

CINT

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The Center for Integrated Nanotechnologies

Nanomaterials

Integration

A U.S. DOE Nanoscale Science Research Center

Megawatts from Nanowatts

Sean J. Hearne

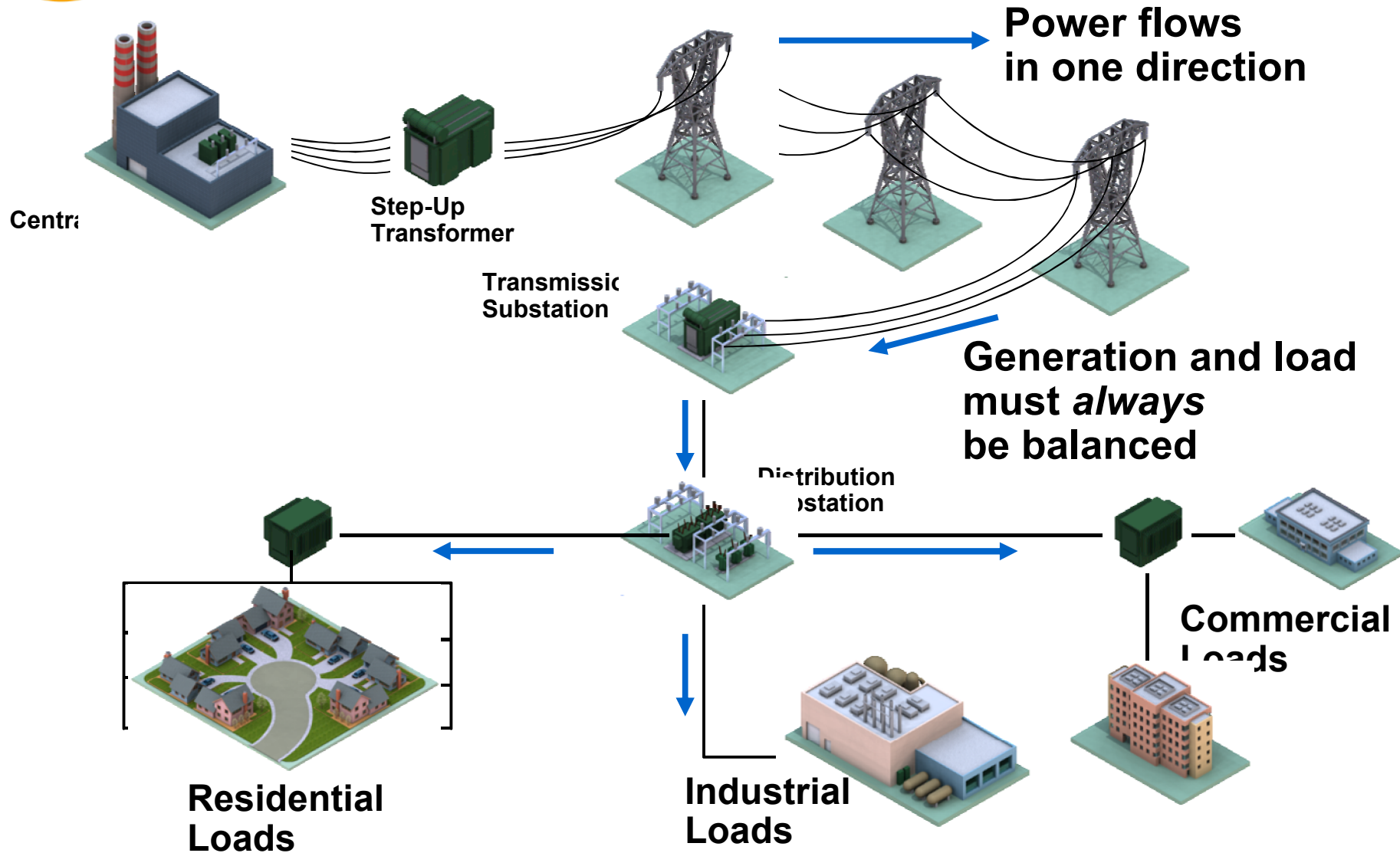
The Center for Integrated Nanotechnologies

Sandia National Laboratories



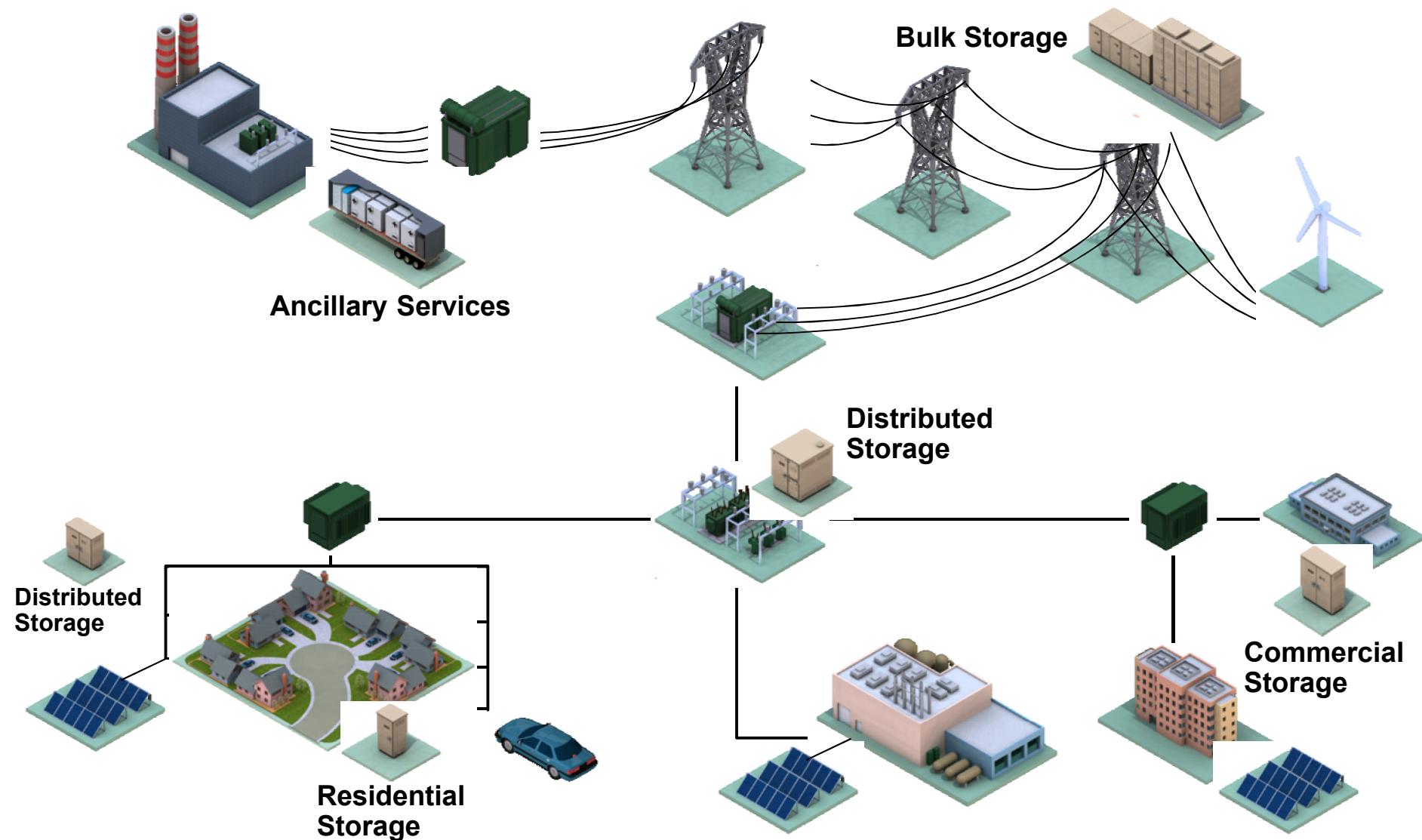


How the Electricity Grid Works Today

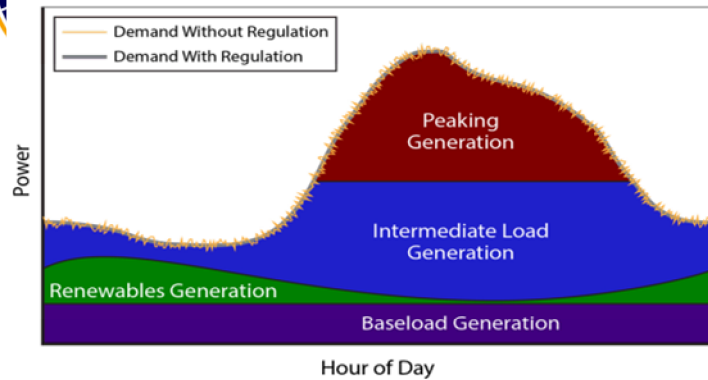




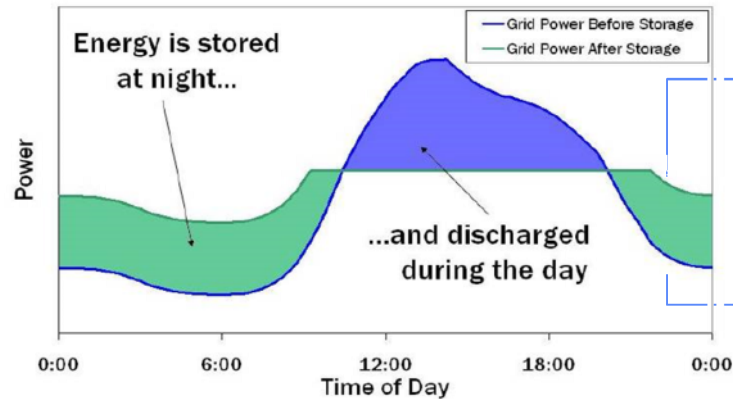
The Grid is Evolving



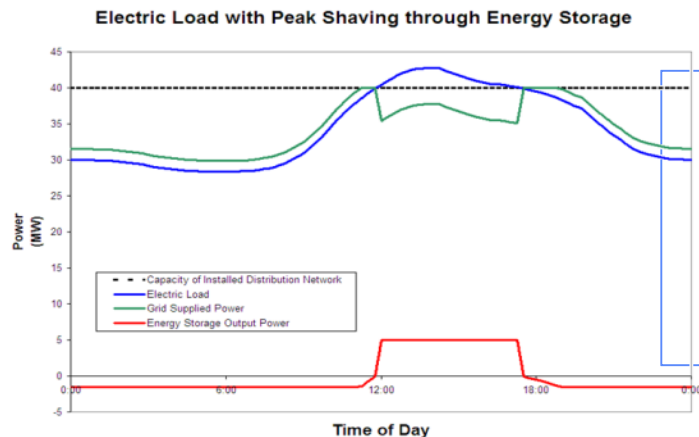
Uses of Energy Storage



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



Why isn't storage everywhere?

