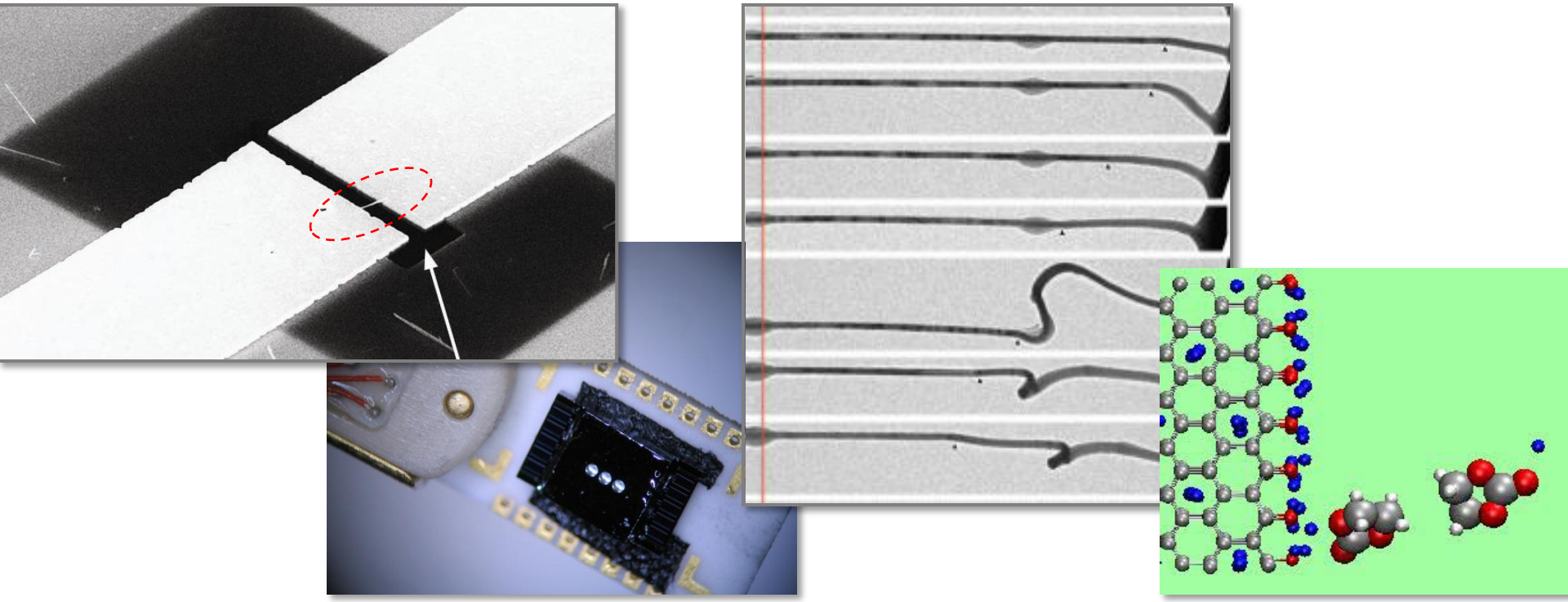
Research at Sandia on Li-ion Batteries: *In situ* TEM and Atomic-scale Modeling

SAND2011-4066C



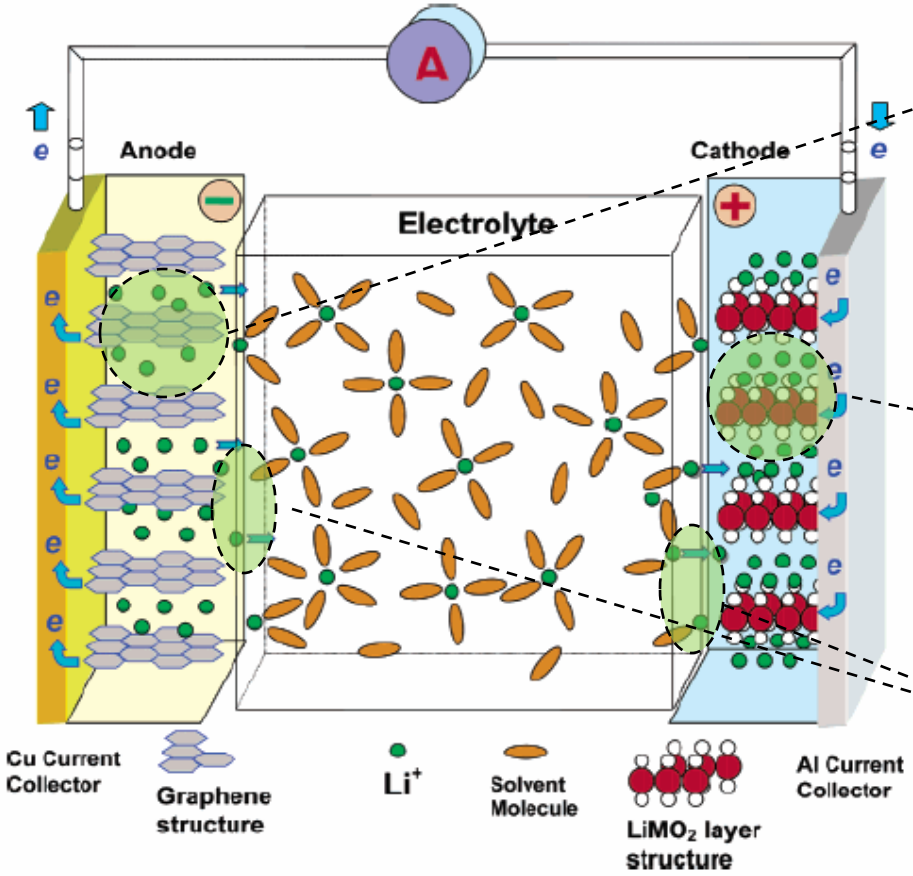
John Sullivan, Jian Yu Huang, and Kevin Leung

Sandia National Labs*, Albuquerque, NM

-- May 17, 2011 --

*Sandia National Laboratories is a multi-program laboratory operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin company, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Some of the Materials-Related Scientific Challenges in Li-ion Batteries



Report of the Basic Energy Sciences Workshop on Electrical Energy Storage, April 2-4, 2007

<u>Anodes</u>

- structural mechanisms to accommodate large strains
- kinetics of Li ion transport

<u>Cathodes</u>

- kinetics of Li ion transport
- electrical transport

<u>Electrolyte interfaces</u>

- solid electrolyte interphase (SEI) formation
- SEI stability

Focus Topics in this Talk

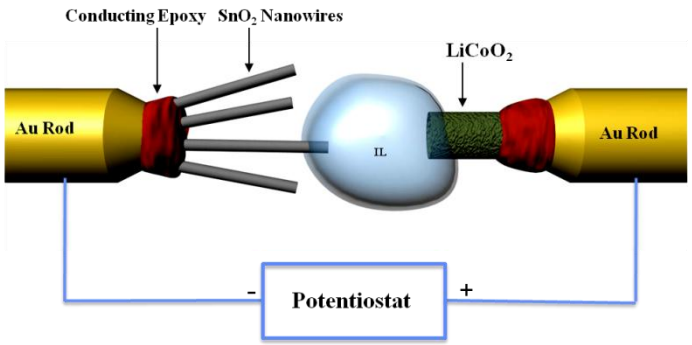
- ***in situ* TEM**
- **atomic-scale modeling**
- **battery abuse testing**
- **coarse-grain modeling**
- **nanoscale electrochemical measurements**
- **optical characterization**
- **new material development**

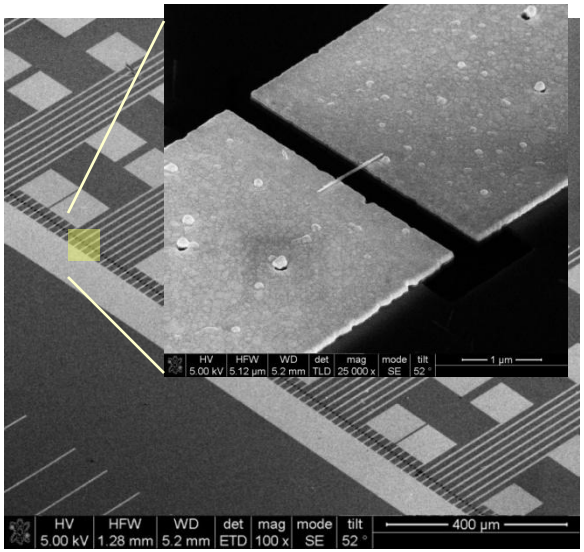
Our *in situ* TEM approach: isolate the nanostructure plus *in situ* TEM electrochem.

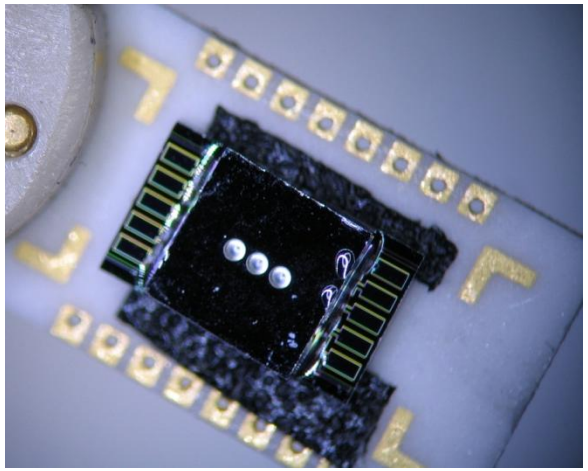
I. sample assembly inside TEM
- use ionic liquid electrolytes

II. on-chip assembly
- use ionic liquid electrolytes inside TEM
- standard electrolytes outside TEM

III. assemble in a sealed chip
- use standard electrolytes inside TEM







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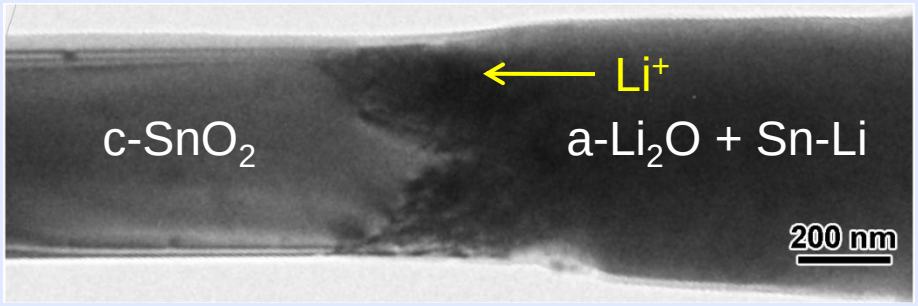
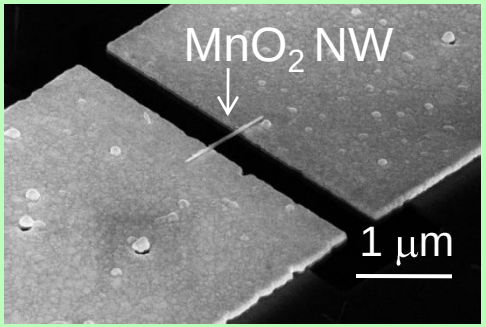
Experiments in Nanoscale Li-ion Electrochemistry: A Three-pronged Effort

1. Structural and mechanical characterization by *in situ* TEM
   - strain accommodation during lithiation
   - initiation of defects (e.g. dislocations/ cracks)
   - kinetics of lithiation



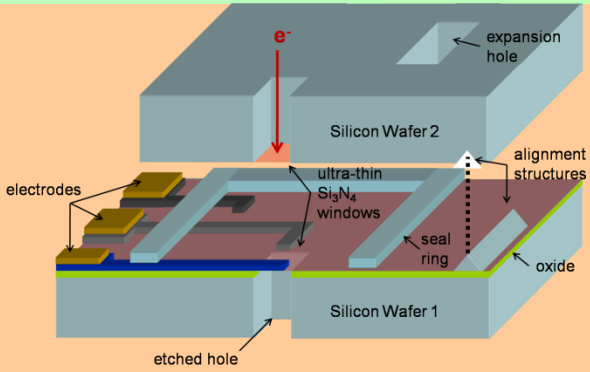
Huang, *et al.*, Science (2010).

2. Single nanoparticle and batch electrochemical studies
   - correlating electrochemical properties to structure
   - size-dependent behavior



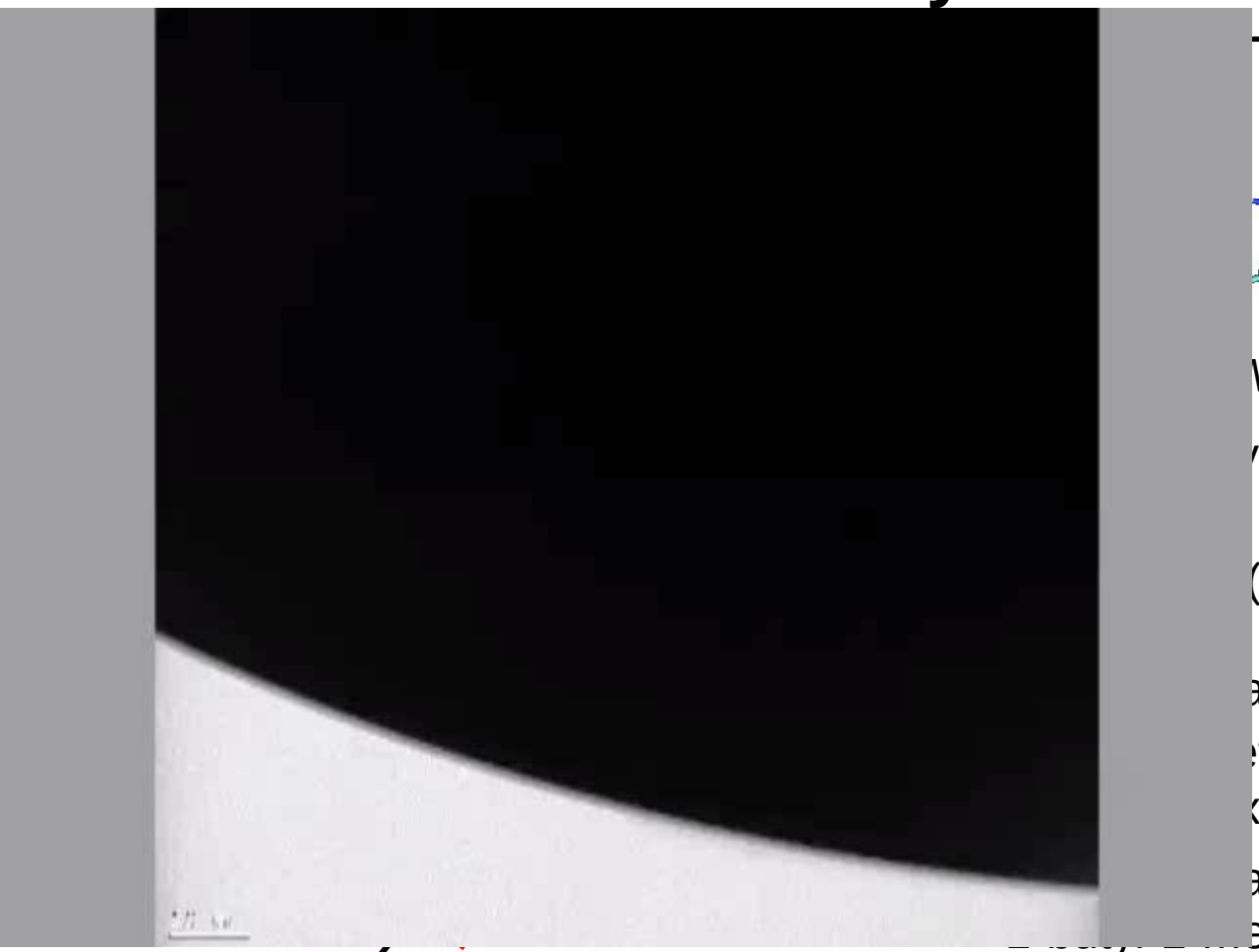
Subramanian, *et al.*, *in submission to NanoLett* (2011).

3. Electrode/electrolyte interface studies
   - SEI formation (composition and morphology)
   - SEI evolution, aging, and stability during cycling

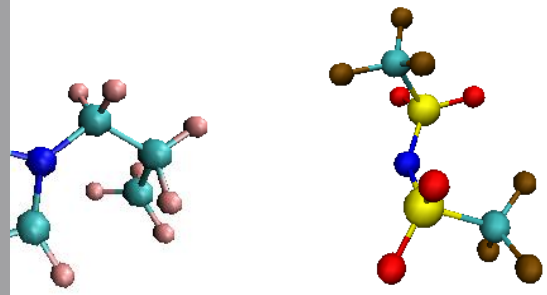


Sullivan, *et al.*, Proc. SPIE (2010).

How do you do liquid electrochemistry in a TEM? -- ILs



ionic liquid spanning a hole



MPI *TFSI*

yl-3-propylimidazolium (DMPI)

(trifluoromethylsulfonyl)imide (TFSI) + Li-TFSI

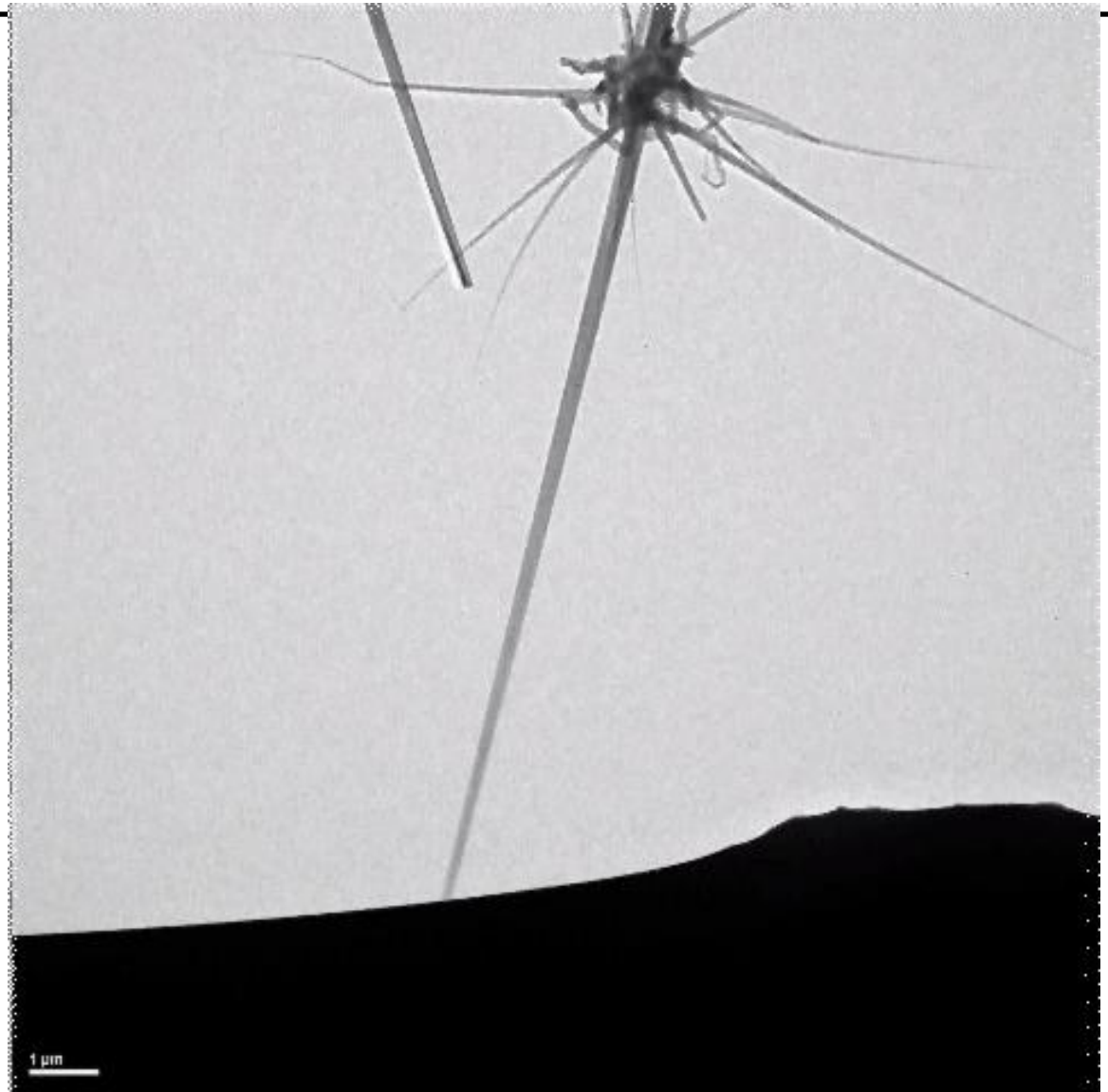
also

ethylimidazolium kafluorophosphate+ $LiPF_6$

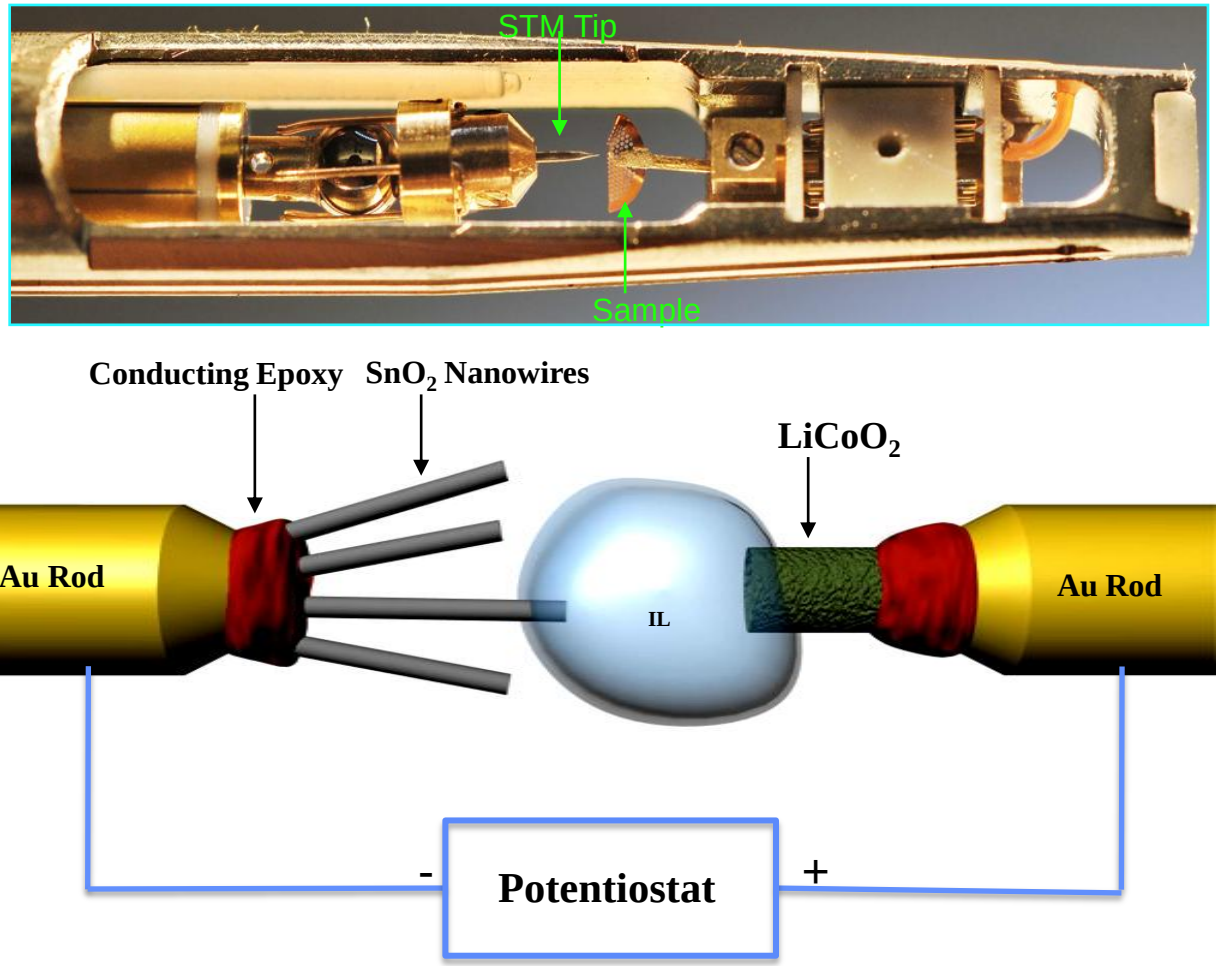
and

ethylpyrrolidinium-TFSI + Li-TFSI

Capillary action of ionic liquids on Si in the TEM.



