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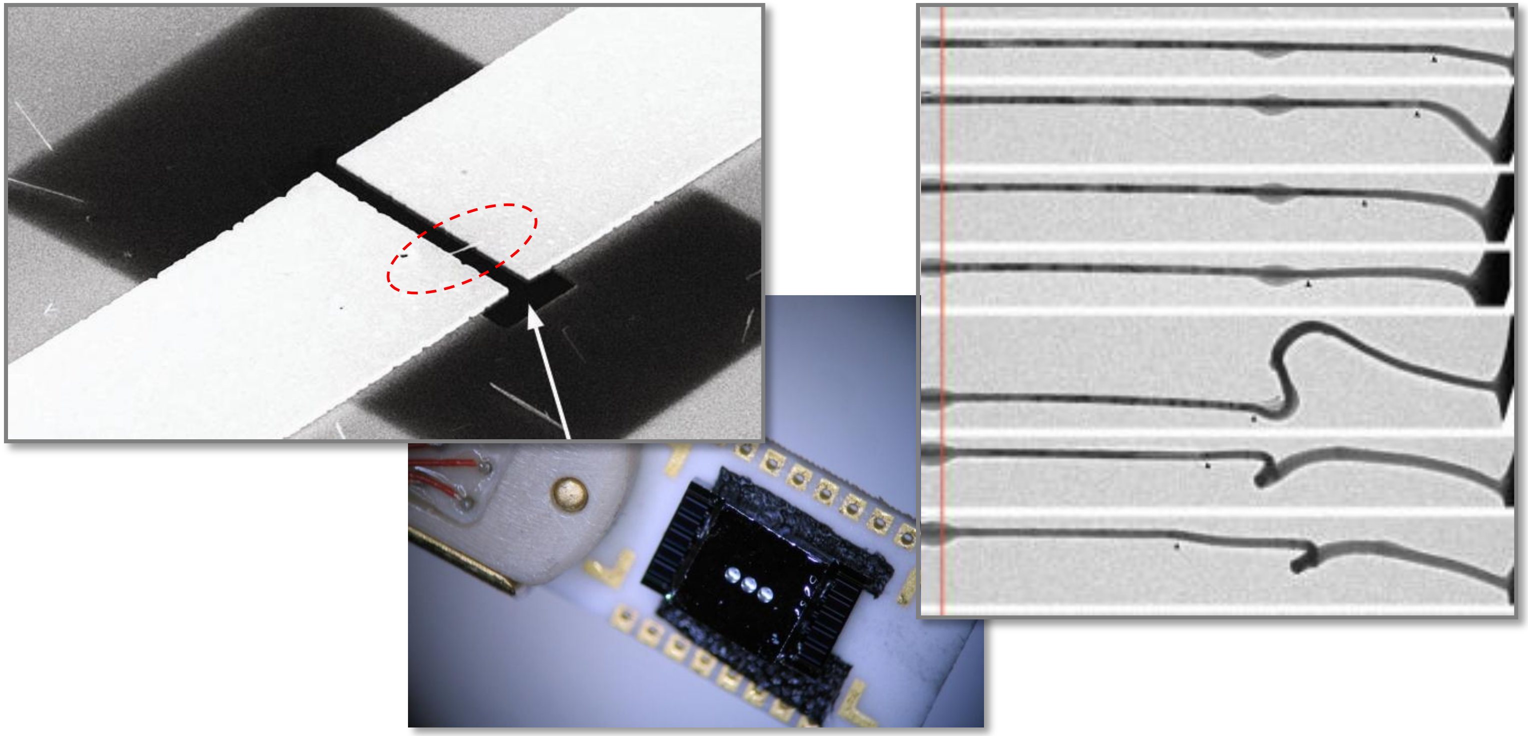
Electrochemistry at the Nanoscale



John Sullivan and Jian Yu Huang

Center for Integrated Nanotechnologies (CINT)

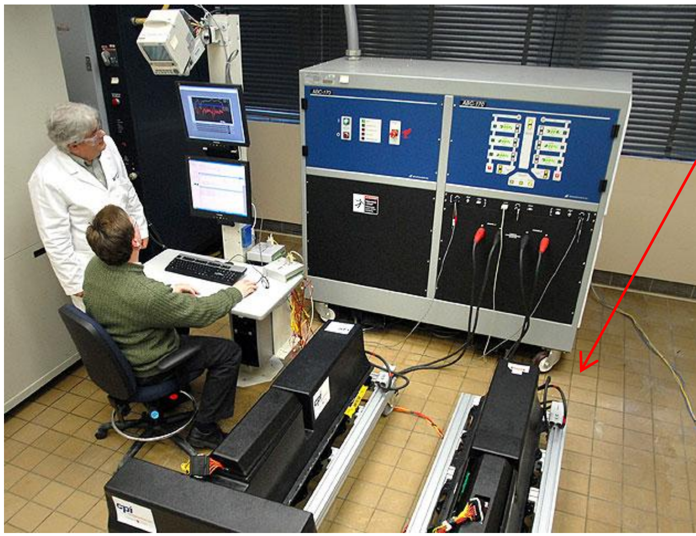
Sandia National Labs*, Albuquerque, NM

-- Defense Science Study Group, July 28, 2011 --

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

Batteries are BIG but the solution to the problems are small.

http://www.popularmechanics.com/cars/news/pictures/Chevy_Volt_Slideshow



- 16 KWh Li-ion battery pack for the Chevy Volt (175 kg)
- 90Wh/kg max capacity, 50 Wh/kg normal

- Comparison: WWII era electric torpedo battery pack ≈ 4 KWh, 550 kg (7.3 Wh/kg)

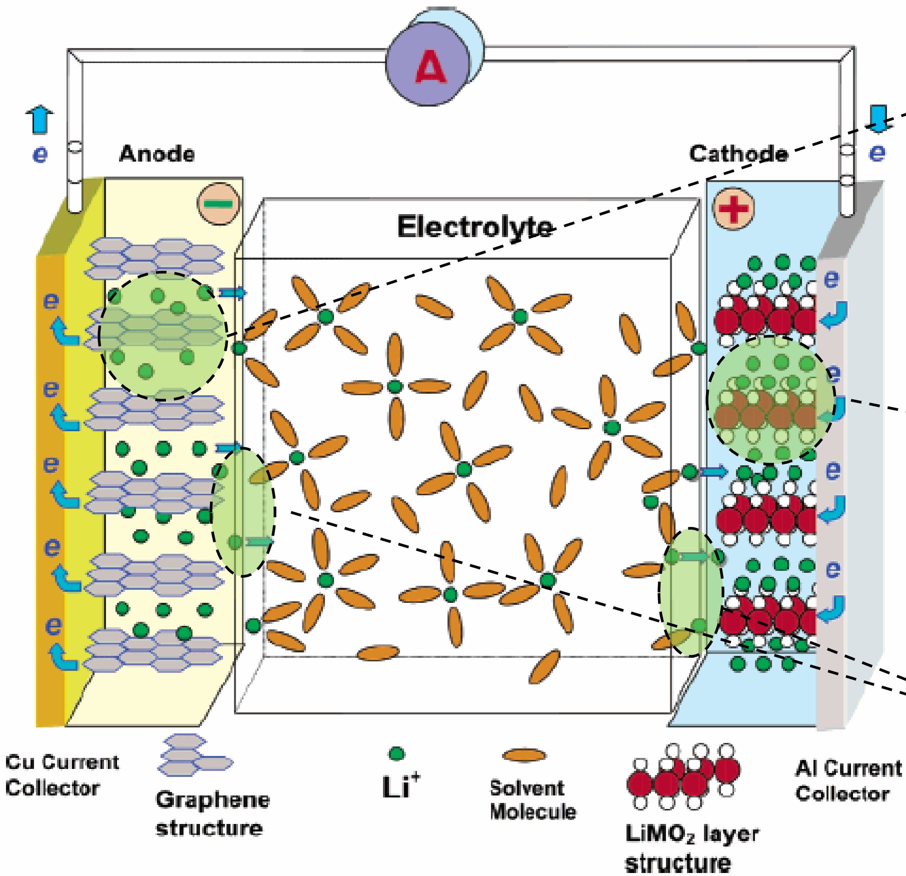
Lots of Energy!: Chevy Volt battery pack ≅ 9 kg of C4 explosive

How do we increase the capacity?

- New anode materials (e.g. Si) offer up to 10X Li storage capacity at the anode (compared to graphite)
- New cathodes (e.g. $LiNi_{0.5}Mn_{1.5}O_4$) offer ~ 25% higher cell voltage
- **Problem**: Materials have limited lifetime

Need a nanoscale focus

Scientific Challenges in Li-ion Batteries



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

Anodes

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

Cathodes

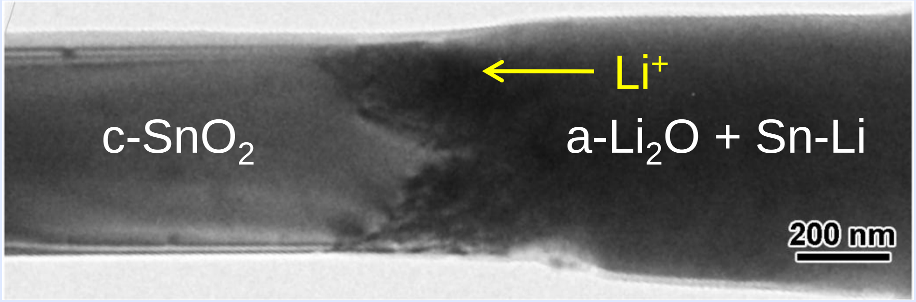
- kinetics of Li ion transport
- electrical transport

Electrolyte interfaces

- solid electrolyte interphase (SEI) formation
- SEI stability

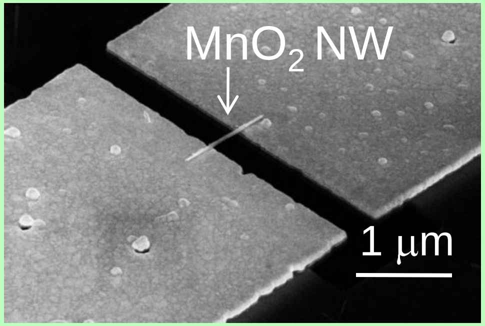
Nanoscale Electrochemistry at CINT: Three Approaches

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



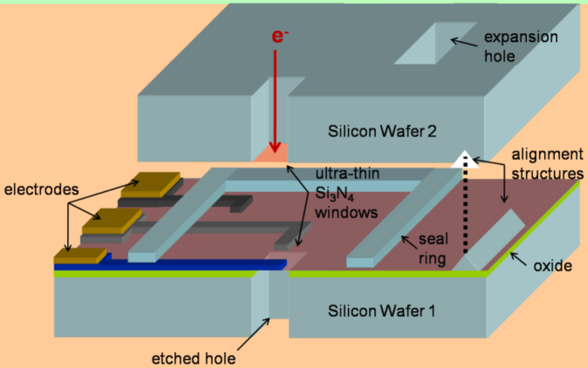
Huang, *et al.*, Science (2010).

