# Etched Silicon Nanowires as Anodes


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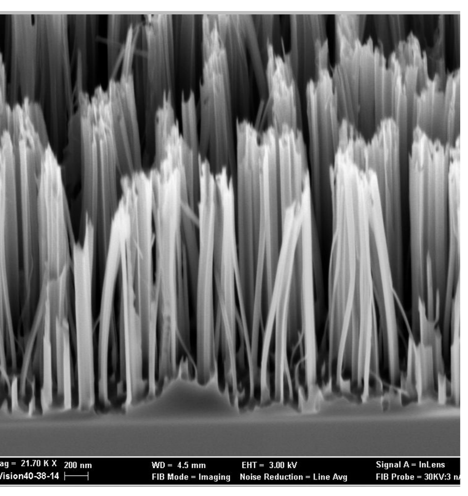

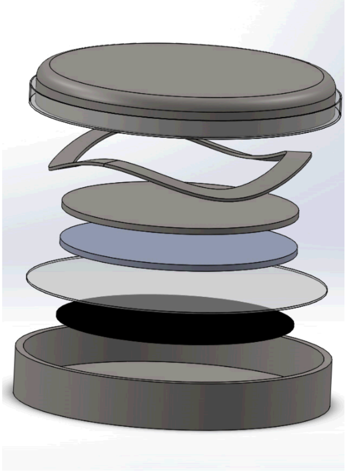

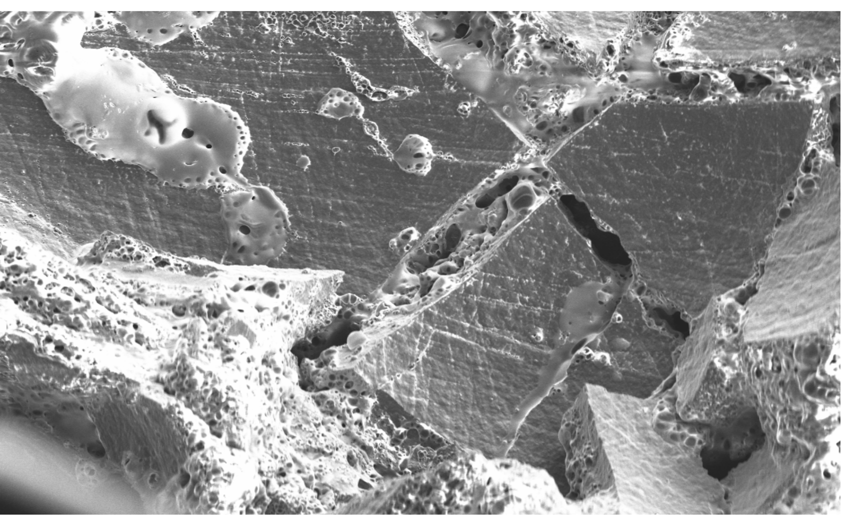

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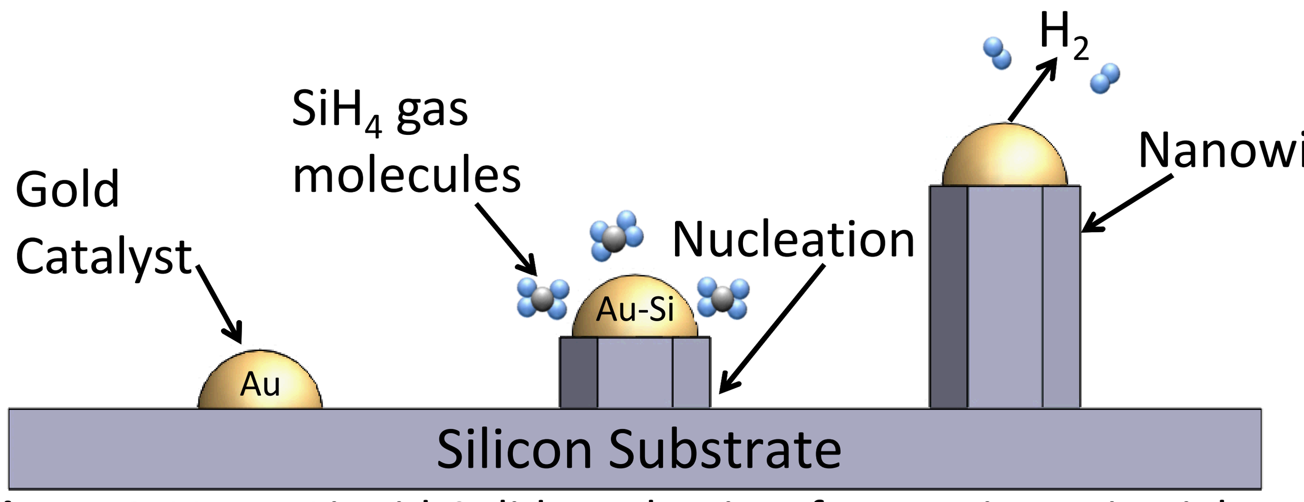
## Introduction