Electrochemistry inside the TEM: Lithiation of a SnO_2 NW anode.



Jian Yu Huang, *et al.*, "In situ observation of the electrochemical lithiation of a single SnO_2 nanowire electrode," Science **330**, 1515 (2010).

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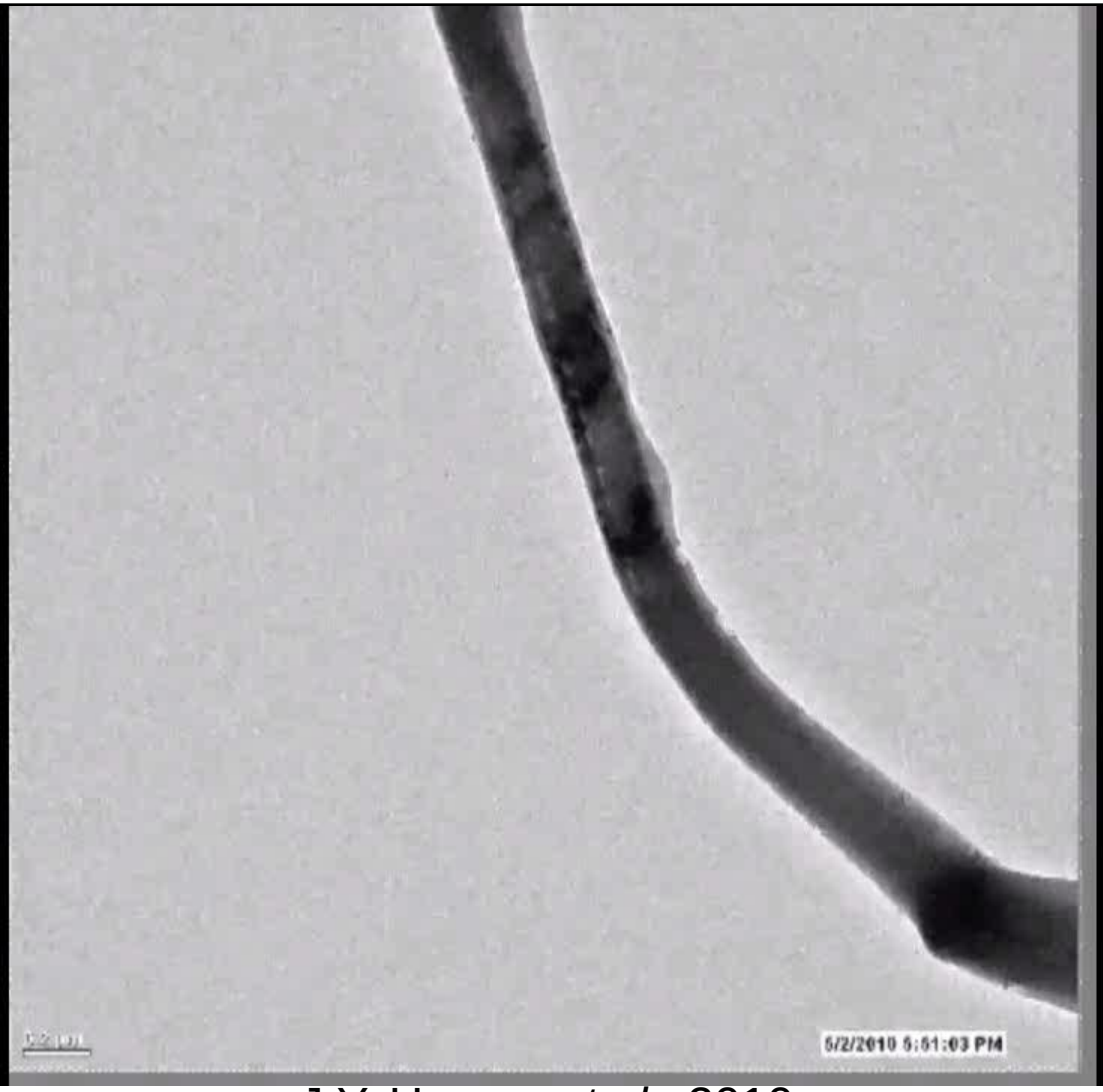
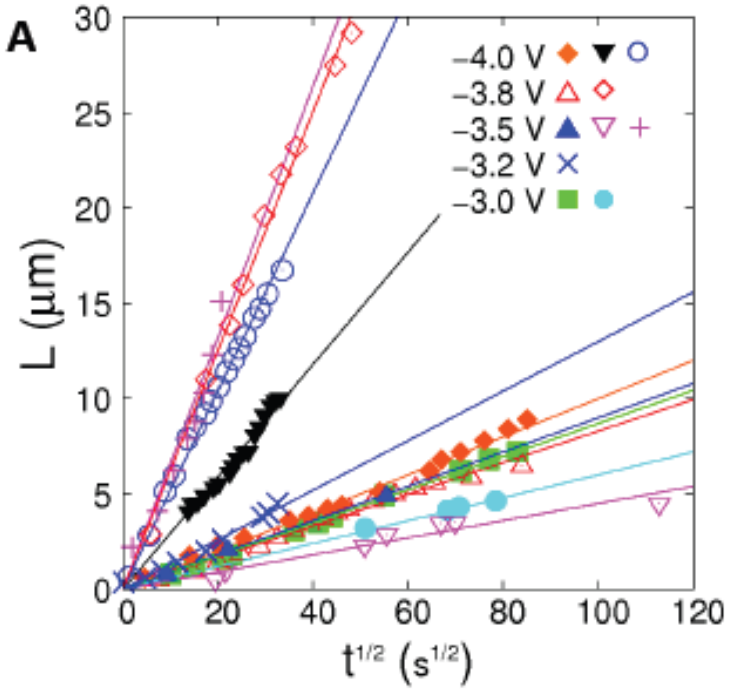
Lithiation creates amorphous Li_2O + Sn-Li and a lengthening of the NW.



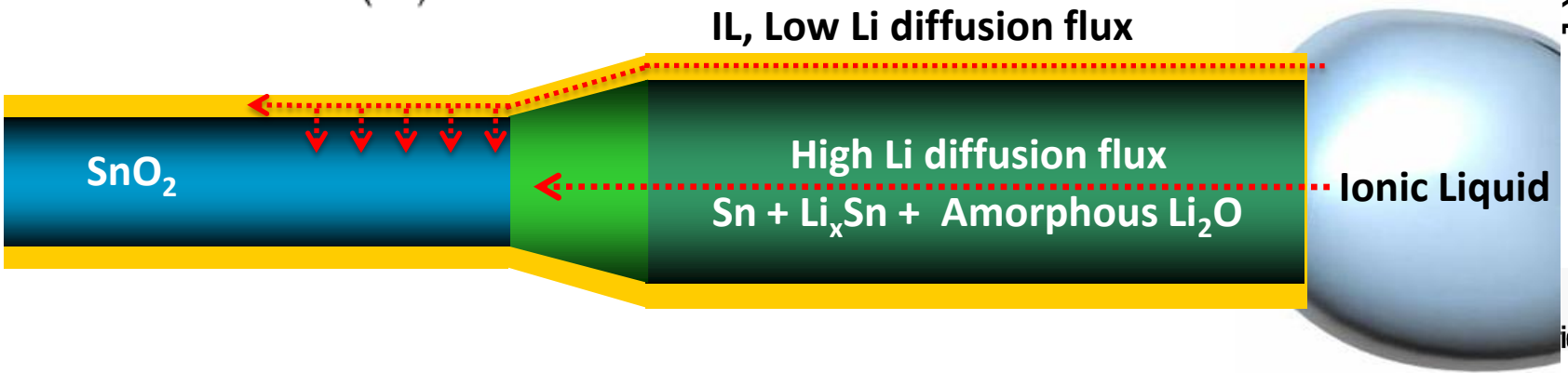
J.Y. Huang, *et al.*, 2010.

The reaction is diffusion-limited: limited by Li^+ flux through Li_2O.

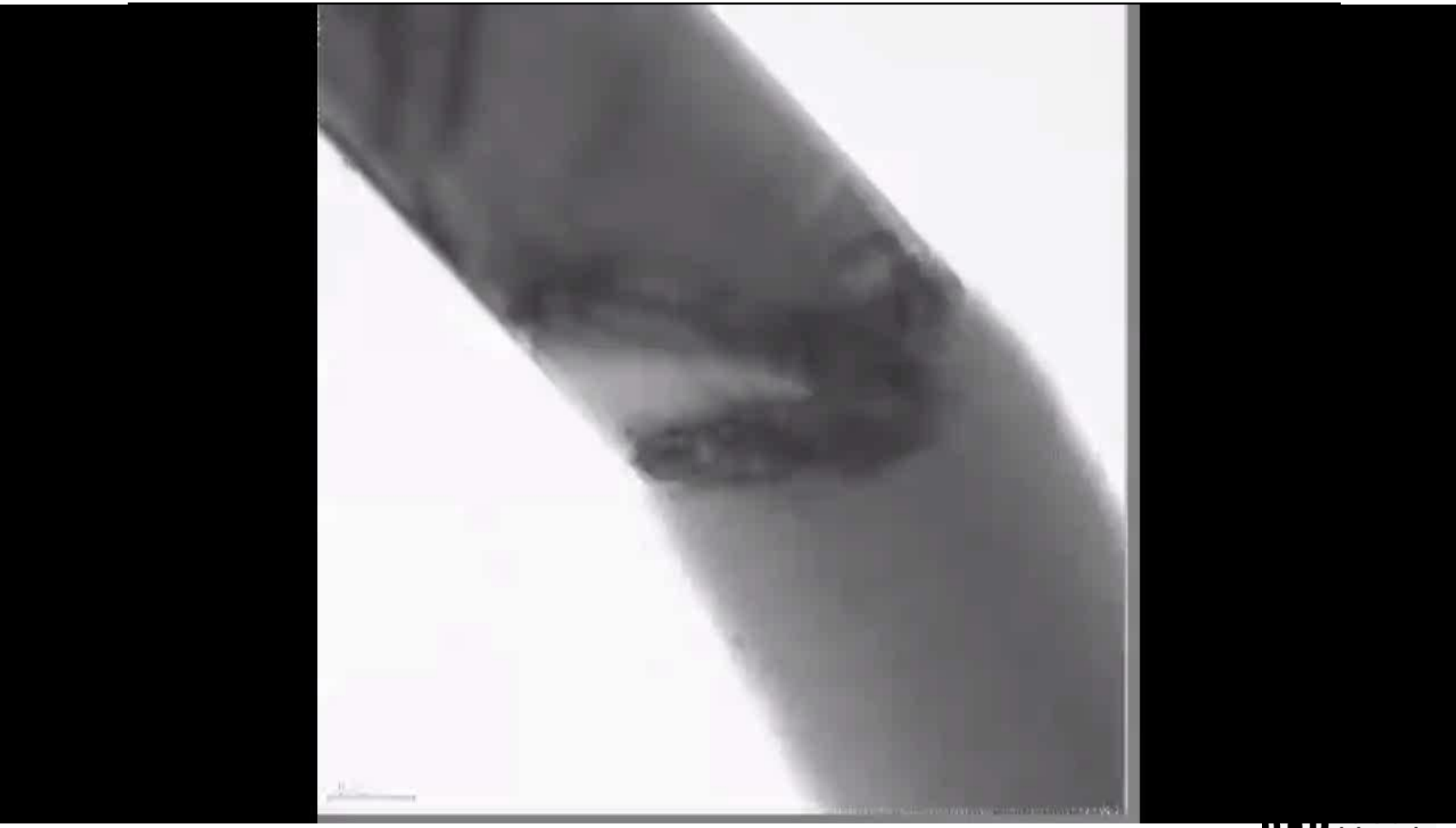


- diffusion-limited kinetics ($t^{1/2}$)
- diffusivities of 0.05 to 5 x 10^{-14} m^2/sec

J.Y. Huang, *et al.*, 2010.

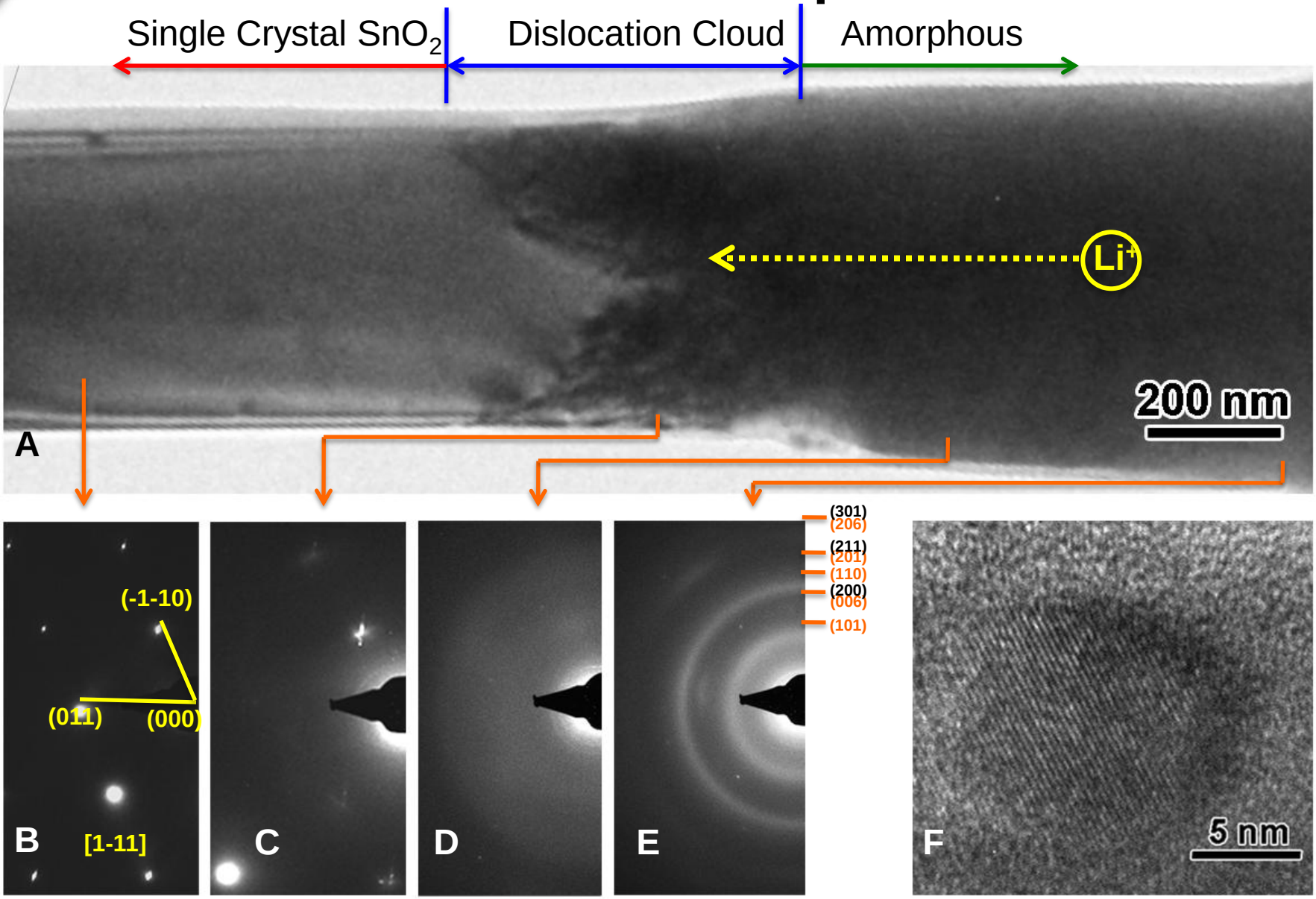


Imaging the strain accommodation mechanism.



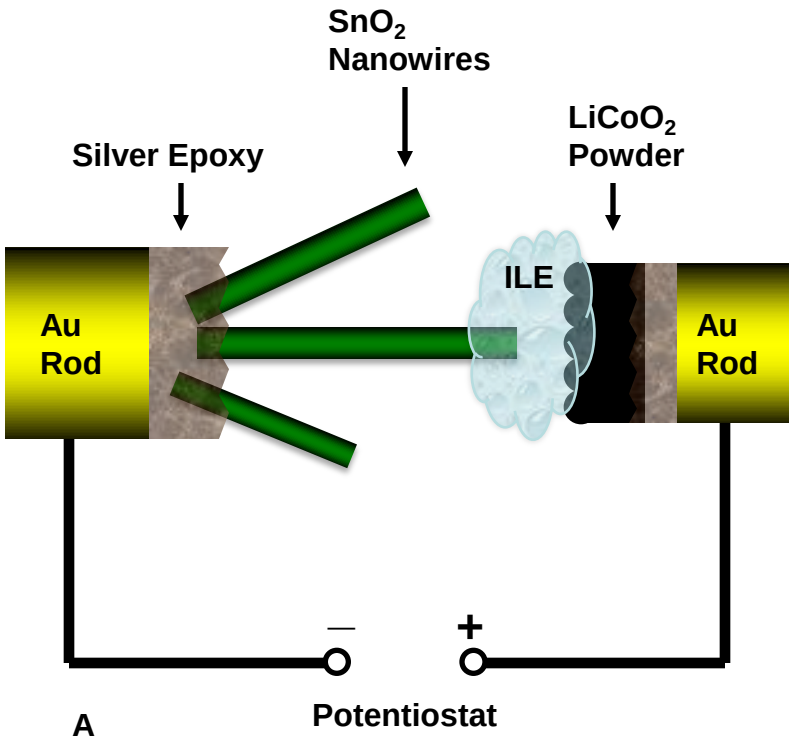
J.Y. Huang, *et al.*, 2010.

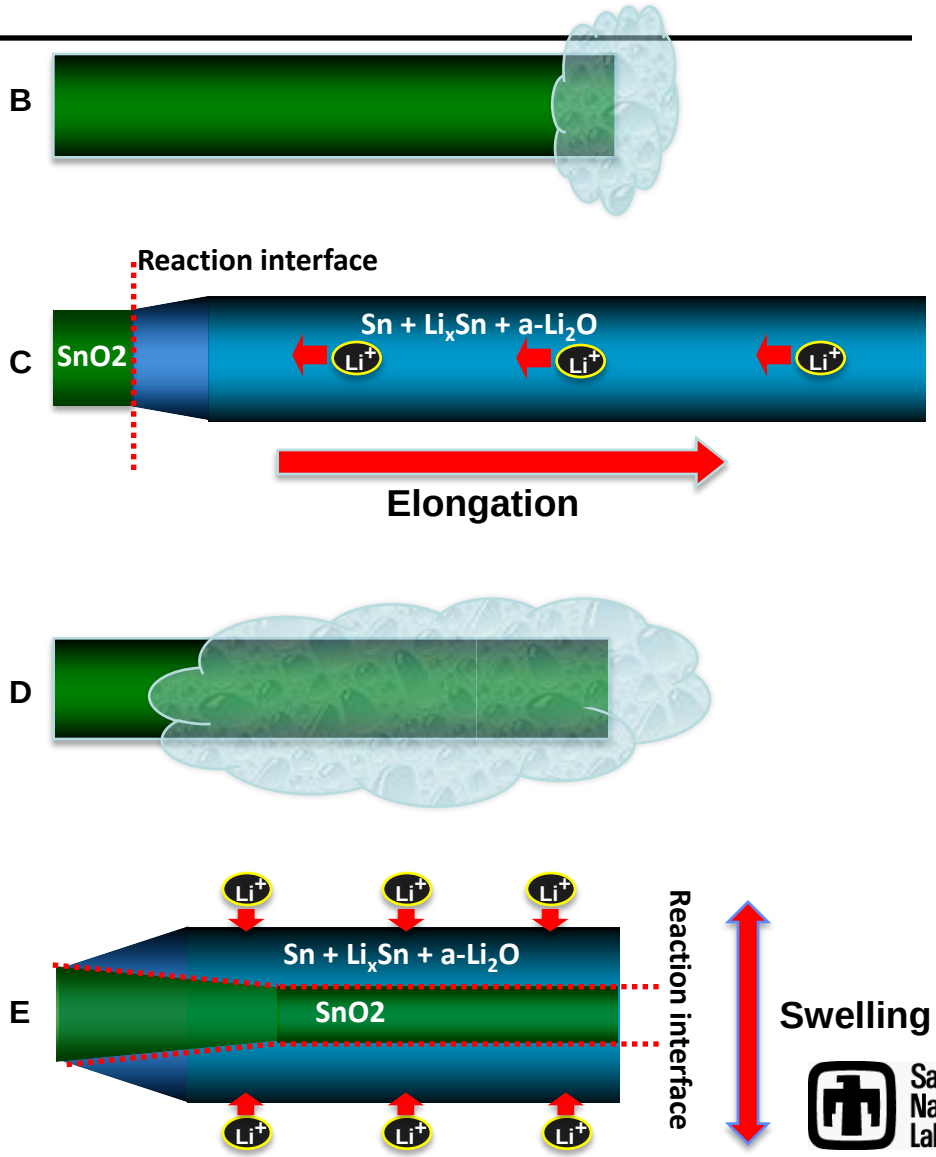
A snapshot in time showing the rxn front and the phases.



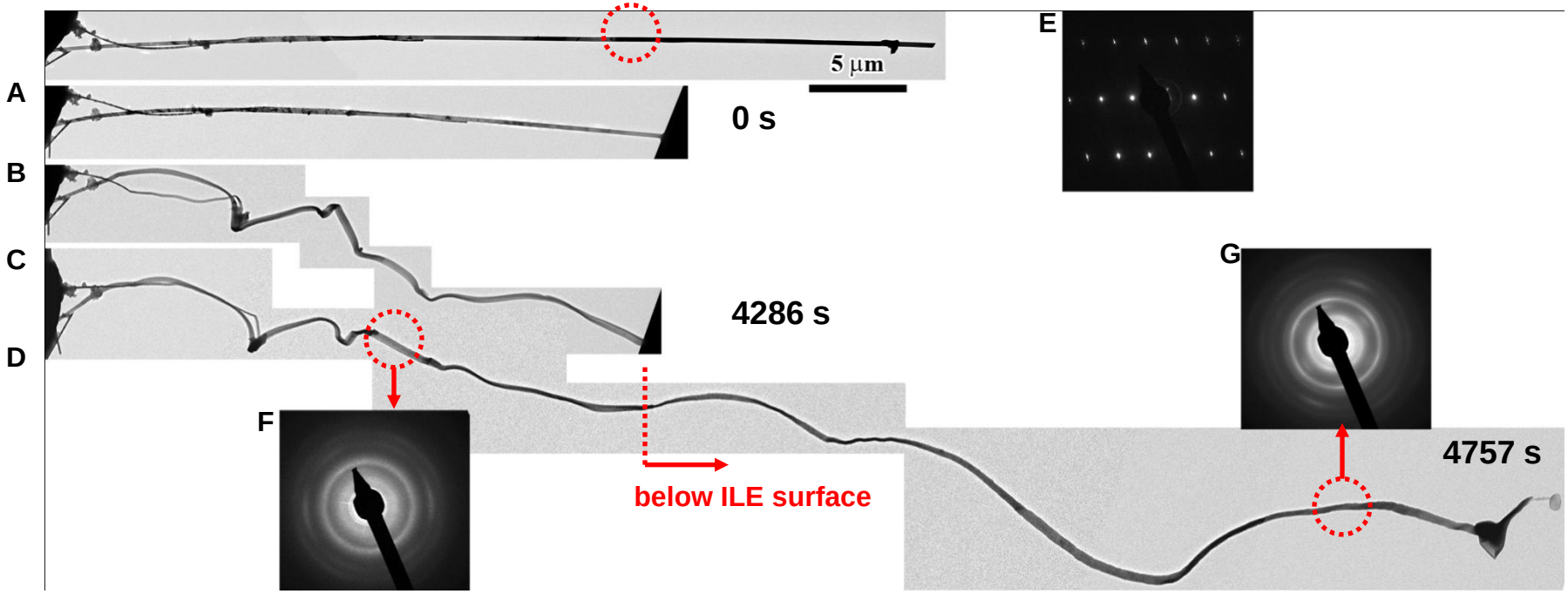
J.Y. Huang, *et al.*, 2010.

Is the morphology just a consequence of the measurement geometry?