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



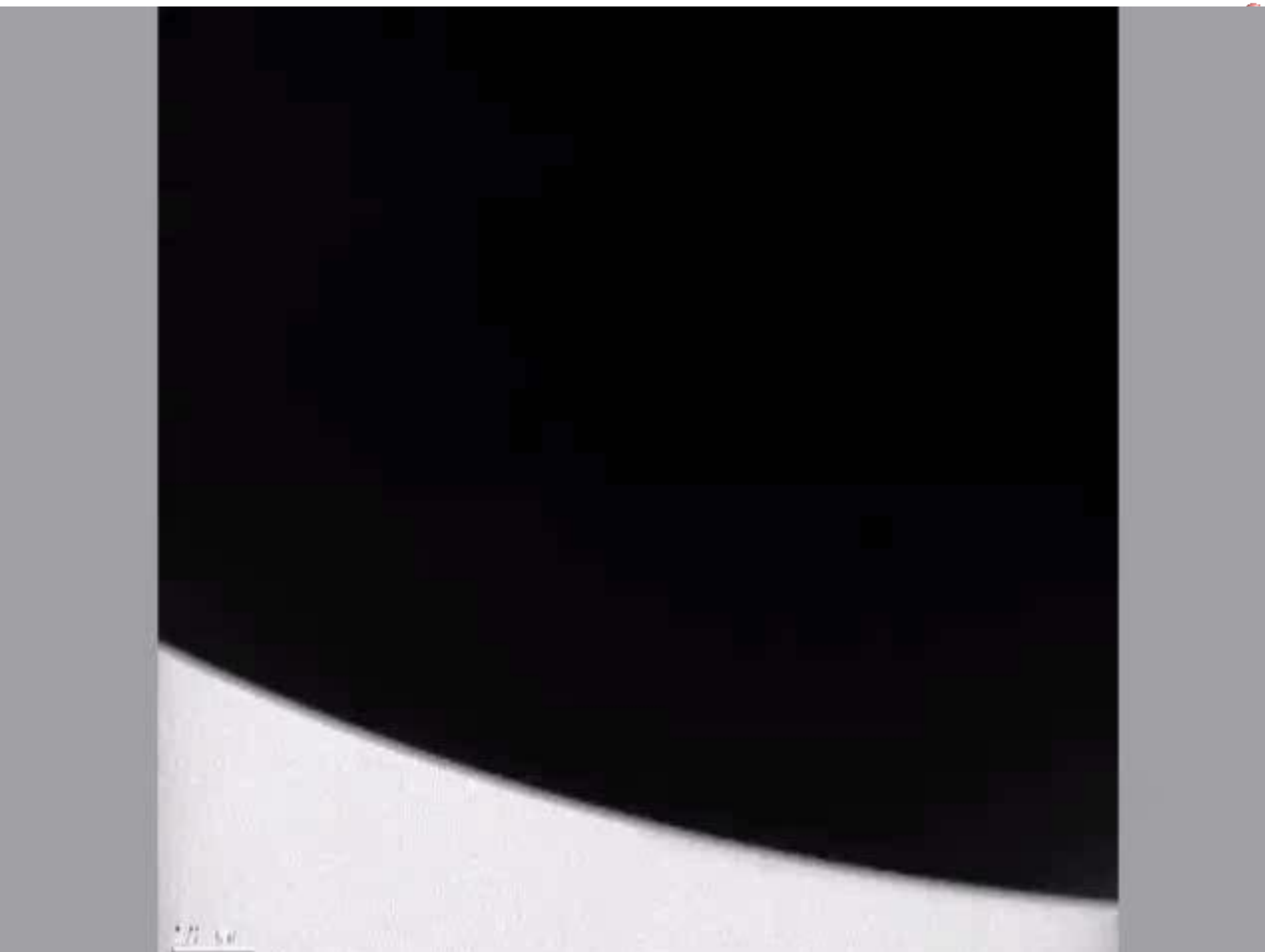
Subramanian, *et al.*, *in submission to NanoLett* (2011).

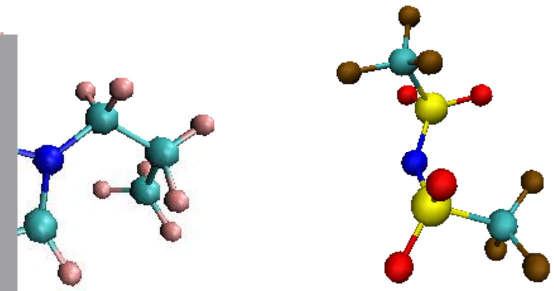
3. Electrode/electrolyte interface studies
   - SEI formation (composition and morphology)
   - SEI evolution, aging, and stability during cycling



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

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





MPI

TFSI

yl-3-propylimidazolium
(DMPI)

(trifluoromethylsulfonyl)imide
(TFSI) + Li-TFSI

also

ethylimidazolium

kafluorophosphate+ $LiPF_6$

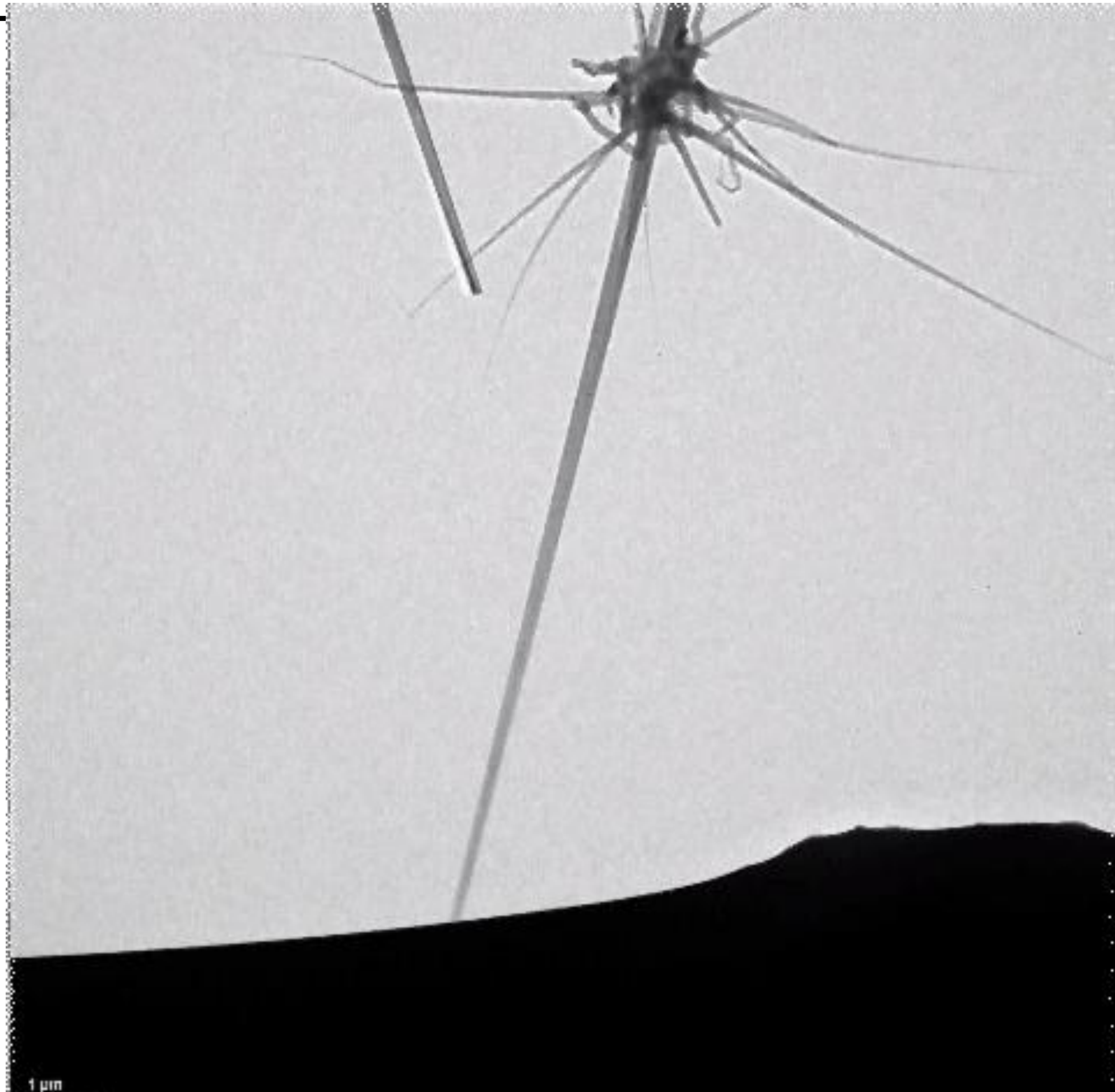
and

ethylpyrrolidinium-TFSI

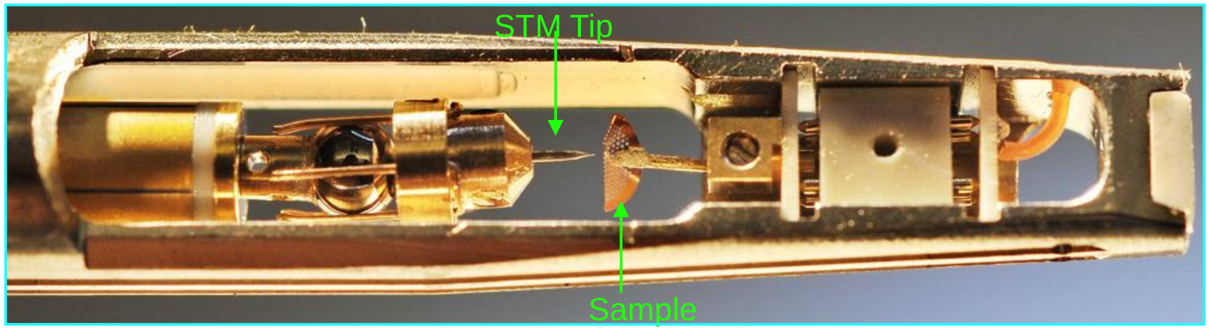
Li-TFSI

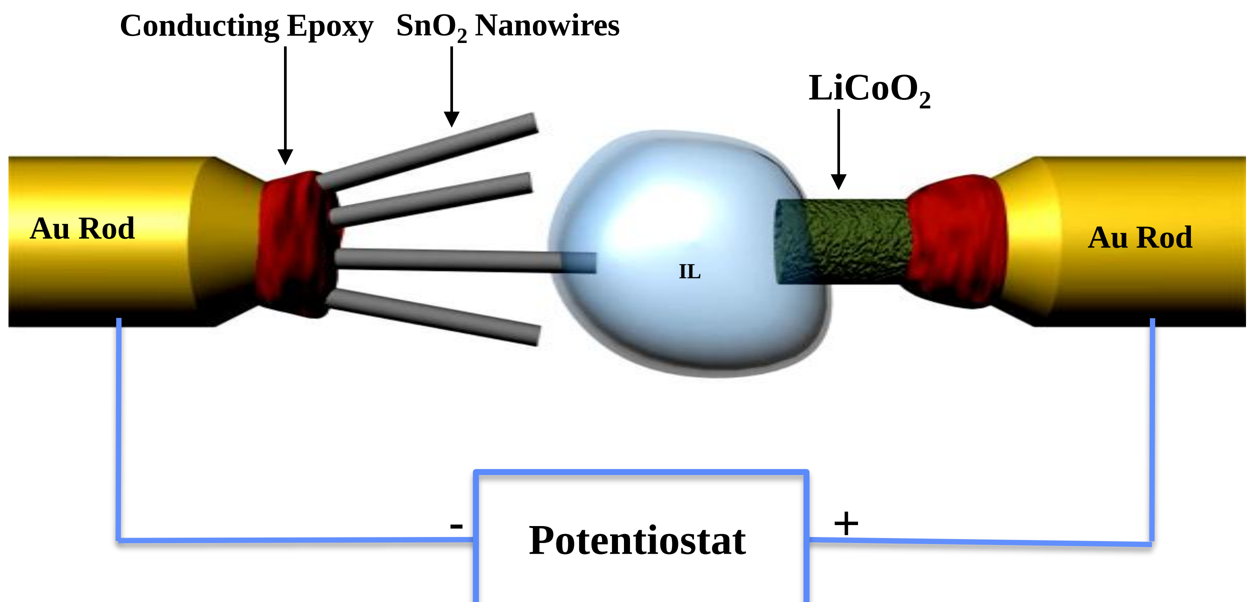
Ionic liquid spanning a hole

Capillary action of ionic liquids on Si in the TEM.