The cost is too high for the value of services provided

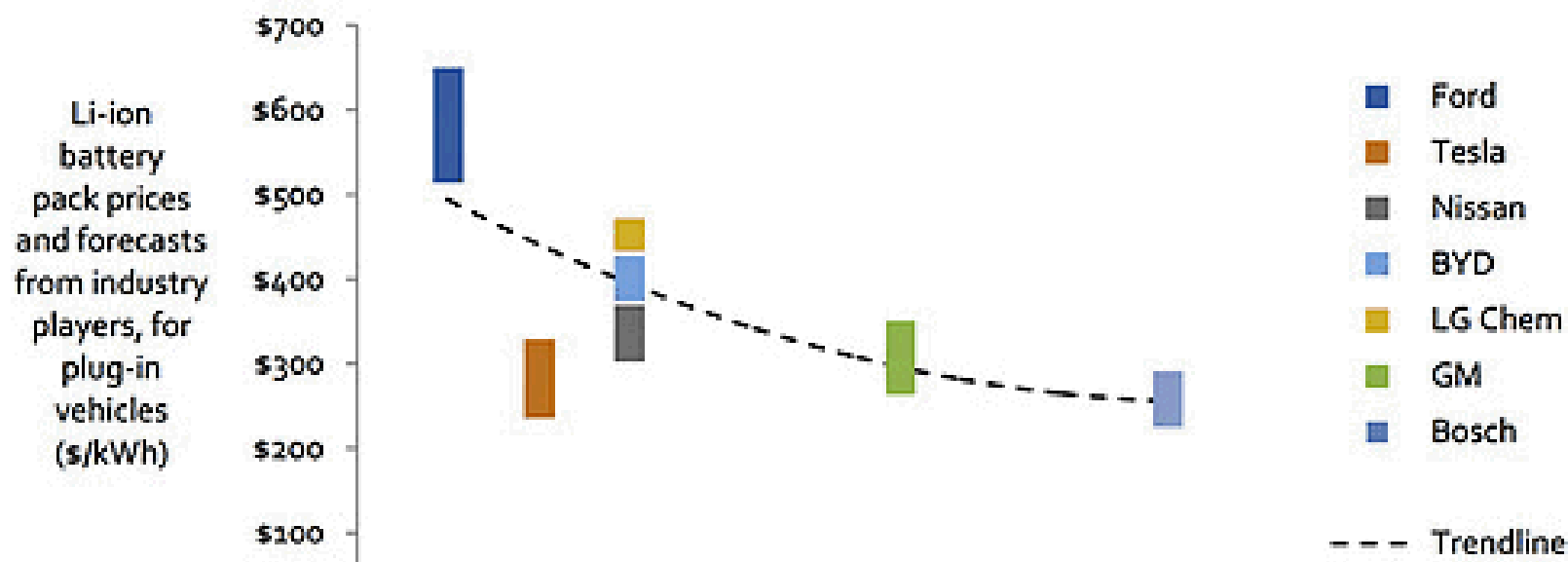


Energy Storage only makes money for the owner when electrons are flowing.



Let's dive deeper: Li-ion Battery Cost

Despite a Huge Historical Spread in Li-Ion Prices, They Are Beginning to Converge – and Keep Falling

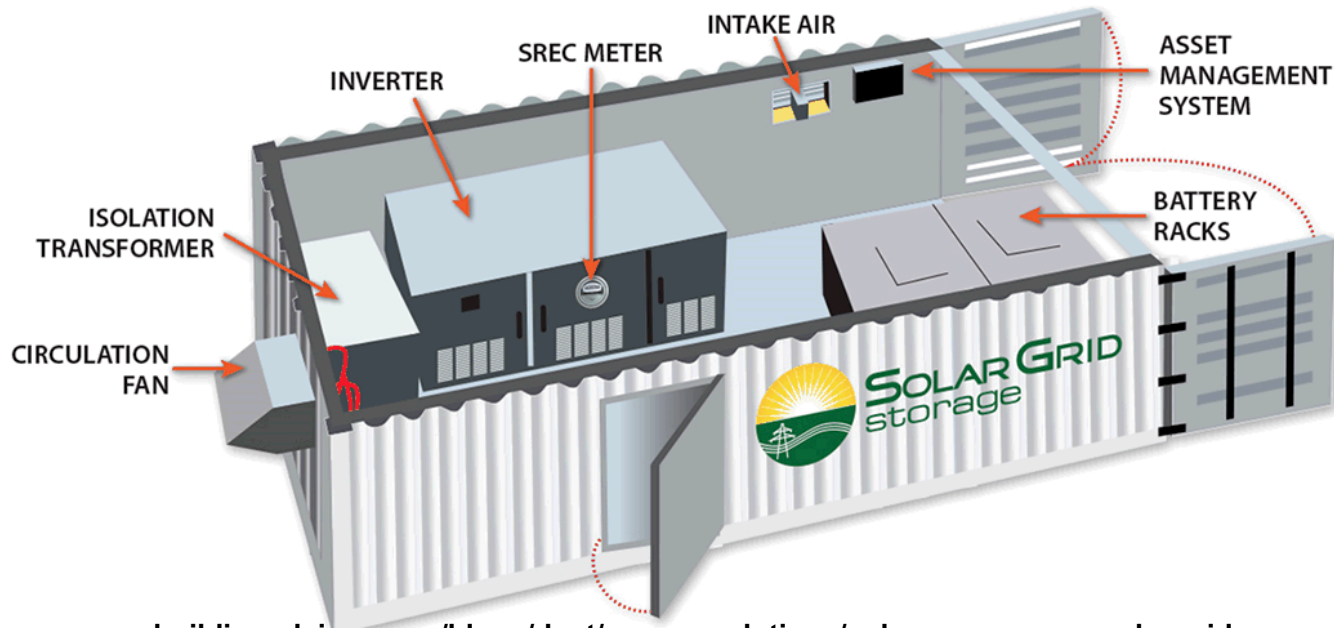


Cost of the battery pack is ~\$300/kWh

Source: Lux Research, Inc.
www.luxresearchinc.com



Balance of System is the Main Cost



<http://www.greenbuildingadvisor.com/blogs/dept/energy-solutions/solar-energy-can-make-grid-more-resilient>

****Cost of the system is ~US\$670 / kWh**

Total cost = ~US\$1000 / kWh

****Luis Ortiz, *Grid-Scale Energy Storage Balance of Systems 2015-2020: Architectures, Costs and Players*, Energy Storage – Greentech Media, January 2016**