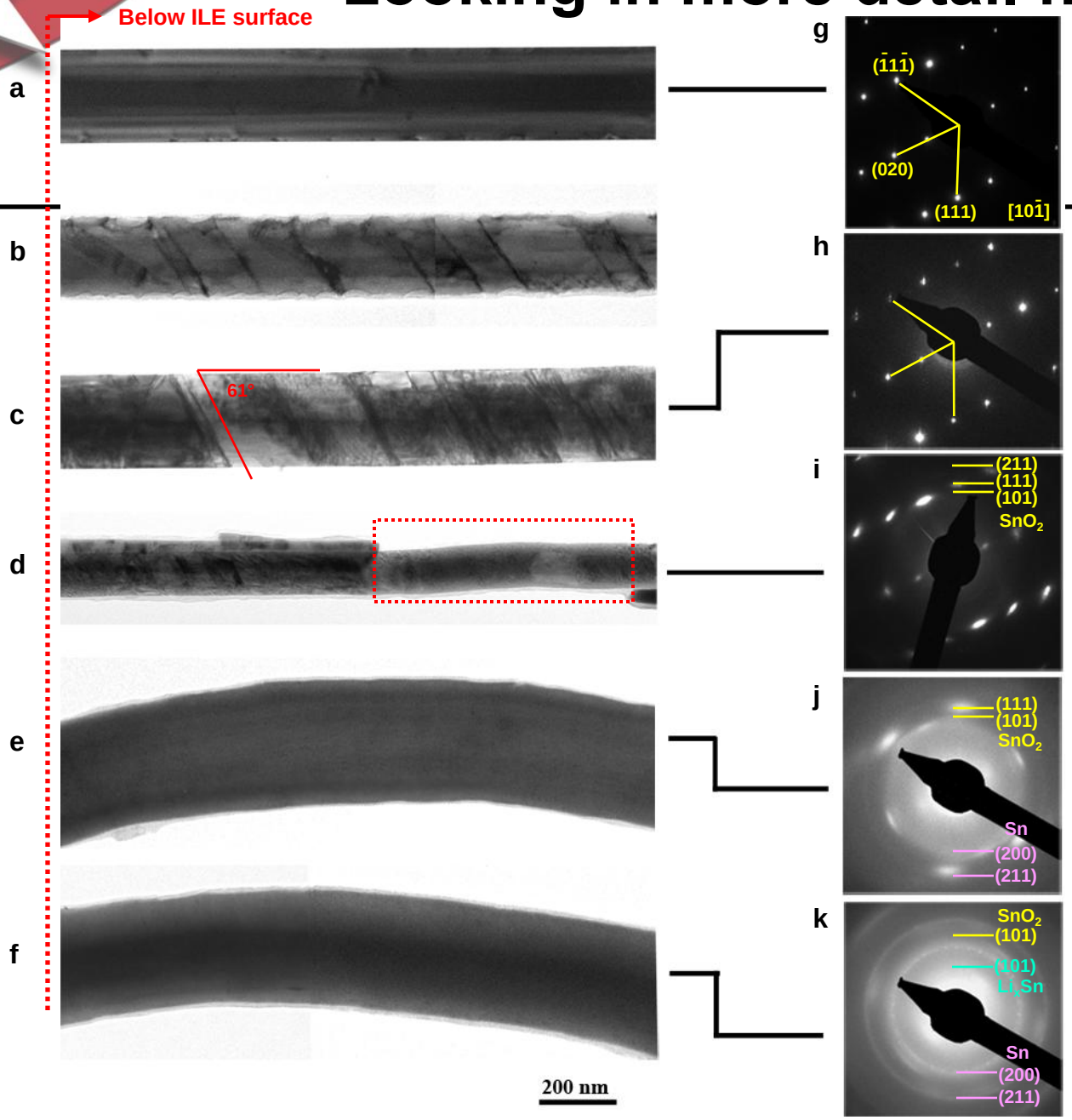


Same morphology is observed for a "flooded" geometry.



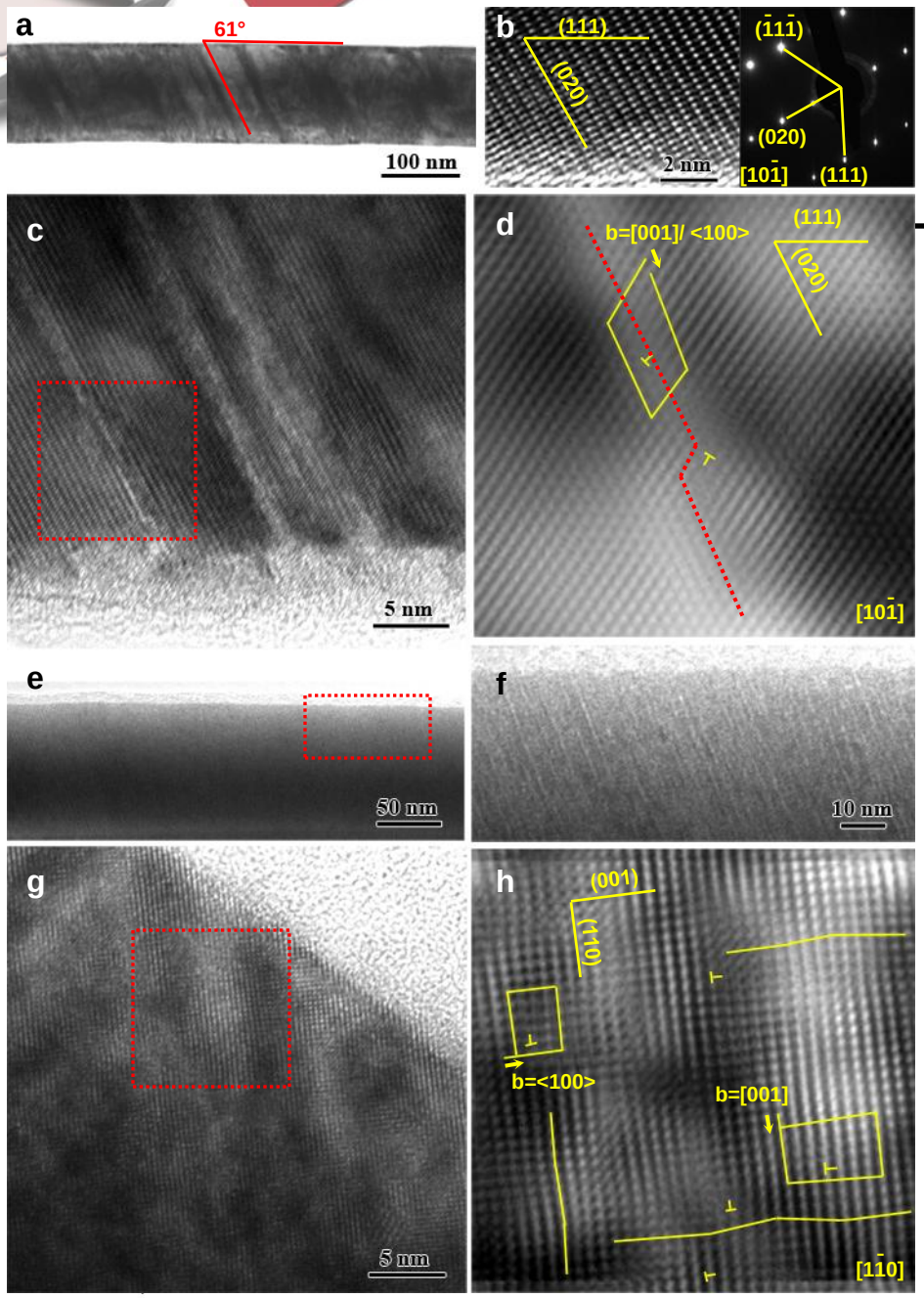
J.Y. Huang, *et al.*, unpublished.

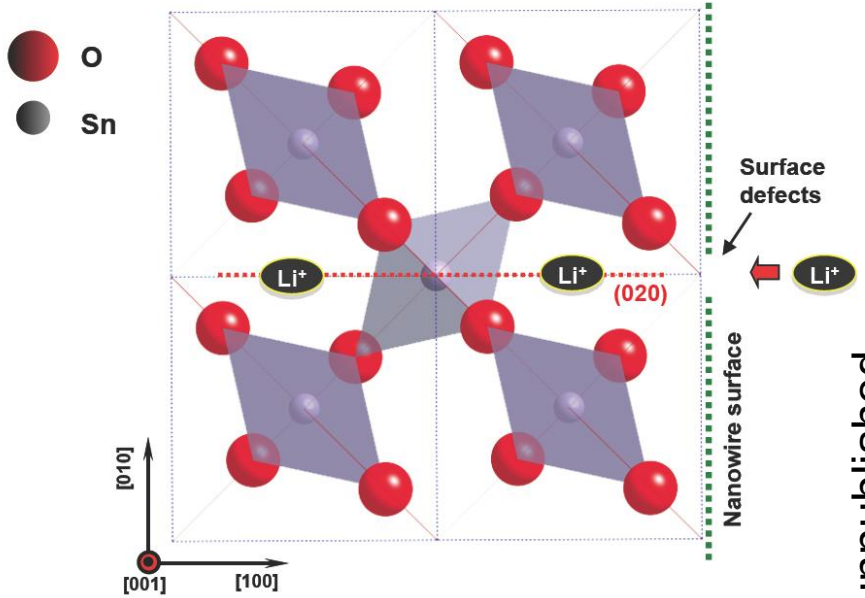
Looking in more detail …

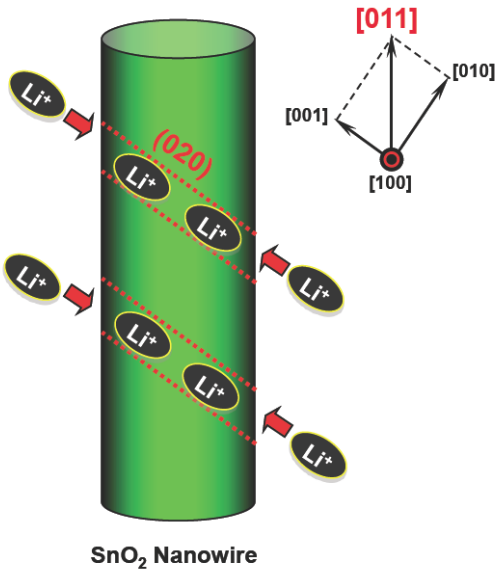


J.Y. Huang, *et al.*, unpublished.

More details …







J.Y. Huang, *et al.*, unpublished.

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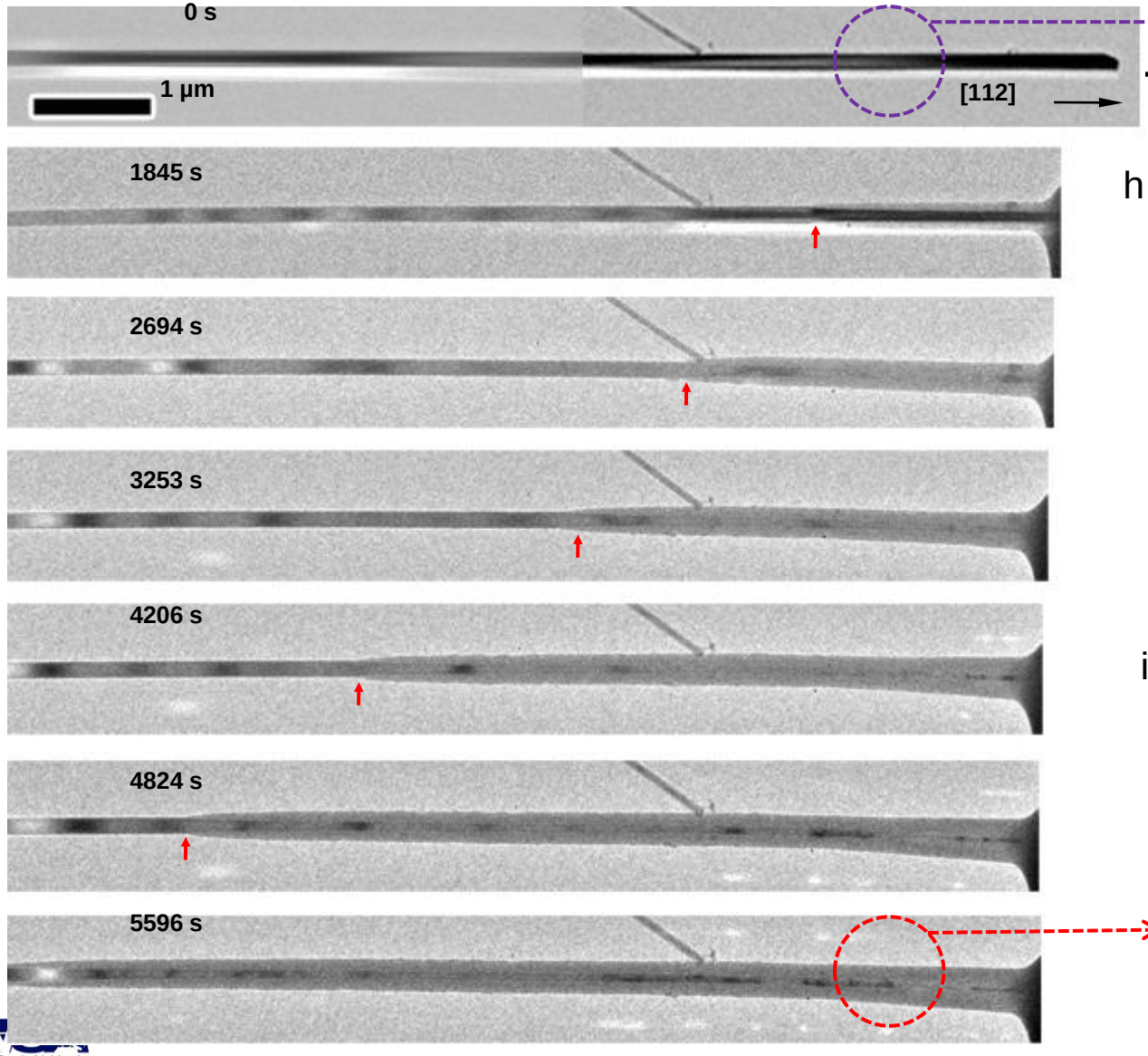
Do all nanowire anodes behave the same? The story with Si.

J.Y. Huang, *et al.*, Nano Lett. (in submission)



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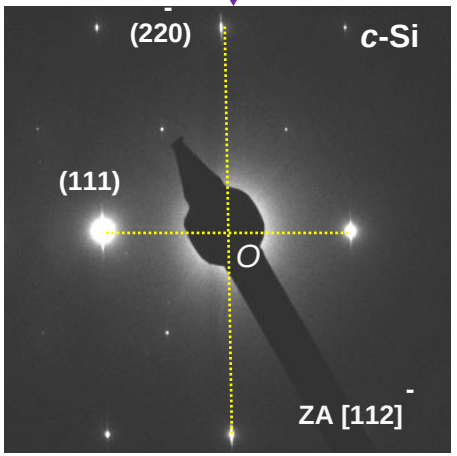

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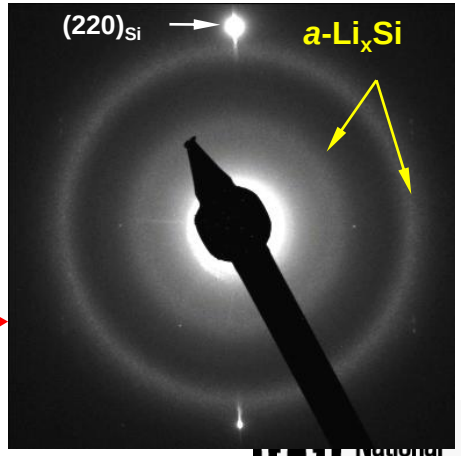

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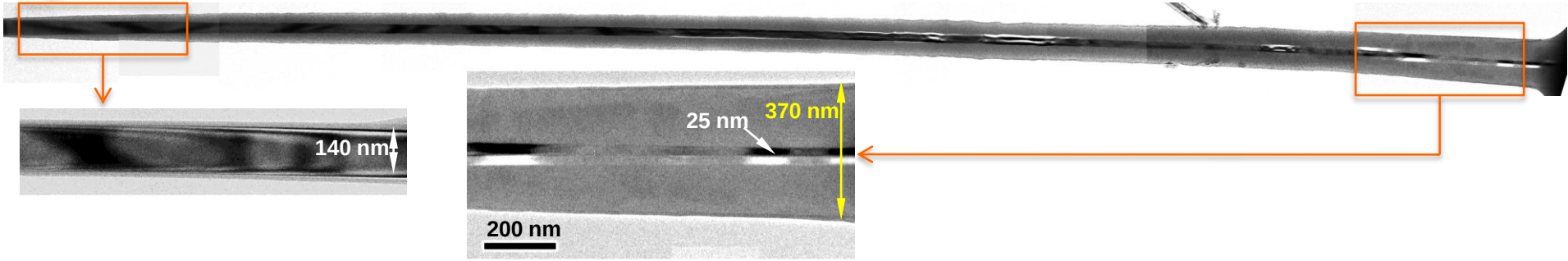
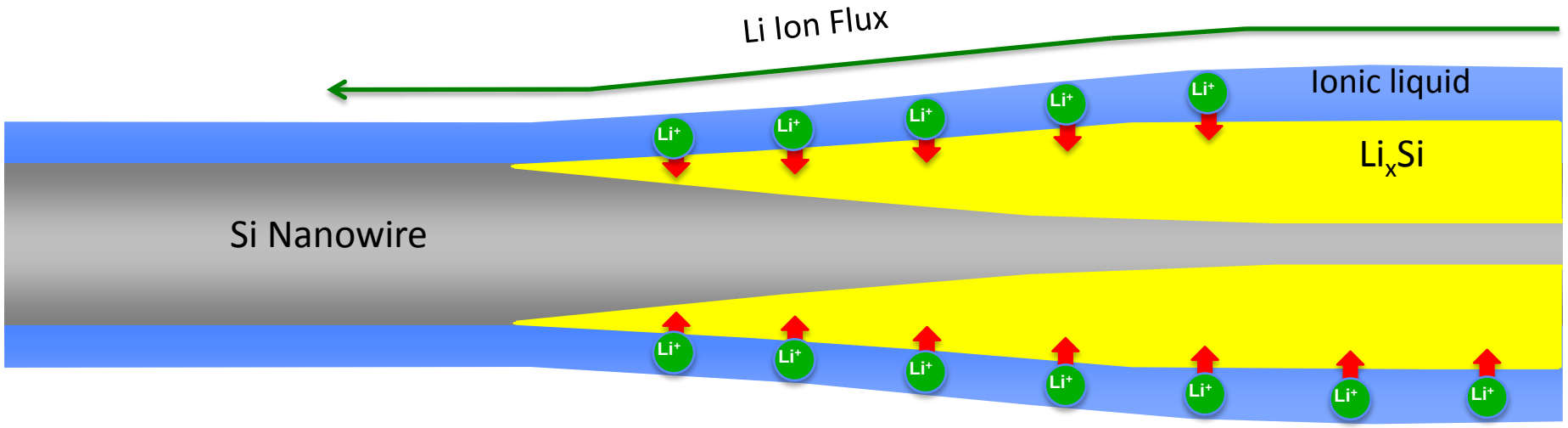
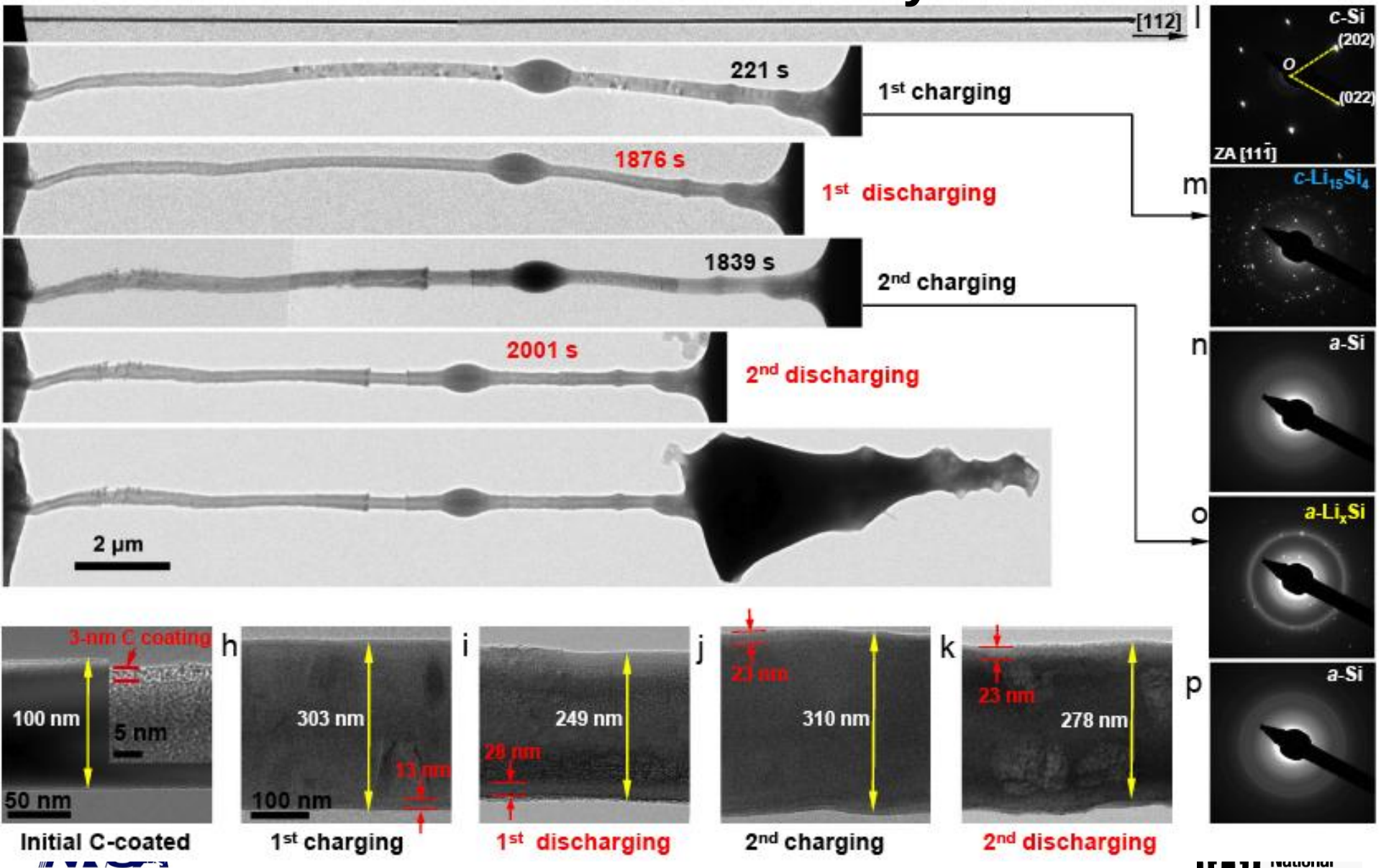
Lithiation of Si leads to a core-shell structure.



