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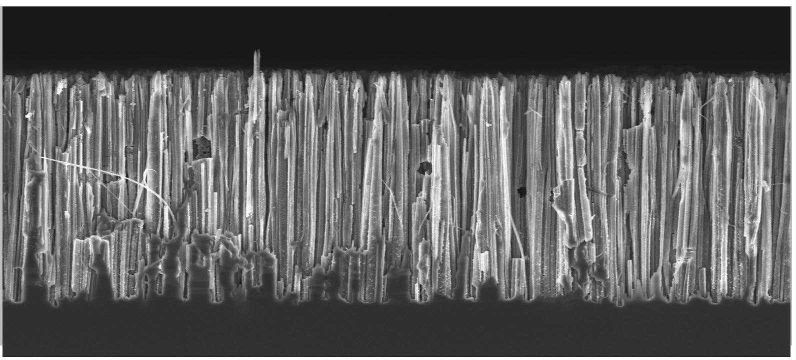
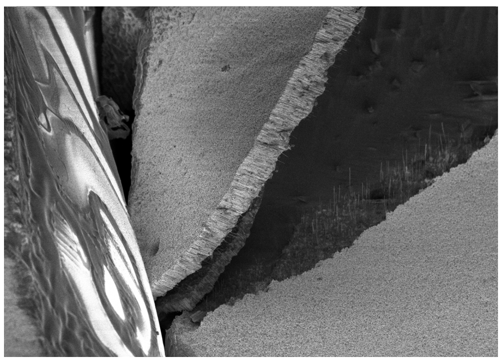
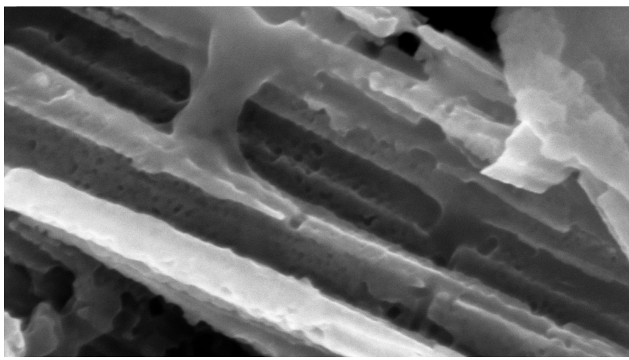

Chemically Etched Silicon Nanowires As Anodes for Lithium-Ion Batteries

Hannah Height

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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Overview

- Motivation and background
- Silicon nanowire manufacturing methods
- Experimental setup and procedure
- Results and SEM imaging
- Conclusions
- Future work

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Motivation

- Aerospace applications
  - Lighter battery packs

- Electric vehicles
  - Longer driving distances

- Personal Electronics

http://www.dailytech.com/Boeing+787+Unveiled+in+the+Virtual+World/article5278.htm
Matulka, R., Electric Cars: Increasingly More Available and More Appealing to the Public. *Mother Earth News*. Online. 2012. Accessed April 11, 2016.
http://www.digitaldocrepair.com/wp-content/uploads/2013/12/digital-devices.png

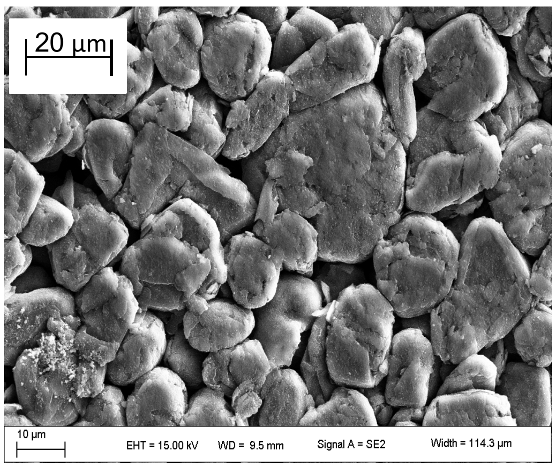
Current Technology

- Current technology

  Graphite

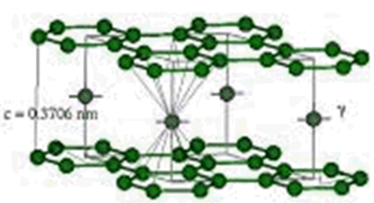
  $LiC_6 \rightarrow 372$ mAh/g

  Expansion: ~10%



Courtesy of: Chelsea Snyder

- Carbon
- Lithium



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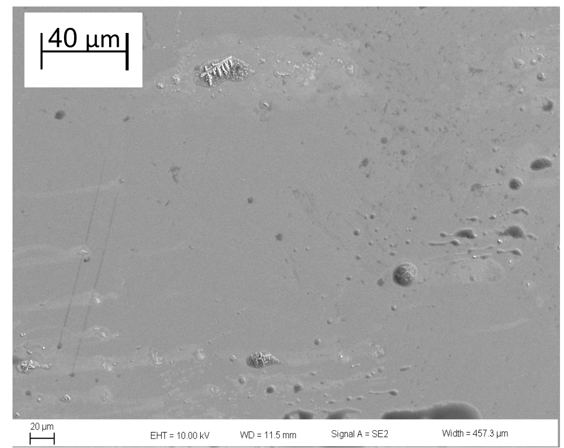
- Future technology

