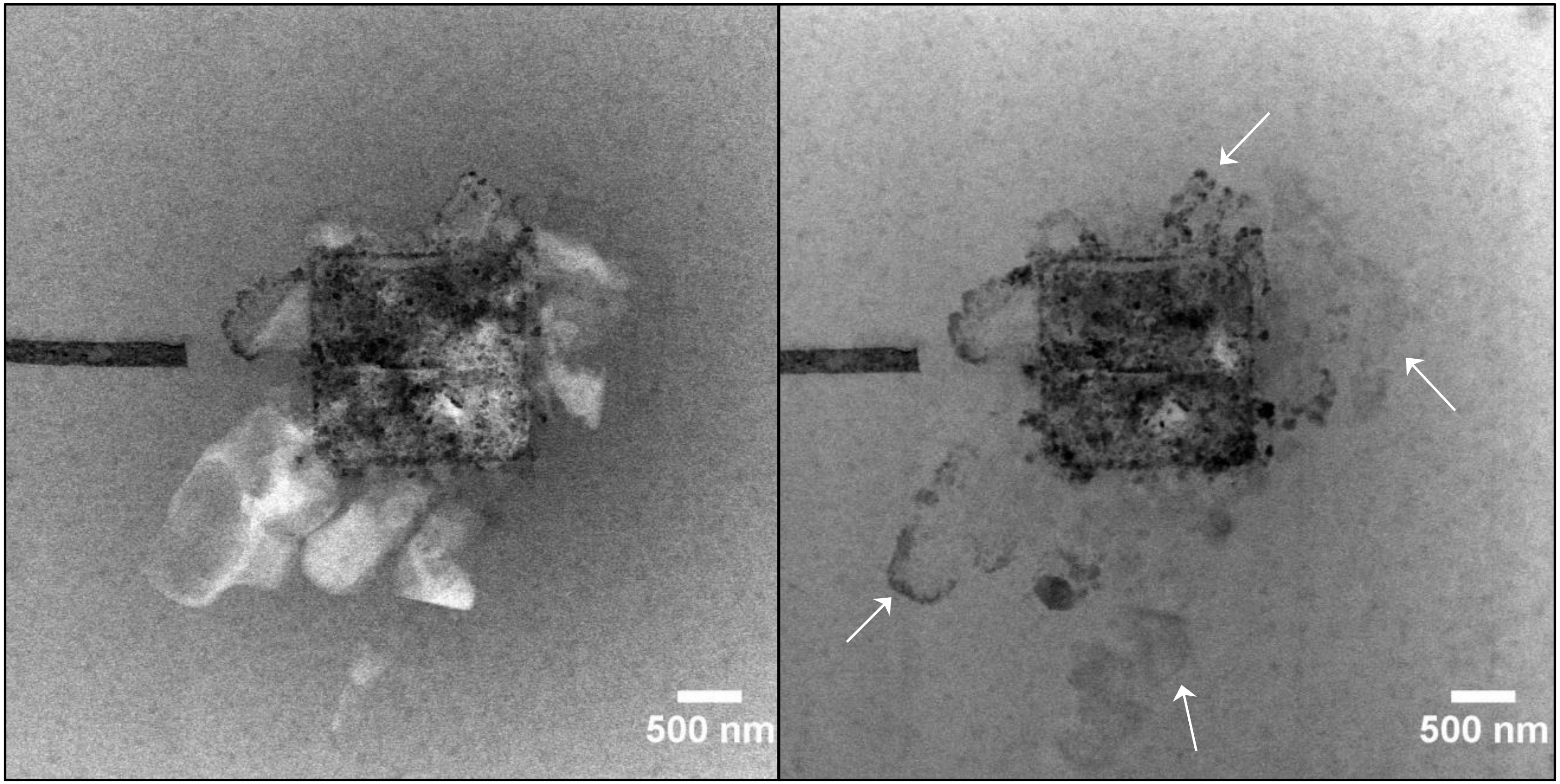
WE#3 : No Beam



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

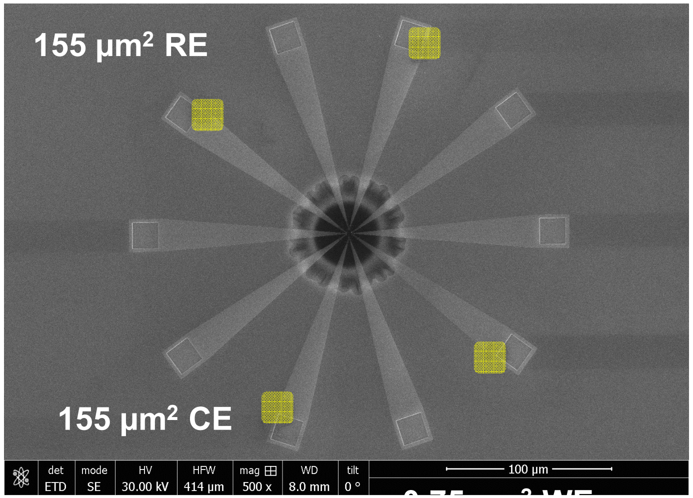
Li Morphology: Limited Beam Influence

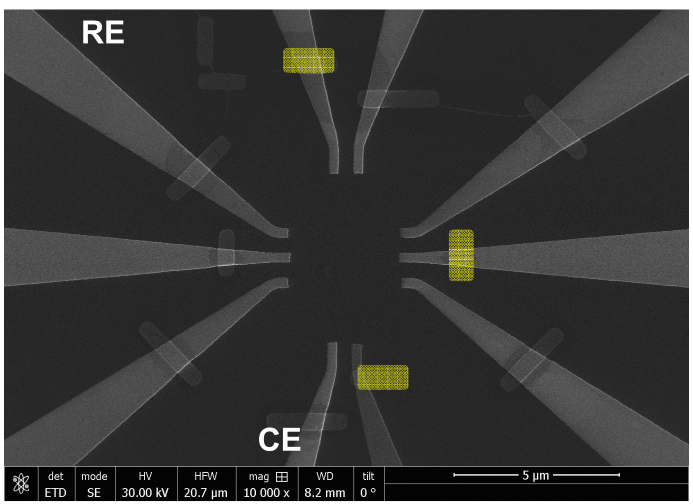