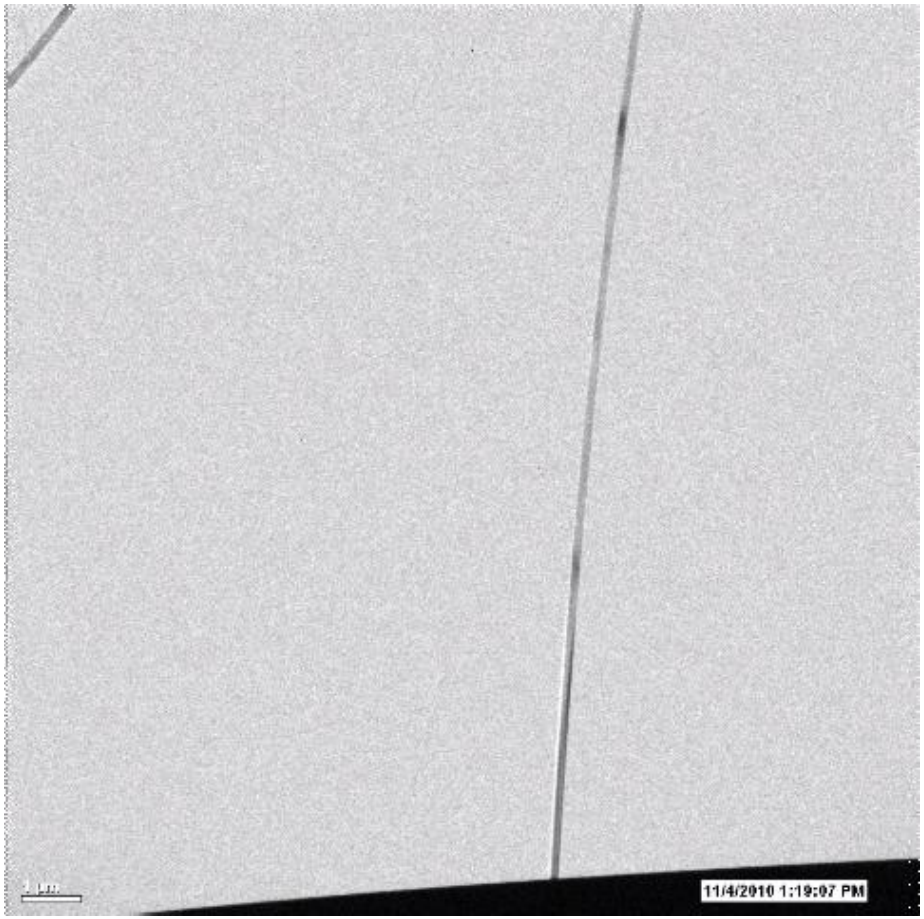


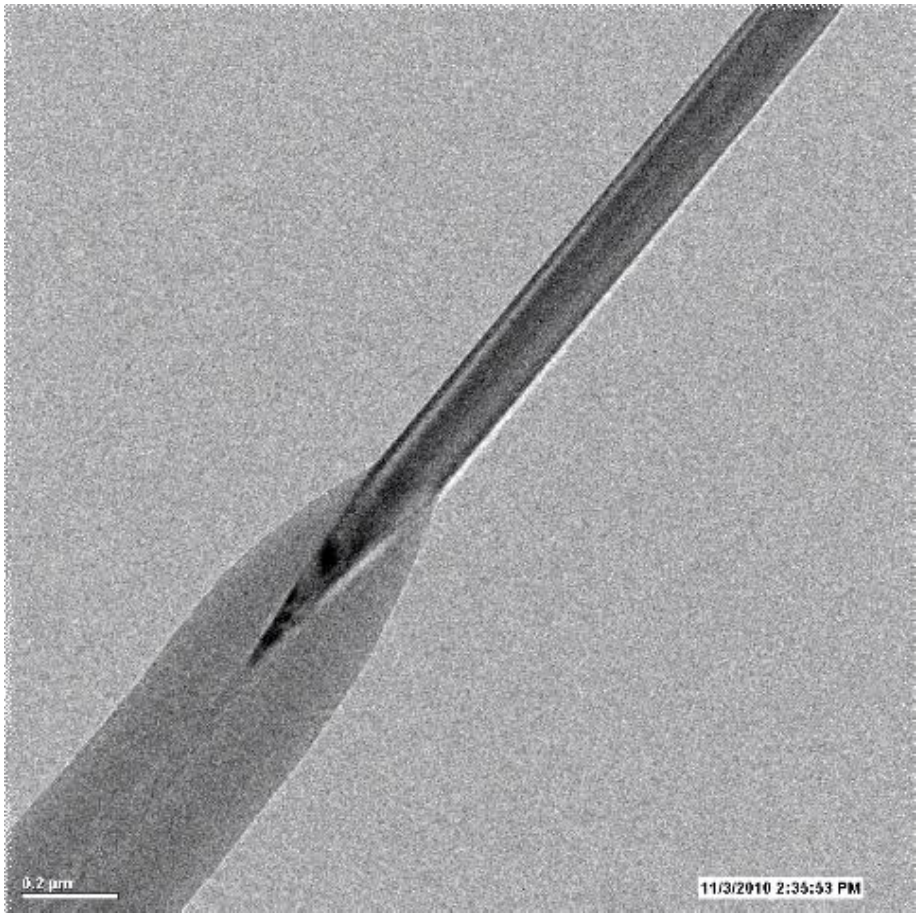
- Core-shell structure; Conical shape of the core
- Reaction from surface to the interior
- No elongation, no dislocations

Changing the reaction kinetics by changing electrical conductivity: C-coated Si.

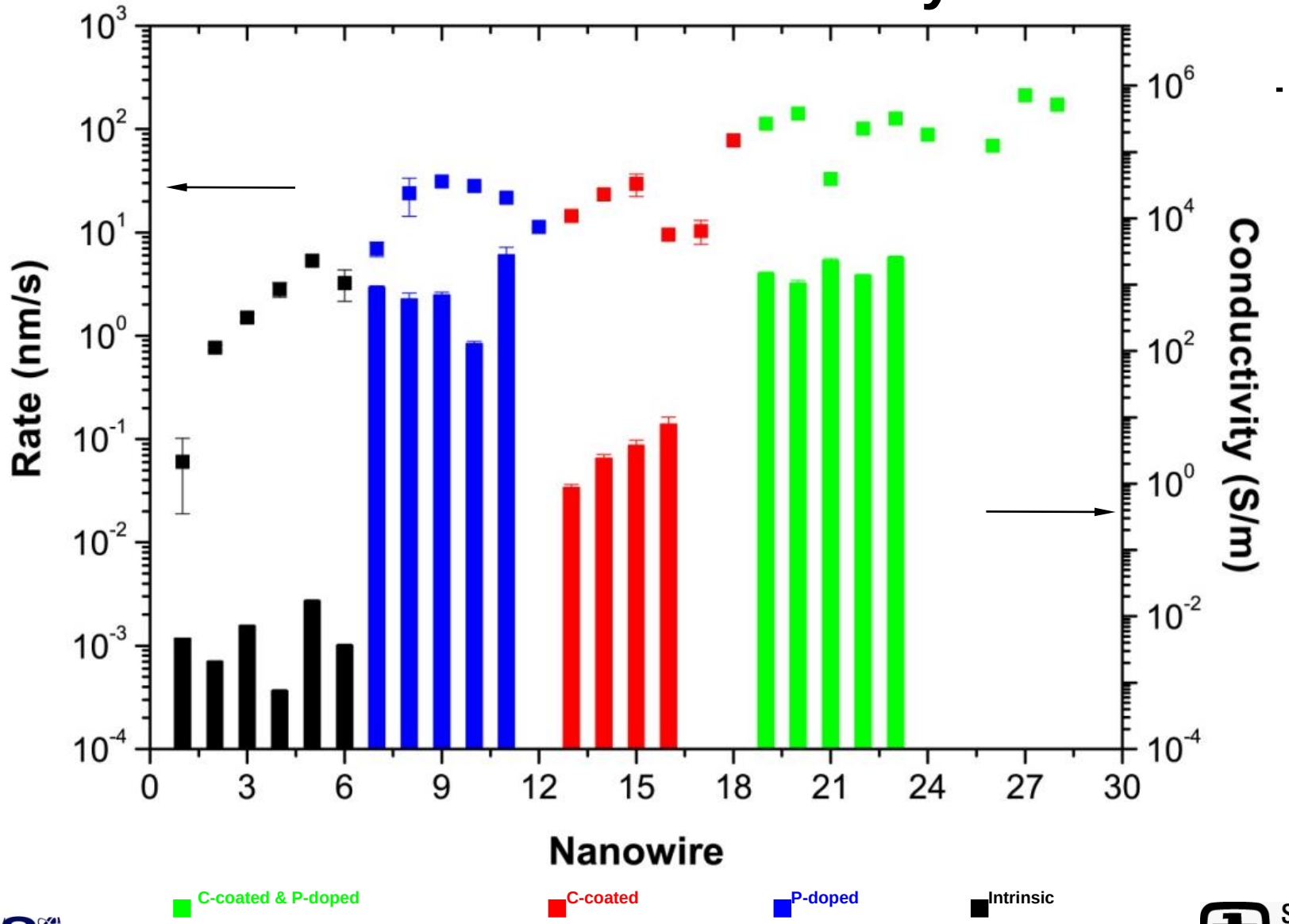


Similar kinetics are observed between C-coated and heavily phosporus-doped Si.

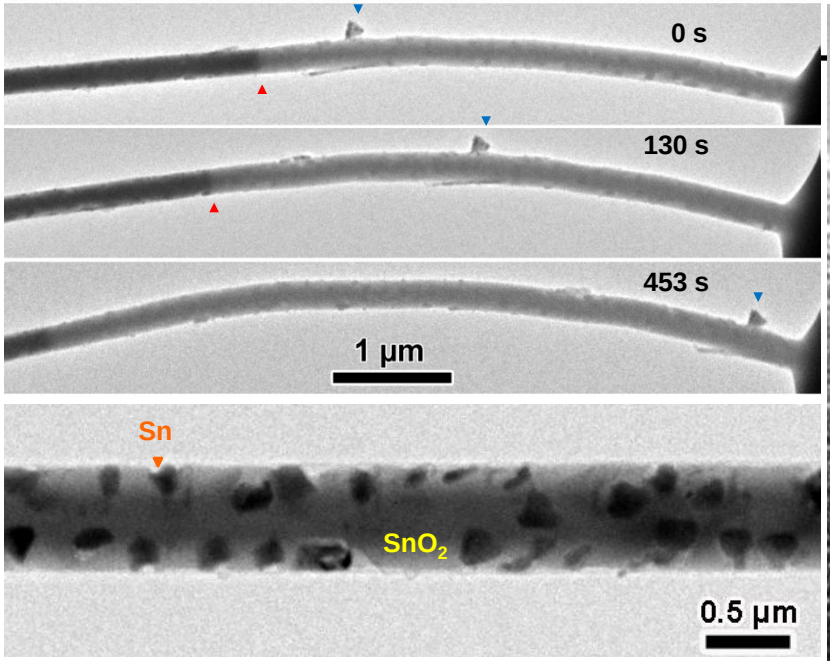


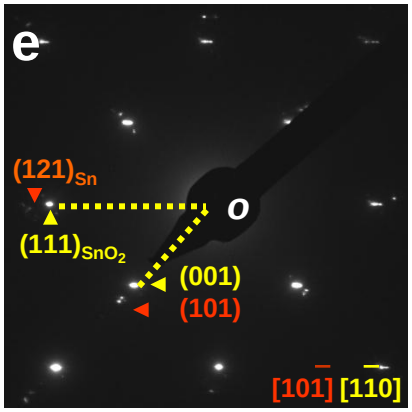


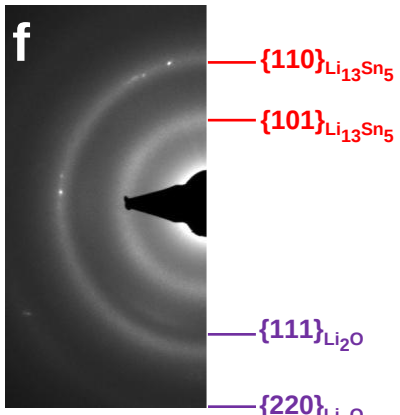
Comparison of lithiation rate and electrical conductivity.

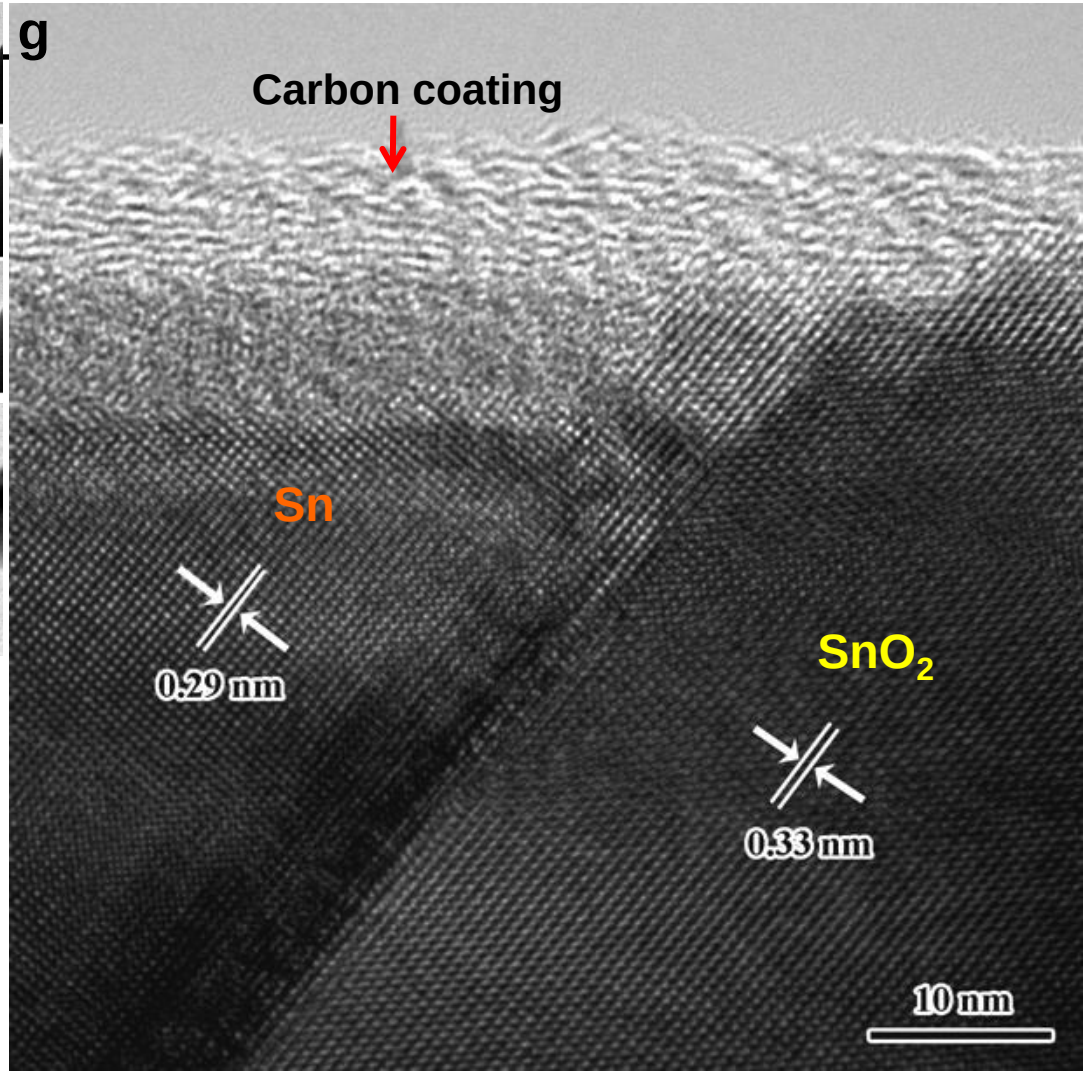


What about C-coating the SnO_2 nanowires?



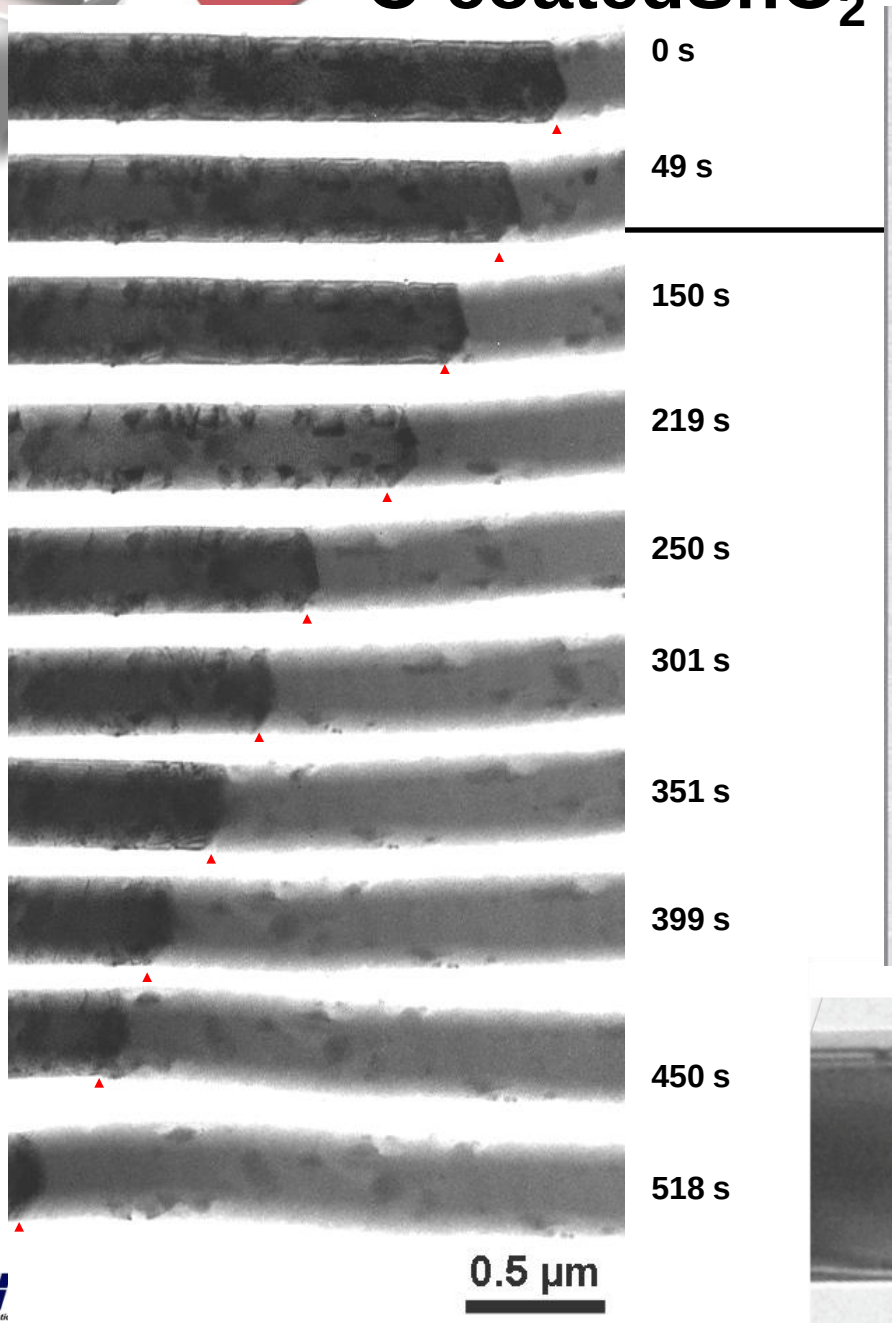


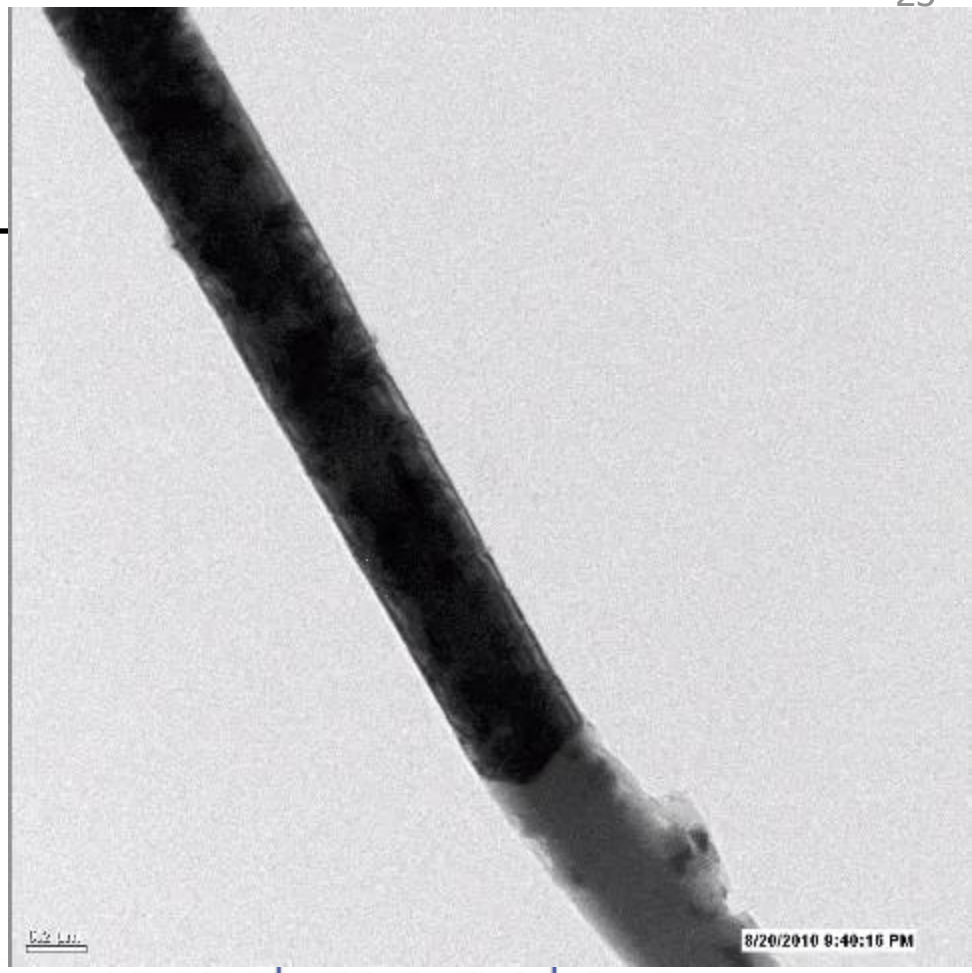


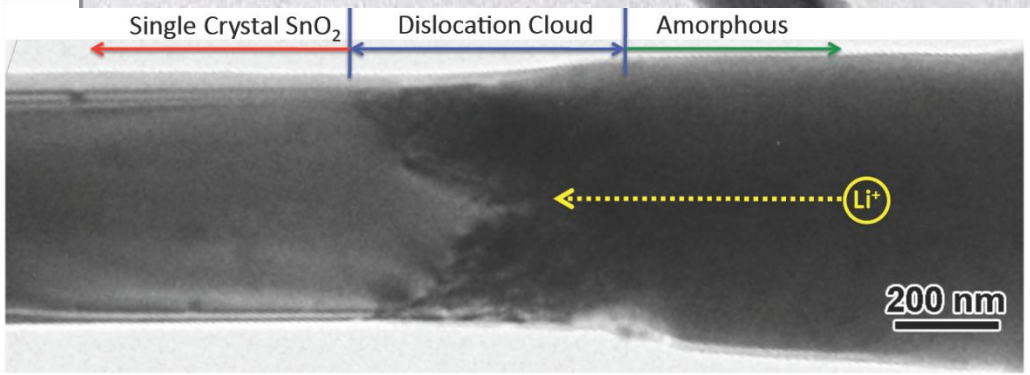


J.Y. Huang, *et al.*, accepted in ACS Nano

C-coatedSnO_2

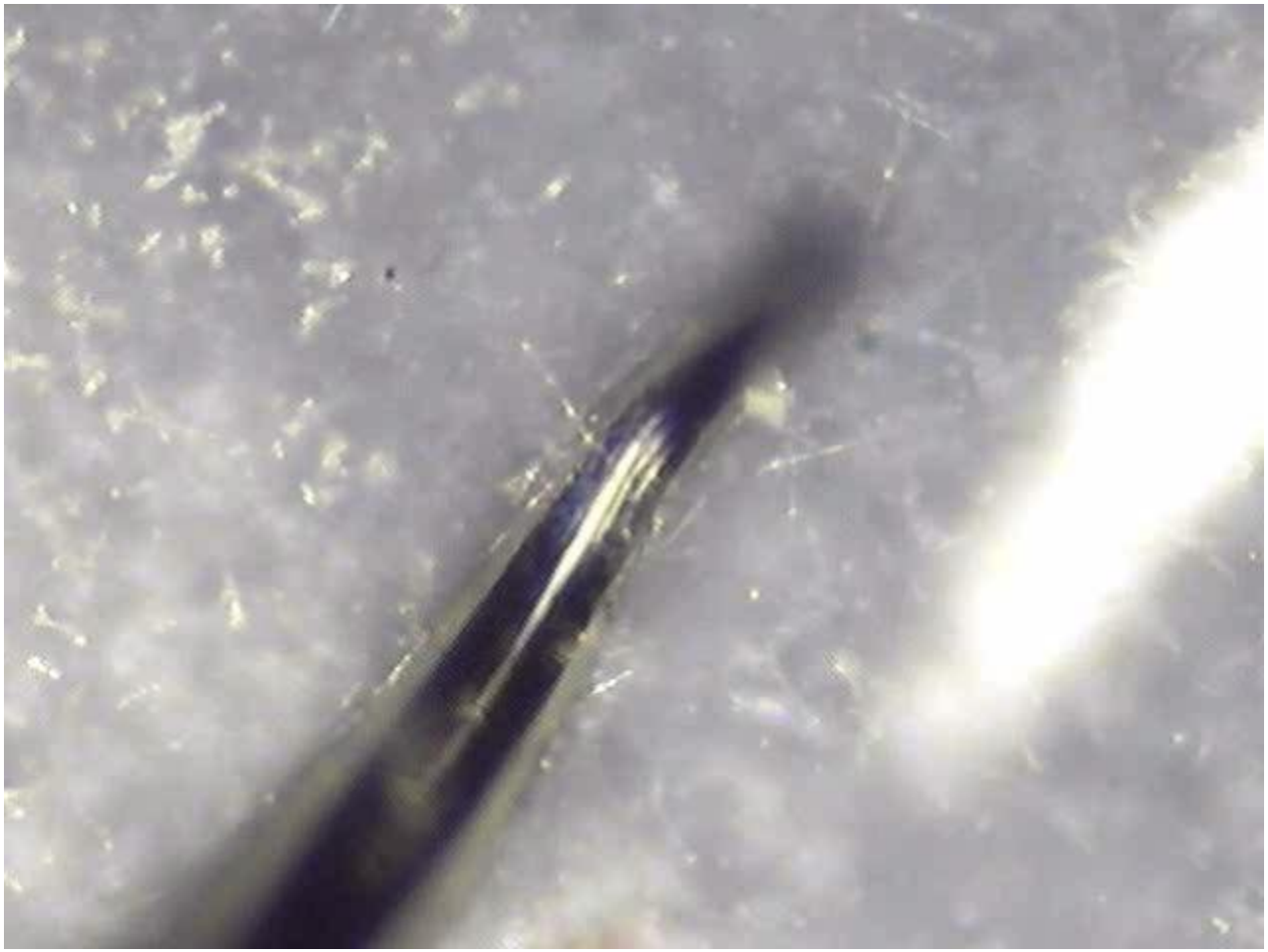






How do we make *in situ* TEM of battery materials an easy to use tool?