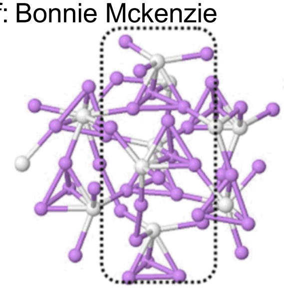
  Silicon

  $Li_{15}Si_4 \rightarrow 3{,}578$ mAh/g

  Expansion: ~270%



Courtesy of: Bonnie Mckenzie



- Silicon
- Lithium

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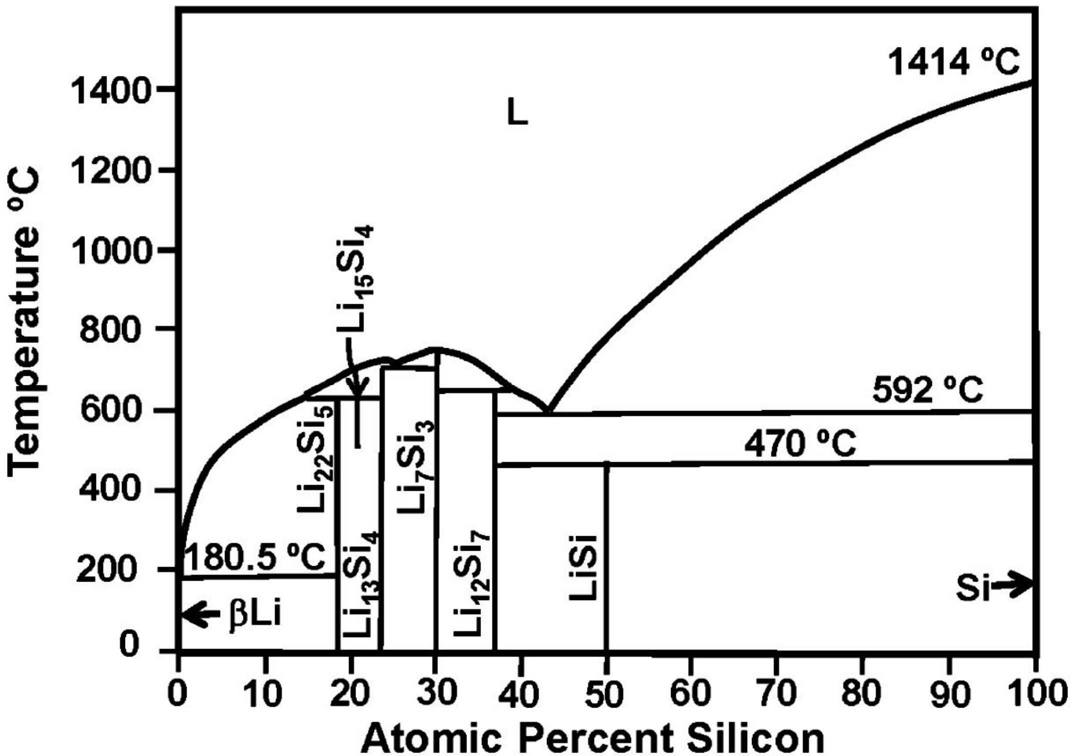
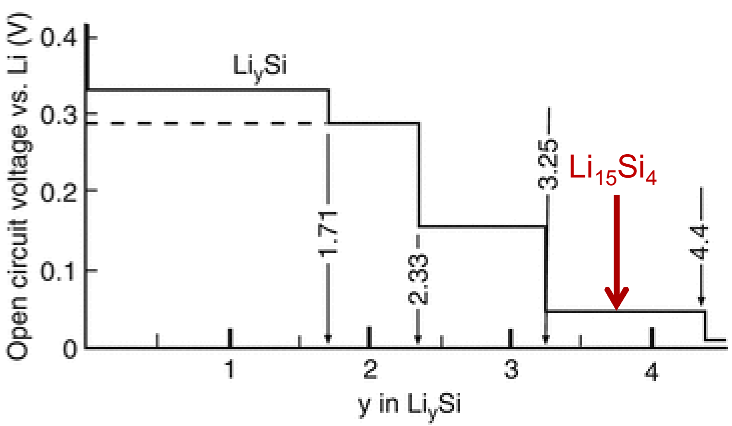
Hatchard, T. D.; Dahn, J. R. *J. Electrochem. Soc.* **2004**, *151*, A838.

Lithiation of Silicon



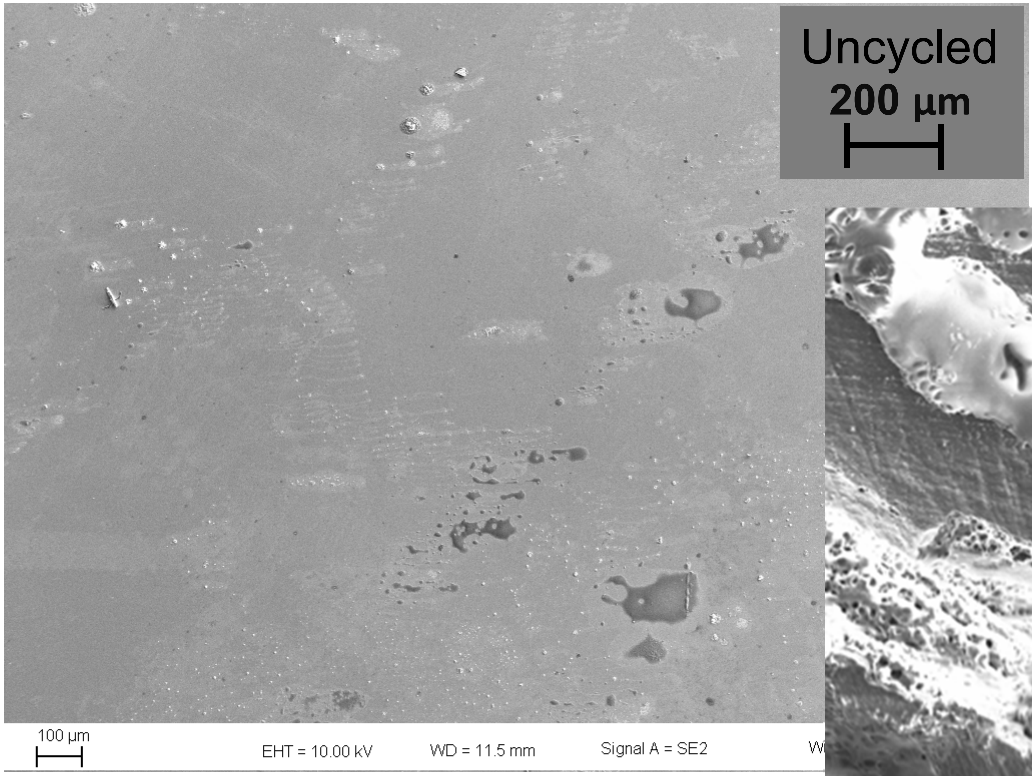
Phase	Capacity (mAh/g)
LiSi	954
Li_7Si_3	2226
$Li_{12}Si_7$	1636
$Li_{13}Si_4$	3101
$Li_{15}Si_4$	3578
$Li_{22}Si_5$	4198

- $Li_{15}Si_4$ forms at room temperature and low voltages
- Crystallization from amorphous phase causes fracturing