Lithium ion batteries are becoming increasingly prevalent as they have many advantages over other battery chemistries. They exhibit high specific energy and energy density. They also have a low self-discharge rate, long cycle life, and can operate in a wide temperature range. Currently Li-ion batteries consist of a lithium cobalt oxide ($LiCoO_2$) or lithium manganese oxide ($LiMn_2O_4$) cathode and a carbonaceous anode. Electrode materials with higher specific capacities are required to advance Li-ion battery technology as its applications continue to shrink in size. Silicon has a theoretical capacity roughly 10 times higher than carbonaceous anodes which is why it is the focus of this research.

## Background

$LiC_6$ has a theoretical capacity of 372 mAh/g while $Li_{15}Si_4$, an alloy formed at room temperature and low voltage, has a theoretical capacity of roughly 3,579 mAh/g.[2] This capacity originates from the ability of a single silicon atom to accommodate 4.4 lithium atoms in the lattice. Unfortunately, silicon has a volume expansion of approximately 270% upon lithiation compared to 10% in graphite anodes.[3] This causes the electrode particles to fracture which leads to a loss of capacity with cycling. Silicon nanostructures experience the same volume expansion as bulk silicon, but are able to accommodate the expansion without fracturing. Nanowires are the primary nanostructure being researched as a viable replacement for carbonaceous anodes. Commonly, silicon nanowires are grown epitaxial with a metallic impurity and a gas containing the reactive species. This method is expensive as it requires metallic impurities such as gold, high temperatures, and a clean environment.




$$SiH_4 \rightarrow Si + 2H_2$$

**Figure 1.** Vapor-Liquid-Solid mechanism for growing epitaxial silicon nanowires.

Etching is an alternate method that uses a silver template and chemicals such as hydrofluoric acid to etch Si nanowires from the top down.[4] This method produces single crystalline, dislocation free nanowires without the additional expenses associated with growing them.

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

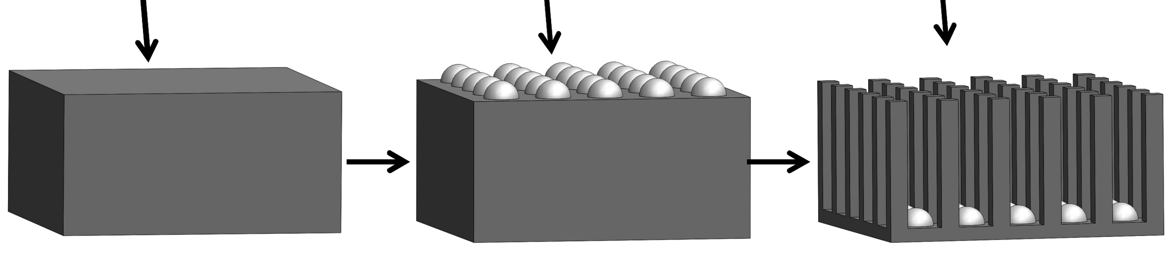
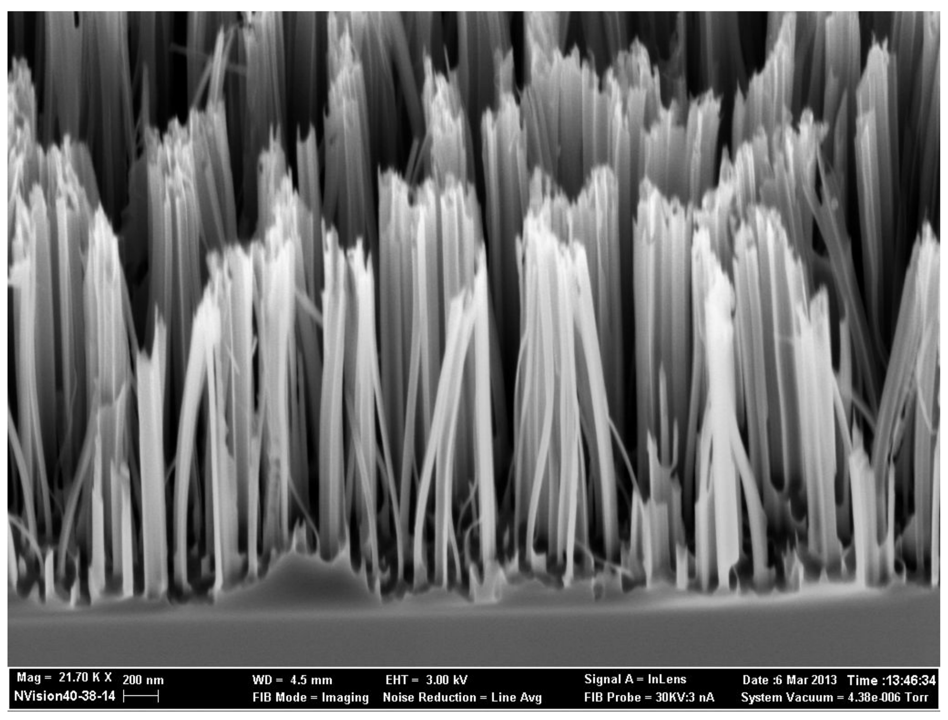