WE#1 : < 3.84 e-/Å^2 Total Dose During Electrochemistry



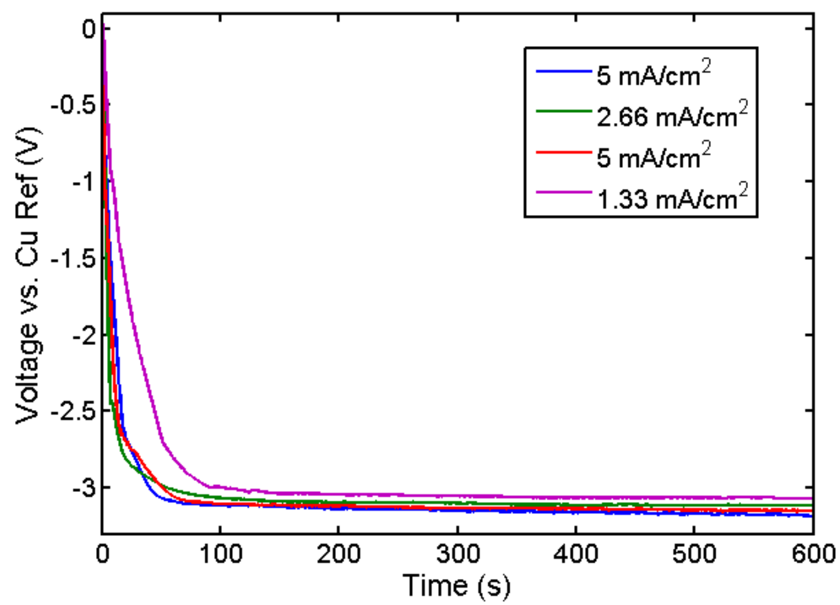
Increased contrast from SEI is observed about the edges of dissolved Li deposits
Shows impact of electron beam degradation of the electrolyte