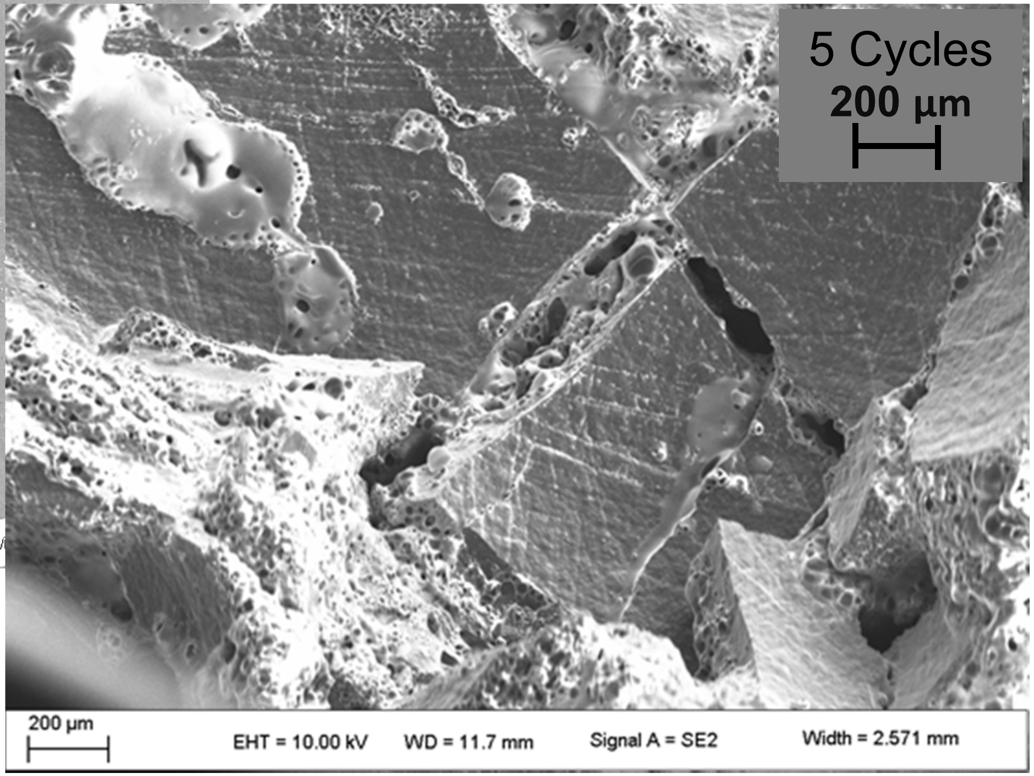


Gu, M.; Wang, Z. G.; Connell, J. G.; Perea, D. E.; Lauhon, L. J.; Gao, F.; Wang, C. M. *ACS Nano* **2013**, *7*, 6303.
Beattie, S. D.; Larcher, D.; Morcrette, M.; Simon, B.; Tarascon, J. M. *J. Electrochem. Soc.* **2008**, *155*, A158.
Hatchard, T. D.; Dahn, J. R. *J. Electrochem. Soc.* **2004**, *151*, A838.
http://link.springer.com/referenceworkentry/10.1007%2F978-1-4419-0851-3_496

Challenges



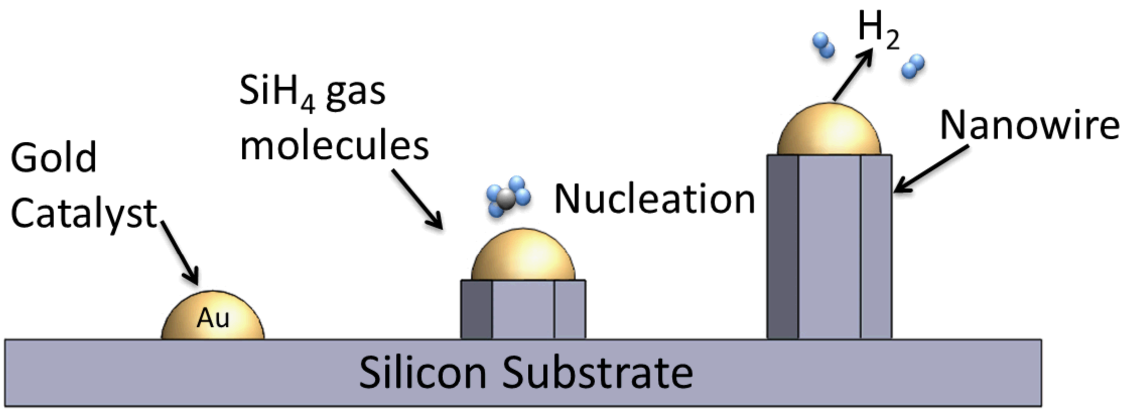
Courtesy of: Bonnie Mckenzie

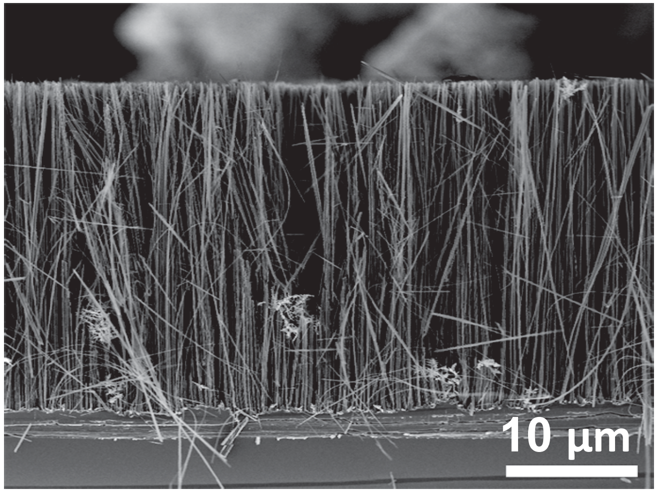


- Silicon expands ~270% upon lithiation
- Rapid loss of capacity

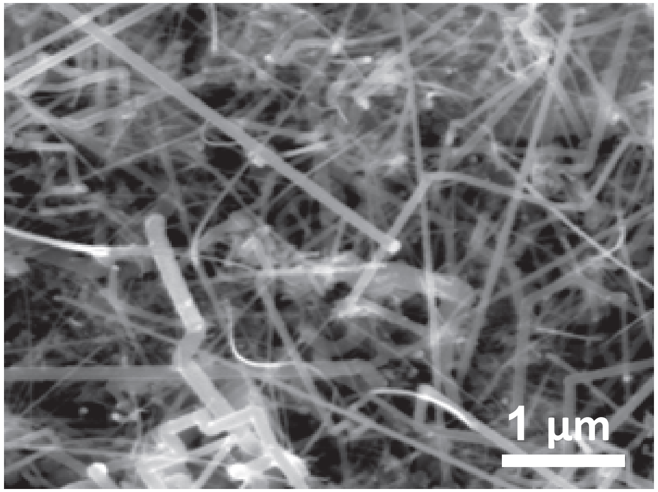
Vapor-Liquid-Solid Mechanism

$$SiH_4 \rightarrow Si + 2H_2$$





Hochbaum, A. I.; Chen, R.; Delgado, R. D.; Liang, W.; Garnett, E. C.; Najarian, M.; Majumdar, A.; Yang, P. *Nature* **2008**, *451*, 163.



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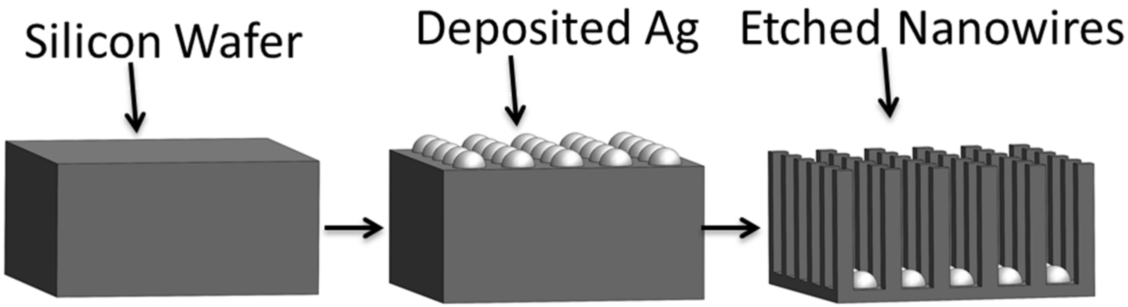
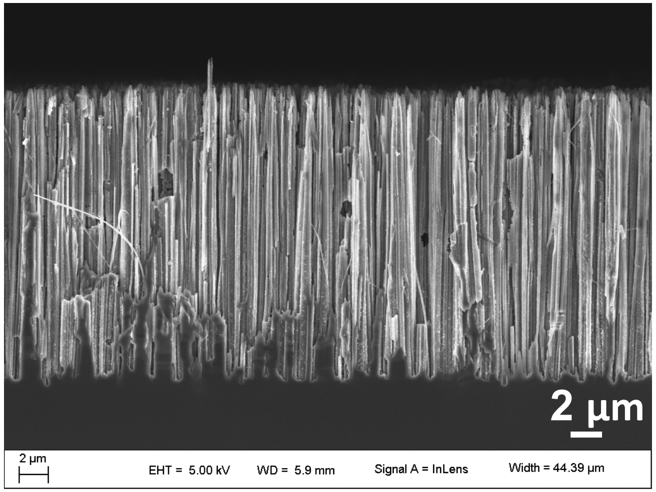
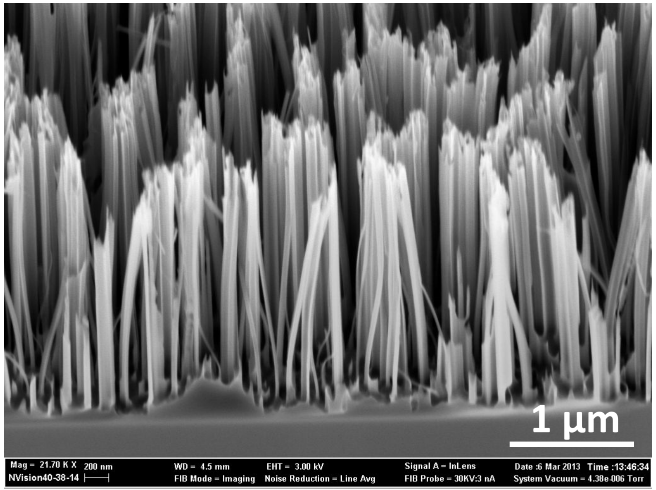
Metal Assisted Chemical Etched