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



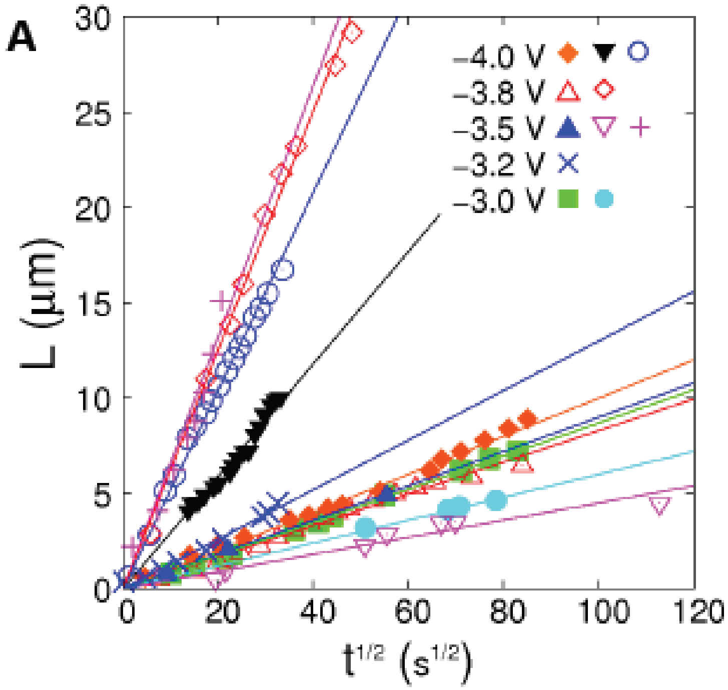


Jian Yu Huang, *et al.*, “In situ observation of the electrochemical lithiation of a single SnO_2 nanowire electrode,” Science **330**, 1515 (2010).

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

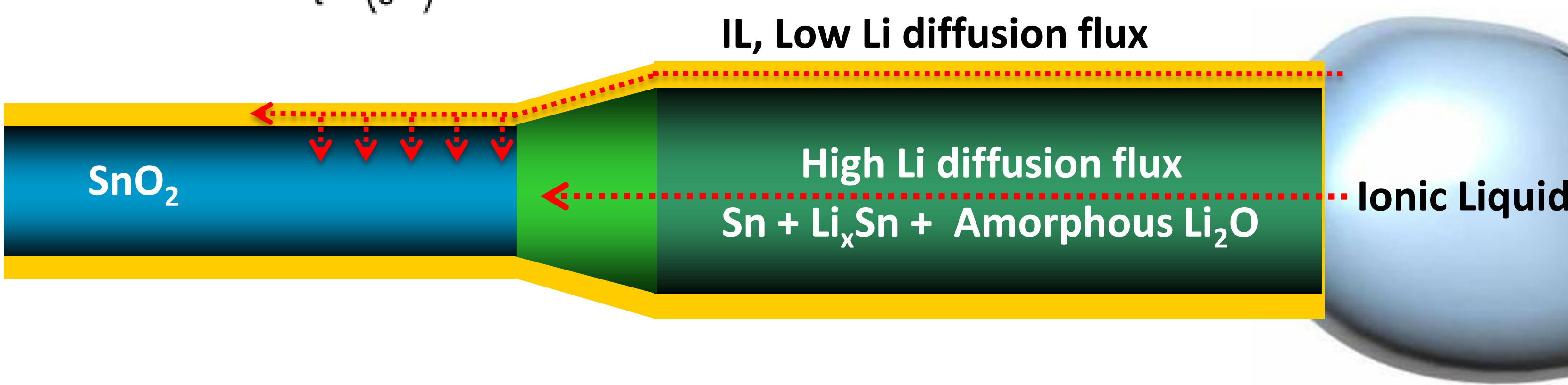
J.Y. Huang, *et al.*, 2010.

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.

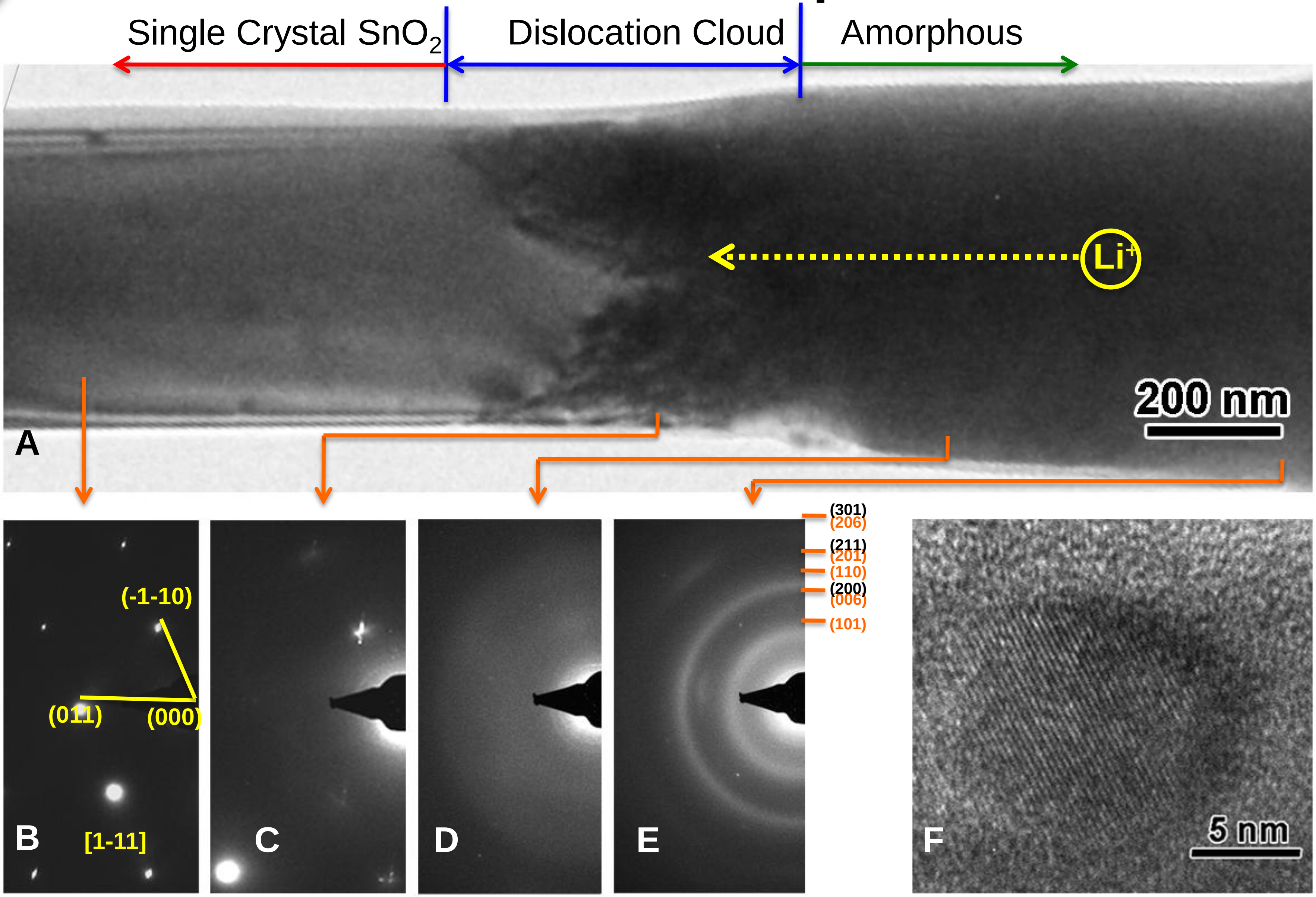


ies

Imaging the strain accommodation mechanism.

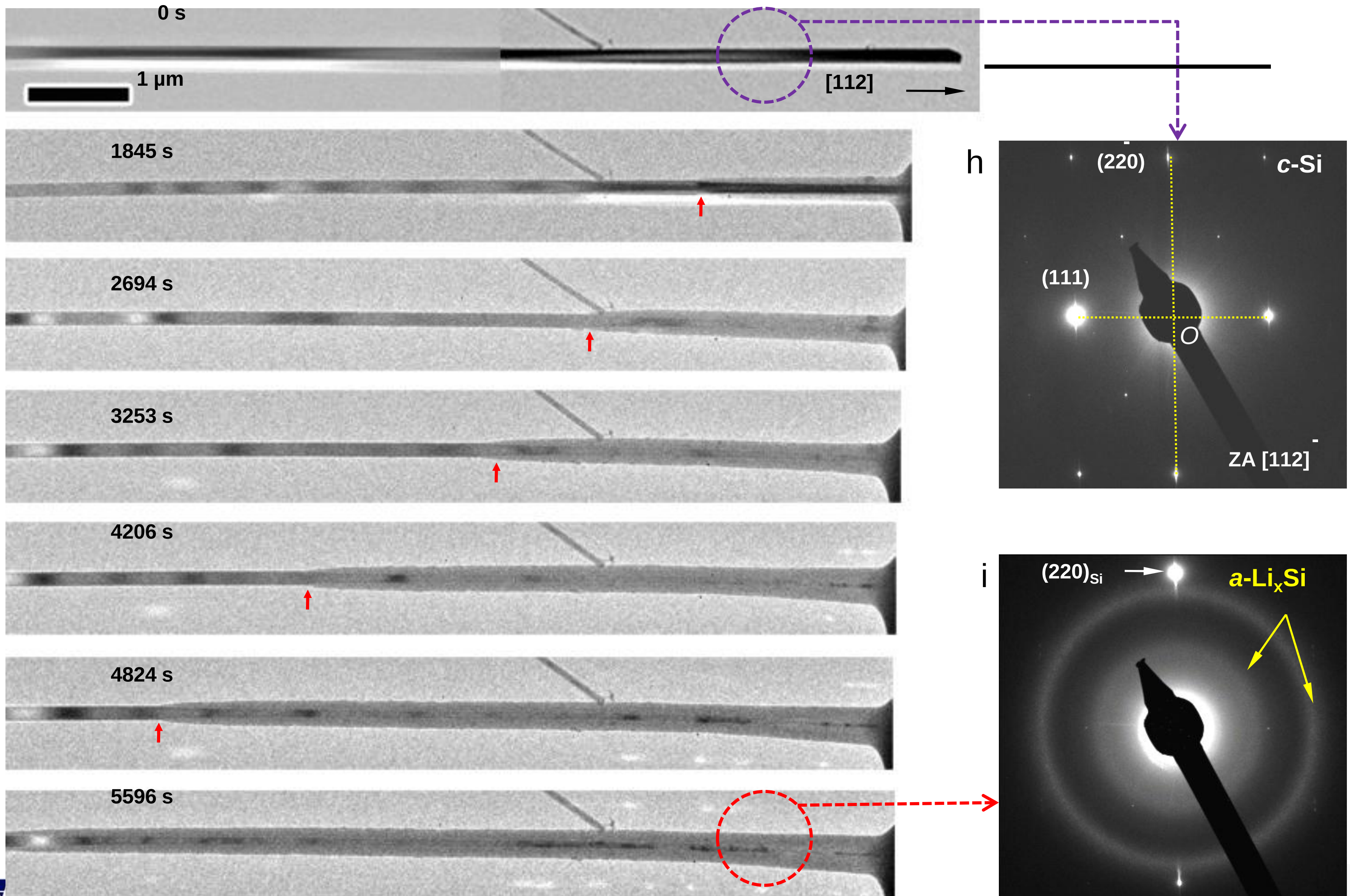
J.Y. Huang, *et al.*, 2010.