Current Density Dependence on Li Morphology

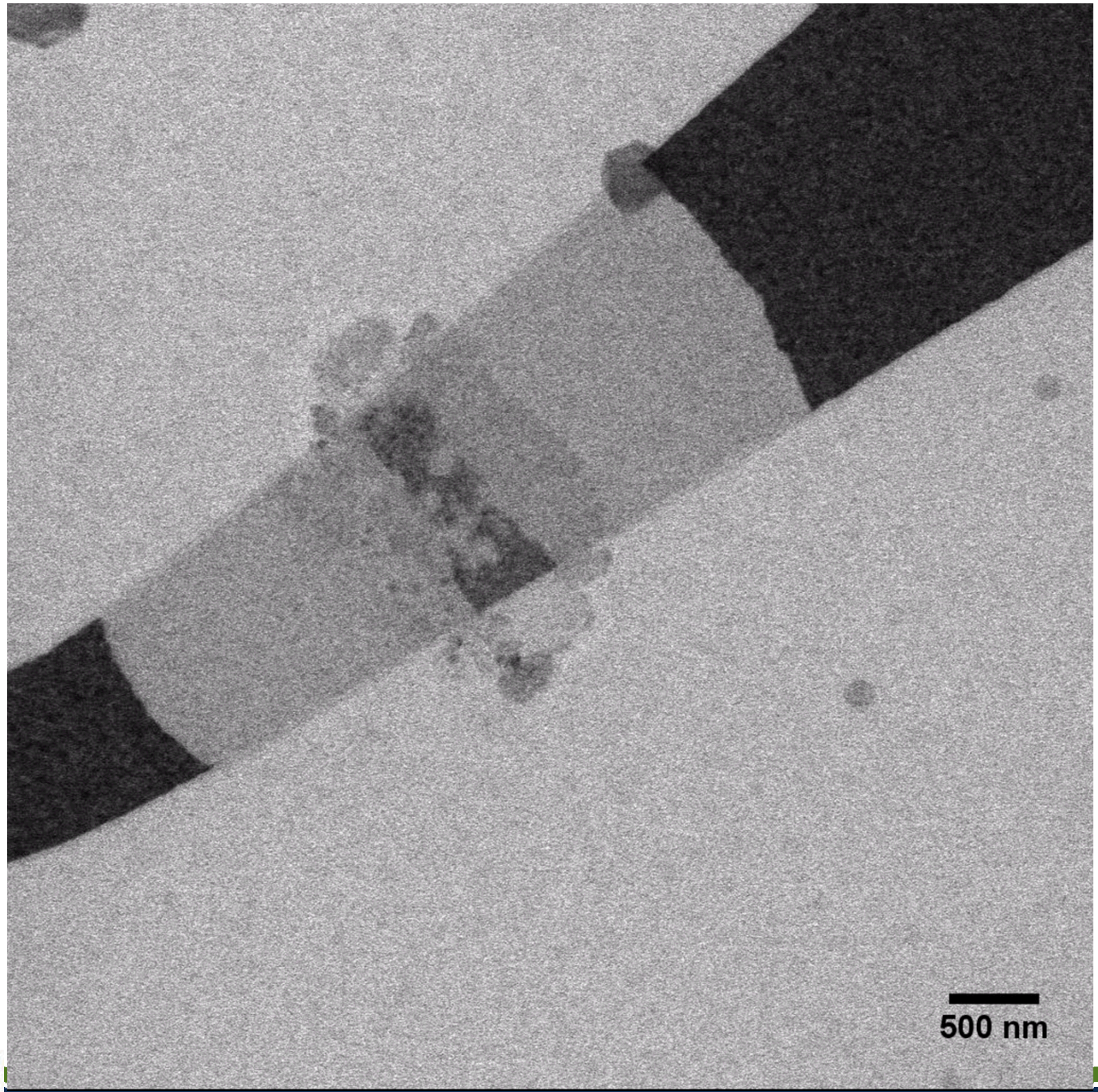




- 40 nm Cu electrodes (5 nm Ti adhesion layer)
- W electrodes coated with Al_2O_3/SiO_2 (40 nm) passivation layer
- Cu WE Area: 0.75 µm²
- Cu RE & CE Areas : 155 µm²
- 4M LiFSI in DME (3 ppm H_2O)
- Dose per frame: 0.03 – 0.28 e^-/Å²
- Electrolyte Thickness: > 1.5 µm



Where is Li depositing during Cycling?



- Ni WE Area: ~1 μm^2
- Ni RE & CE Areas : 100 μm^2
- Electron Beam Dose: < 2.53 e
- Dose per frame: 0.03 e$^-$/Å^2
- Electrolyte Thickness: 500 nm