making an in situ TEM sample



~ 20 μm

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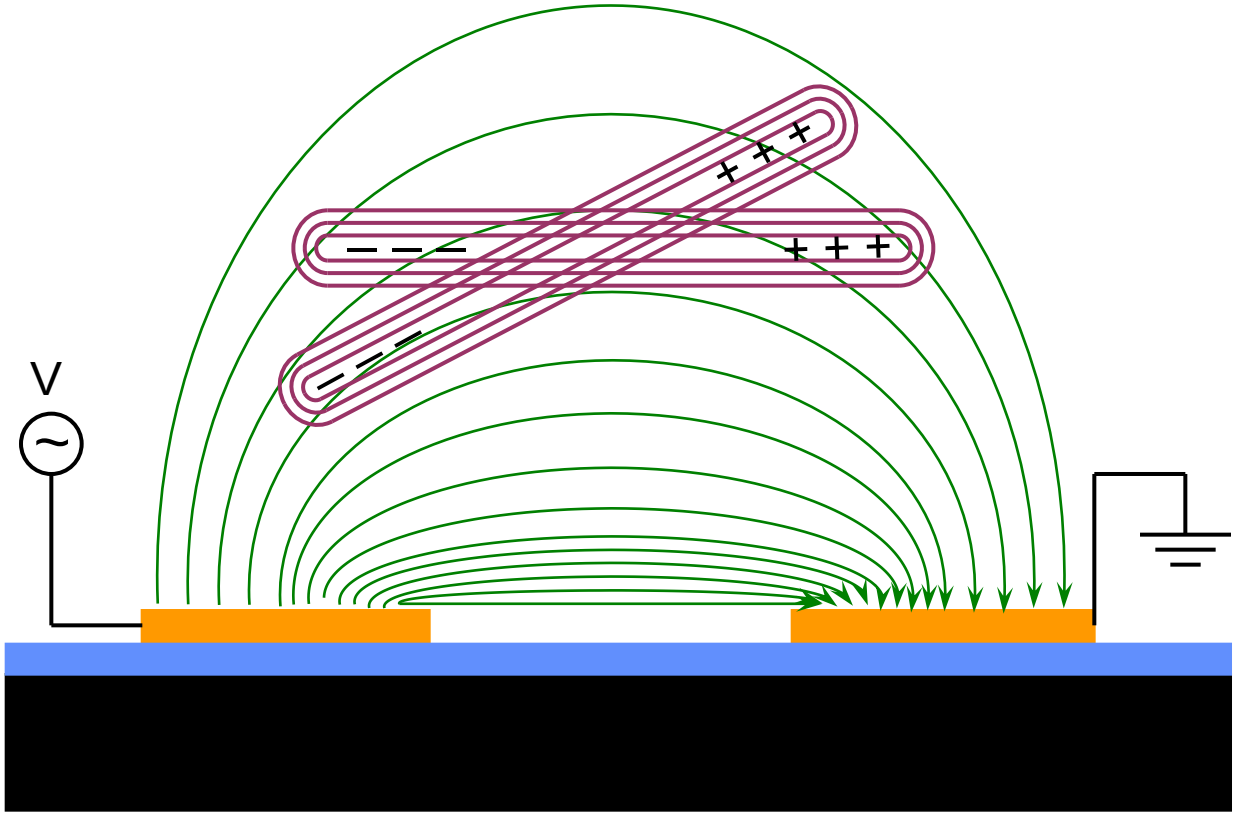
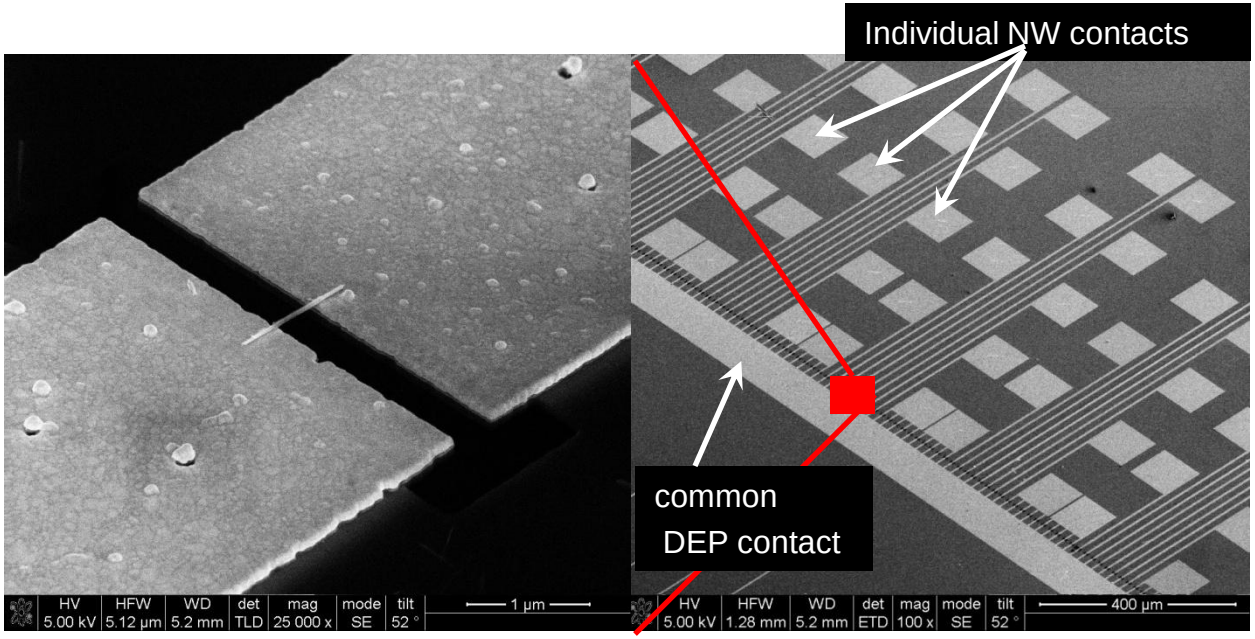
How do we easily assemble and measure "lots" of different battery materials?

Dielectrophoresis (DEP) assembly

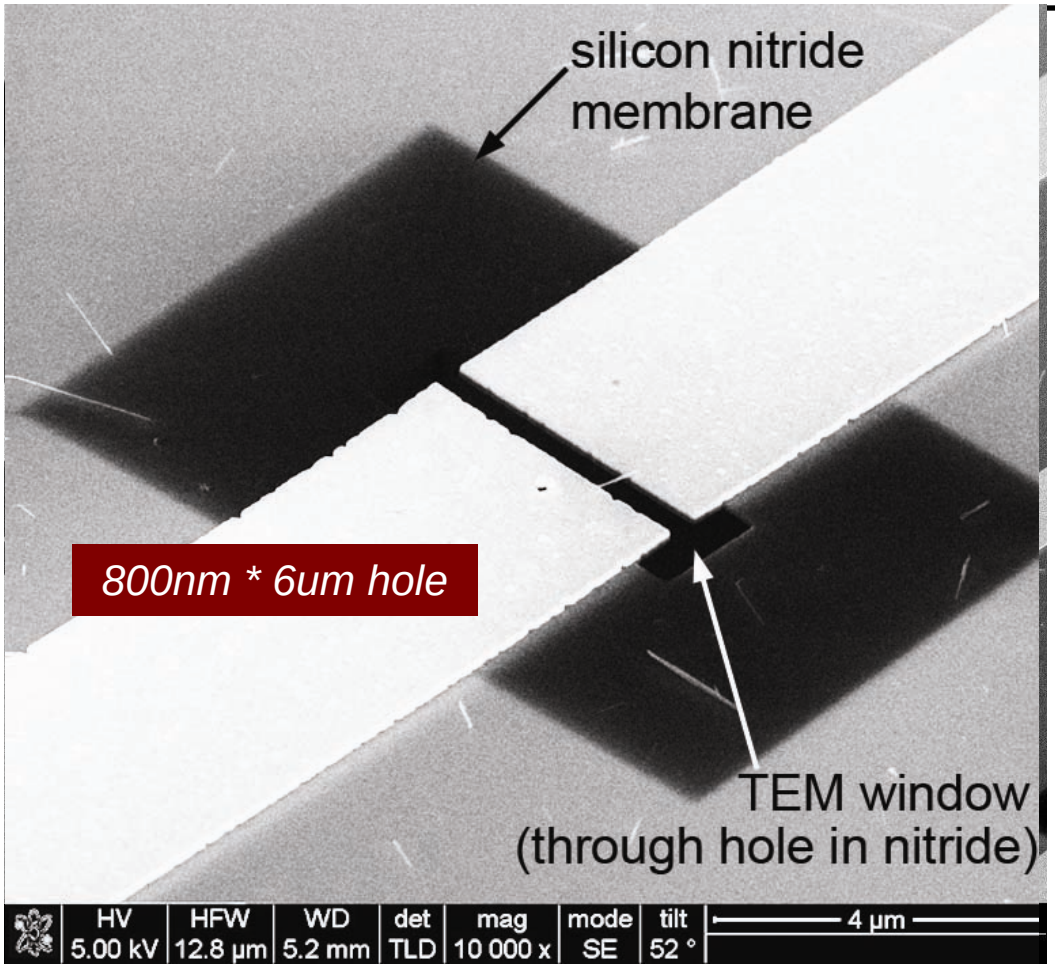


A chip-based platform for *in situ* TEM.



A. Subramanian, *et al.*," Single nanowire structural, electrical, and electrochemical characterization during lithium insertion," (in submission to Nano Lett), 2011.

Hybrid Nanofabrication Platform for *in situ* TEM

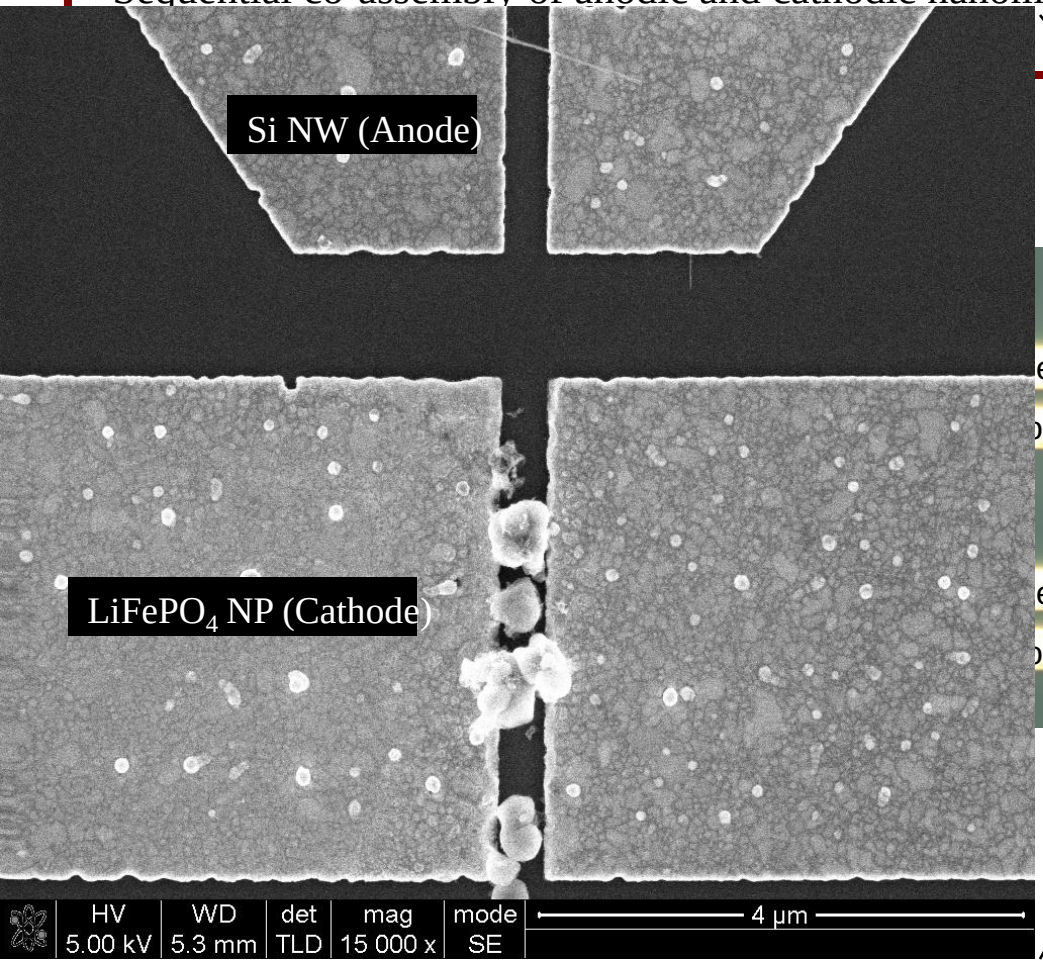


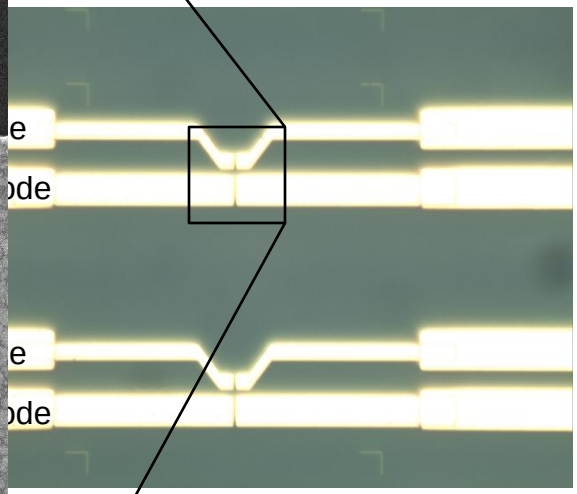
A. Subramanian, *et al.*, 2011.

Battery Materials Co-Assembly

Co-assembled, DEP-based integration of NW / NP Anodes & Cathodes

- Sequential co-assembly of anodic and cathodic nanomaterials onto the same chip using DEP





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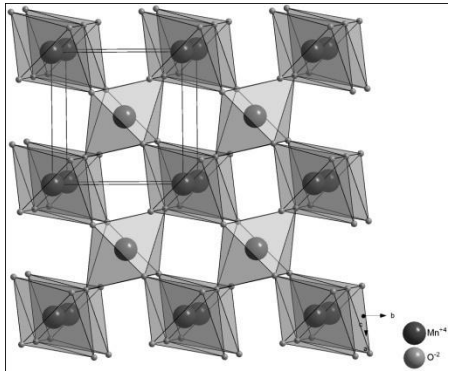
Test Case: β-MnO_2 NWs

β-MnO_2

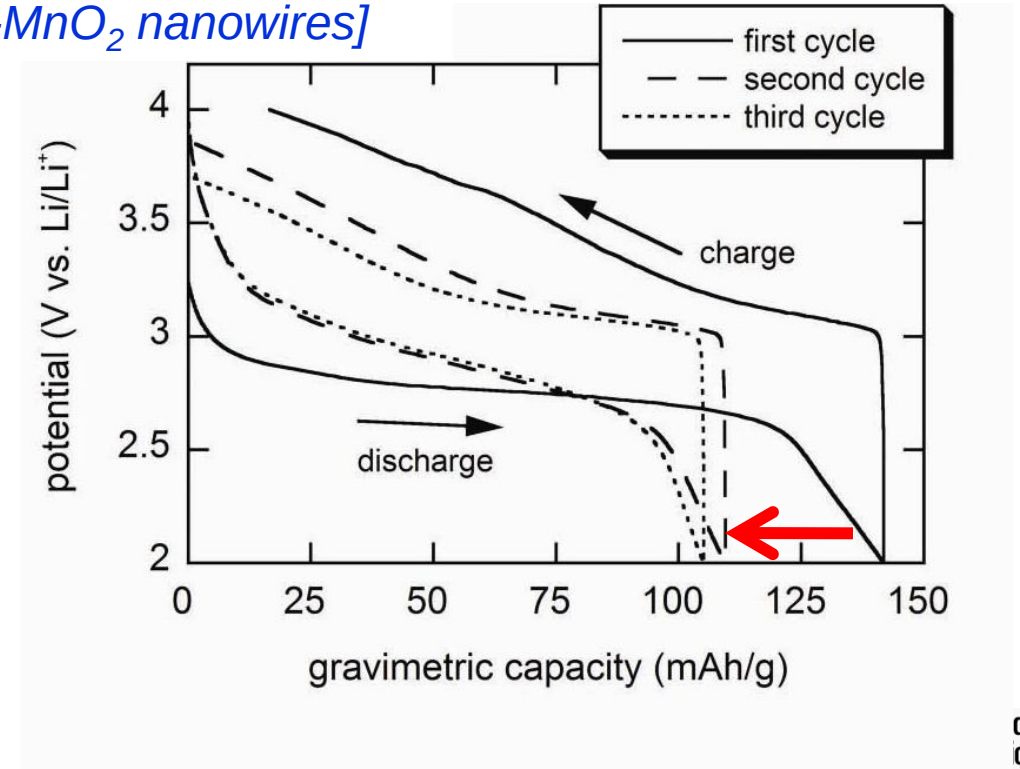
P42/mnm
***a* = 4.3983(3) Å**
***c* = 2.8730(3) Å**



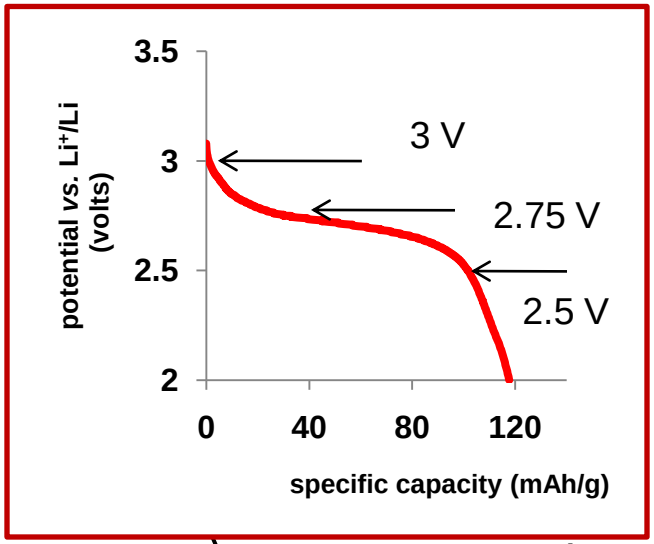
1 x 1 ion channels

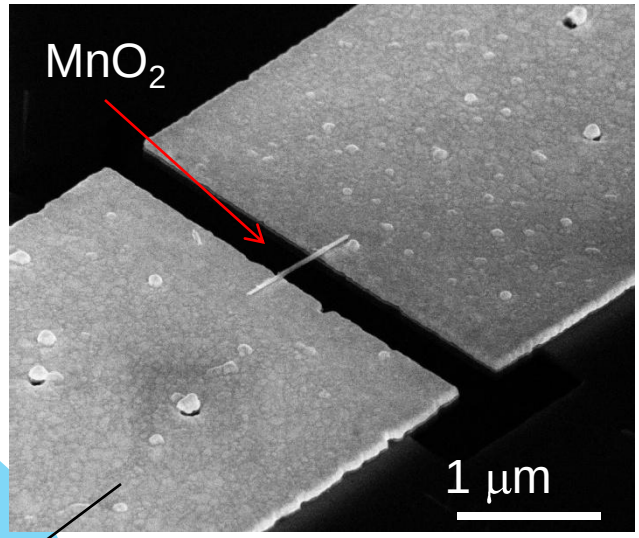
What are the structural and electrical changes that occur after the first cycle?

[data from 260 μg of β-MnO_2 nanowires]



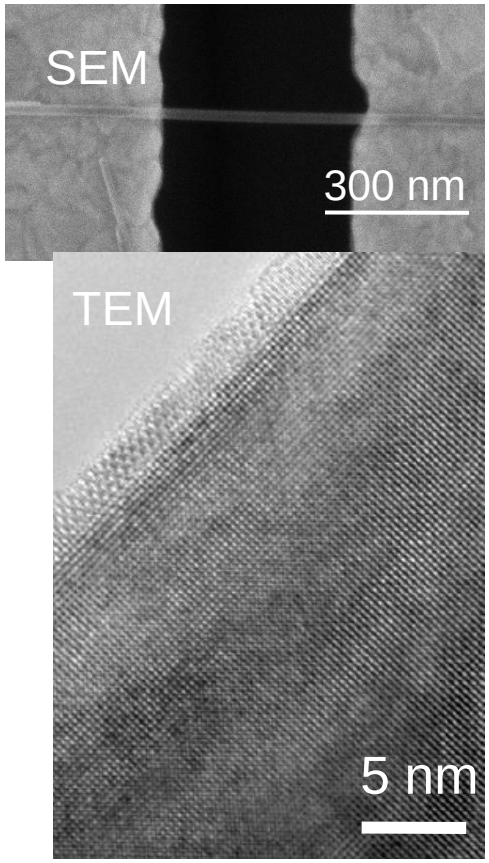
Ex-situ lithiation is performed, followed by characterization.



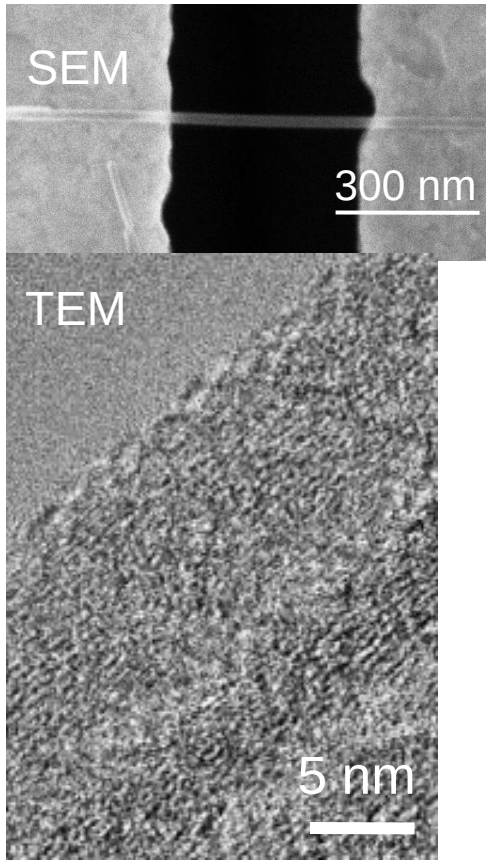


First cycle lithiation disorders the lattice and increases the resistivity → kinetic limitations.