$Si + 4Ag^{+} \rightarrow Si^{4+} + 4Ag^{0}$





Courtesy of: Bonnie Mckenzie



Smith, Z. R.; Smith, R. L.; Collins, S. D. *Electrochim. Acta* **2013**, *92*, 139.

Manufacturing Comparison

Vapor-Liquid-Solid (VLS) Mechanism

Advantages:	Disadvantages:
Single crystalline	High temperature
Dislocation free	Clean room
	Expensive Catalyst

Metal Assisted Chemical Etching

Advantages:	Disadvantages:
Single crystalline	Uses hydrofluoric acid
Fast process	Silicon wafer needed
Room temperature	Loss of material
Affordable catalyst	

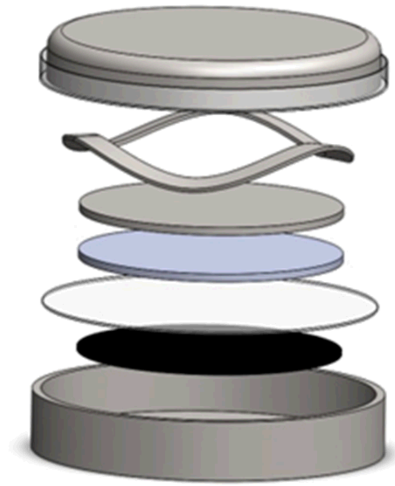
1. Cheaper than vapor-liquid-solid method
2. More easily implemented into production facility
3. More mechanically sound than grown nanowires

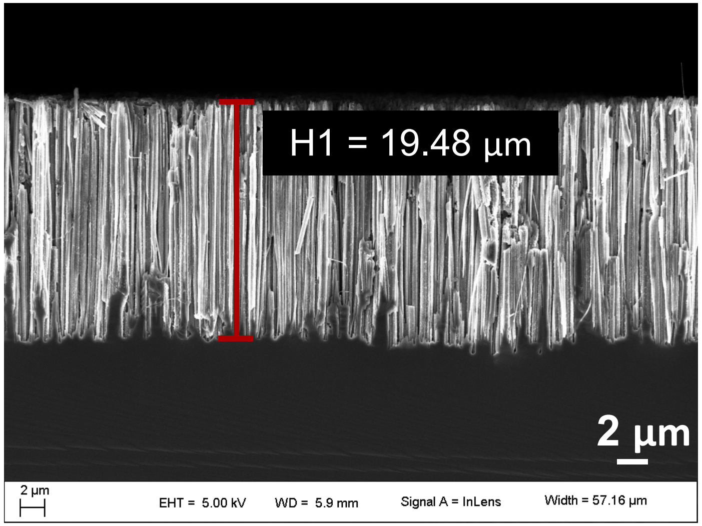
Experimental Set up

- Half-cell configuration
  - Cyclic voltammetry
  - Chrono-voltammetry (charge/discharge)
  - SEM/EDS

Working Electrode: Silicon
Counter Electrode: Lithium metal
Electrolyte: 3:7 EC:EMC + 1.2M $LiPF_6$

- Capacity determined by mass of nanowires (30% surface coverage)
- Actual capacity used for long cycling
- All tests performed in controlled environment (~25°C)
- No carbon conductive phase in bulk

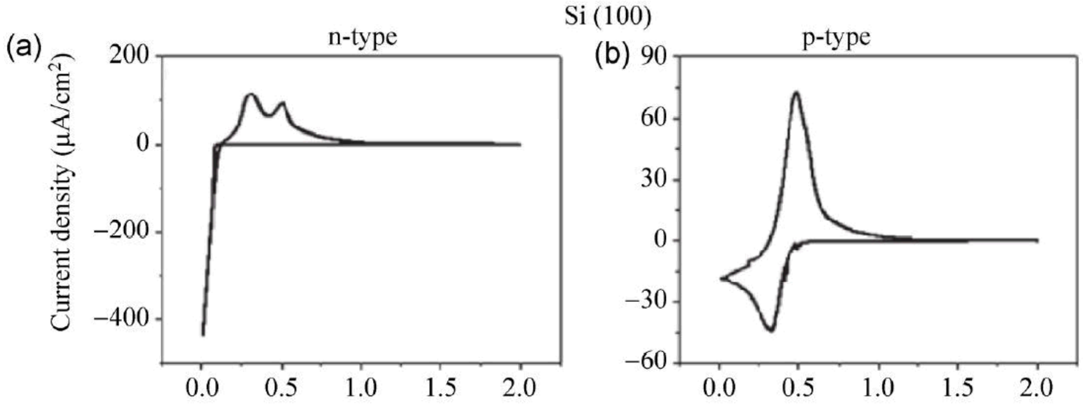




Courtesy of: Bonnie Mckenzie

Smith, Z. R.; Smith, R. L.; Collins, S. D. *Electrochim. Acta* **2013**, *92*, 139.