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



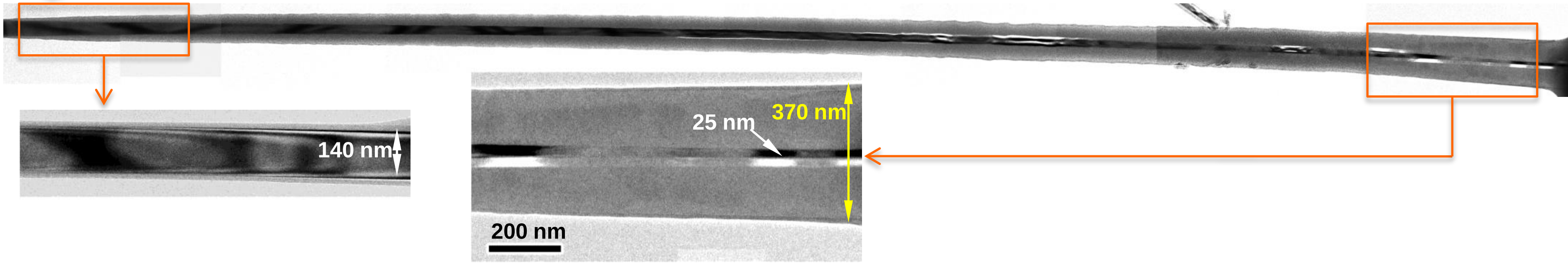
J.Y. Huang, *et al.*, 2010.

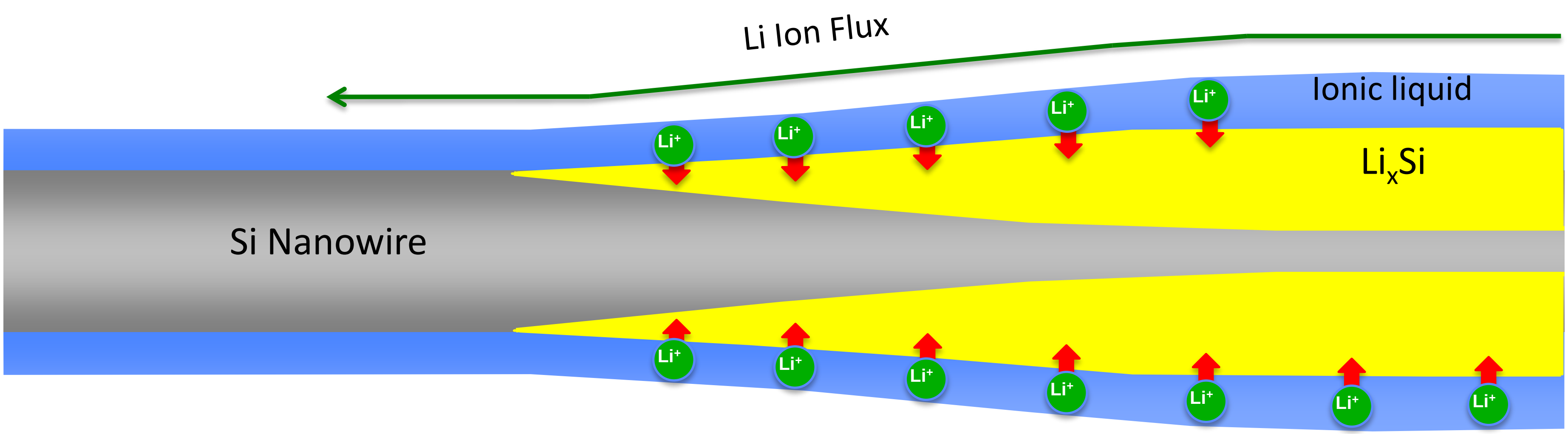
Do all nanowire anodes behave the same? The story with Si.



J.Y. Huang, *et al.*, Nano Lett., 2011 (DOI: 10.1021/nl200412p)

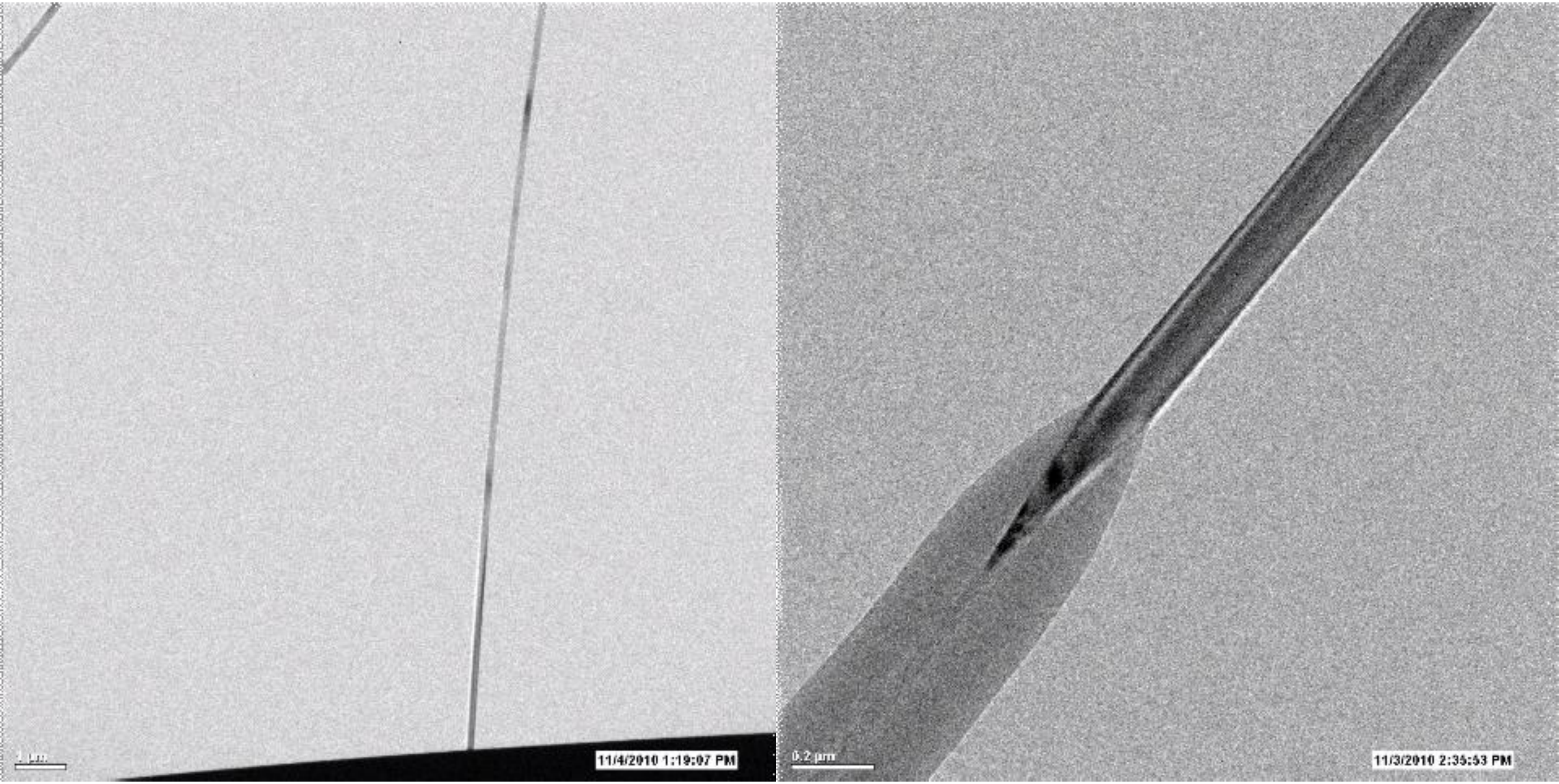
Lithiation of Si leads to a core-shell structure.





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

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



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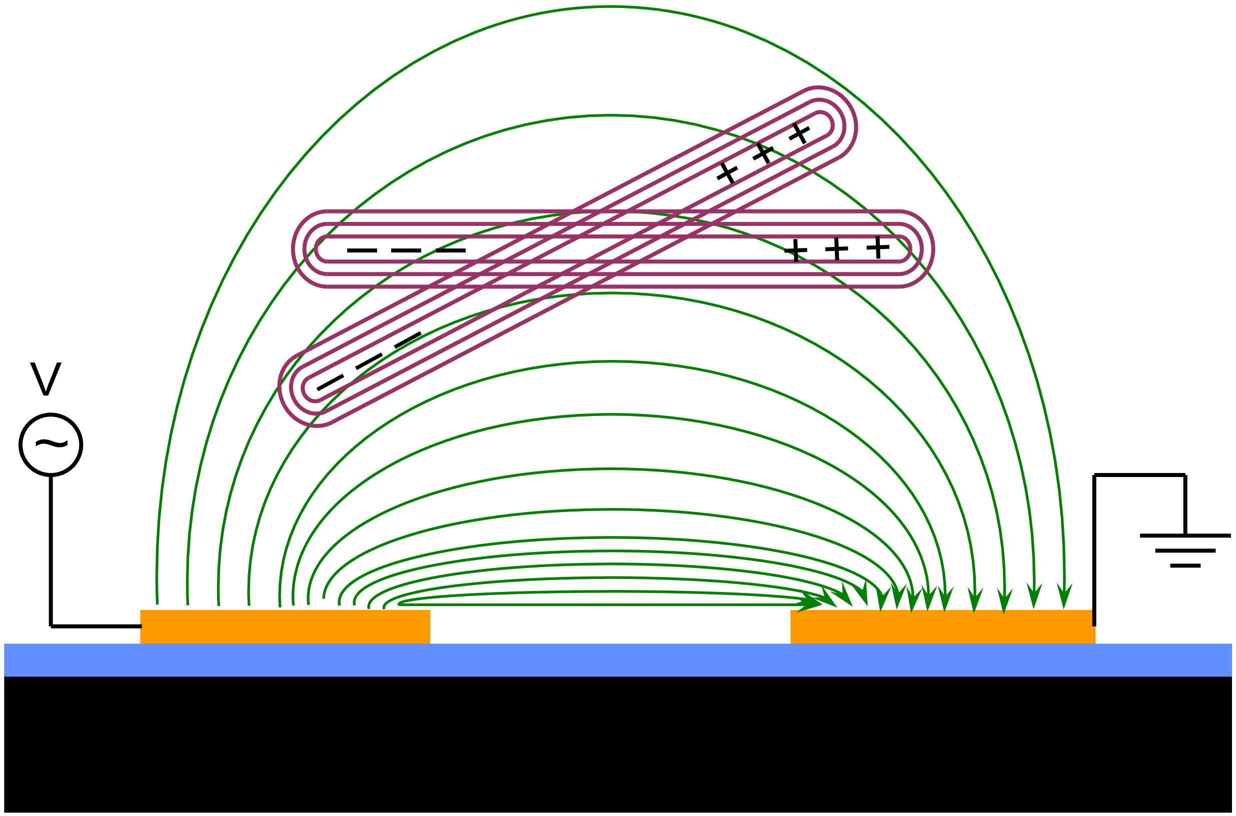
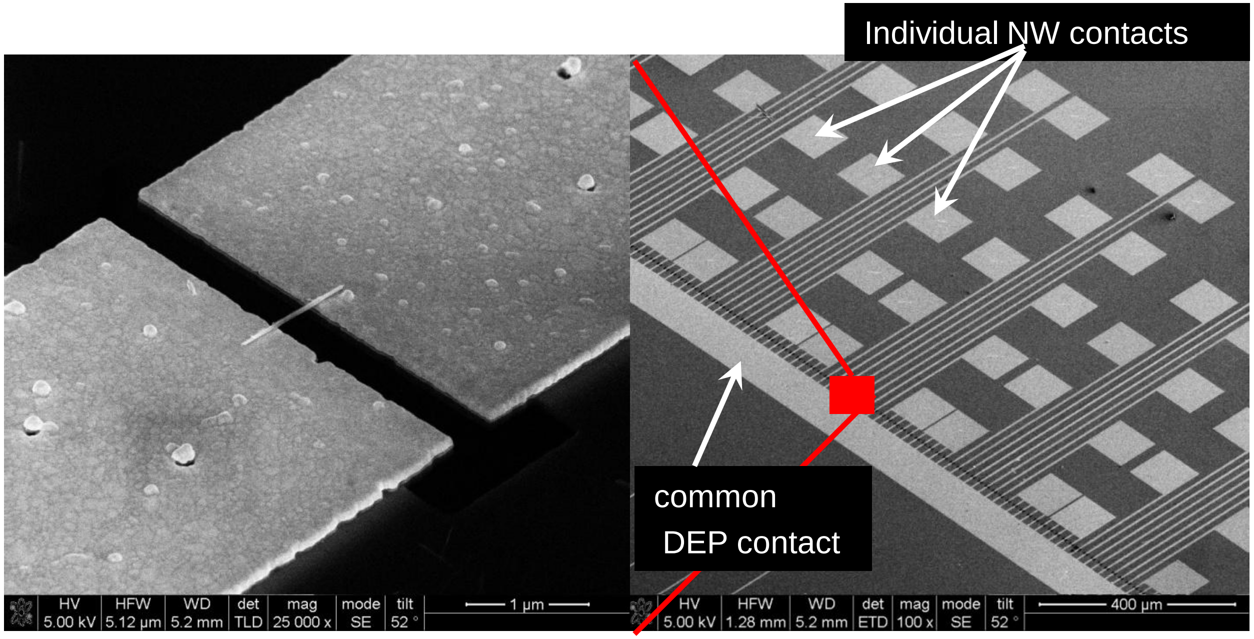
How do we easily assemble and measure "lots" of different battery materials?