Value of Grid Storage

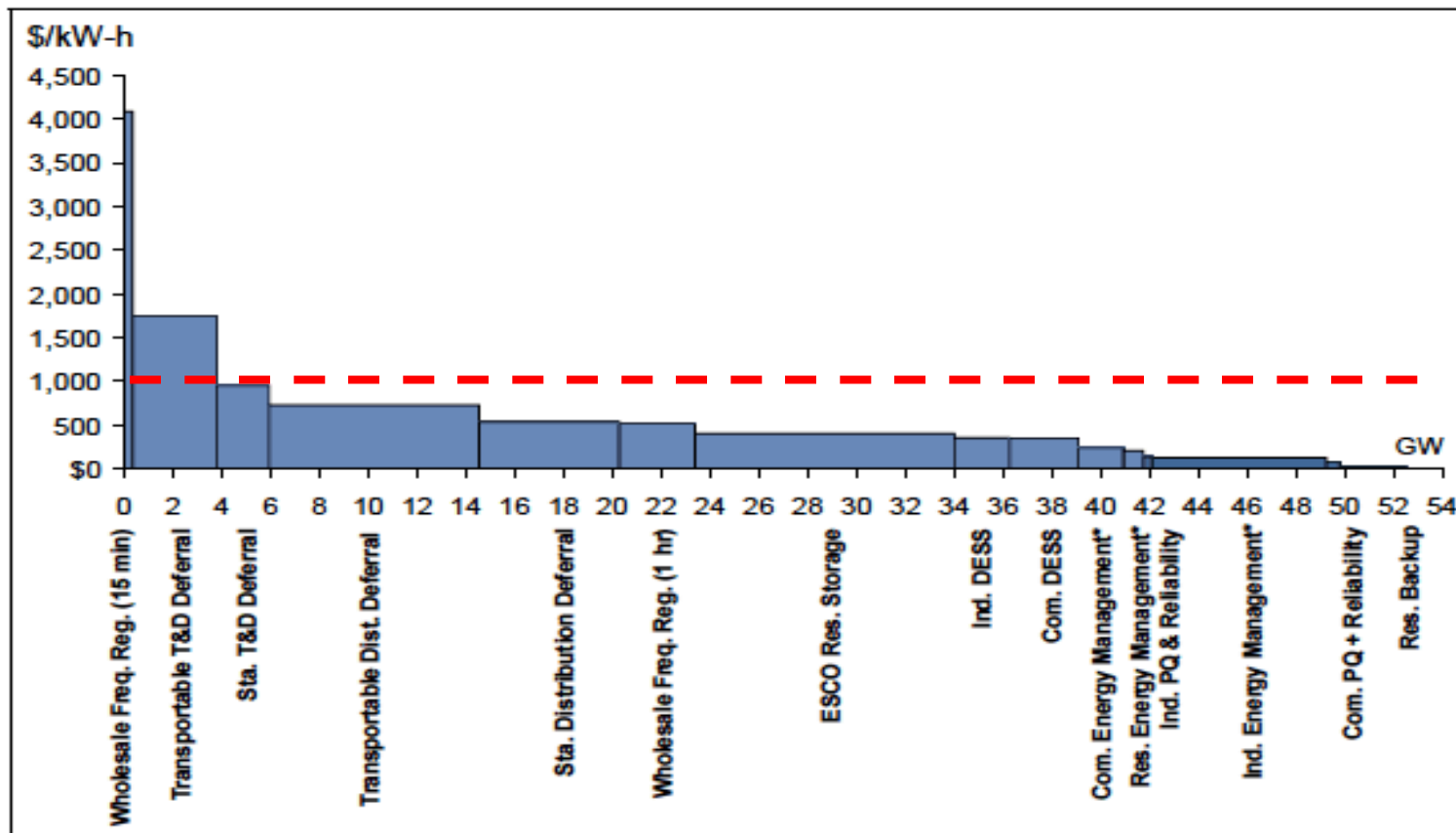


Figure 13
Estimated Target Market Size and Target Value Analysis

Source: EPRI, 2010

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



Energy Storage Technologies

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

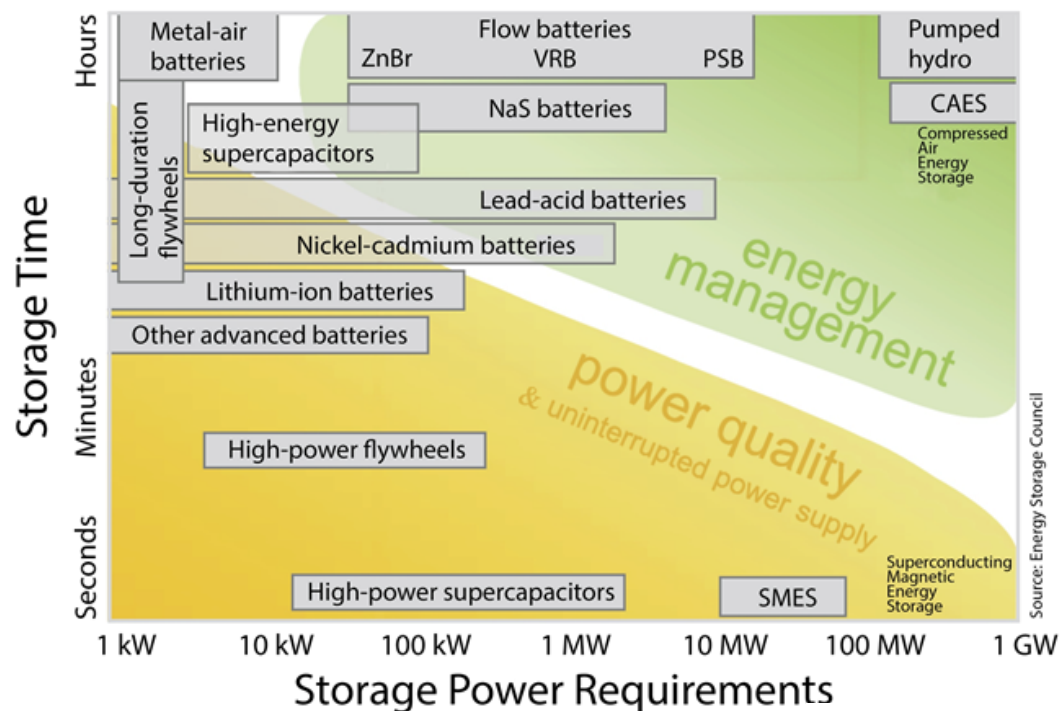
Two regimes, multiple technologies:

Power – short discharges (sec to min):

flywheels, capacitors, SMES, some batteries

Energy – long discharges (min to hr):

batteries, H₂ fuel cells, CAES, pumped hydro



Source: Energy Storage Council



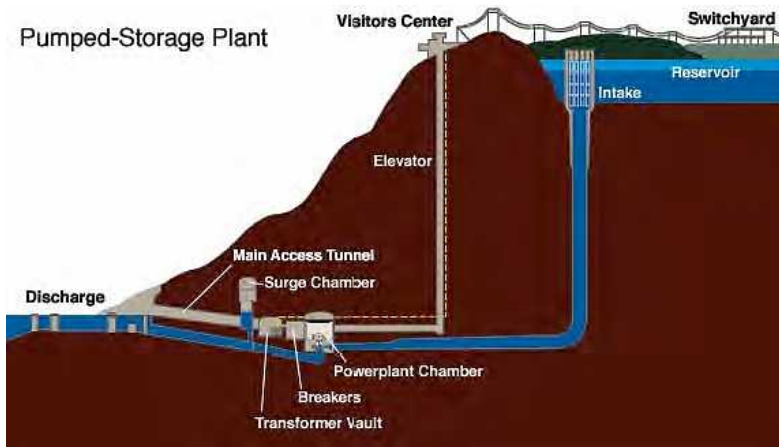
Is Pumped Hydro the Answer?

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 (~10 trailer trucks)

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!**

919 cubic meters =
10 tractor trailers





What about Li-ion Batteries?



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

With the cost of the batteries \$500 /kWh, so 0.5MWh is \$250k

Total cost = \$420k

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



But...



Let's consider the degradation cost of Tesla batteries

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

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

Current average electricity cost in USA = US\$0.09 kWh

So, using your Tesla S to store energy for the grid is a losing proposition because of degradation 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

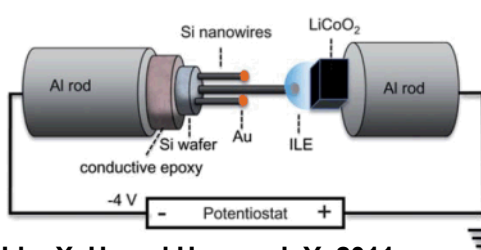
[2] http://my.teslamotors.com/fr_CA/forum/forums/battery-degradation-finally-some-data ₁₂



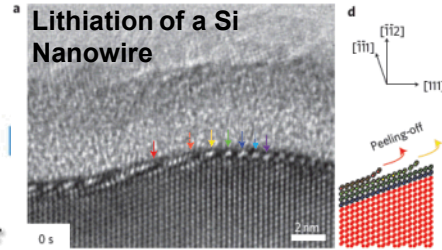
The Nanostructural source of Li-ion Battery Degradation



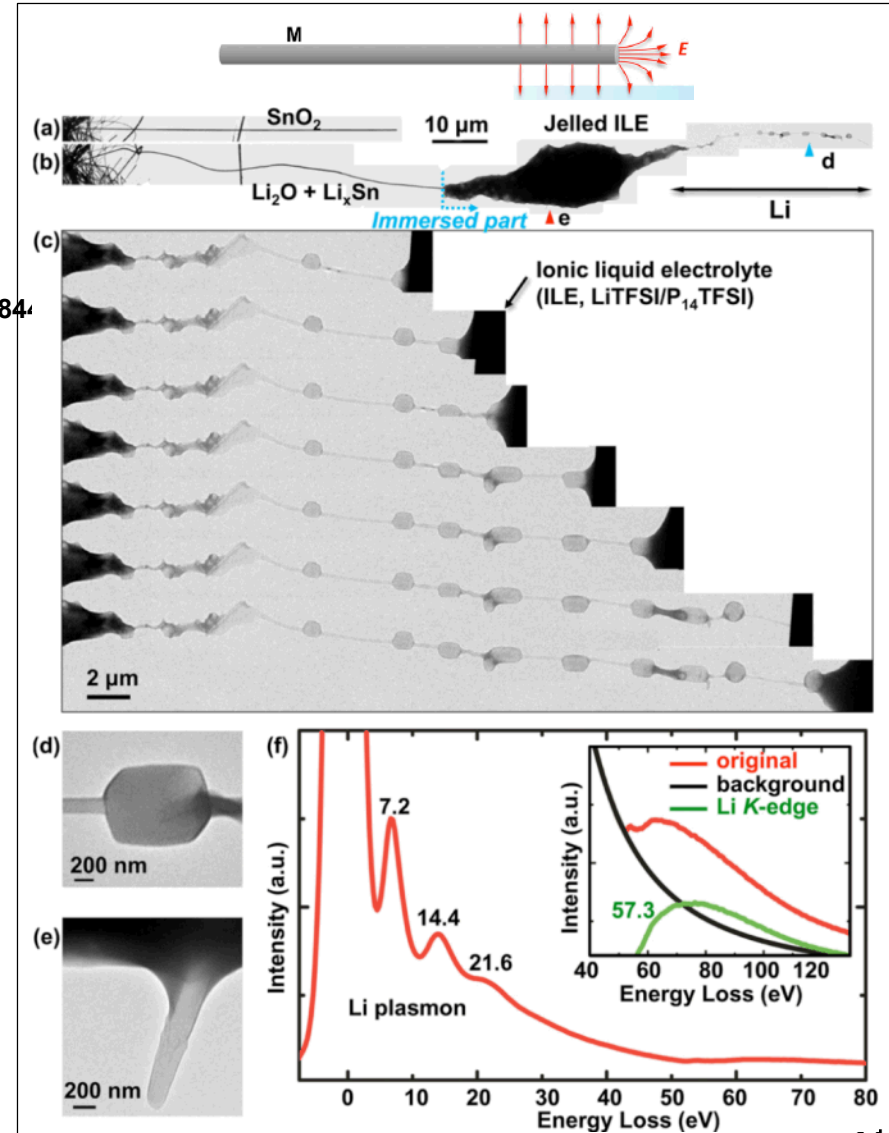
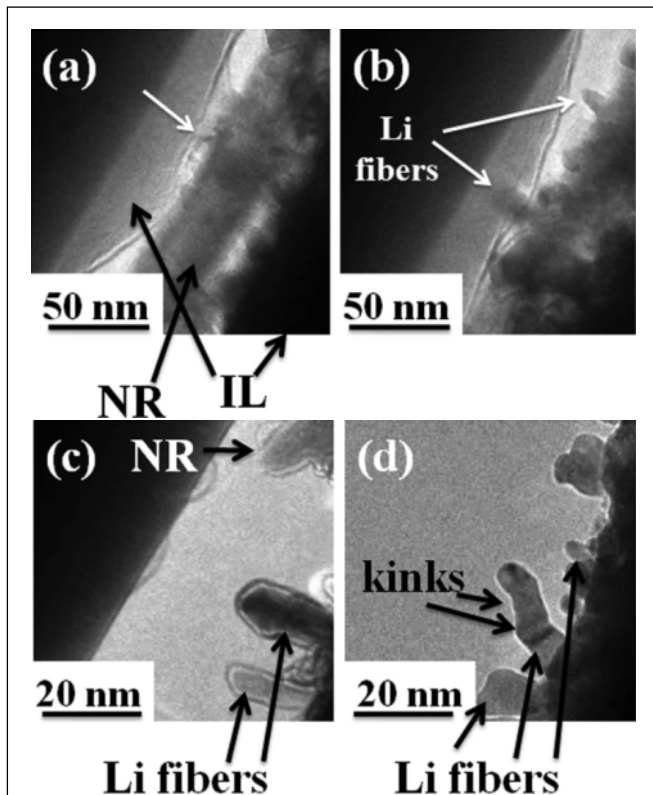
Vacuum Environment: Li Dendrite Formation