Models that Explain Li Deposition Morphology

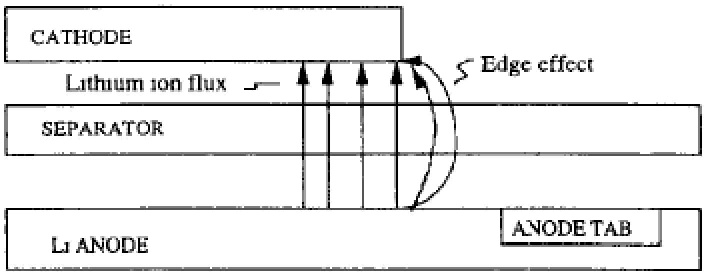
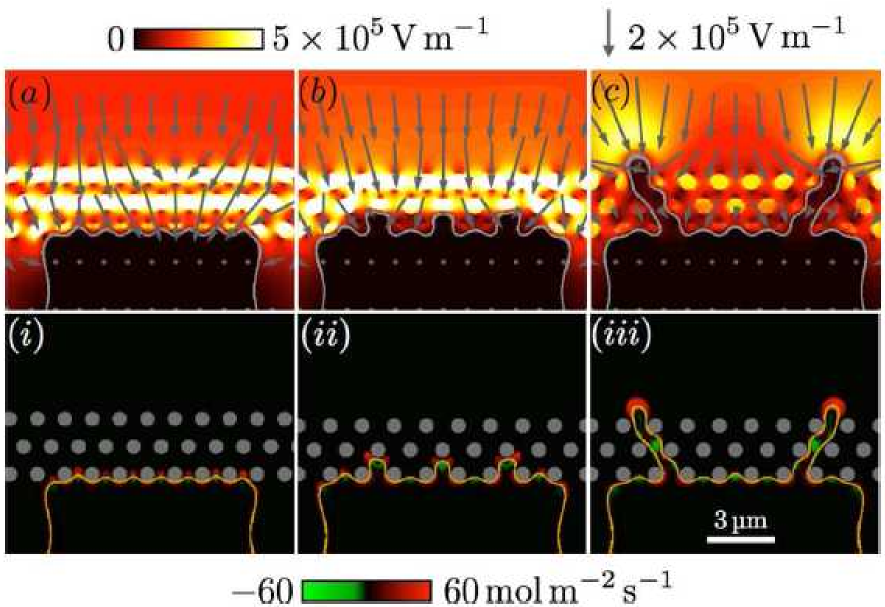
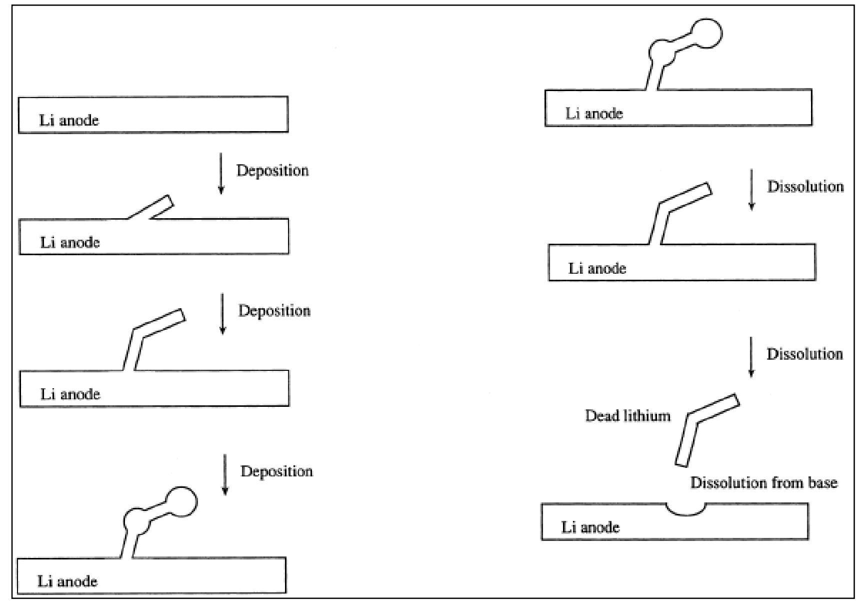


Fig 4 Lithium anode cut at the end of the cathode during cycling

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

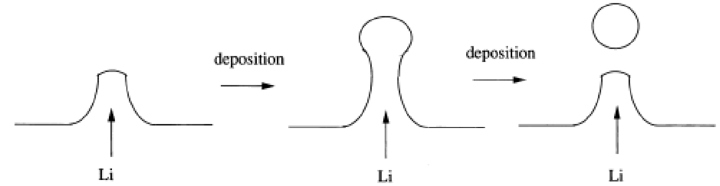


Jana A. et al. 2015. J. Power Sources 275, 912.



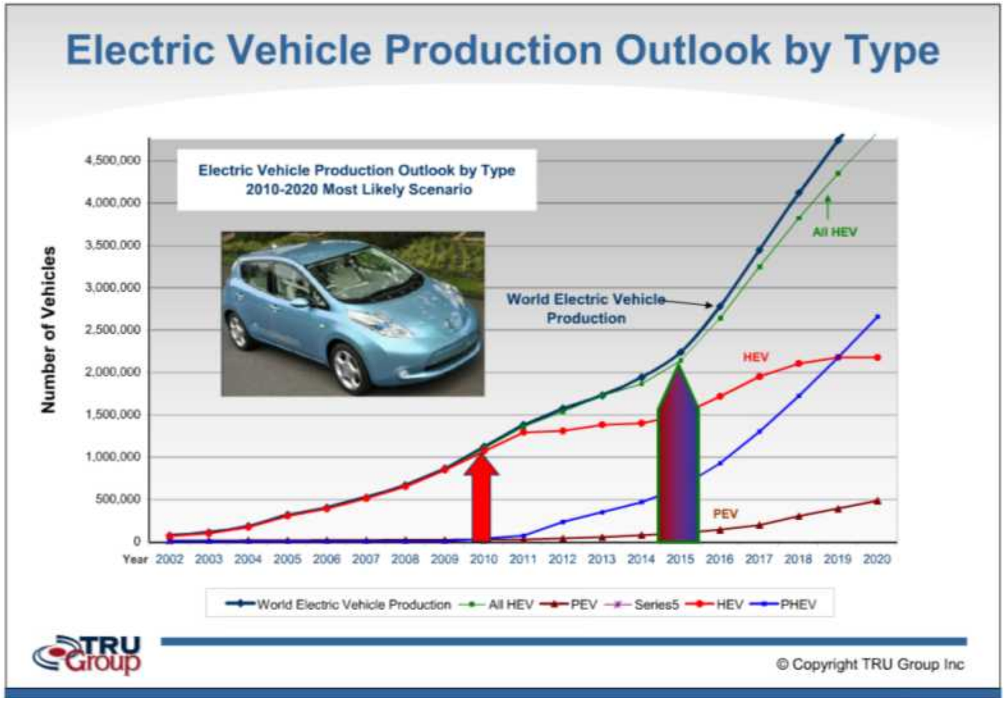
Yamaki, J.-i. et al. 1998. J. Power Sources 74, 219.