Cyclic Voltammetry Results

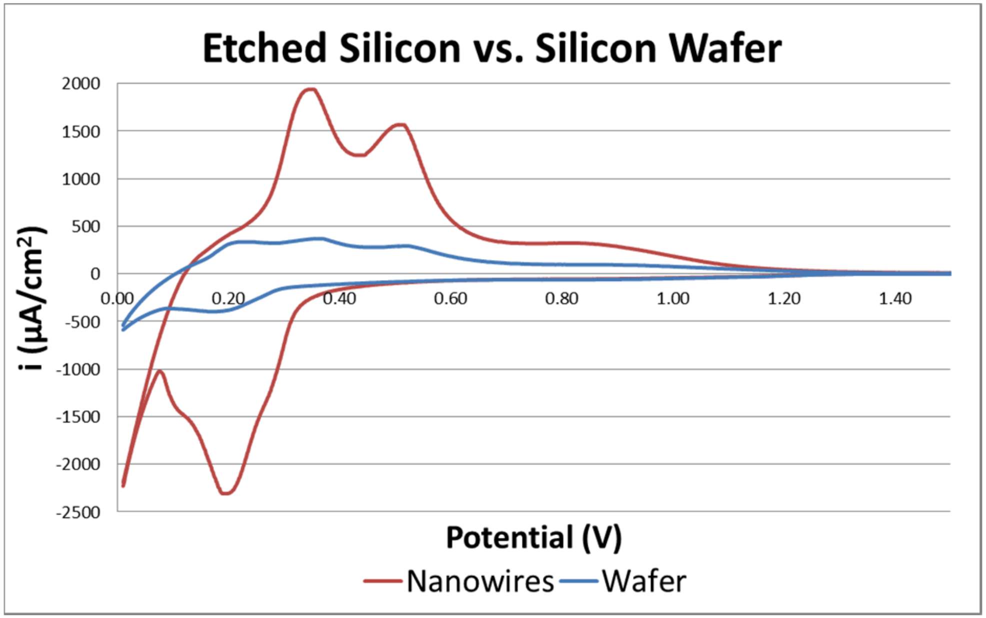


Long, B. R.; Chan, M. K. Y.; Greeley, J. P.; Gewirth, A. A. *J. Phys. Chem. C* **2011**, *115*, 18916.

Working Electrodes: n-type P doped Si
p-type B doped Si

Counter Electrode: Li ribbon

Scan Rate: 200 μV/s



Working Electrodes: p-type P doped Si
Silicon Nanowires

Counter Electrode: Li metal

Scan Rate: 25 μV/s

Temperature: 25°C

Chrono-voltammetry Results

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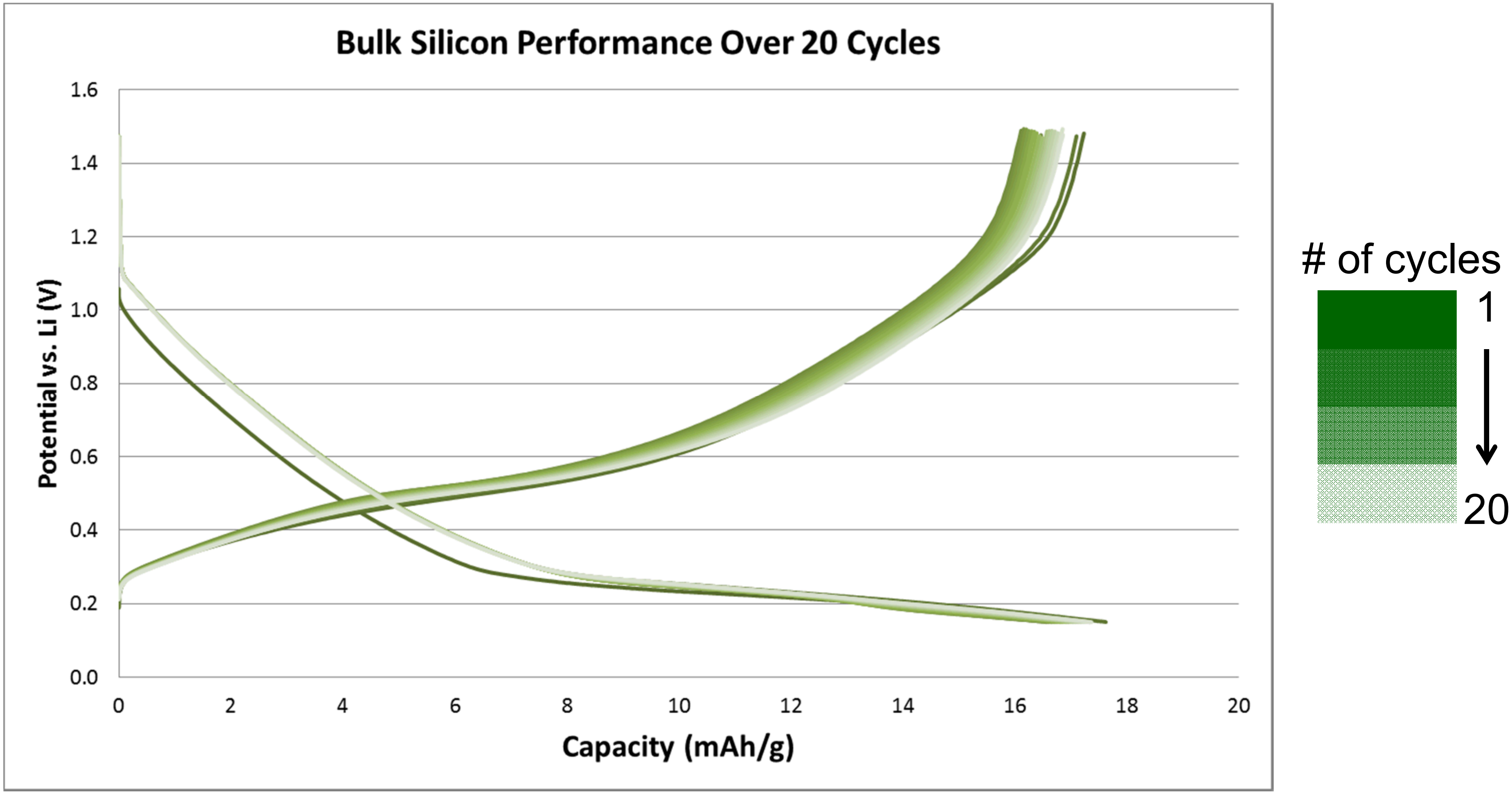