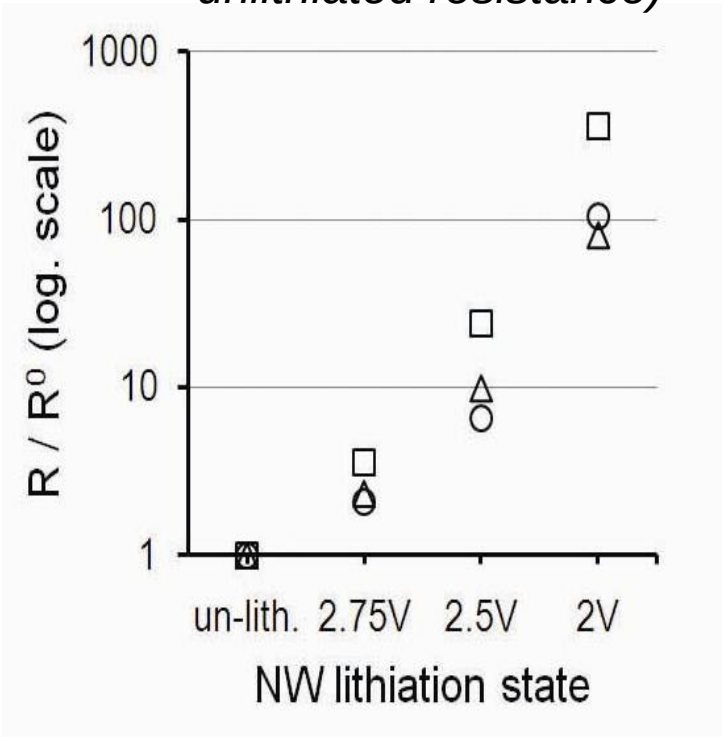
before lithiation



after lithiation



electrical changes
(ratio of lithiated to unlithiated resistance)



A. Subramanian, *et al.*, 2011.

- capacity fade is due to ***kinetic*** limitations
- can also see this by rate-dependent charging studies

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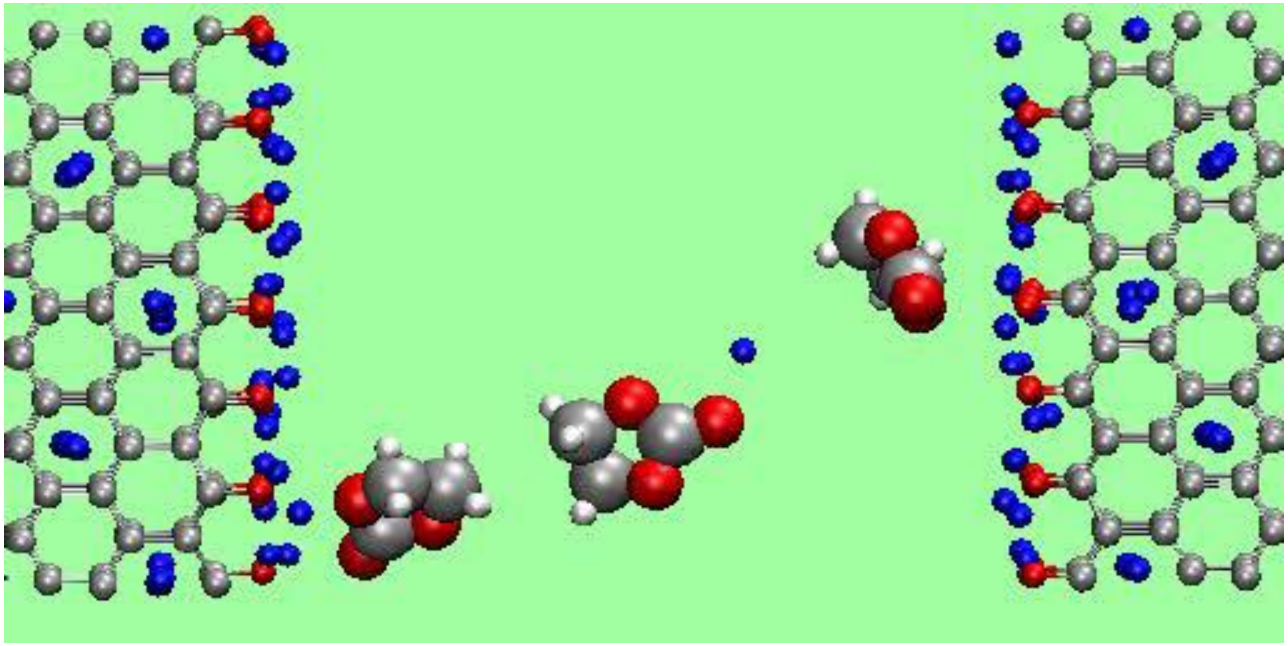
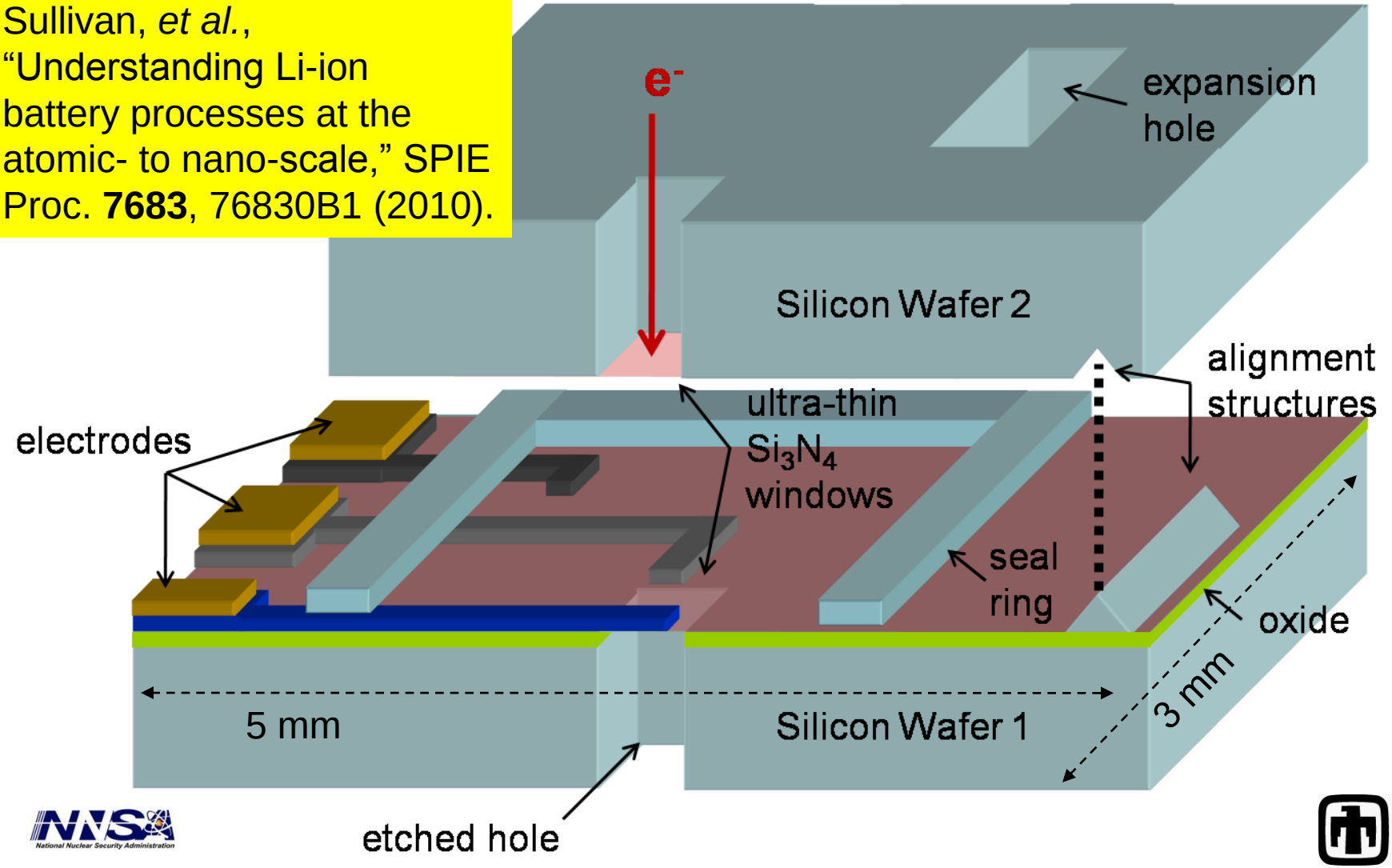
What about the interaction of the electrode material with real battery electrolytes?



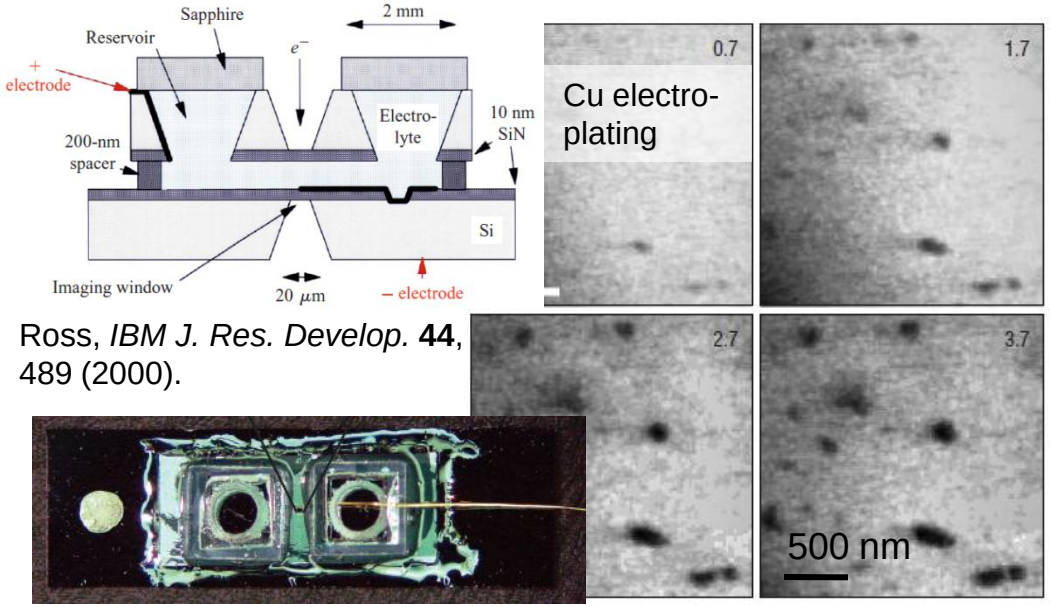
Kevin Leung *and J. Budzien, Phys. Chem. Chem. Phys. (2010).*

Our approach: develop *in-situ* electrochemical platforms for TEM.

Sullivan, *et al.*, "Understanding Li-ion battery processes at the atomic- to nano-scale," SPIE Proc. **7683**, 76830B1 (2010).

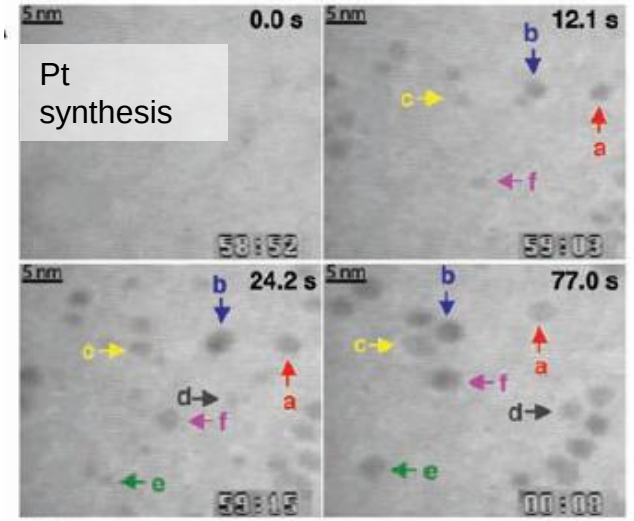


There has been limited *in-situ* liquid-cell TEM work.

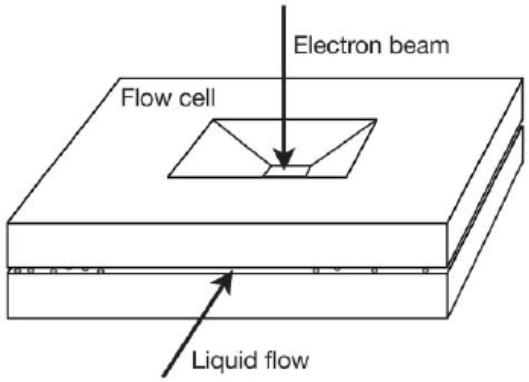


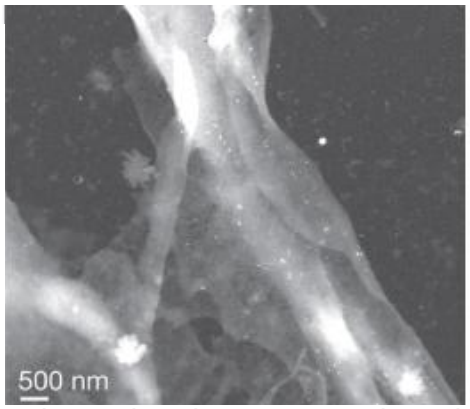
Ross, *IBM J. Res. Develop.* **44**, 489 (2000).

Williamson et al., *Nature Mater.* **2**, 532 (2003).



Zheng et al., *Science* **324**, 1309 (2009).





de Jonge et al., *Proc. Natl. Acad. Sci.* **106**, 2159 (2009).

also …

Thiberge et al., *Proc. Natl. Acad. Sci.* **101**, 3346 (2004).

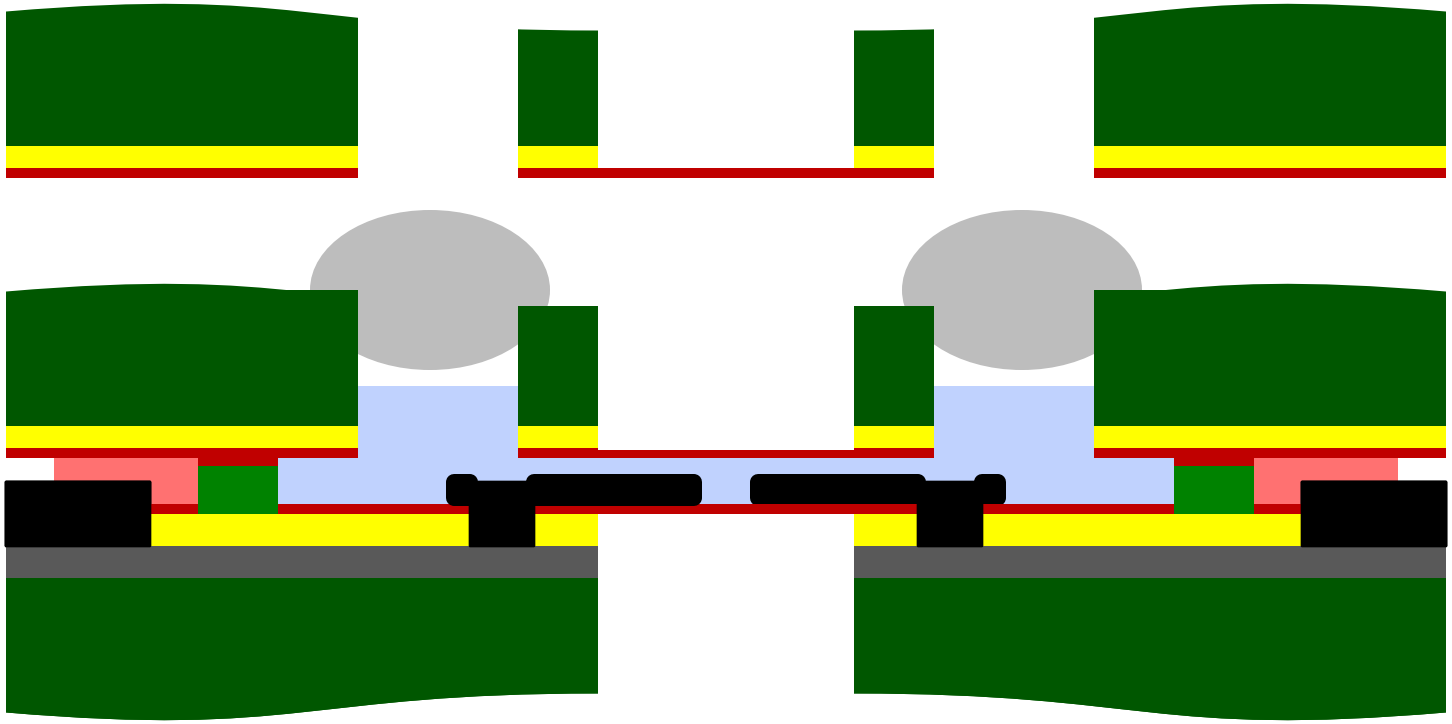
Liu et al., *Lab Chip* **8**, 1915 (2008).

National Nuclear Security Administration

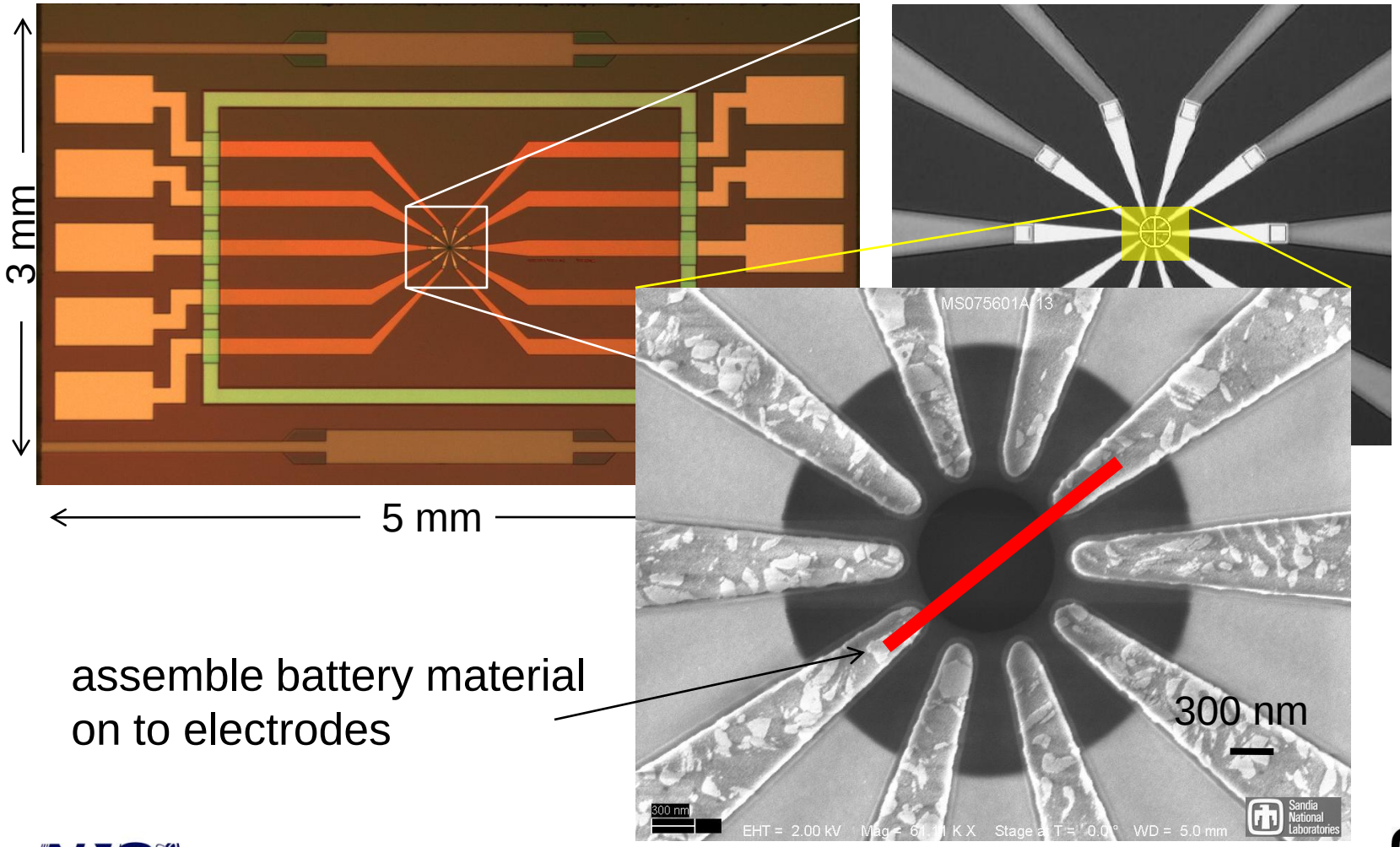
Sandia National Laboratories

Assembly requires alignment, sealing, filling, and capping.

1. Align top and bottom chips
2. Epoxy seal (Epotek 301 – used industrially for Si chips)
3. Fill with electrolyte
4. Cap fill holes

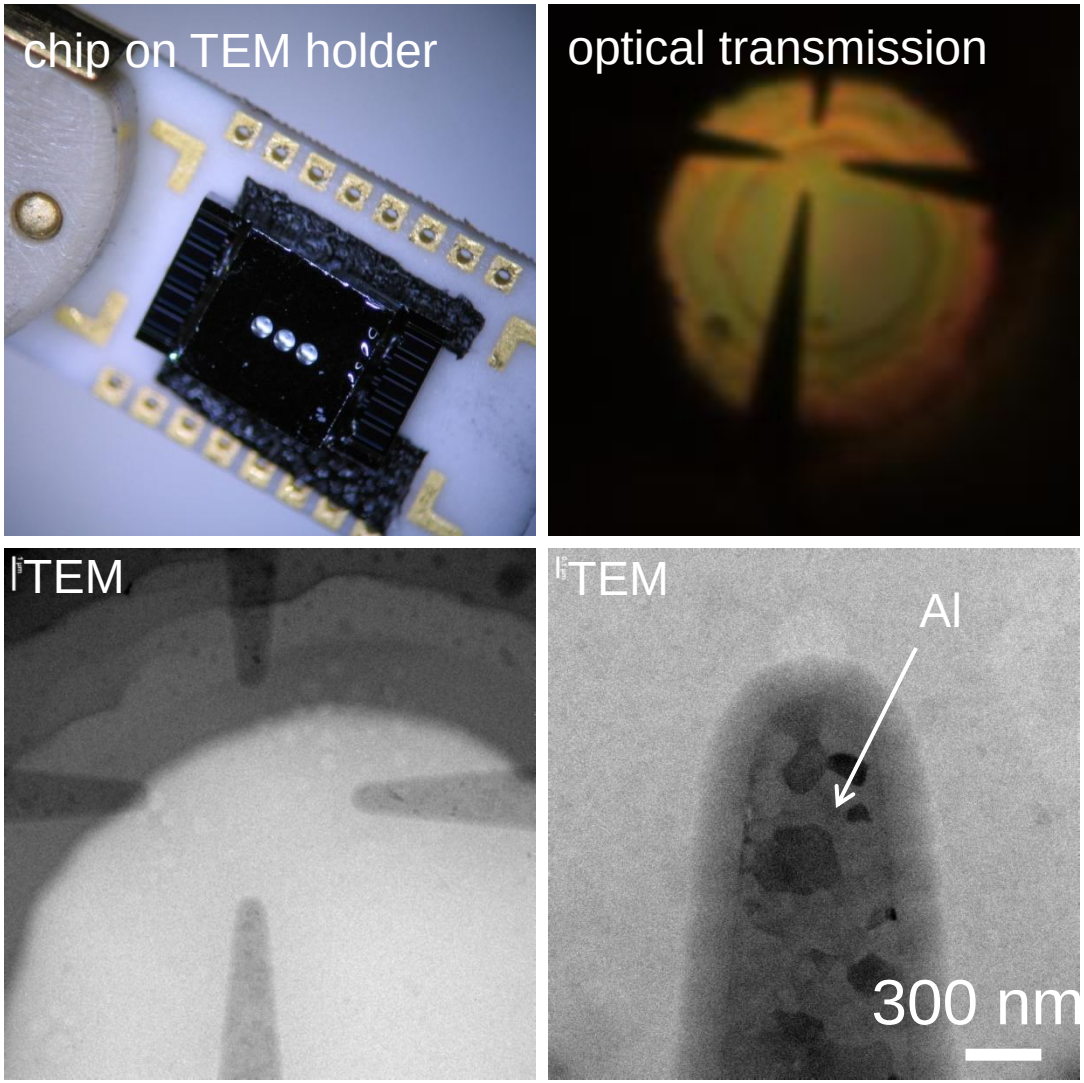


More than three electrodes are provided: enables field-driven assembly.