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



2020 Transportation Market Size

- Though motivation for xEV's is decreased with low fuel costs, the market is still large.
- An optimistic 2020 estimate of >4.5M xEV on the road.
- **Represents a vehicle storage market of potentially ~45GWh of storage by 2020** (assume 10kWh per xEV).

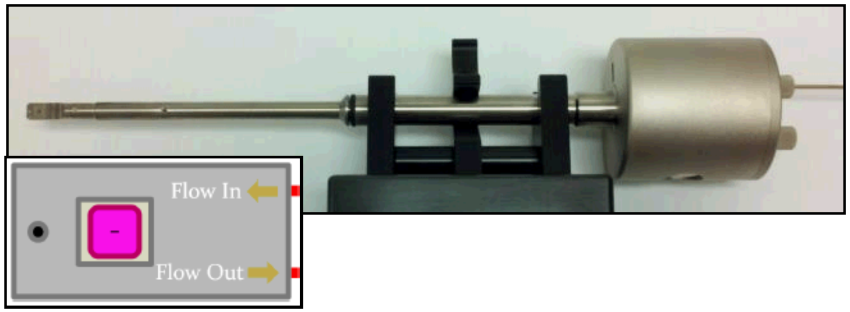


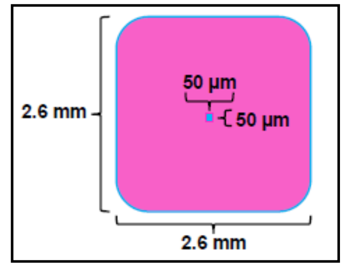
Presidential mandate of 100M xEV on the road, would result in ~1,000GWh of storage (assuming 10kWh per xEV)

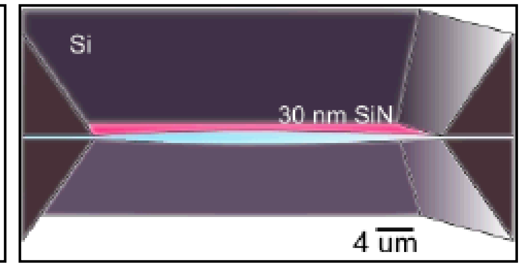
Sandia National Laboratories

Liquid Cell Transmission Electron Microscopy

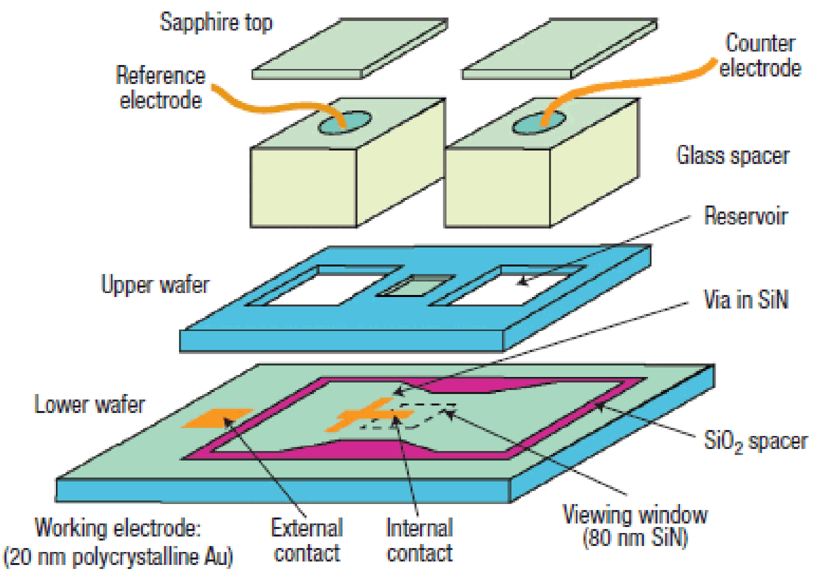
Commercial Microfluidic Liquid Cell TEM Holder