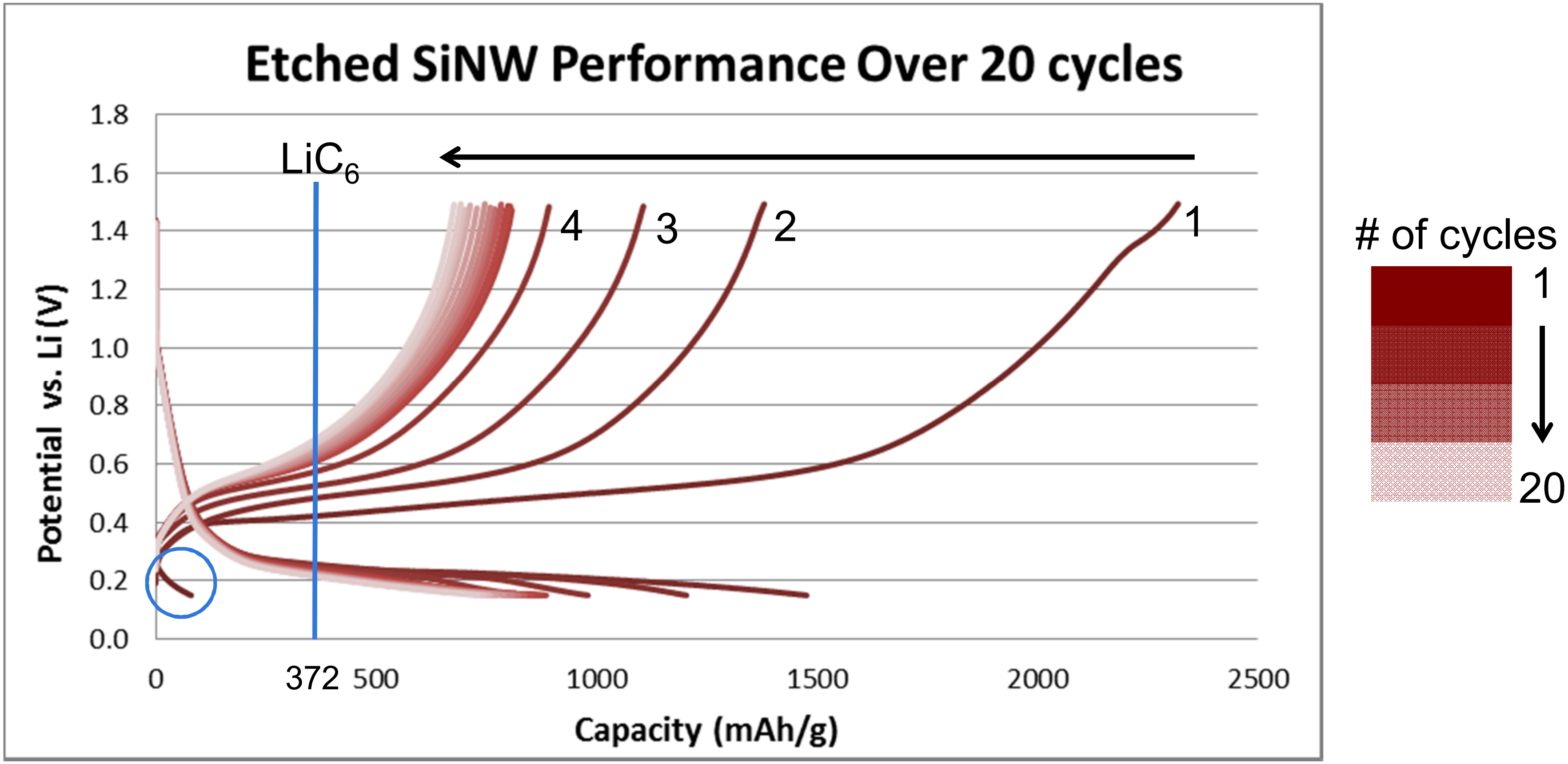
Temperature: 25˚C

Rate: C/10

Mass: 0.0965 g

- Only penetrating 0.48% of wafer
- ~3.15 µm out of 650 µm

Chrono-voltammetry Results



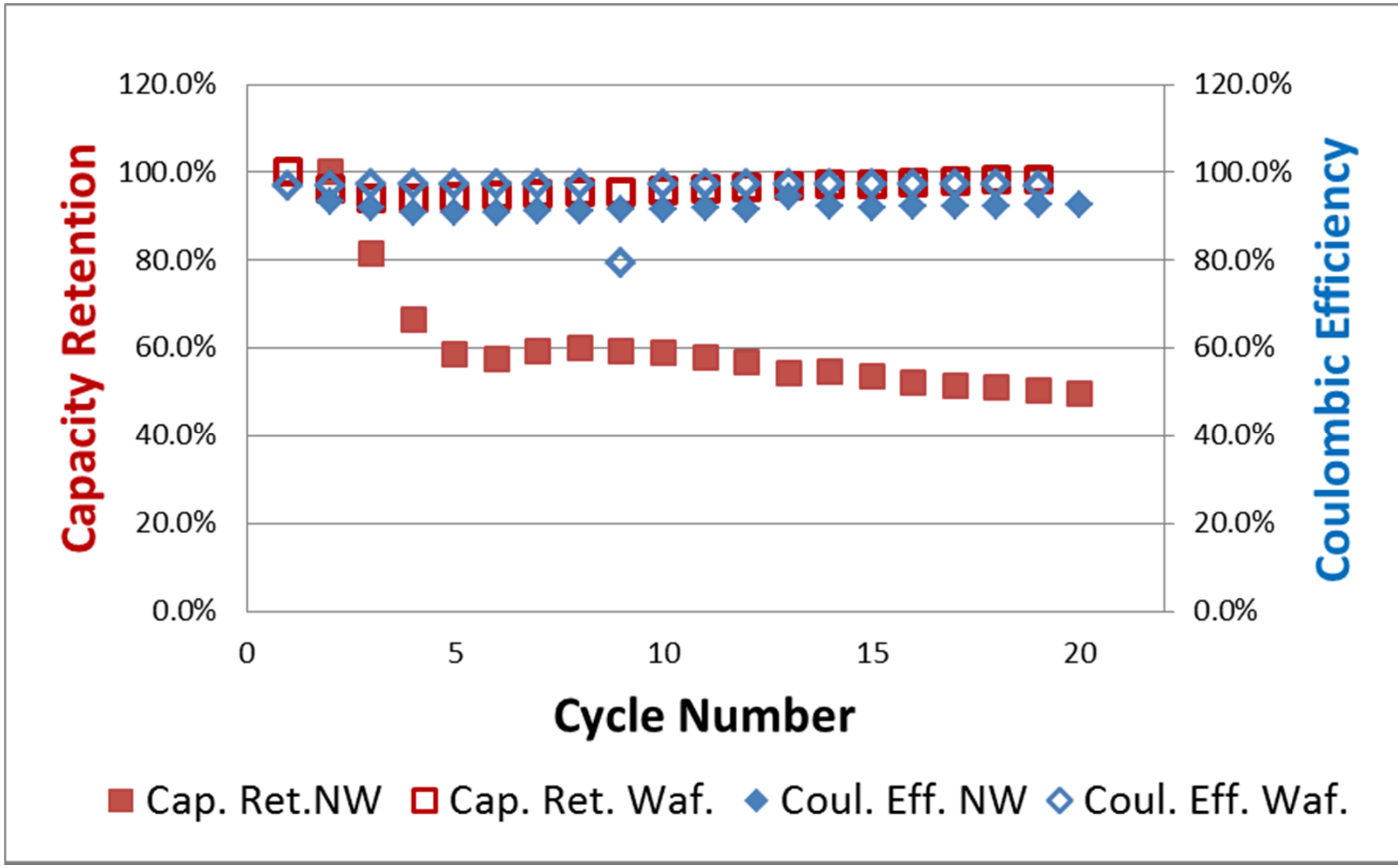
Temperature: 25˚C

Rate: C/10

Mass: 0.00469 g

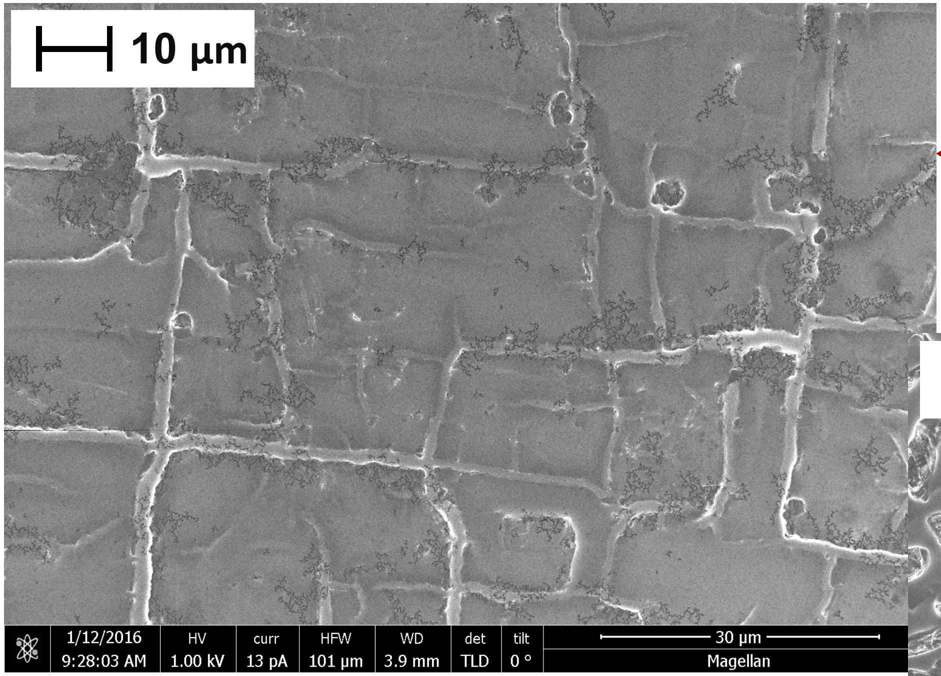
- Discharge = lithiation of silicon
- After 3 formation cycles at C/100