Dielectrophoresis (DEP) assembly

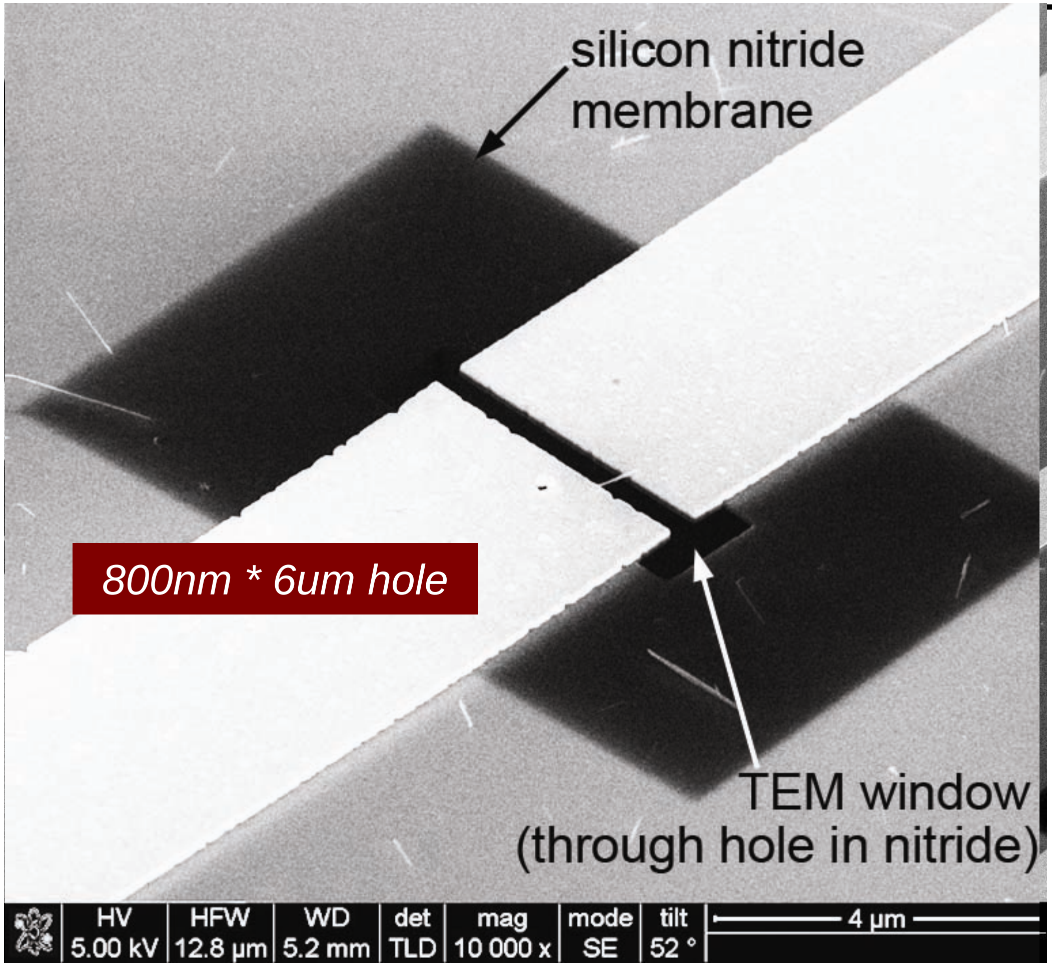


A chip-based platform for *in situ* TEM.



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

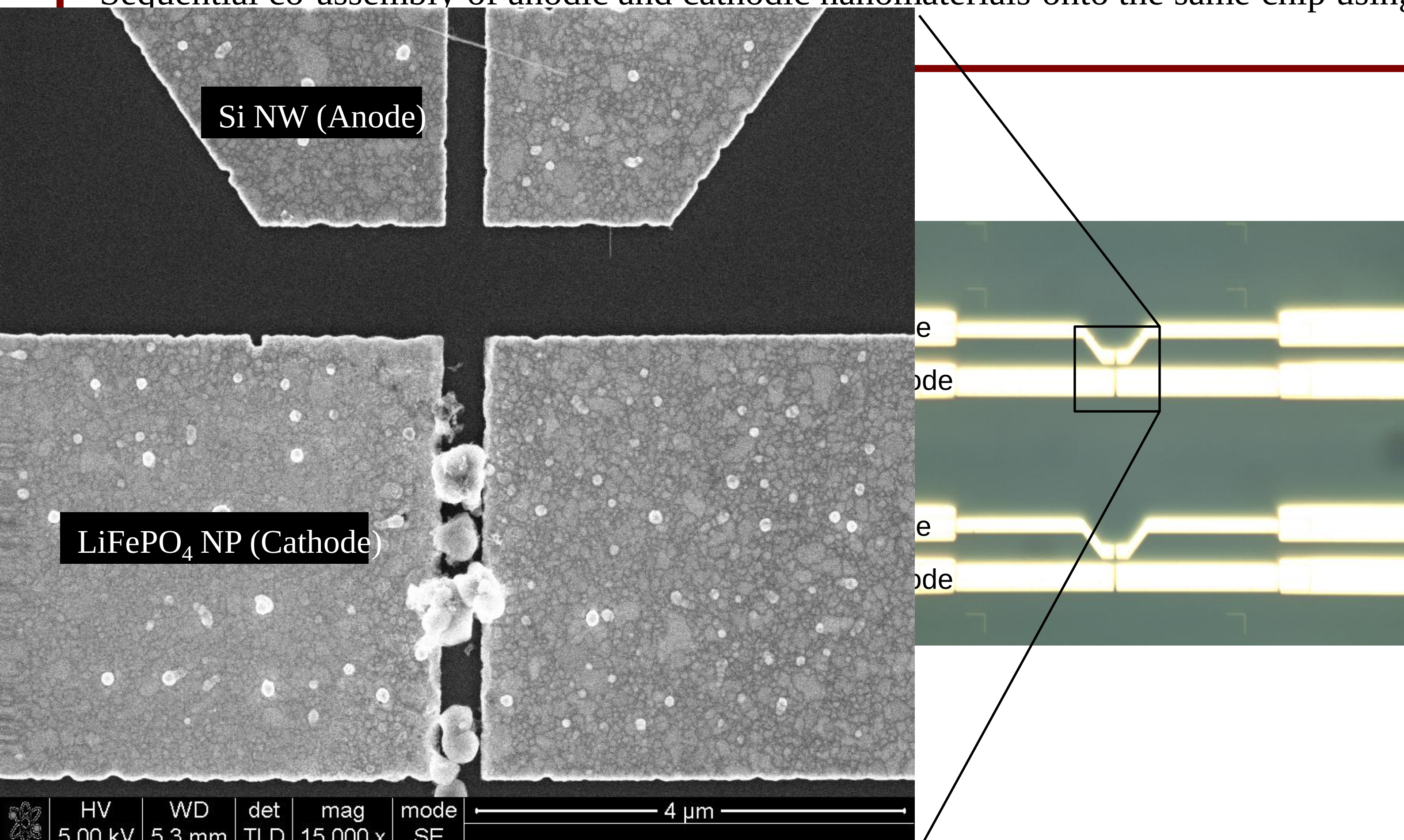


A. Subramanian, *et al.*, 2011.

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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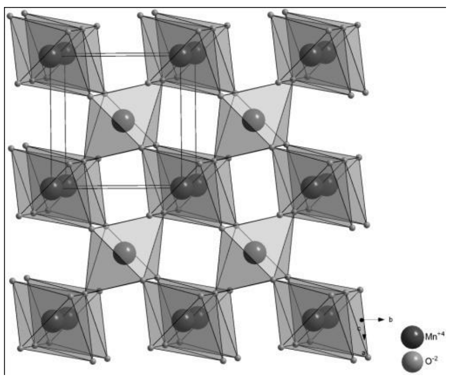
Test Case: β-MnO_2 NWs