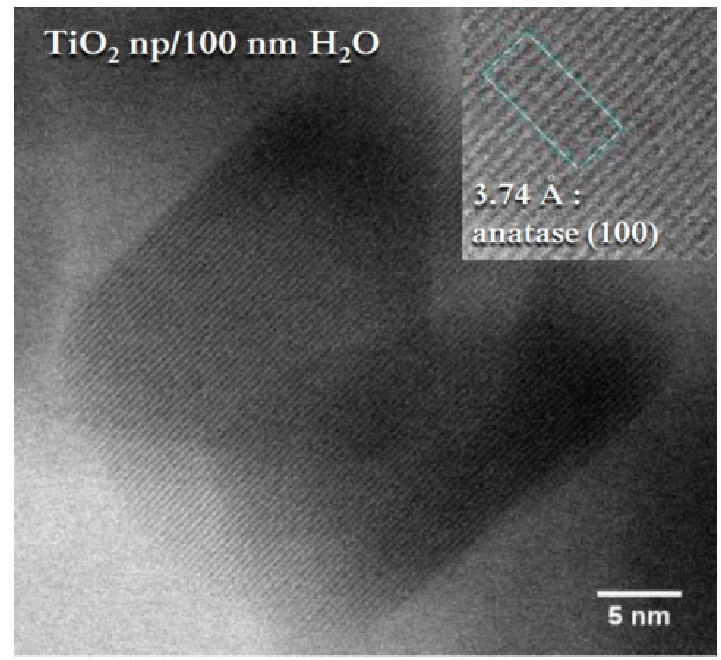




Custom MEMS-based Liquid Cell



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



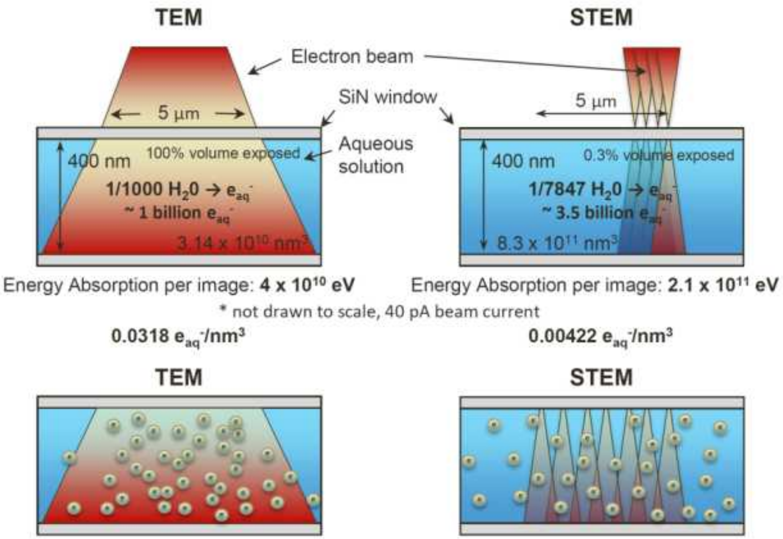
Electron Dose:

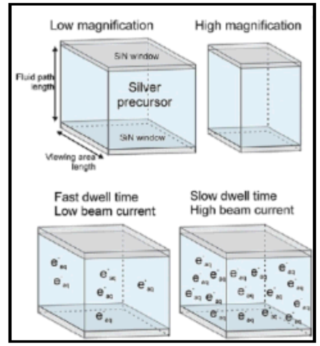
ACSTEM: >10^4 e^-/A^2

Low Dose STEM: >1 e^-/A^2

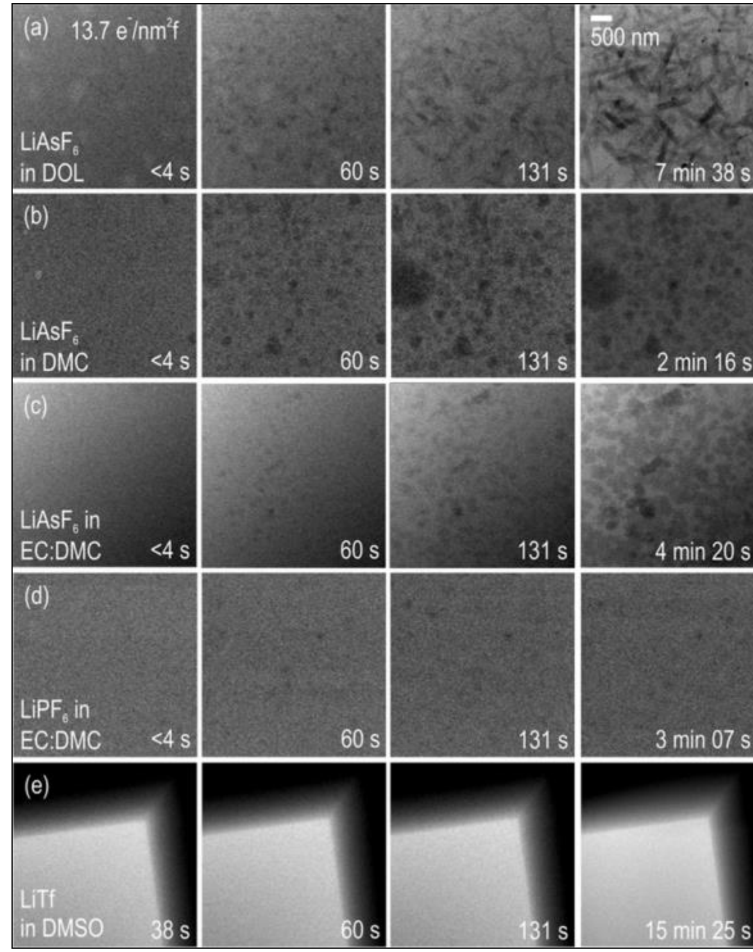
Electron Beam Damage on Liquids

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



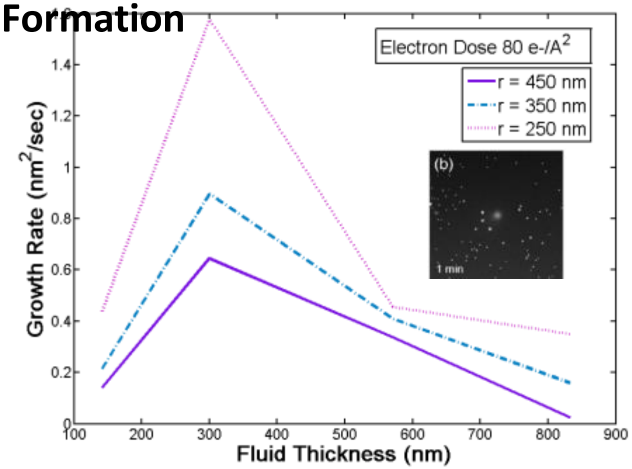


Woehl et al. ACS Nano 6, 8599 (2012).



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

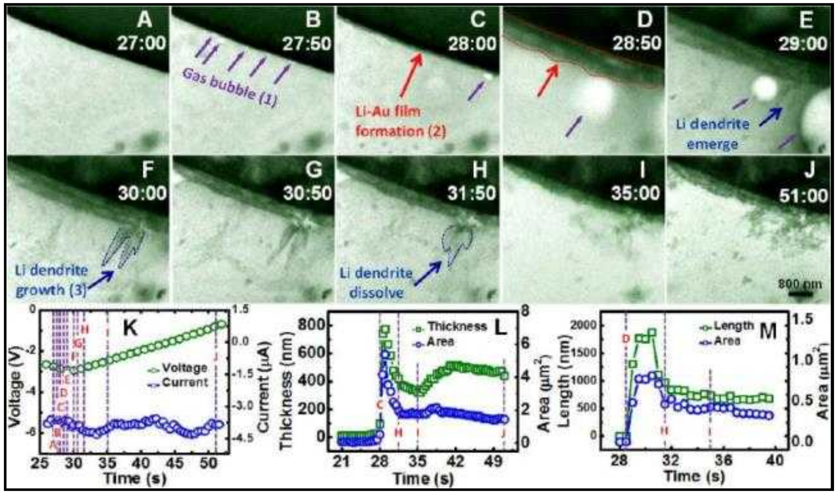
Thickness dependence on Beam Induced Radical Formation



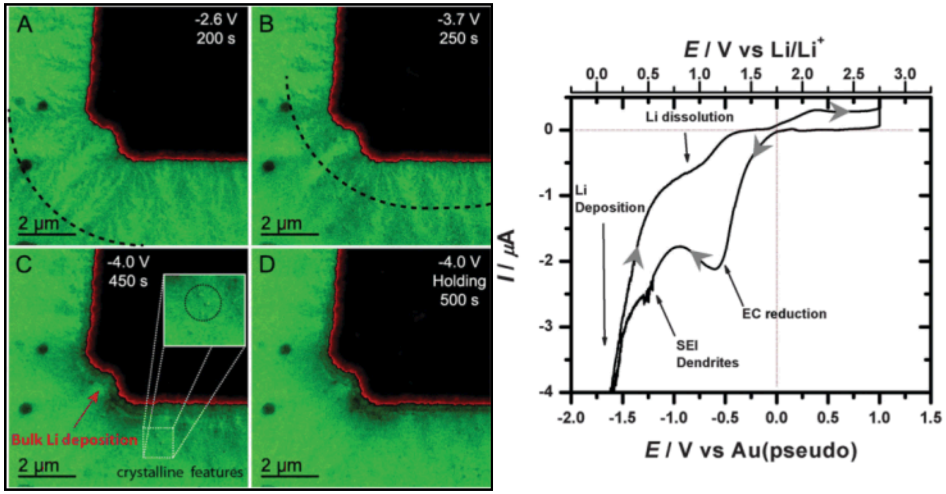
- **Maximum solvated electrons at ~ 300 nm thick liquid layers**