- C rate based on data from formation cycles

Capacity Retention and Coulombic Efficiency

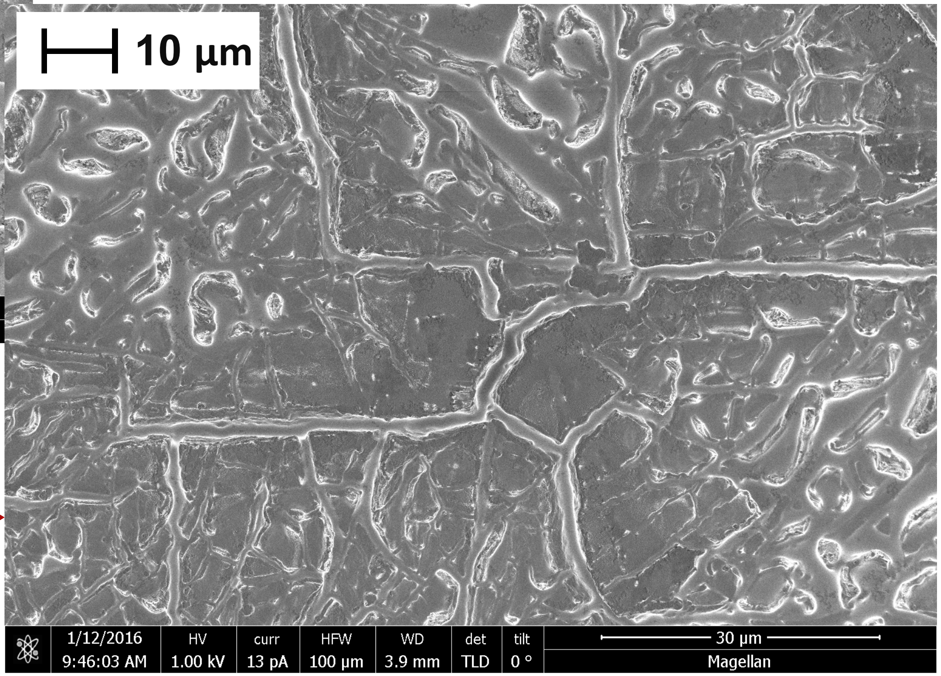


- Low coulombic efficiency for nanowires (consistent with literature)

Bulk Silicon Wafers

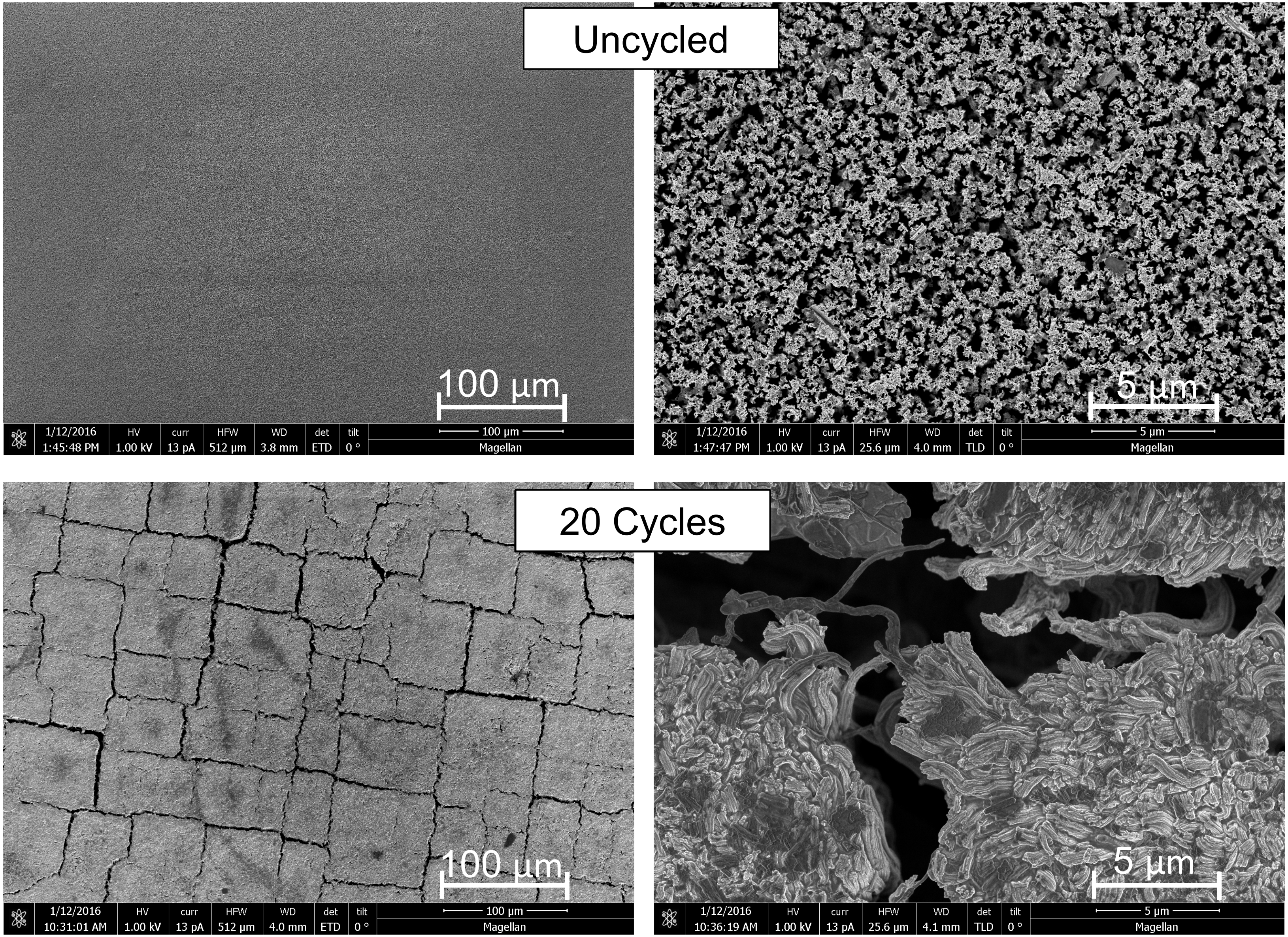


Bulk Silicon Wafer
10 cycles at C/10
Room Temperature (~25°C)
3:7 EC:EMC + 1.2M $LiPF_6$