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



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

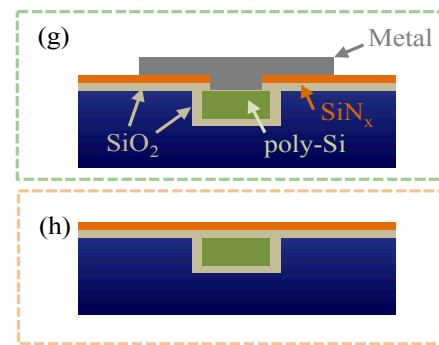
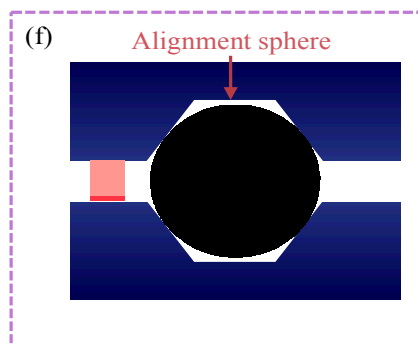
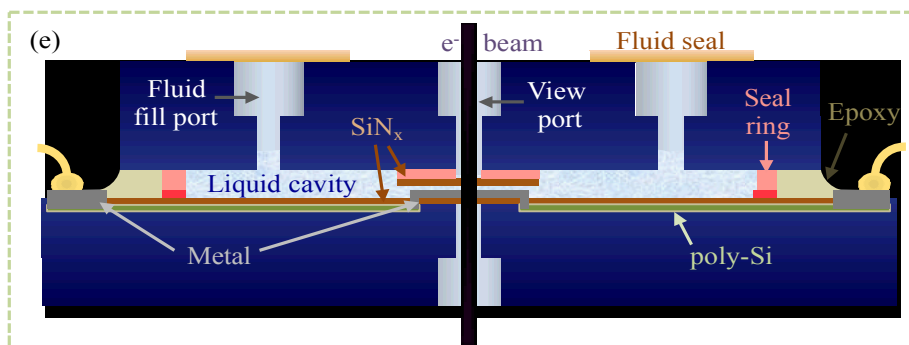
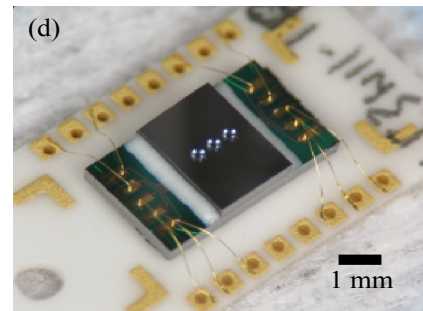
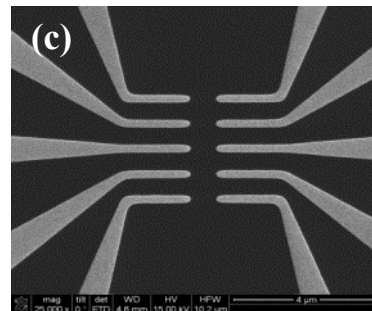
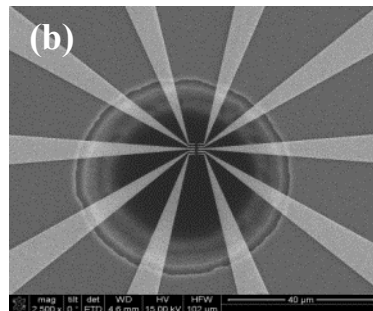
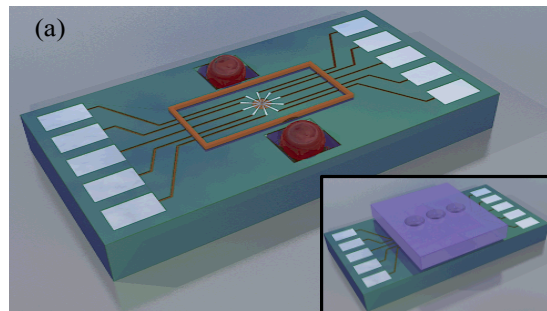


Liu, X. H. et al. 2011. Appl. Phys. Lett. 98, 183107.



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



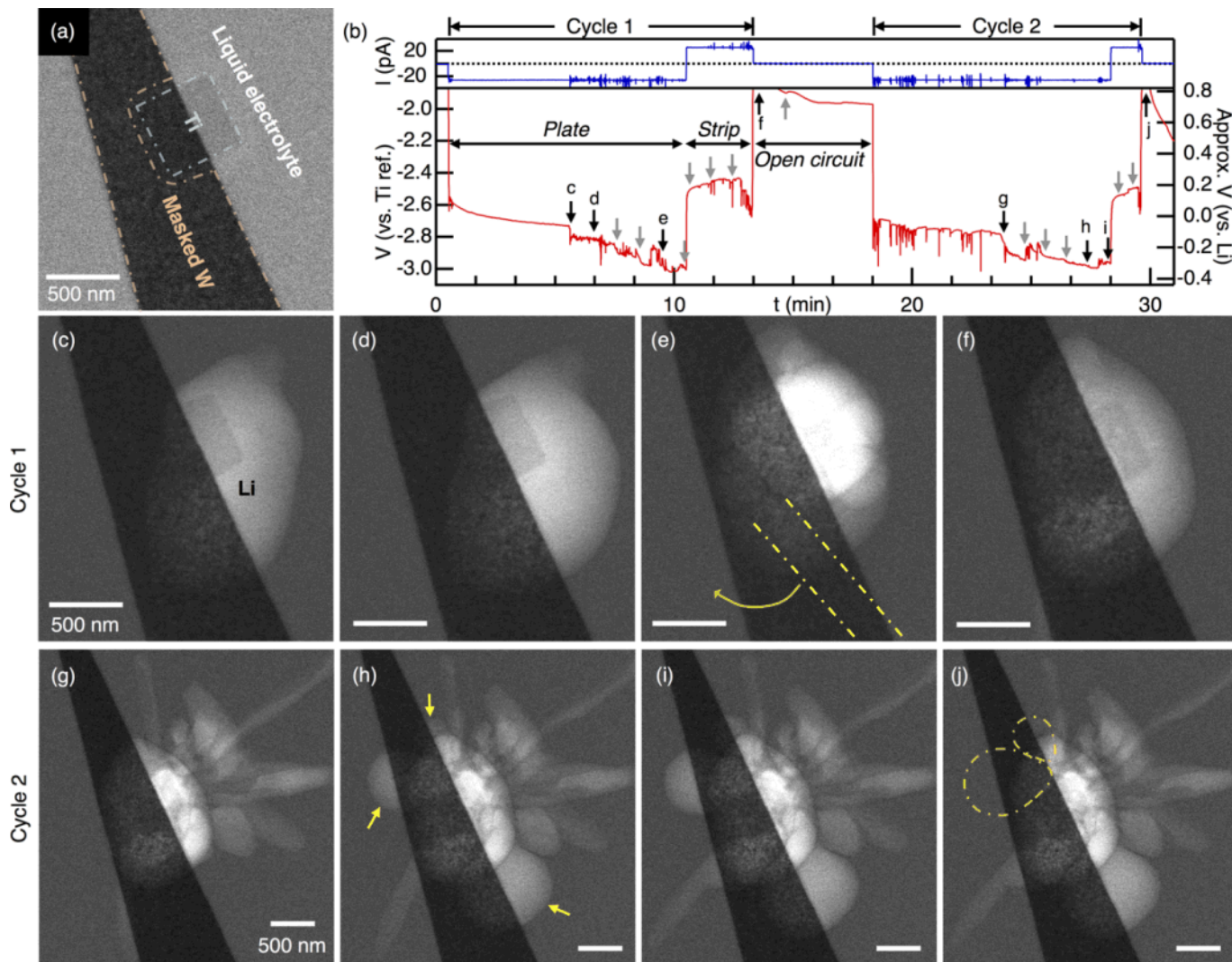
Reproducible electrochemical control during imaging