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

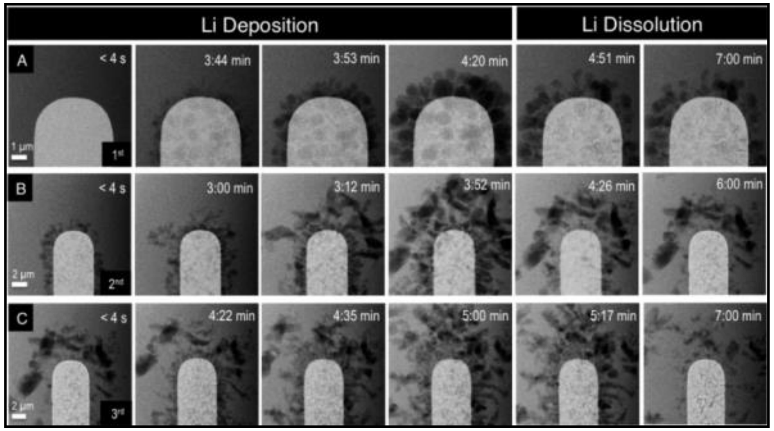
Li Deposition in Closed TEM Liquid Cell



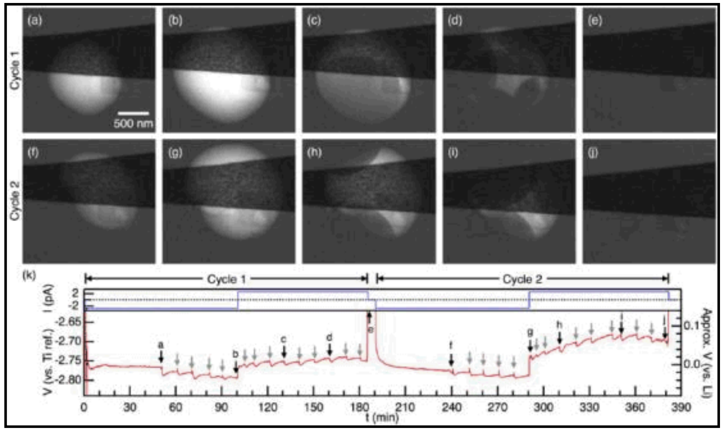
Zeng et al. (2014) Nano Letters 14(4) 1745-1750.



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

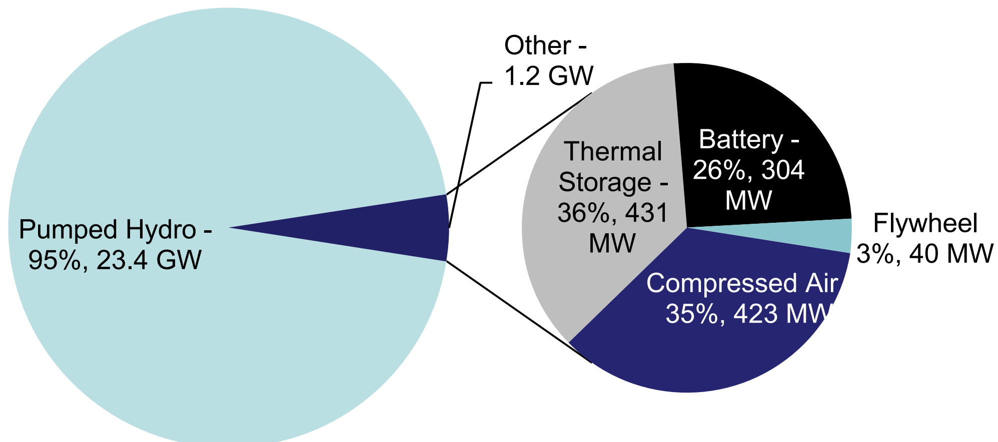


Medhi et al. (2015) Nano Letters 15, 2168-2173.



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

The Distribution of Storage Types



Pumped Hydro is king!

http://www.energystorageexchange.org/ (data cited as of July 2013)