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

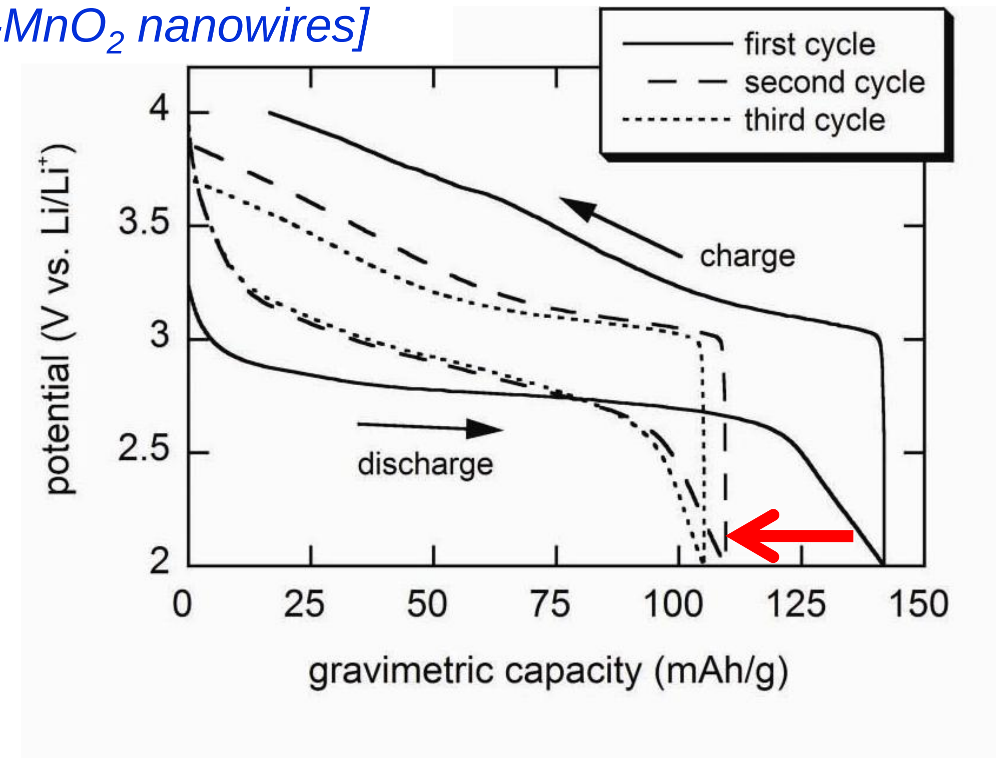
β-MnO_2

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

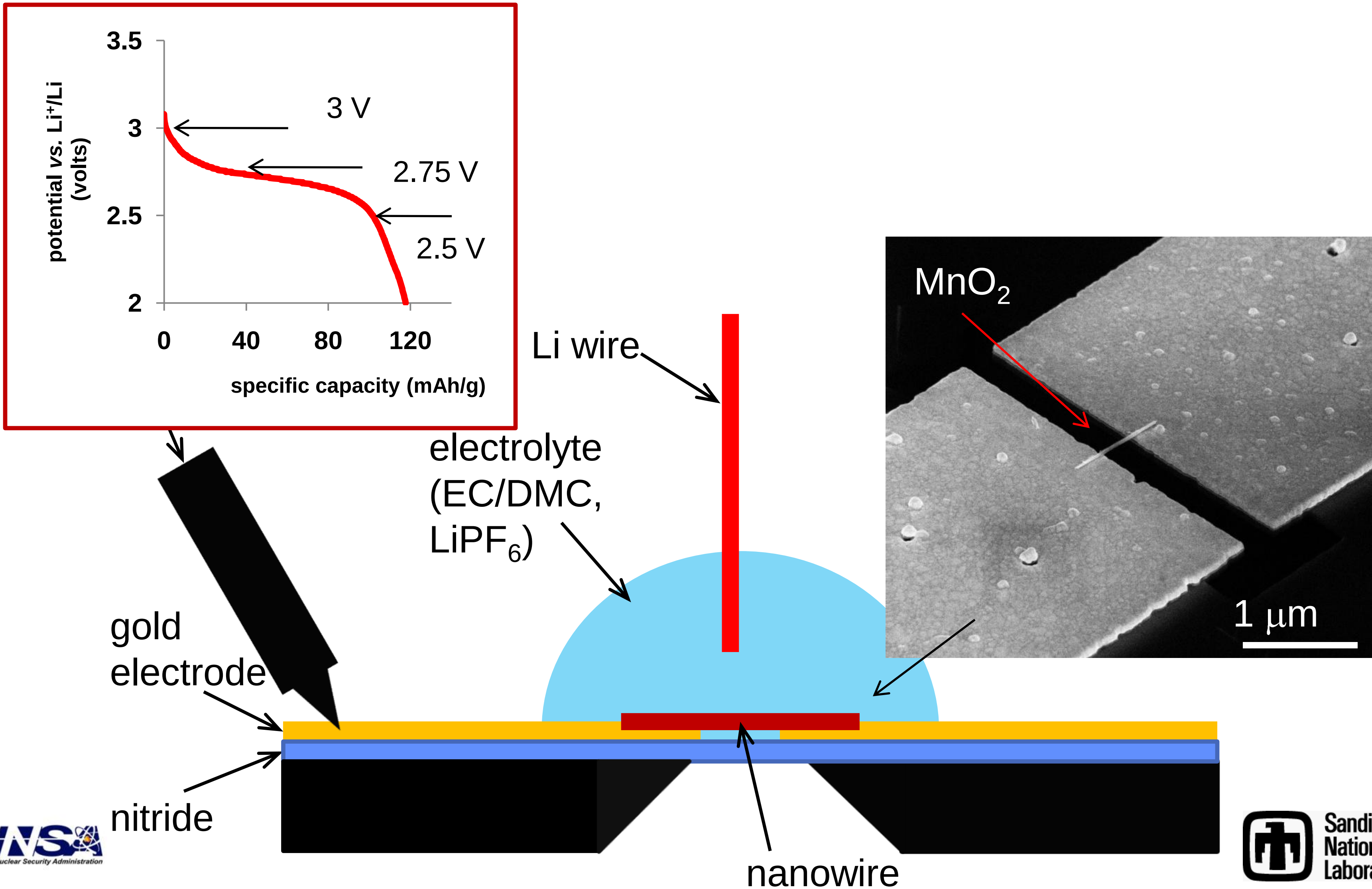


1 x 1 ion channels

[data from 260 μg of β-MnO_2 nanowires]

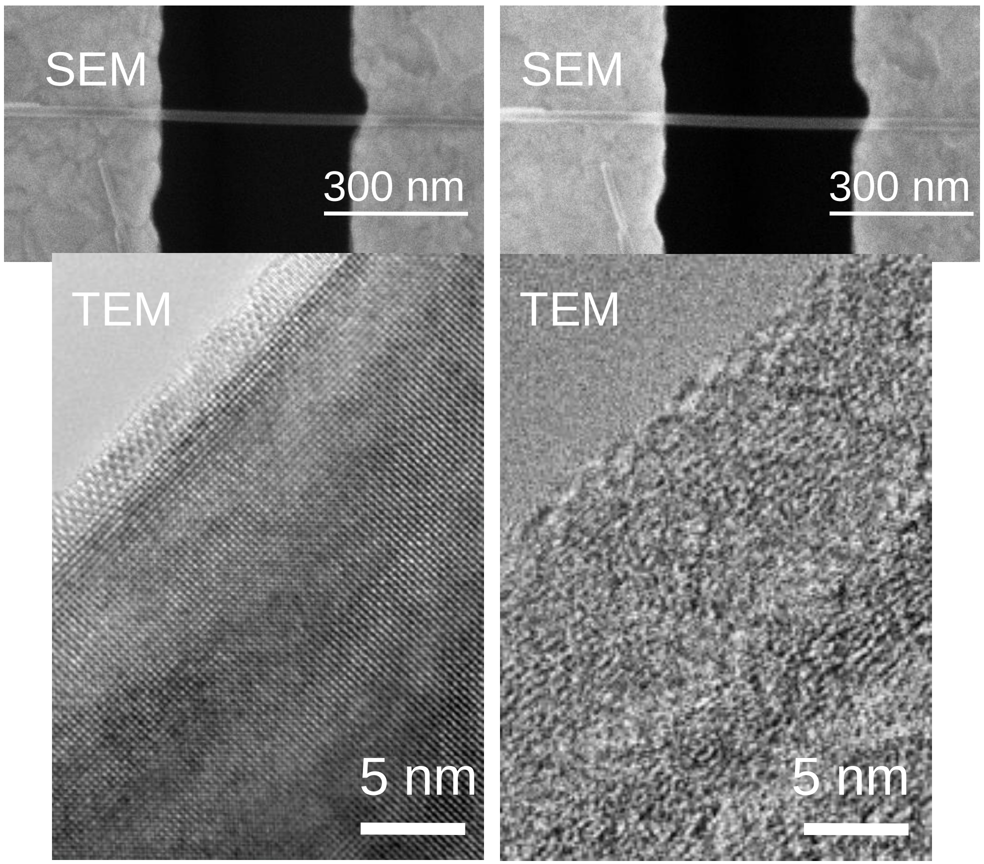


Ex-situ lithiation is performed, followed by characterization.

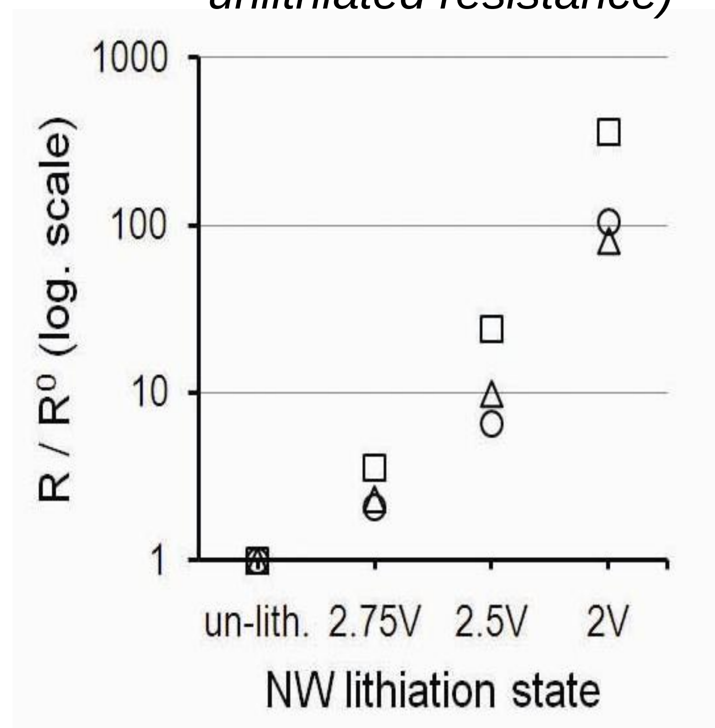


First cycle lithiation disorders the lattice and increases the resistivity → kinetic limitations.