Li Morphology During Cycling

WE: $0.26 \mu\text{m}^2$ Ti electrode
 CE: $750 \mu\text{m}^2$ Ti electrode
 Coated with ALD Al_2O_3
 Liquid thickness: $>1 \mu\text{m}$
 Galvanostatic control: $\pm 10 \text{ mA/cm}^2$
 Electron dose per image: $25\text{-}50 \text{ e}^-/\text{\AA}^2$
 Electrolyte: 1 M LiPF₆ in EC/DMC
 ($>10 \text{ ppm h}_2\text{o}$)

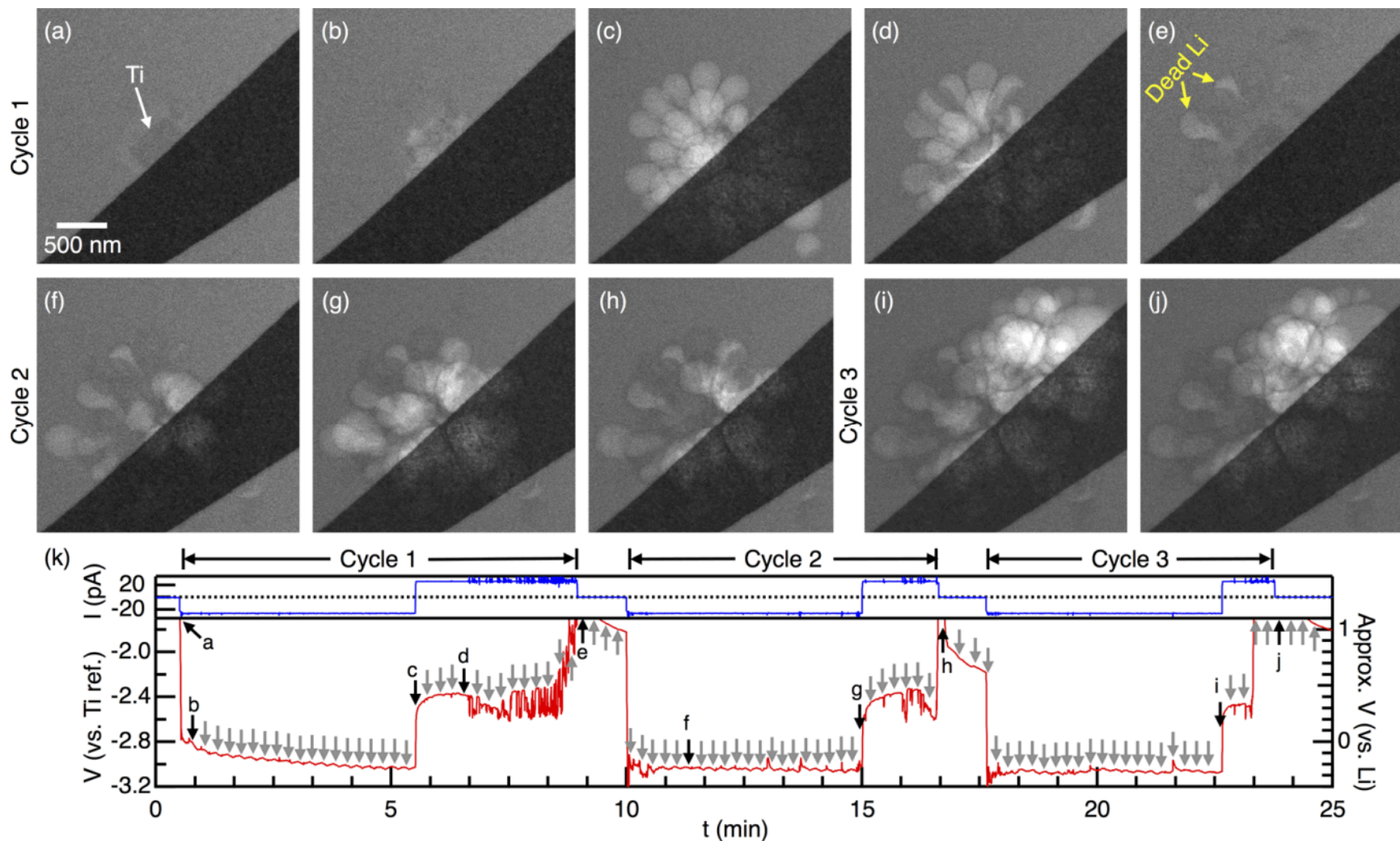
- The electron beam impacted initial Li plating
- Correlate spikes in electrochemical data with nucleation of new Li grains
- Unable to distinguish electrochemically the nucleation of a rounded grain vs. a dendrite





Li Morphology: High E- Beam Dose

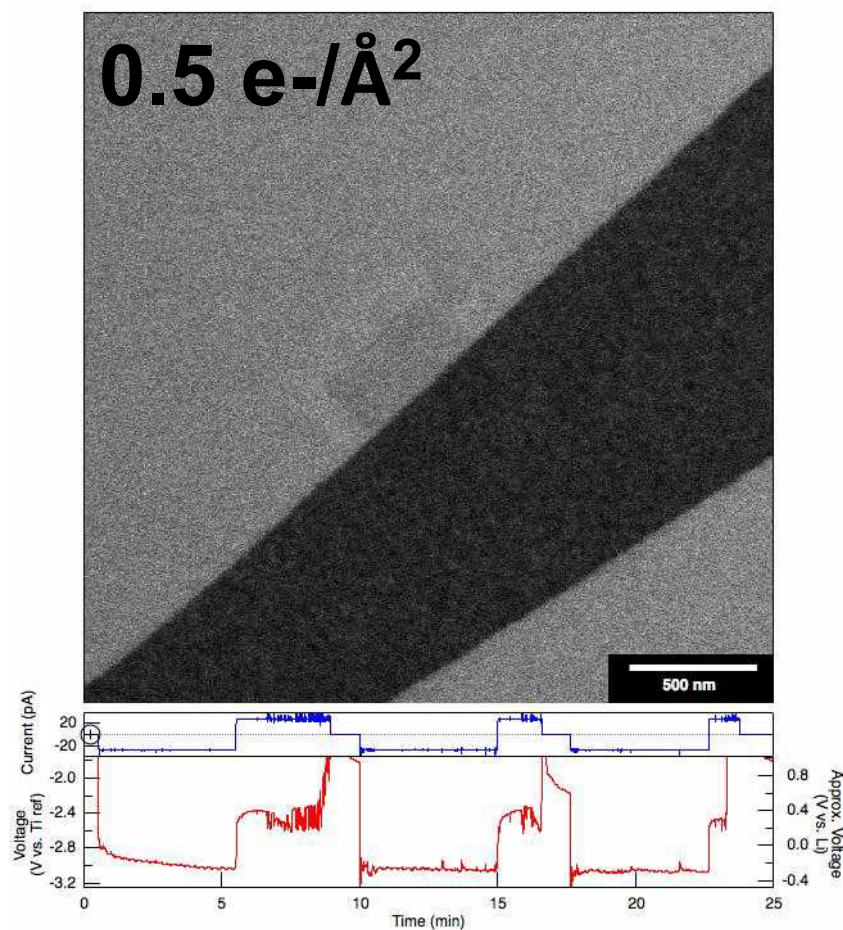
Galvanostatic control at $\pm 10 \text{ mA/cm}^2$, Electron dose per image: $25 - 50 \text{ e}/\text{\AA}^2$, Imaging every 15 seconds



Electron beam increases nucleation and creates rounded Li deposits Leenheer et al., (2015) Nano Lett.