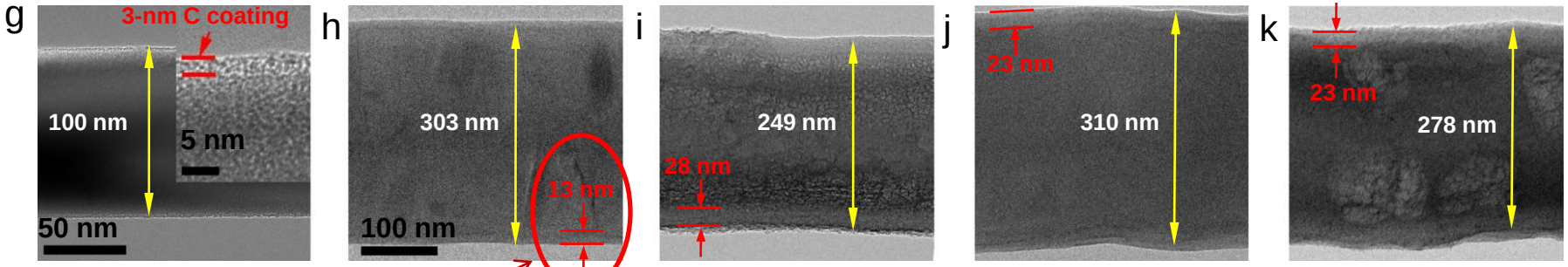


J. P. Sullivan, *et al.*, 2010.

Preliminary testing in the TEM …



SEI morphology and evolution should be visible, as suggested by Si-ILE studies



as prepared

1st lithiation

1st delithiation

2nd lithiation

2nd delithiation

In situ TEM of a carbon-coated Si nanowire during lithiation/delithiation

(Jian Yu Huang, et al.)

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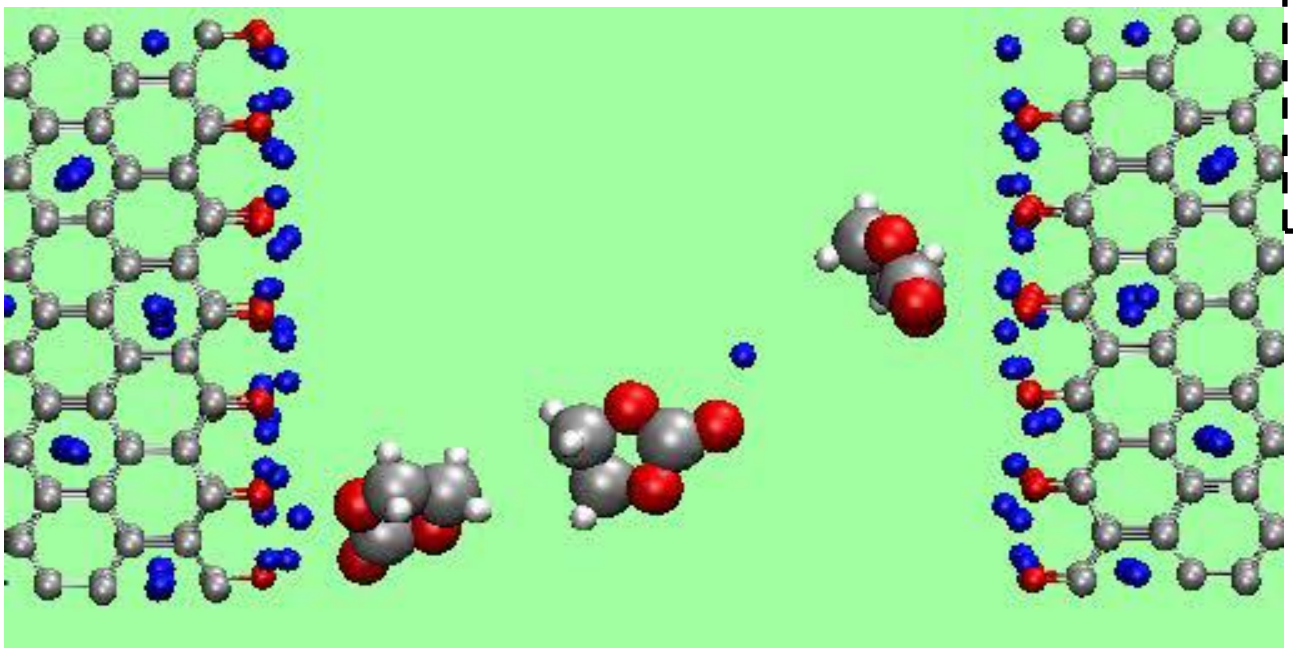
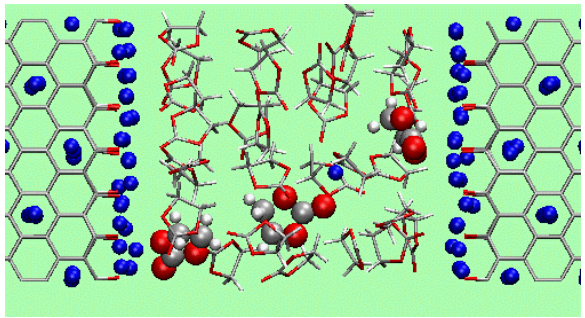
Until we can get there experimentally, what can theory tell us?

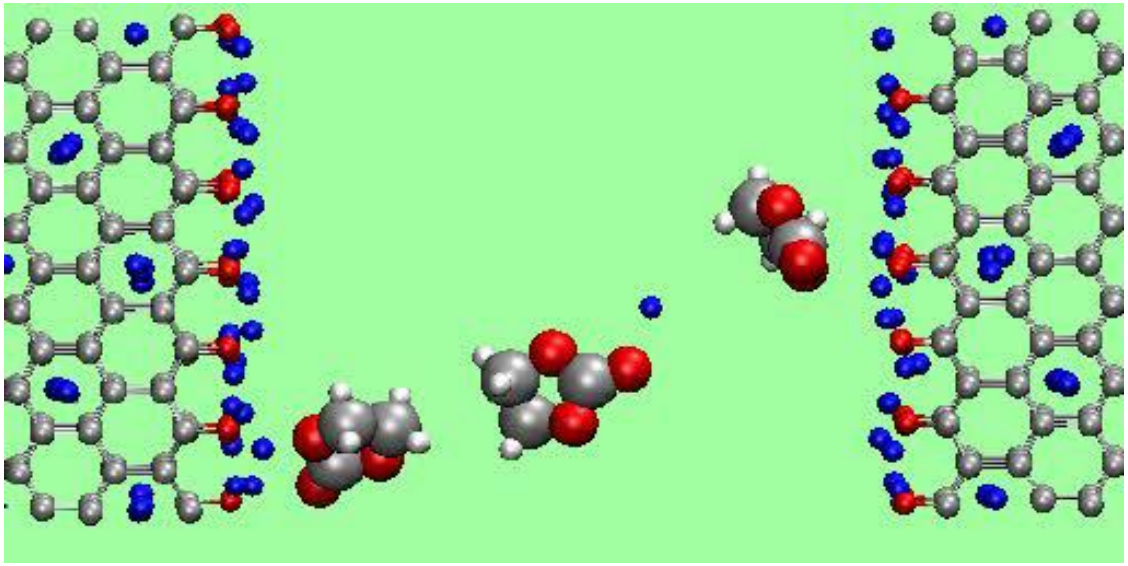


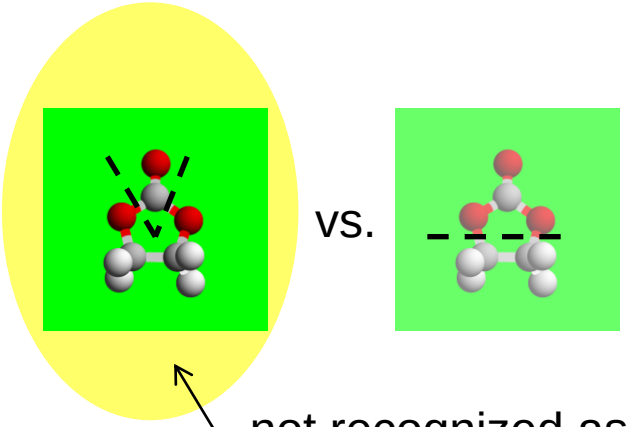


Kevin Leung *and J. Budzien, Phys. Chem. Chem. Phys. (2010).*

(bare graphite electrode immersed in EC)

New SEI reaction pathway discovered by AIMD.





vs.

$EC + 2\ e^- \rightarrow {}^-OC_2H_4O^- + CO$

$^-OC_2H_4O^- + 2\ CO_2 \rightarrow {}^-O_2COC_2H_4OCO_2^-$

not recognized as a mechanism before, but found to dominate on reactive surfaces (e.g. Li^0)

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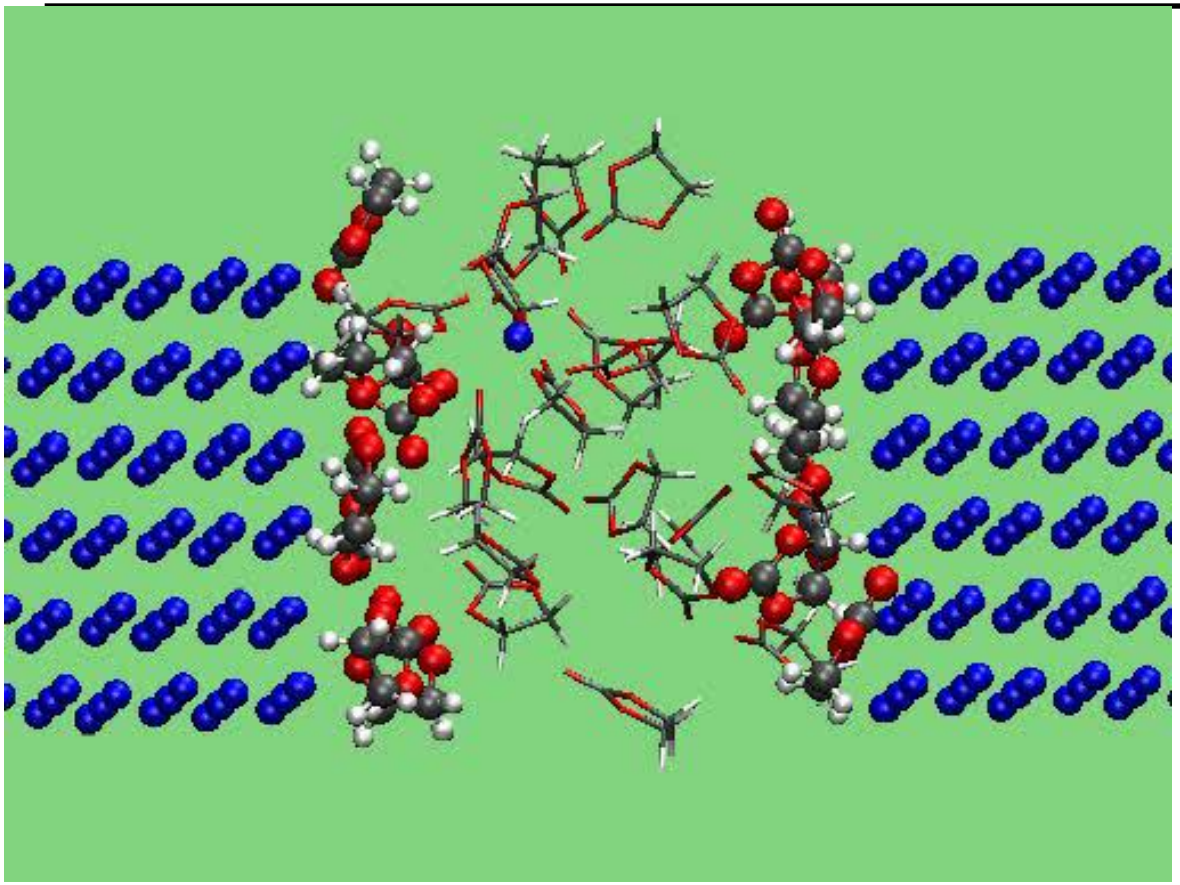
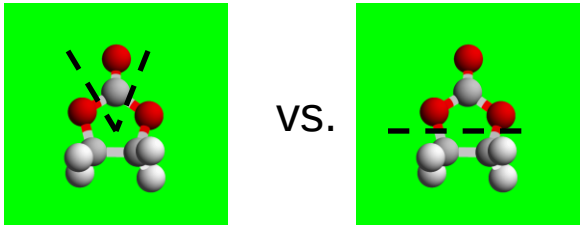
EC liquid breakdown on Li metal electrode also favors CO production pathway.



11/12 EC at the interface decomposes into $OC_2H_4O^{2-}$ + CO, not $C_2H_4 + CO_3^{2-}$



T=350 K

Li metal SEI "film" Intact EC SEI "film" Li metal

Liu, Balbuena, Budzien, Leung, JECS 2011

SEI on LiC_6 and Li metal "similar": Expt: Aurbach, Daroux, Foguy, Yeager, JES 134:1611 (1987)

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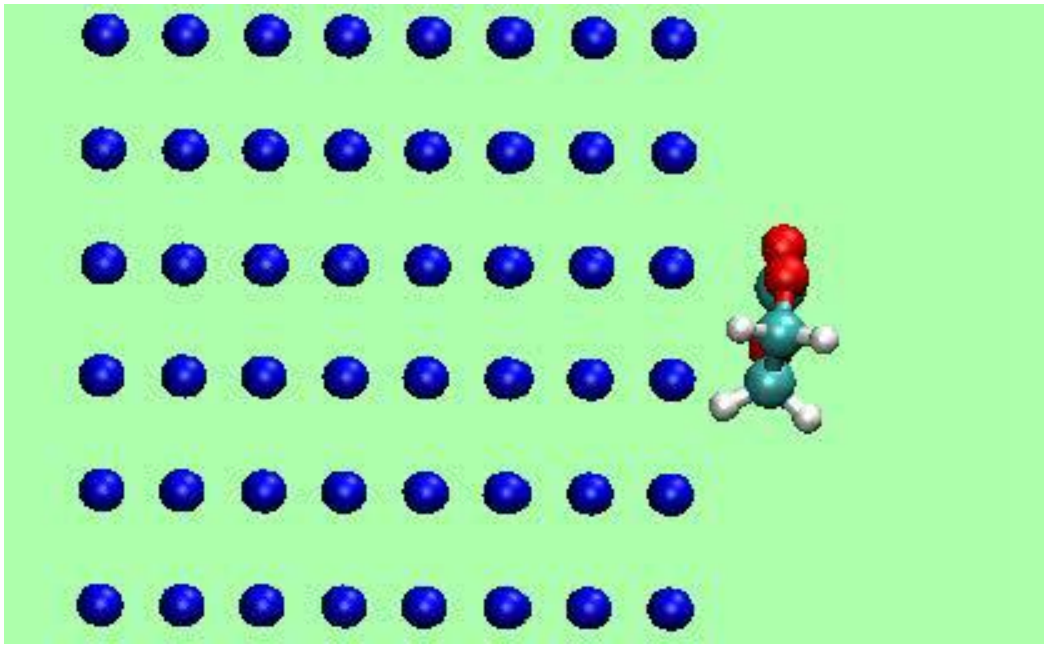
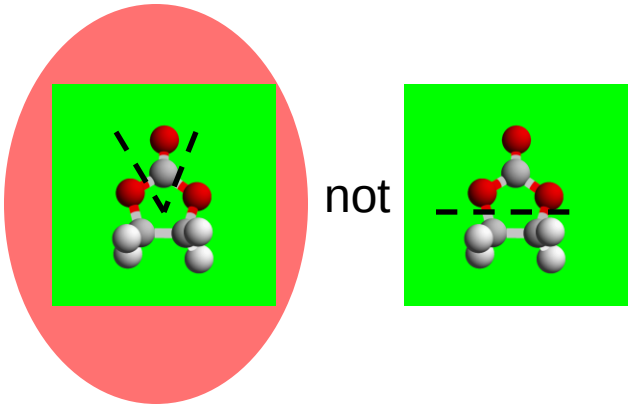
Single molecule EC breakdown on Li metal electrode surface again favors CO.



Li metal

Intact EC



T=350 K

K. Leung, *to be submitted*

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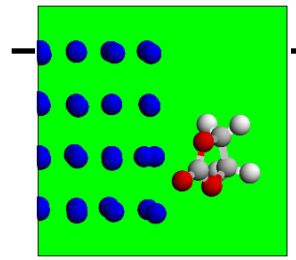
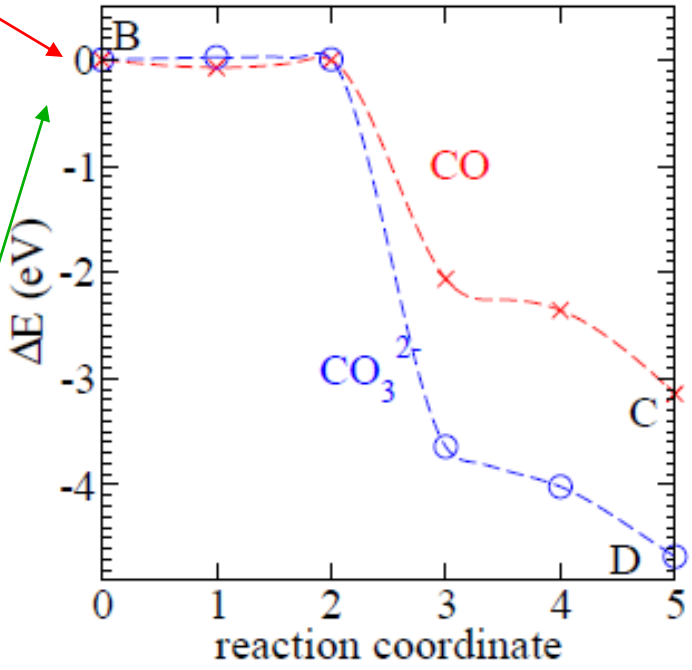
But CO_3^{2-} reaction product is more exothermic -> kinetic limitation.

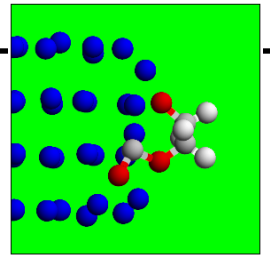


Li metal

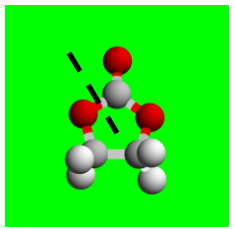
Theory: Han & Lee,Theor. Chem. Acct. 112:106 (2004

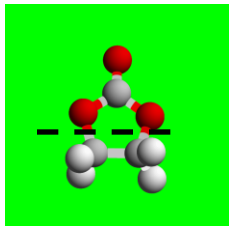


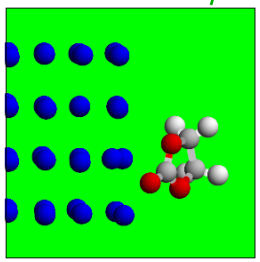
reaction coordination

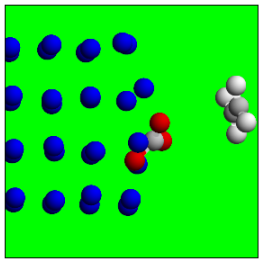


favored due to kinetics









K. Leung, *to be submitted*

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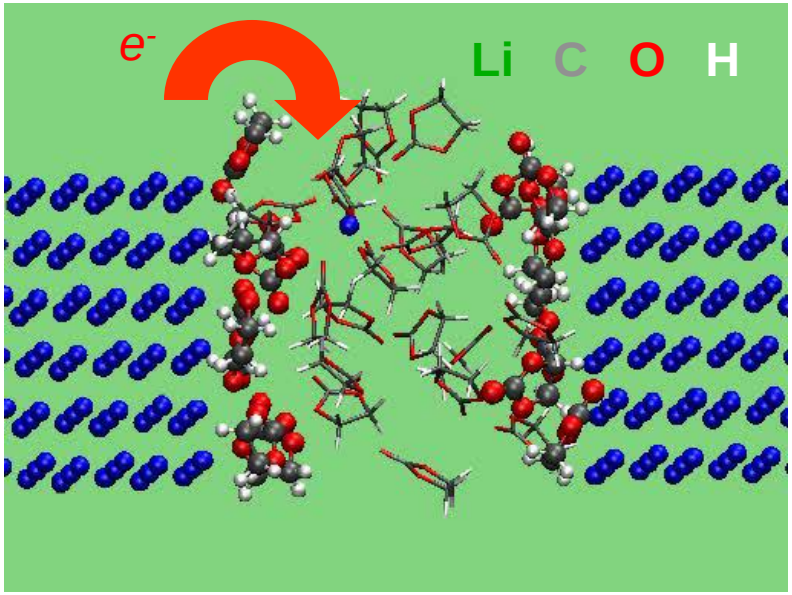
What about later stages of SEI formation?

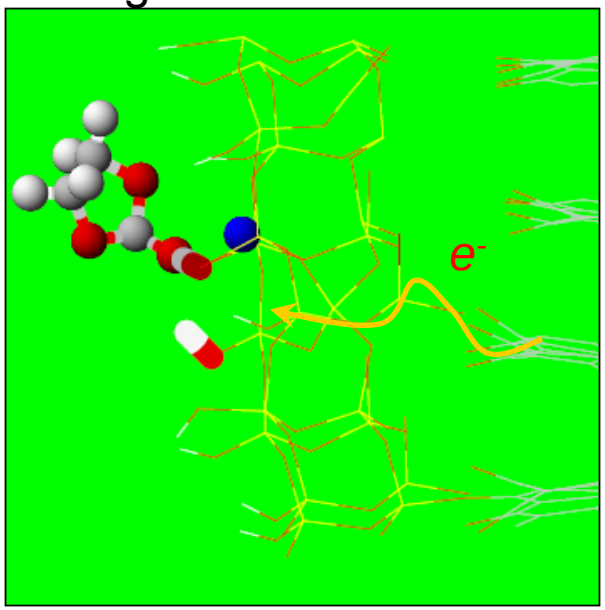
pristine electrode



Li metal Intact EC Li metal

- adiabatic (e^- moves faster than nuclei)
- DFT calculations suffice
- *ab initio* molecular dynamics to follow
- follow bond-breaking in real time

"aged" electrode



Intact EC $LiAlO_2$ Li_xC_6

7 or 10 A thick

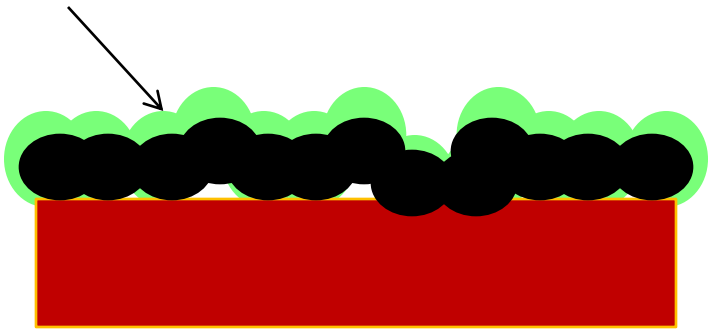
- non-adiabatic (e^- tunnels slowly)
- Focus on electron transfer (Marcus theory)
- Constrained DFT (cDFT)

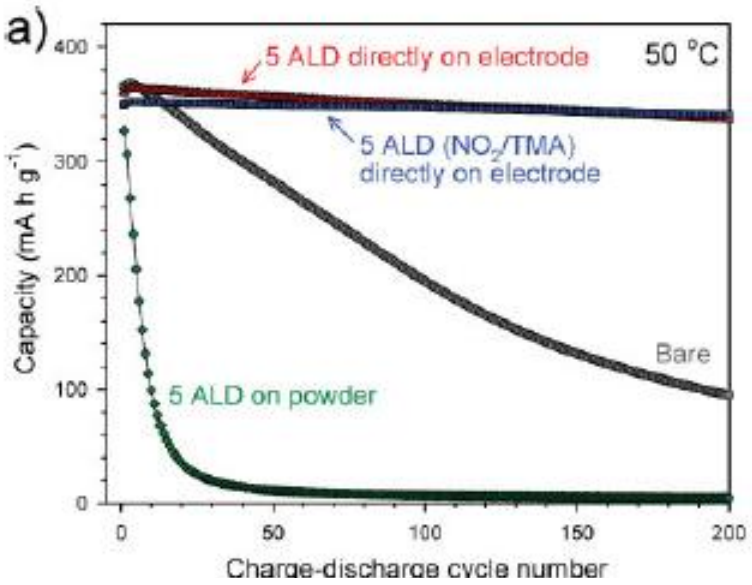
Why $LiAlO_2$?