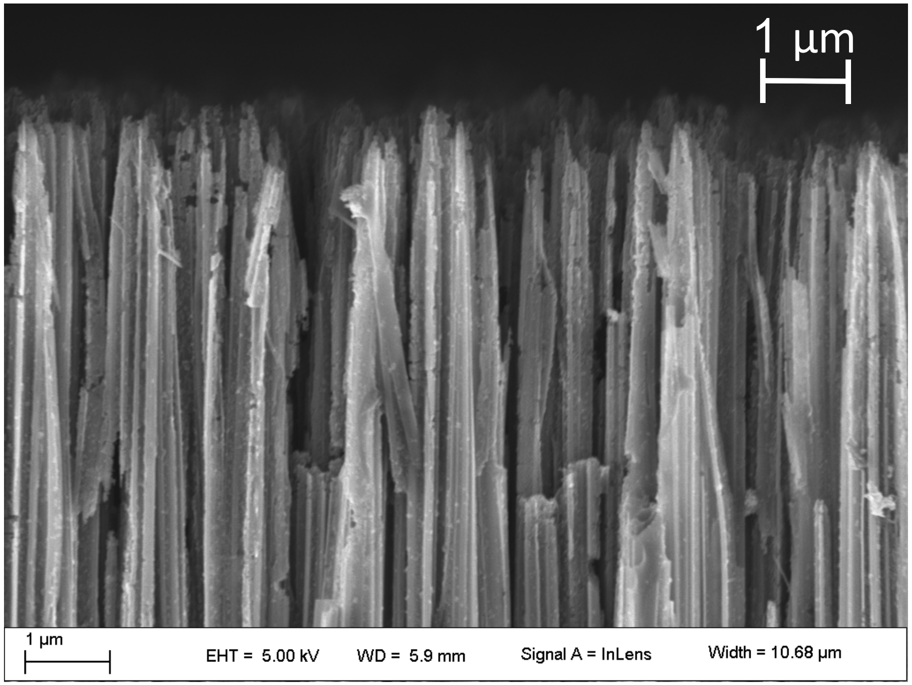


Bulk Silicon Wafer
20 cycles at C/10
Room Temperature (~25°C)
3:7 EC:EMC + 1.2M $LiPF_6$

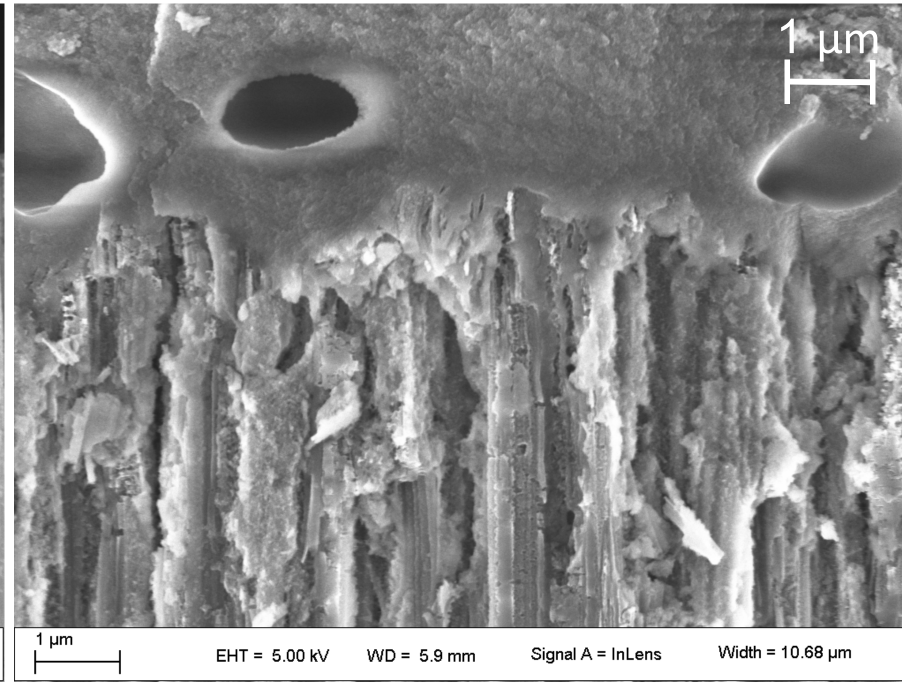
Etched Silicon



SEM Imaging of Silicon Nanowires



Uncycled



Cycled

Conditions:
RT = 25°C
WE: Si NW
CE: Li metal

Conclusions

- Etched silicon nanowires are capable of achieving capacities twice as large as graphite anodes even after 20 cycles.
- Mechanically sound, stayed relatively intact during cycling
- Low coulombic efficiency
- 49.5% capacity retained after 20 cycles

Future Work

- Identify capacity dependence on etch time and concentration
- Run silicon nanowire anodes in full cell
- Run anodes for more cycles (50+ cycles)

Acknowledgements

Christopher Apblett

Jonathan Coleman

Scott D. Collins

Kyle Fenton

Brian Perdue

Bonnie Mckenzie

Chelsea Snyder

Richard Grant

Backup Slides

Silicon Nanowires		
Cycle	**Coulombic Efficiency**	**Capacity Retention**
1	-	-
2	93.5%	100.0%
3	91.9%	81.5%
4	91.0%	66.4%
5	90.7%	58.5%
6	90.9%	57.5%
7	91.2%	59.4%
8	91.2%	60.0%
9	91.8%	59.4%
10	91.6%	58.9%
11	91.8%	57.8%
12	91.7%	56.7%
13	94.4%	54.5%
14	92.2%	54.8%
15	92.1%	53.6%
16	92.4%	52.3%
17	92.3%	51.5%
18	92.4%	51.2%
19	92.7%	50.5%
20	92.6%	49.5%

Silicon Wafer		
Cycle	**Coulombic Efficiency**	**Capacity Retention**
1	-	-
2	97.0%	100.0%
3	97.1%	96.2%
4	97.3%	94.0%
5	97.3%	94.2%
6	97.3%	94.5%
7	97.2%	94.8%
8	97.3%	95.1%
9	97.2%	95.4%
10	79.4%	95.7%
11	97.2%	96.0%
12	97.2%	96.3%
13	97.2%	96.7%
14	97.2%	97.0%
15	97.2%	97.2%
16	97.3%	97.5%
17	97.2%	97.8%
18	97.2%	98.2%
19	97.2%	98.4%
20	97.1%	98.6%

Theoretical Capacity Calculations

$$q = \frac{nF}{3600\frac{C}{Ah} * M}$$

n = # of electrons
F = 96487 Coulombs/mol
M = 28.09 g/mol for Si

$Li_{15}Si_4$

$$q = \frac{(15)(96487\frac{C}{mol})}{(3600\frac{C}{Ah}) * (4 * 28.09\frac{g}{mol})} = 3.578\frac{Ah}{g}$$