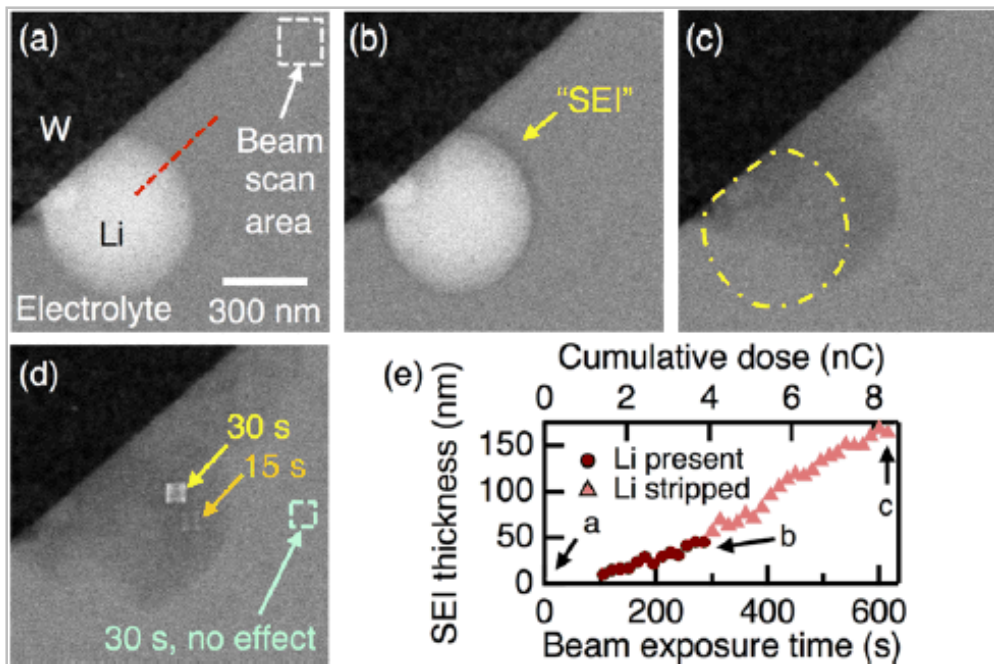
Gratuitous TEM movie



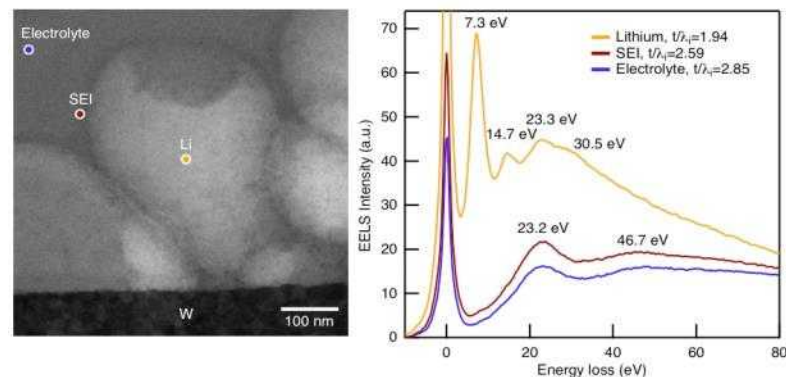
Leenheer et al. (2015) ACS Nano. DOI: 10.1021/acsnano.5b00876.

Beam Effects

Shadow caused by beam

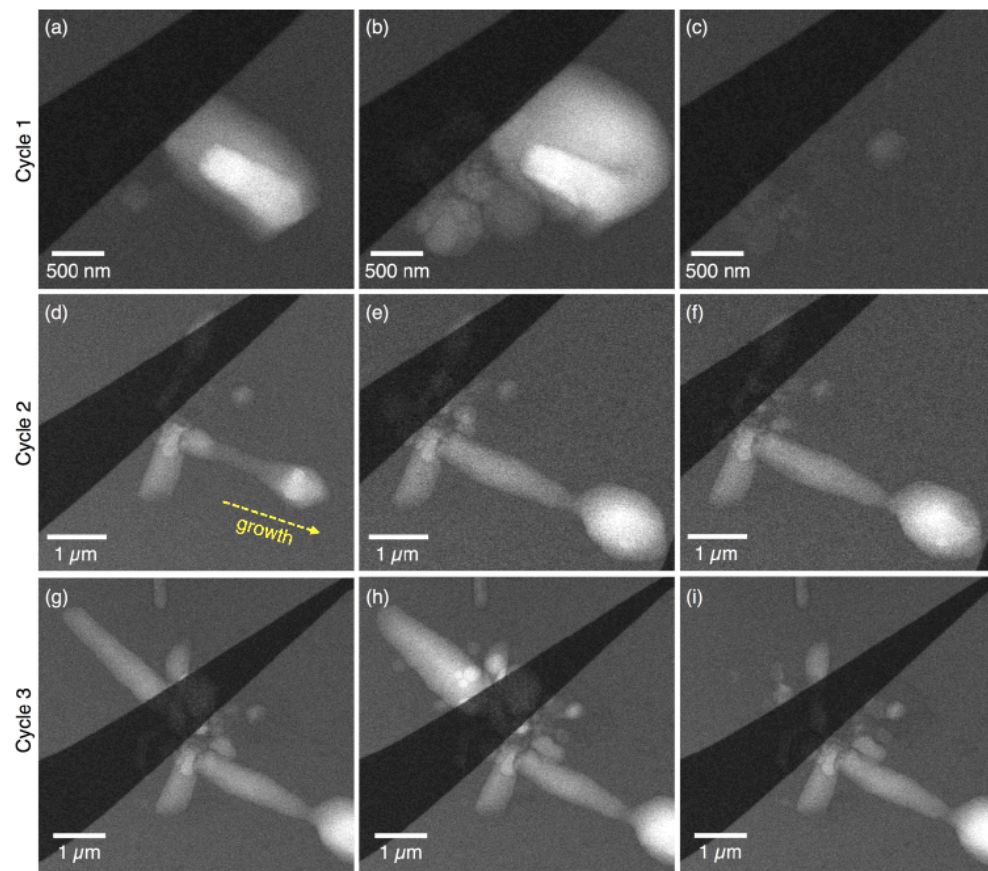


EELS verification that the dark regions are SEI



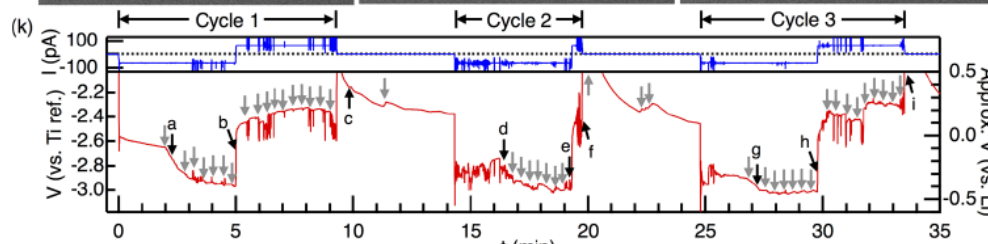


Li Deposition: High Current Density



Galvanostatic control at $\pm 25 \text{ mA/cm}^2$
 Electron dose per image: $12.5 - 25 \text{ e}^-/\text{\AA}^2$
 Imaging every 15 seconds

- Li dendrites observed more readily at higher current densities
- Li dendrites were observed more frequently at later cycles
- 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.

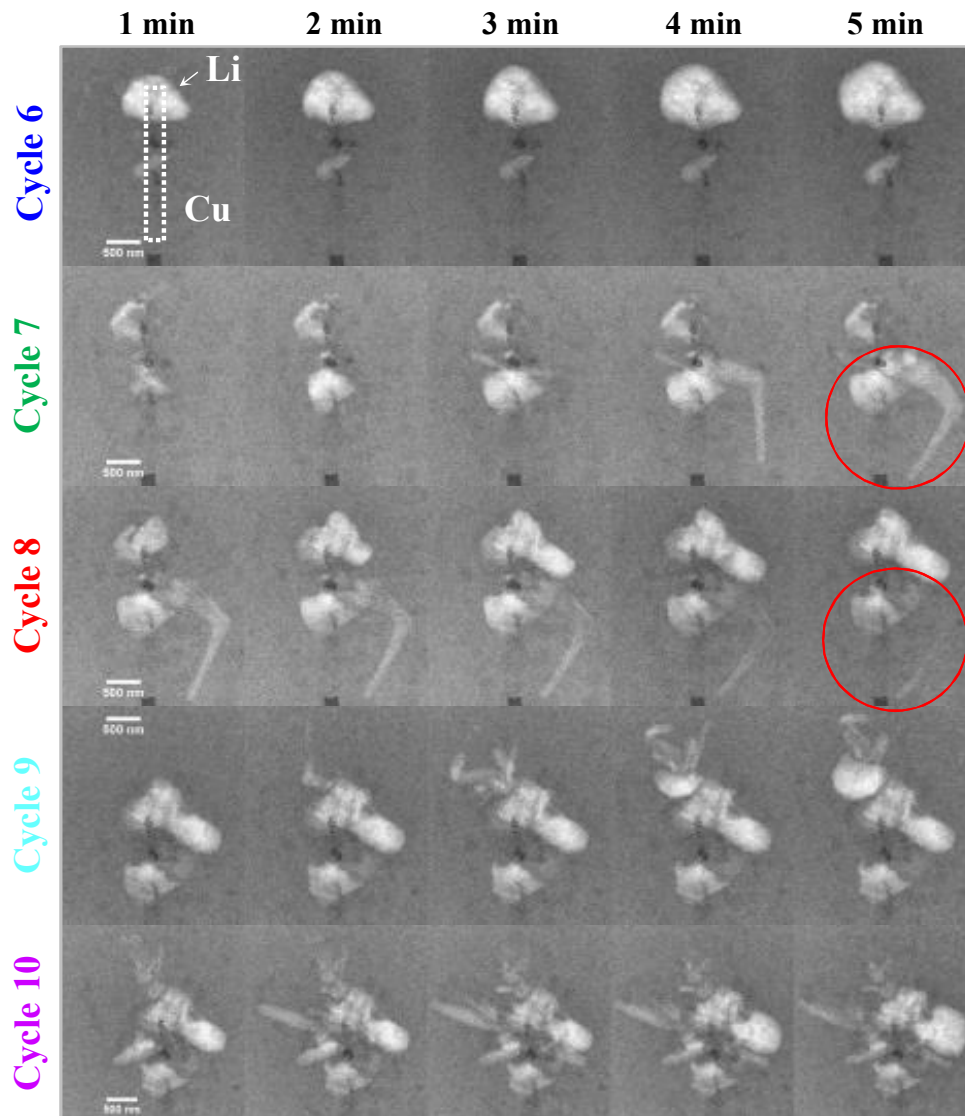
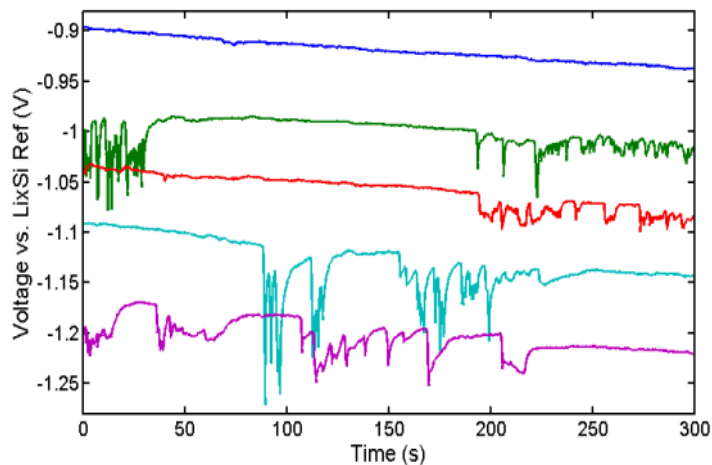