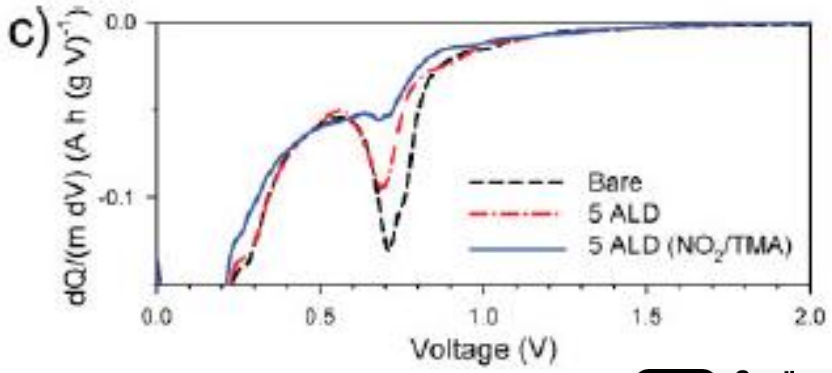
Ultrathin Direct Atomic Layer Deposition on Composite Electrodes for Highly Durable and Safe Li-Ion Batteries Adv. Mater. 22:2172 (2010)

By *Yoon Seok Jung, Andrew S. Cavanagh, Leah A. Riley, Sun-Ho Kang, Anne C. Dillon, Markus D. Groner, Steven M. George,* and *Se-Hee Lee**

ALD a-Al_2O_3 coated graphite







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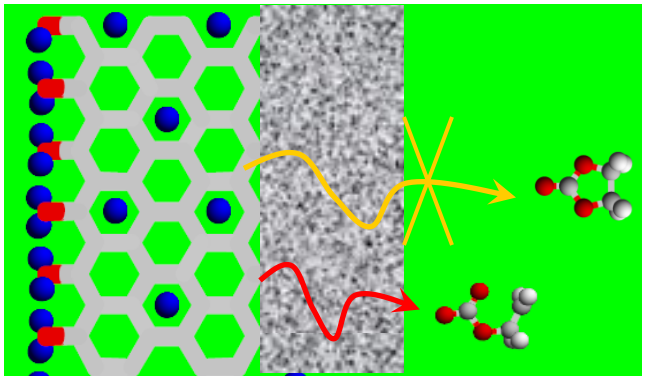
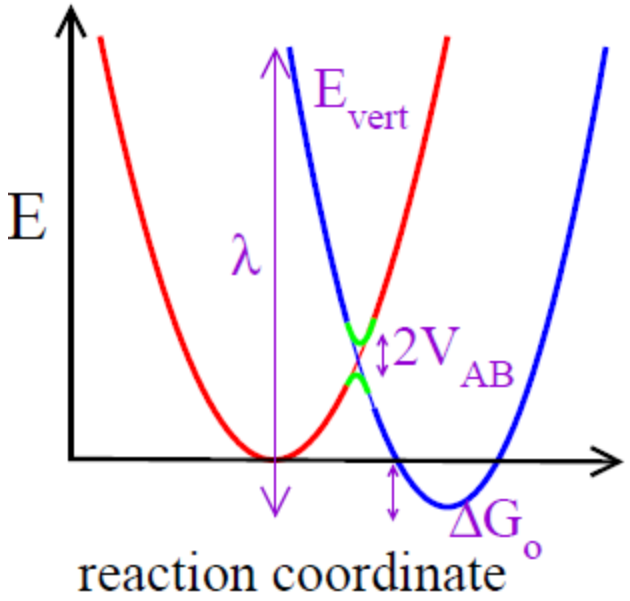
Oxide-coated electrode: focus on e^- transfer to EC (non-adiabatic effects)



can't use DFT

Use Marcus theory to calculate electron transfer rate: focus on λ and V_{AB}



adiabatic

DFT rigorous if no self-interaction error

$$k_{et} = \upsilon_n \exp[-(\lambda/4 - V_{AB})/k_B T]$$

non-adiabatic

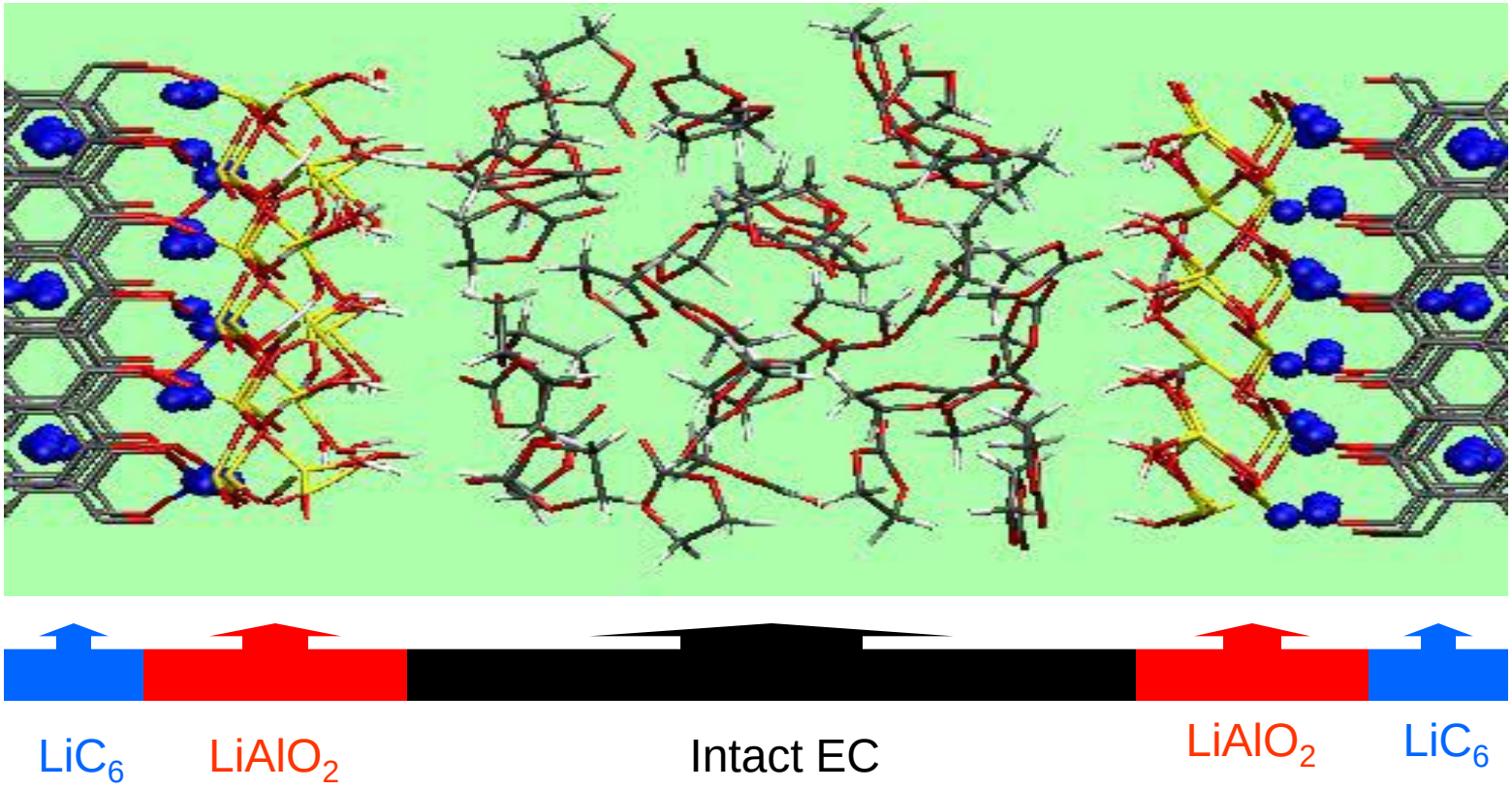
DFT not rigorous; cDFT gives λ and V_{AB}

$$k_{et} = \frac{2\pi |V_{AB}|^2}{\hbar\sqrt{4\pi\lambda k_B T}} \exp\left[-\frac{(\Delta G_o + \lambda)^2}{4\lambda k_B T}\right]$$

NNSA National Nuclear Security Administration

Sandia National Laboratories

EC on 10Å $LiAlO_2$ coating – no decomposition (in 7ps)



($LiAlO_2$ instead of Al_2O_3 as model: has Li embedded on surface, more ordered surface)

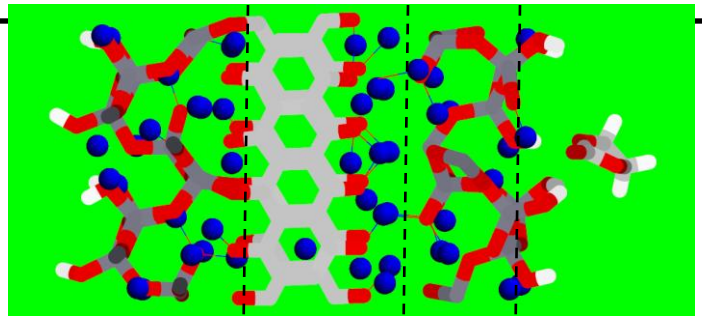
K. Leung, *to be submitted*

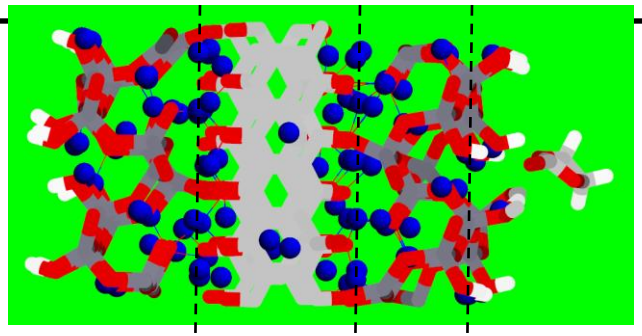
Sandia National Laboratories

The conformation of the EC molecule is critical for e^- transfer.

K. Leung, *to be submitted*

flat EC | **bent EC$^-$**

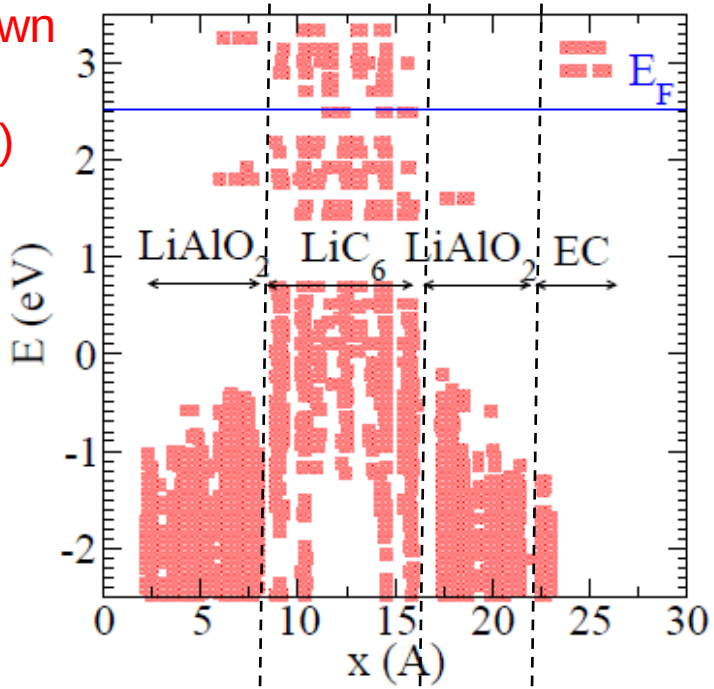


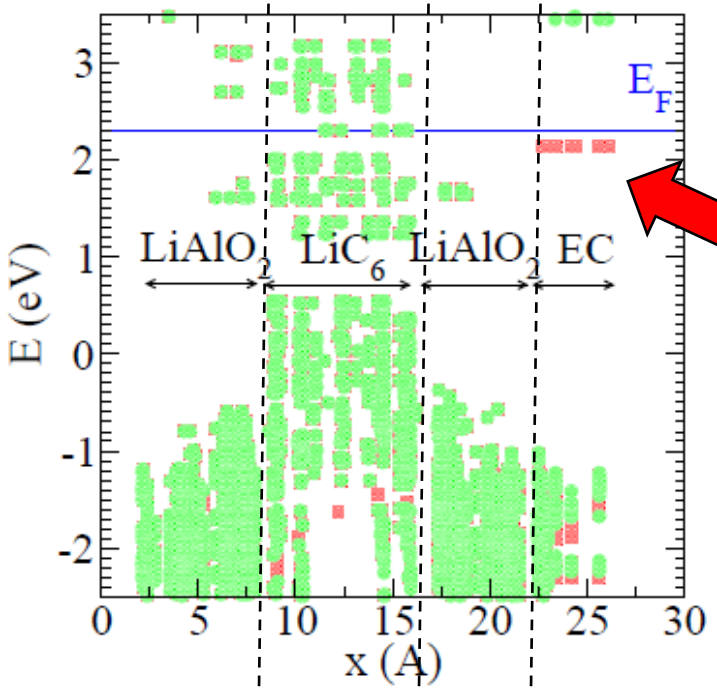


oxide | LiC_6 | oxide | flat EC

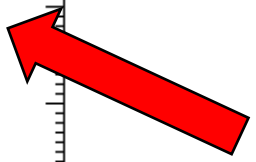
oxide | LiC_6 | oxide | bent EC$^-$

up & down spin (no net spin)

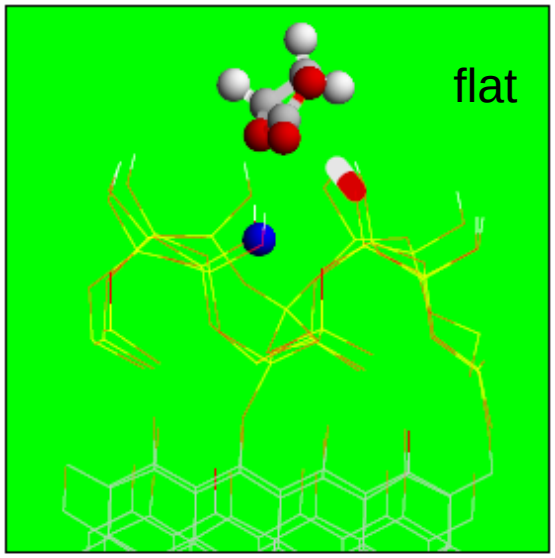


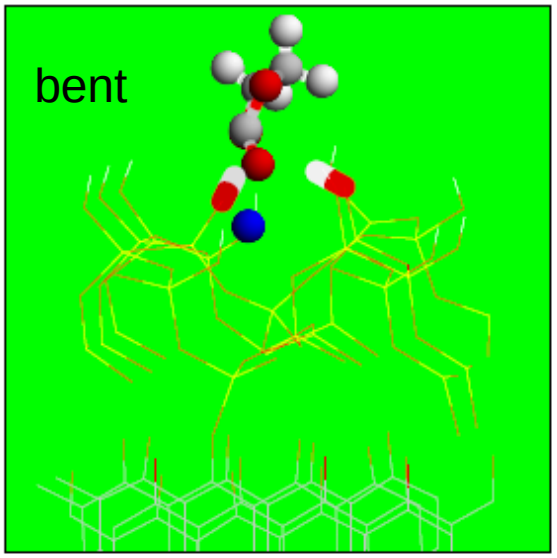


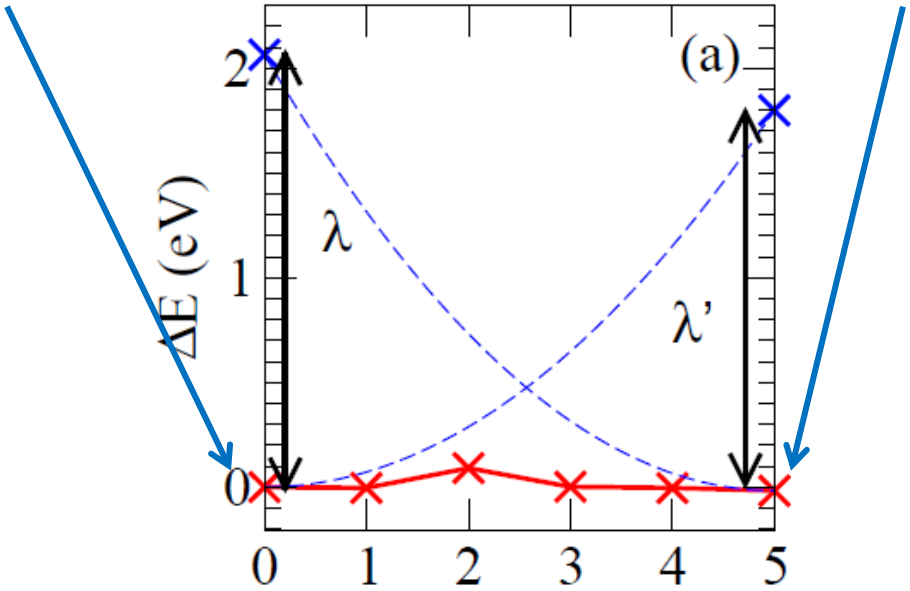
up spin
down spin



What does Marcus theory give for k_{et}?







λ ~ 2 eV (dominates)

V_{AB} ~0.017 eV

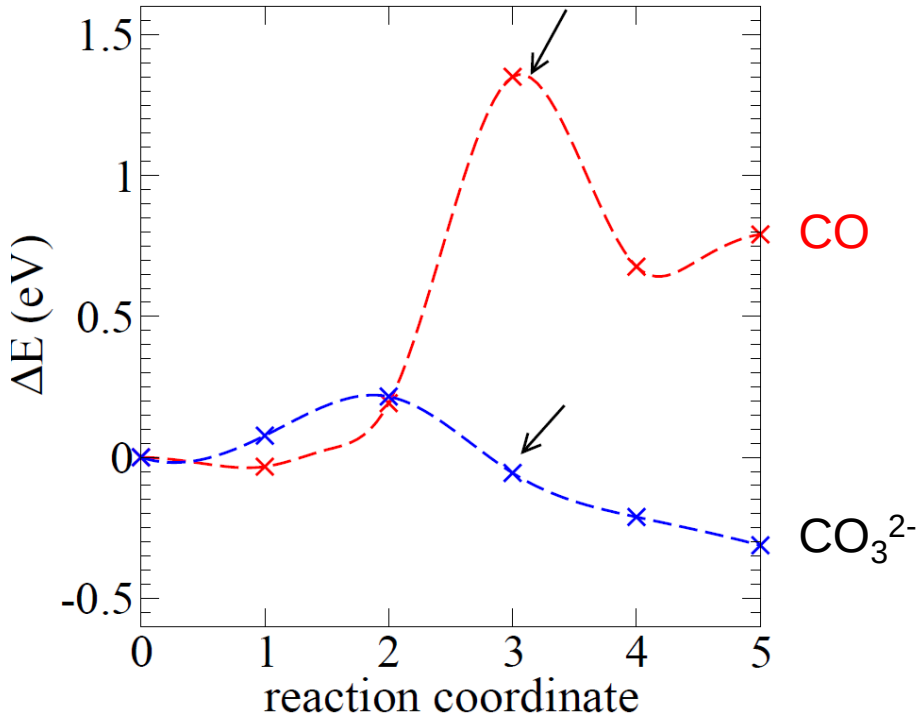
k_{et} ~ 3x10^3 /s

(about 1/3 msec)

K. Leung, *to be submitted*

On 10 Å thick oxide coating: product channel crossover

C-O bond breaking barriers

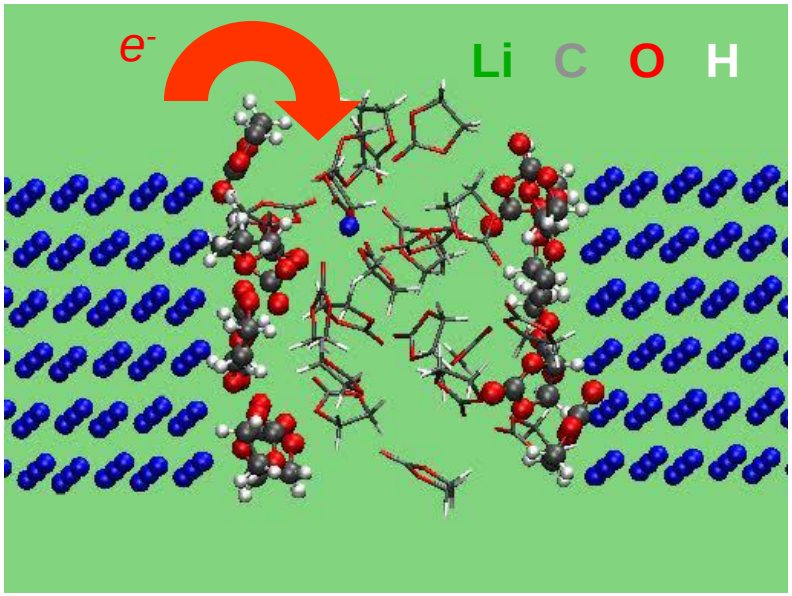


on thicker coating, CO much less favorable than CO_3^{2-} → product channel crossover

K. Leung, *to be submitted*

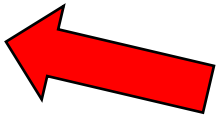
What about later stages of SEI formation?

pristine electrode

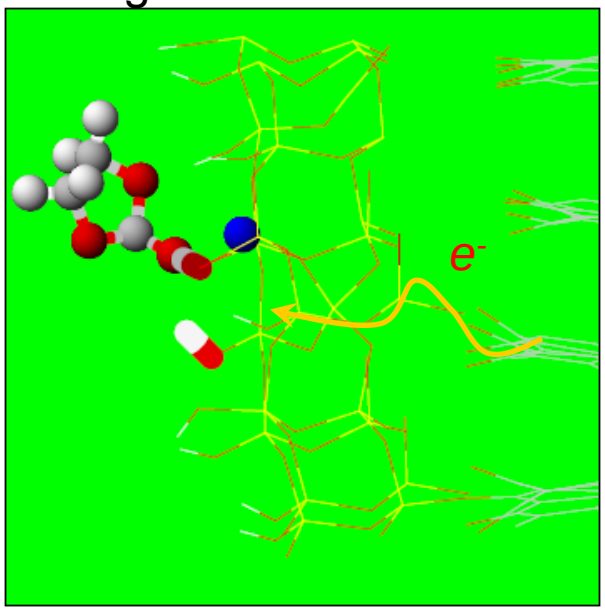


Li metal | Intact EC | Li metal

- two possible reaction pathways
- CO pathway is preferred due to kinetic effects



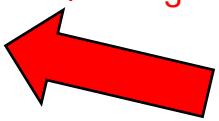
"aged" electrode



Intact EC | $LiAlO_2$ | Li_xC_6

7 or 10 A thick

- kinetics about 9 orders of magnitude slower
- for thicker oxide, CO_3^{2-} pathway is preferred



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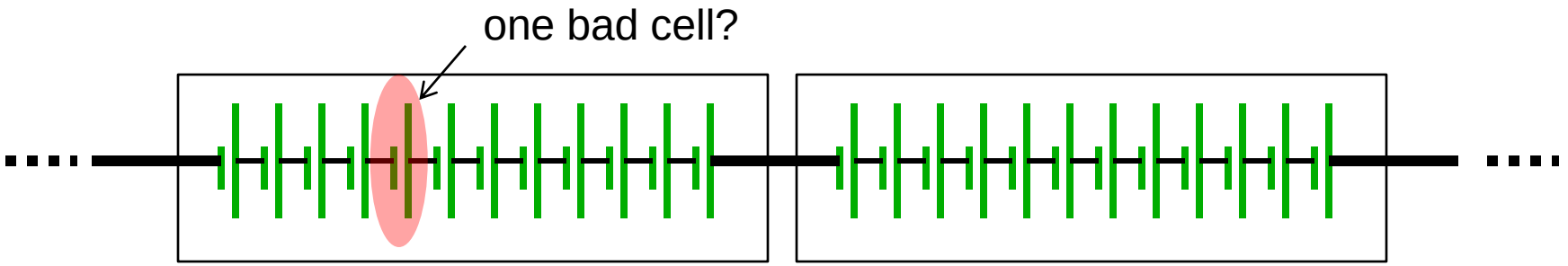
tories

OK, where do we go from here?

- can we move towards predicting battery (not just cell or even half-cell) degradation?
- what do we mean by degradation?
- what about loss in capacity of a vehicle battery pack?



Thermal-induced degradation is important.

- include variable temperature capability in *in situ* TEM
- correlate observed structure (i.e. SEI layer thickness) with electrochemical observables, such as EIS or entropy measurements
- include chemical spectroscopies that can probe chemical species in the electrolyte and electrode interface (SERS, second harmonic generation)
- other …

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Our CINT Users (Rice Univ., U. Penn., U. Pitt., U. MD, …)

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END