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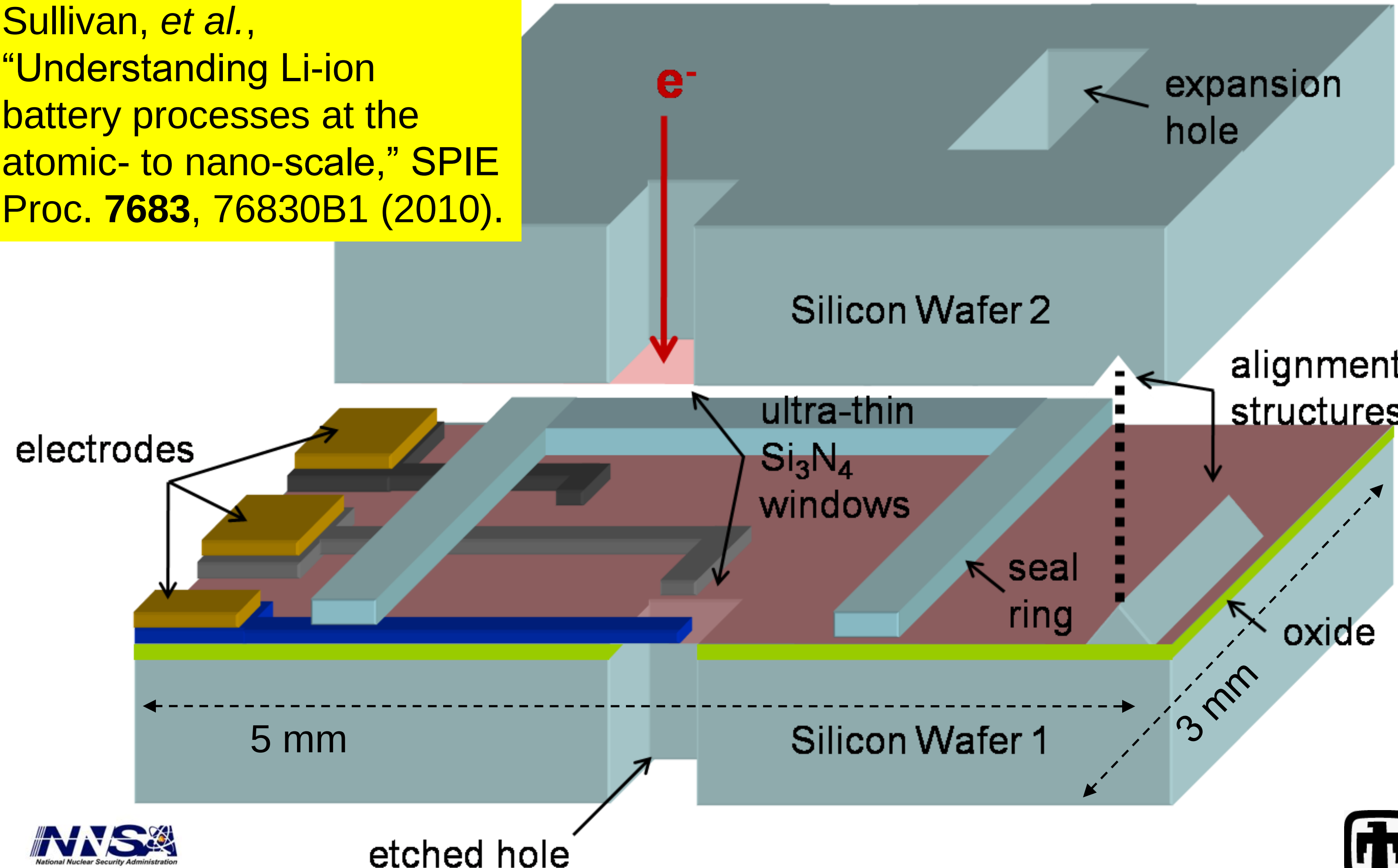
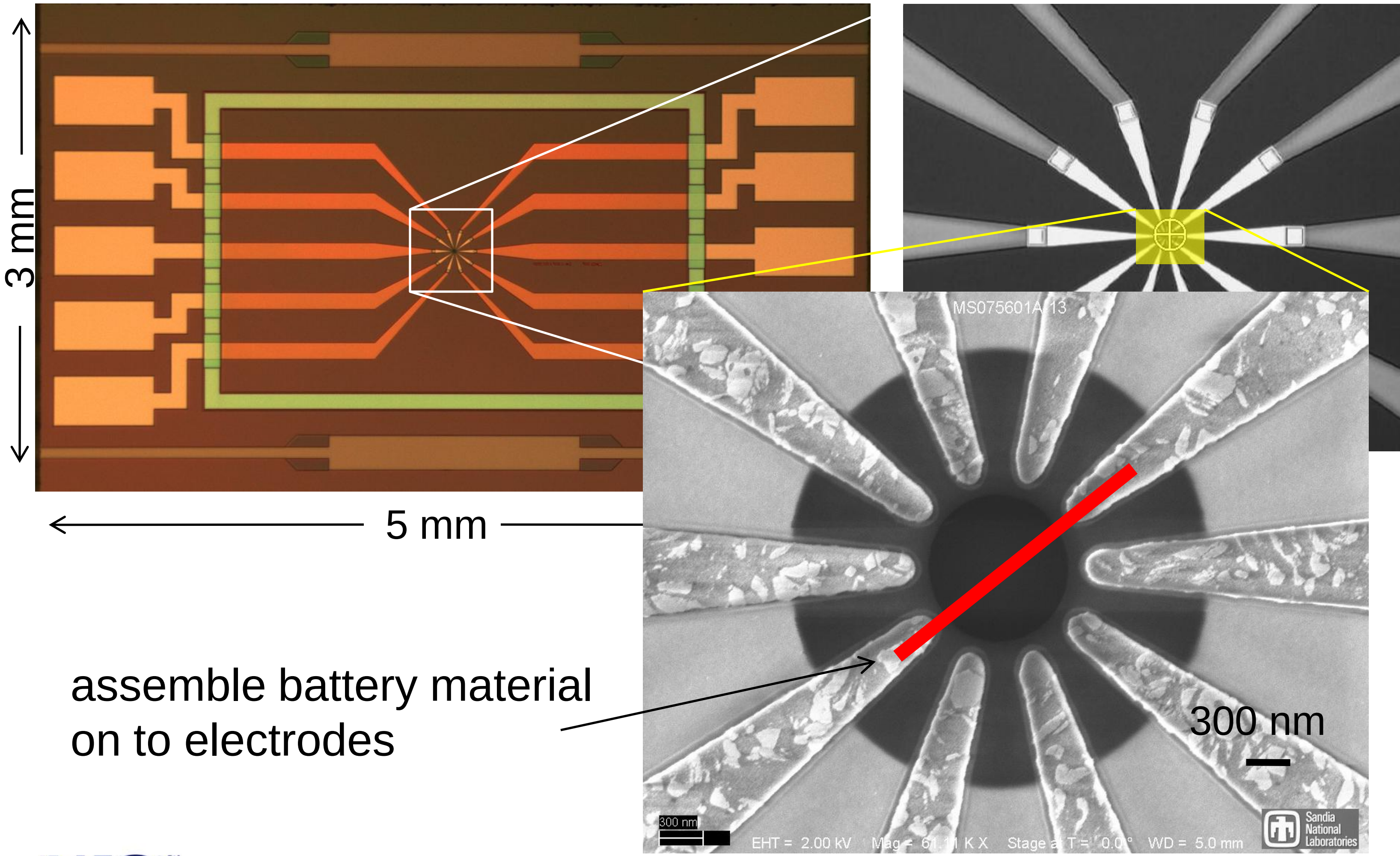
Our approach: develop *in-situ* electrochemical platforms for TEM.

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

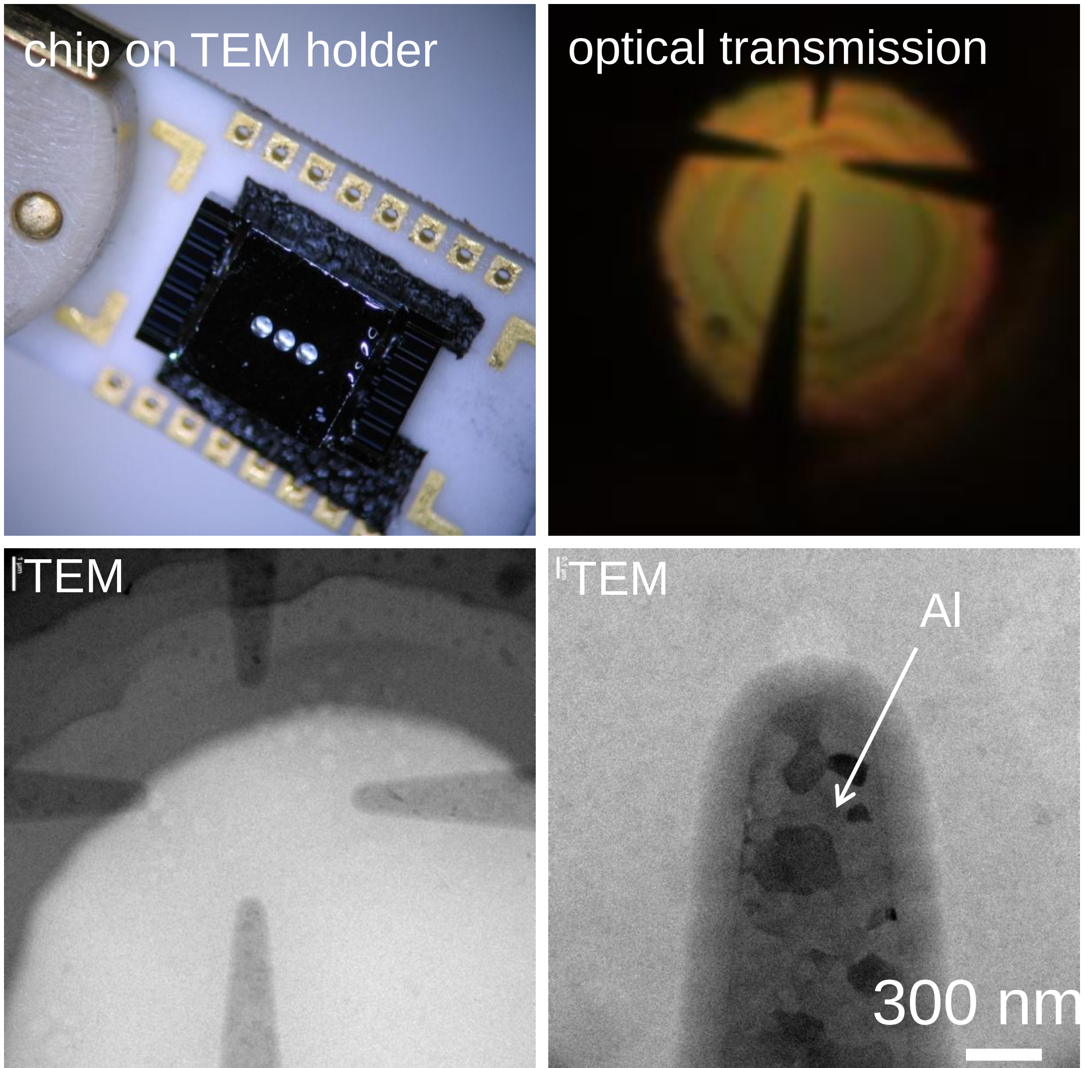


More than three electrodes are provided: enables field-driven assembly.



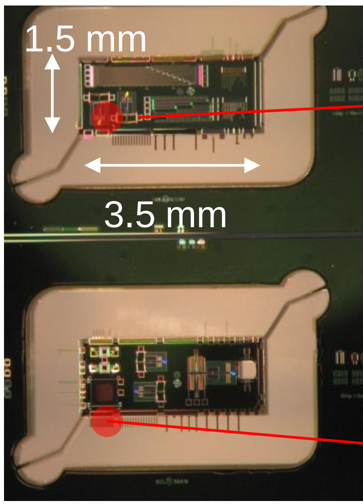
J. P. Sullivan, *et al.*, 2010.