Let's step back and look at the dendrites



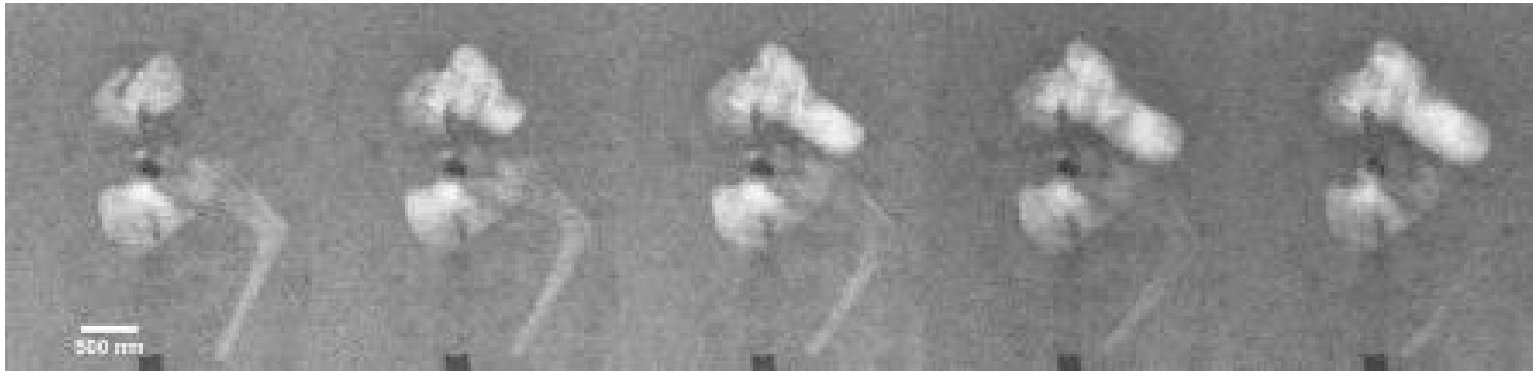
Multiple Cycles and Li Nucleation

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





Li Dendrite breaking off = self-discharge



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



Li Degradation Observations

- Nano-scale morphology can directly impact macroscopic performance.
- Li morphology was observed to be dependent on many factors: electrolyte/salt, SEI, and deposition current density
- Increased number of Li dendrites were observed at higher current densities and as the number of cycles is increased
- The electron beam can influence the growth morphology, even at low dose imaging – we need to reduce the beam damage.





Acknowledgements

The Team

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Reliability



Questions?

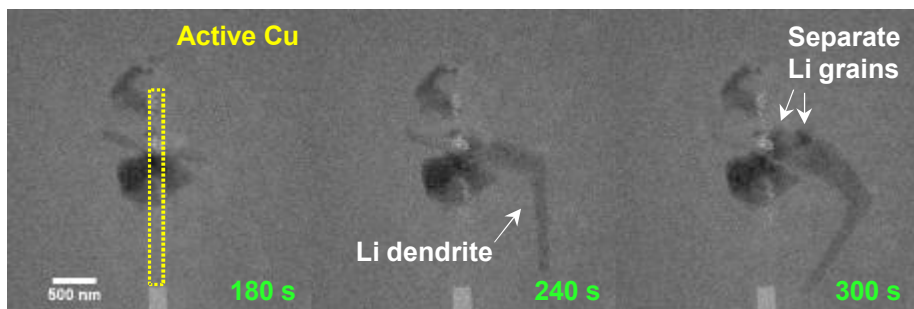


Back up slides

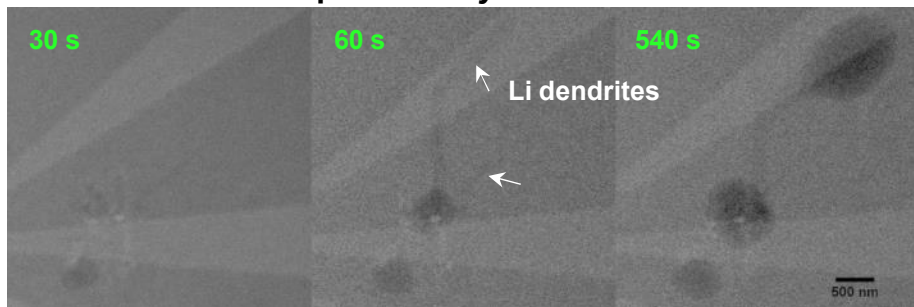
Li Dendrite Disconnection

- 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*

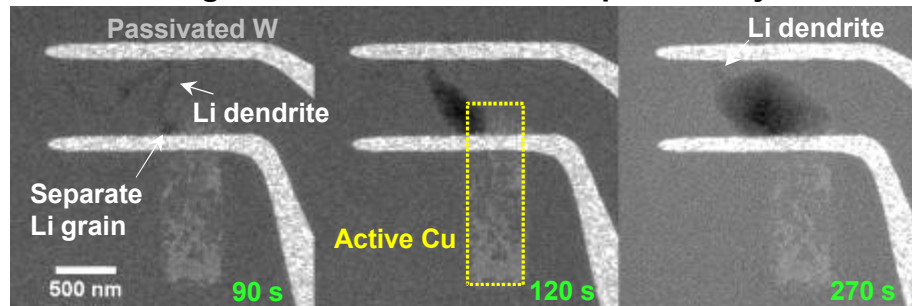
-2.25 mA/cm² on 0.44 μm² Cu: Cycle 7



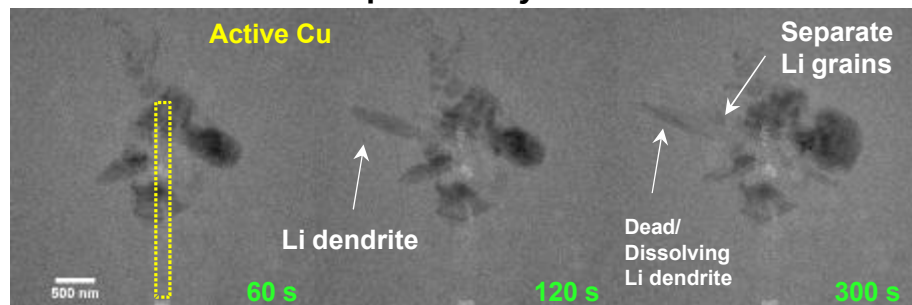
-5 mA/cm² on 0.75 μm² Cu : Cycle 1



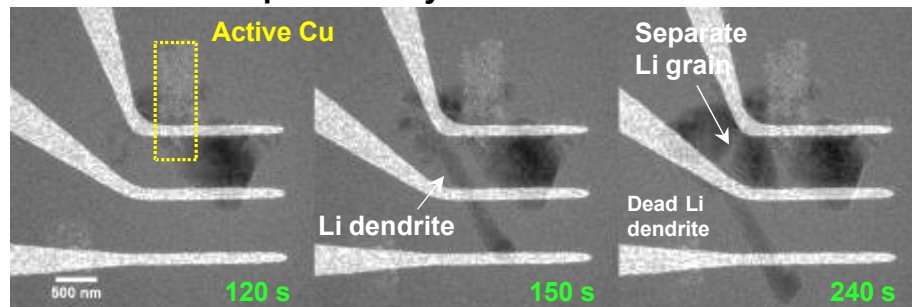
EC-Scanning TEM: -1.33 mA/cm² on 1 μm² Cu: Cycle 1



-2.25 mA/cm² on 0.44 μm² Cu: Cycle 10



-5 mA/cm² on 1 μm² Cu : Cycle 1



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



Galvanostatic Control of Working Electrode

Electric current is kept at a defined set point

We are able to control currents below pA level

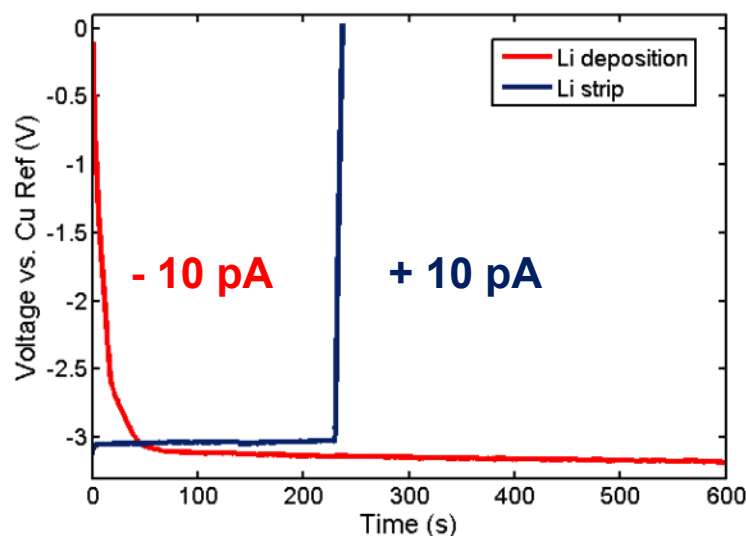
The voltage applied is dependent on the resistance during the measurement, value plotted vs. time