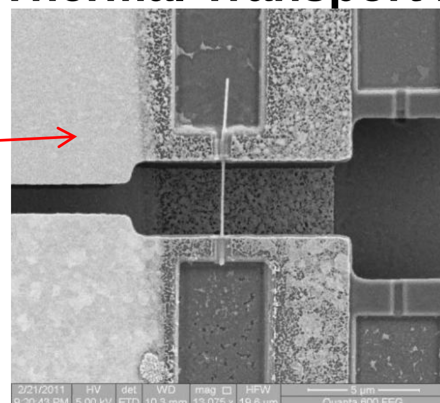
Preliminary testing in the TEM …

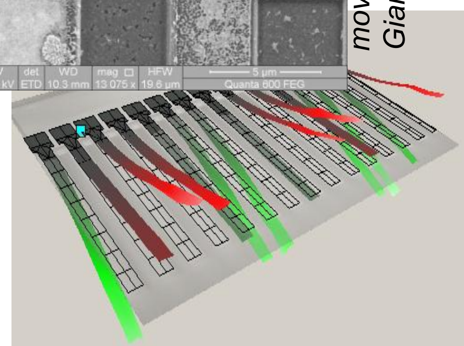


Discovery Platforms at CINT

Nanomechanics and Thermal Transport Discovery Platform



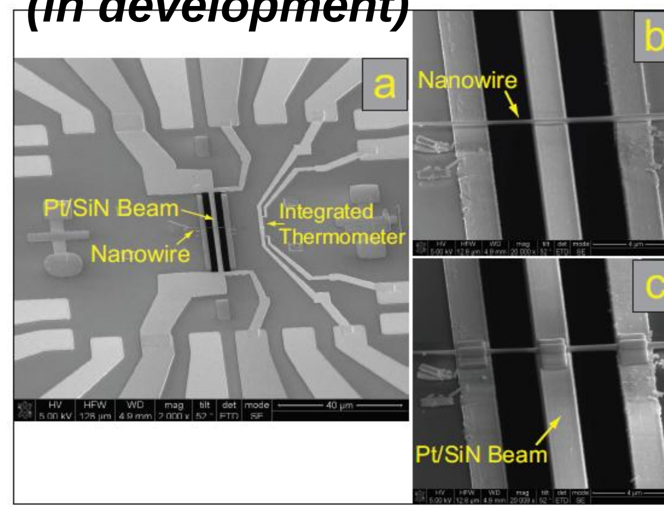




movie courtesy of Dan Gianola's group, U. Penn

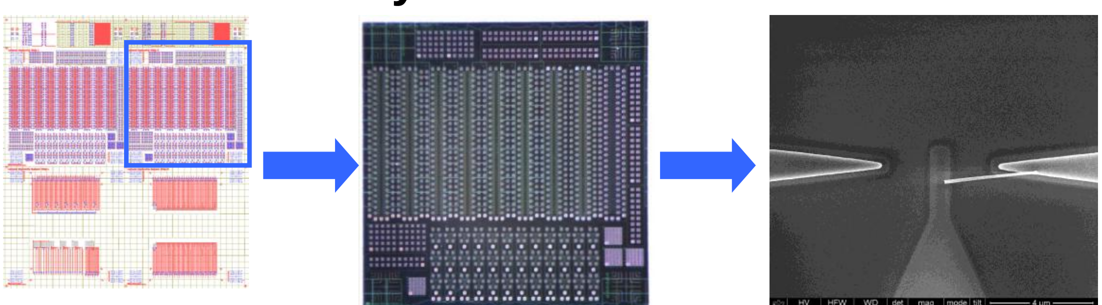
J. P. Sullivan, CINT

Thermal Discovery Platform *(in development)*



C. T. Harris, CINT

Nanowire Discovery Platform



S. T. Picraux, CINT

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ACKNOWLEDGMENTS

Sean Hearne (SNL, NM): technical discussions, management

Xiaohua Liu and Yang Liu (SNL, NM): TEM expts.

Arun Subramanian (SNL, NM): DEP platform and MnO_2 NW expts.

Mike Shaw (SNL, NM): Liquid-cell platform engineering and fab

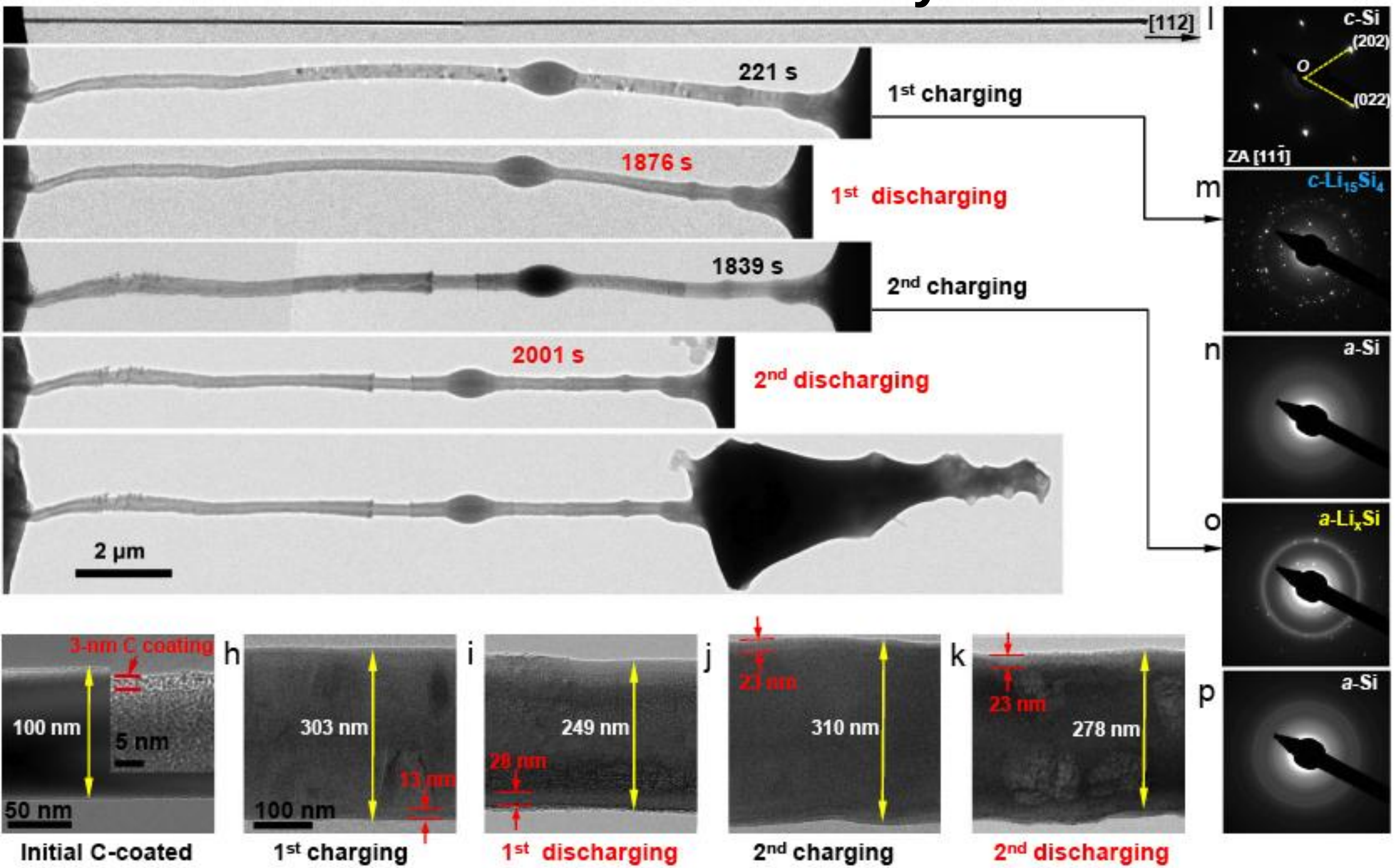
Nick Hudak (SNL, NM): Electrochemistry measurements

Kevin Leung (SNL, NM): *ab initio* calculations of electrode/electrolyte interfaces

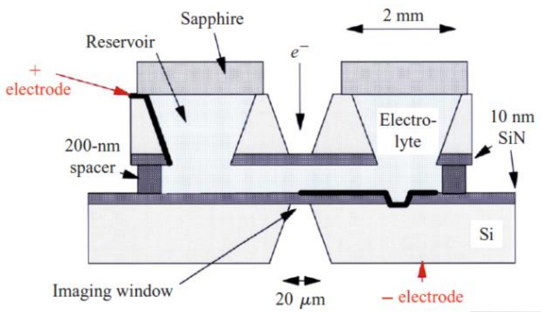
Kevin Zavadil, Rick Muller, Chris Orendorff, Ganesan Nagasubramanian, Kevin McCarty, Carl Hayden & … (SNL, NM) : battery discussions

Our CINT Users – Li Zhong, Li Qiang Zhang, Scott X. Mao, Jun Lou, S. Huang, Ting Zhu, Liang Qi, Akihiro Kushima, Ju Li, Jeong-Hyun Cho, S. T. Picraux, C.M. Wang, W. Xu (U. Pitt, Rice, GA Tech, U. Penn, LANL, PNNL)*:* TEM, nanomaterials, and modeling

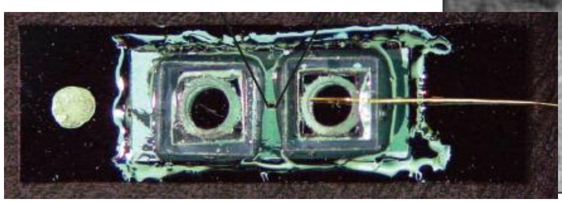
Changing the reaction kinetics by changing electrical conductivity: C-coated Si.

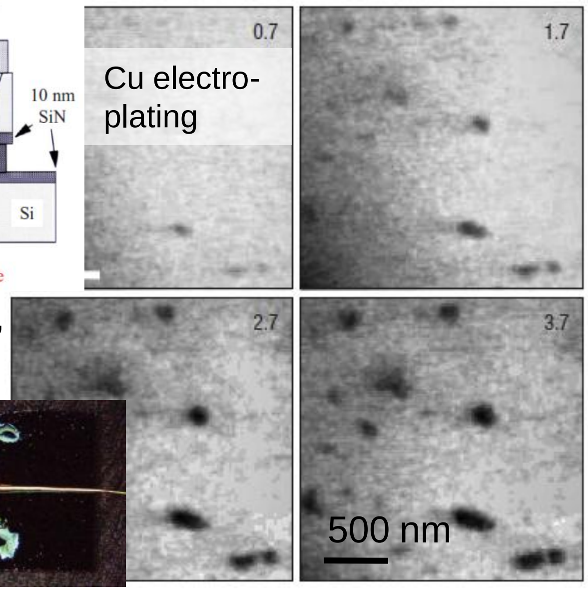


There has been limited *in-situ* liquid-cell TEM work.

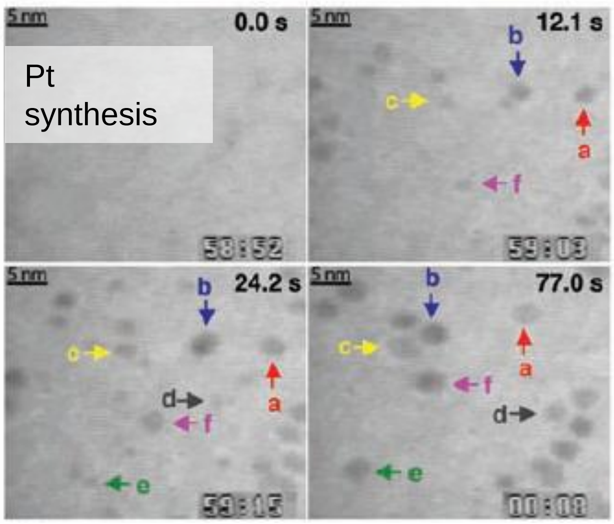


Ross, *IBM J. Res. Develop.* **44**, 489 (2000).

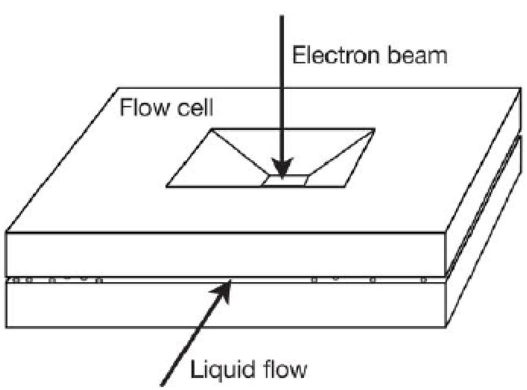


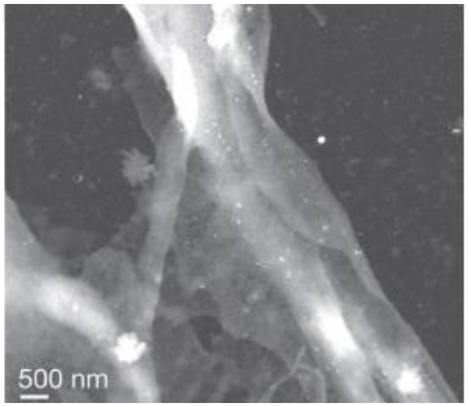


Williamson et al., *Nature Mater.* **2**, 532 (2003).



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).

NNSA National Nuclear Security Administration
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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