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

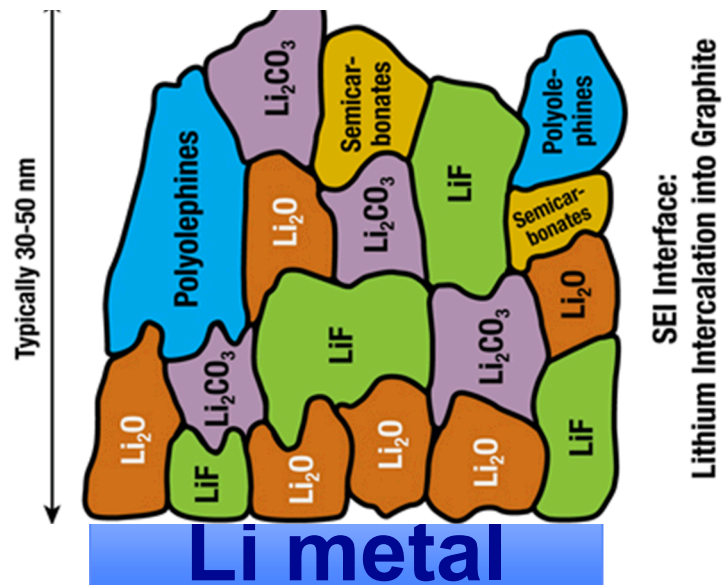
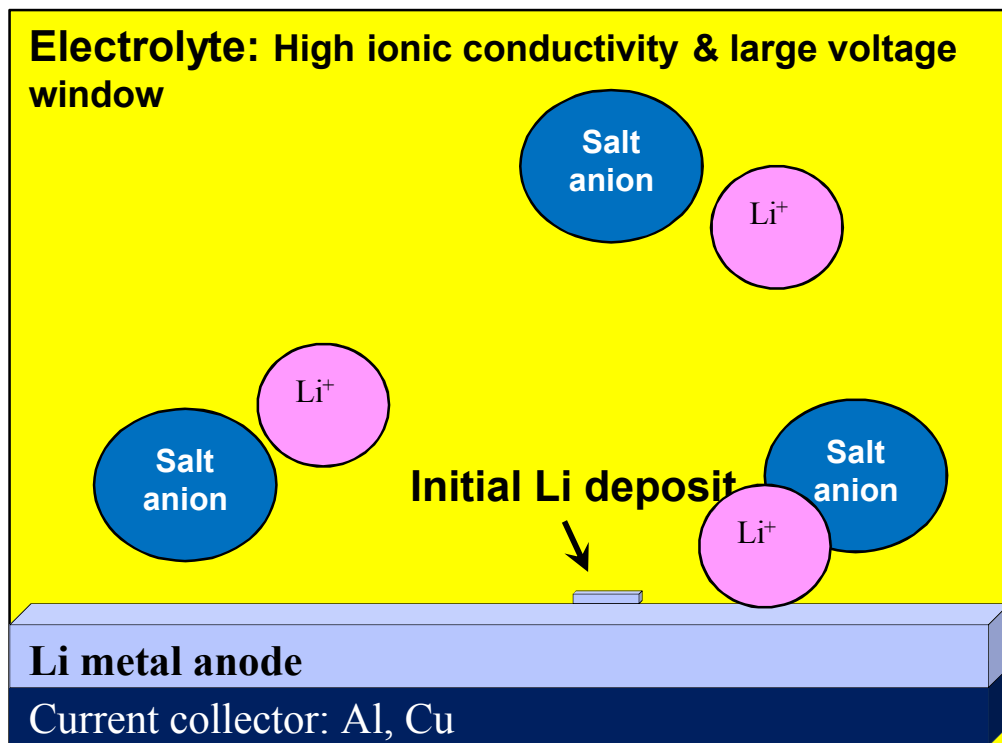
Galvanostatic experiments allow us to directly measure the Coulombic efficiency at each of the deposition/stripping cycles



Coulombic Efficiency: 39.47%



Li Metal – Electrolyte Interface

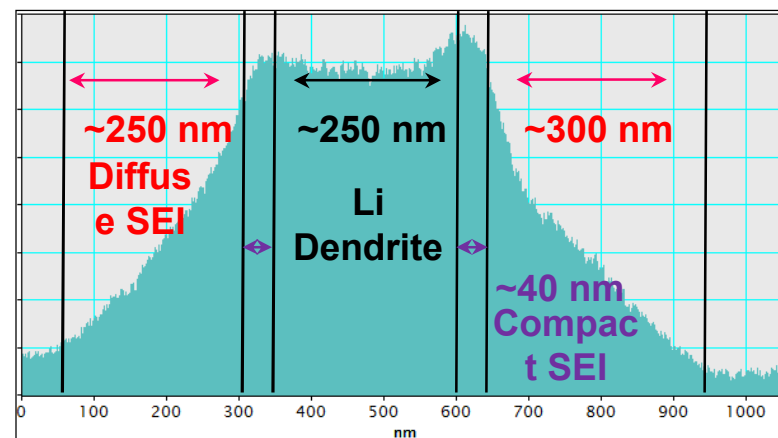
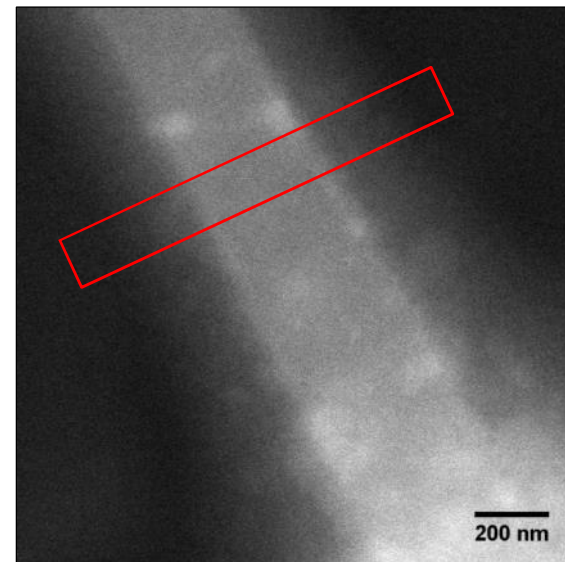
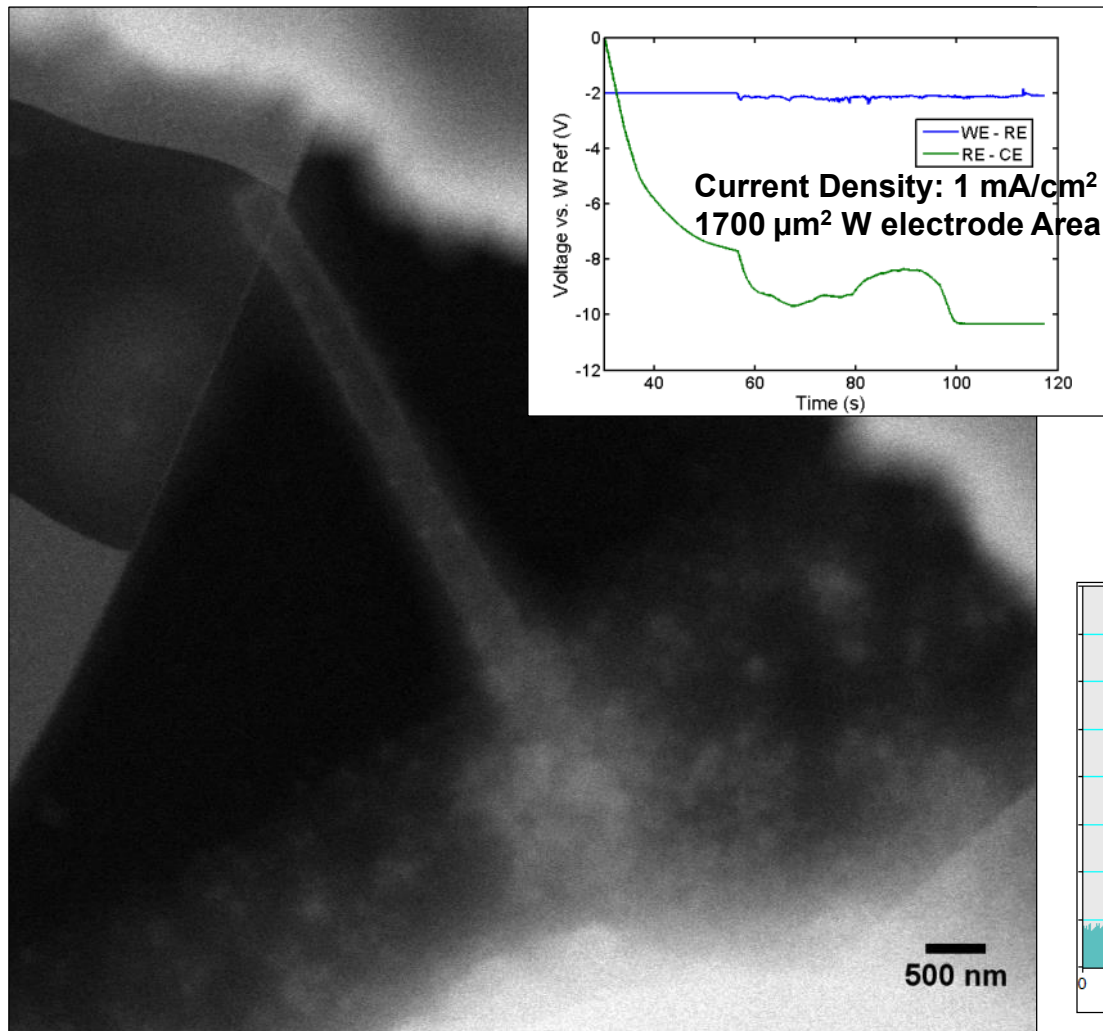


Peled et al. (1997) J. Electrochem. Soc. 144, L208.

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



Li Dendrites formed at High Current Densities



Remove electrolyte to observe structural details in SEI