**Figure 2.** Chemical etching of silicon wafer with silver and hydrofluoric acid to produce nanowires.



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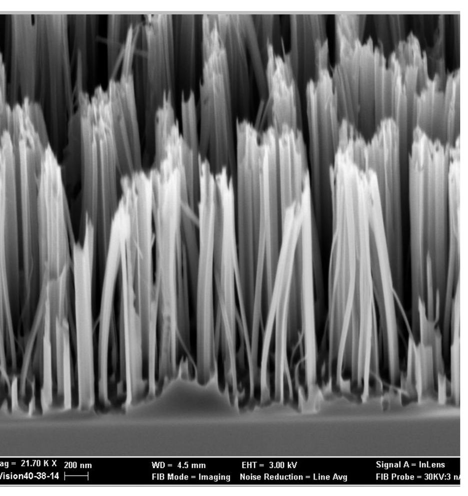
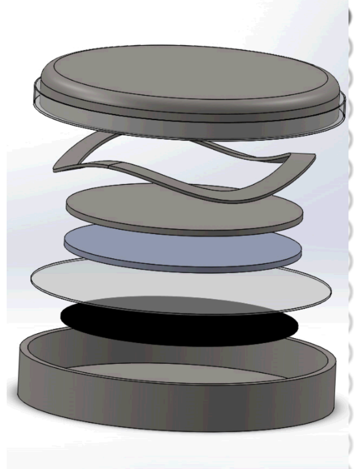
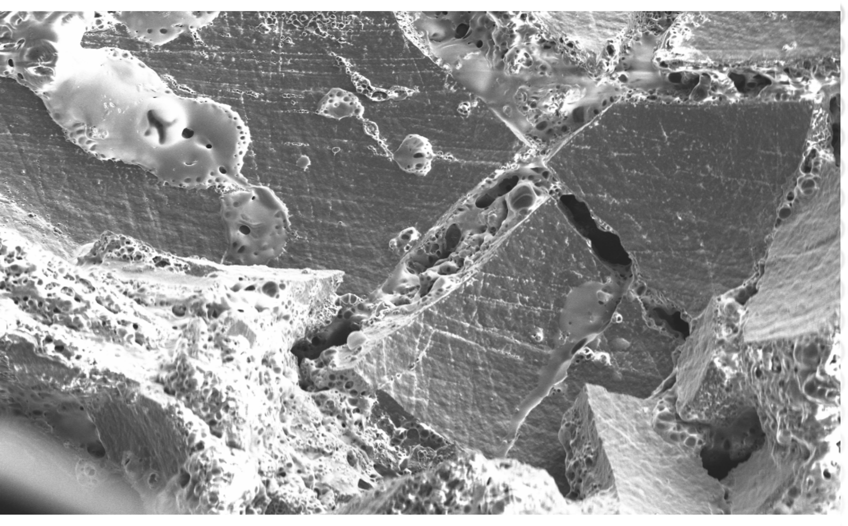
[1] *Linden's Handbook of Batteries,* 4th ed. McGraw-Hill, NY, 2011, pp.26.1-26.40.
[2] S.D. Beattie *et al.*, "Si Electrodes for Li-Ion Batteries – A New Way to Look at an Old Problem," *ECS*, 2007.
[3] R. Benedek, M.M. Thackeray, " Lithium Reaction with Intermetallic-compound electrodes," *Journal of Power Sources,* 2002.
[4] Z.R. Smith, R.L. Smith, S.D. Collins. "Mechanism of nanowire formation in metal assisted chemical etching," *Electrochimica Acta,* 2012.







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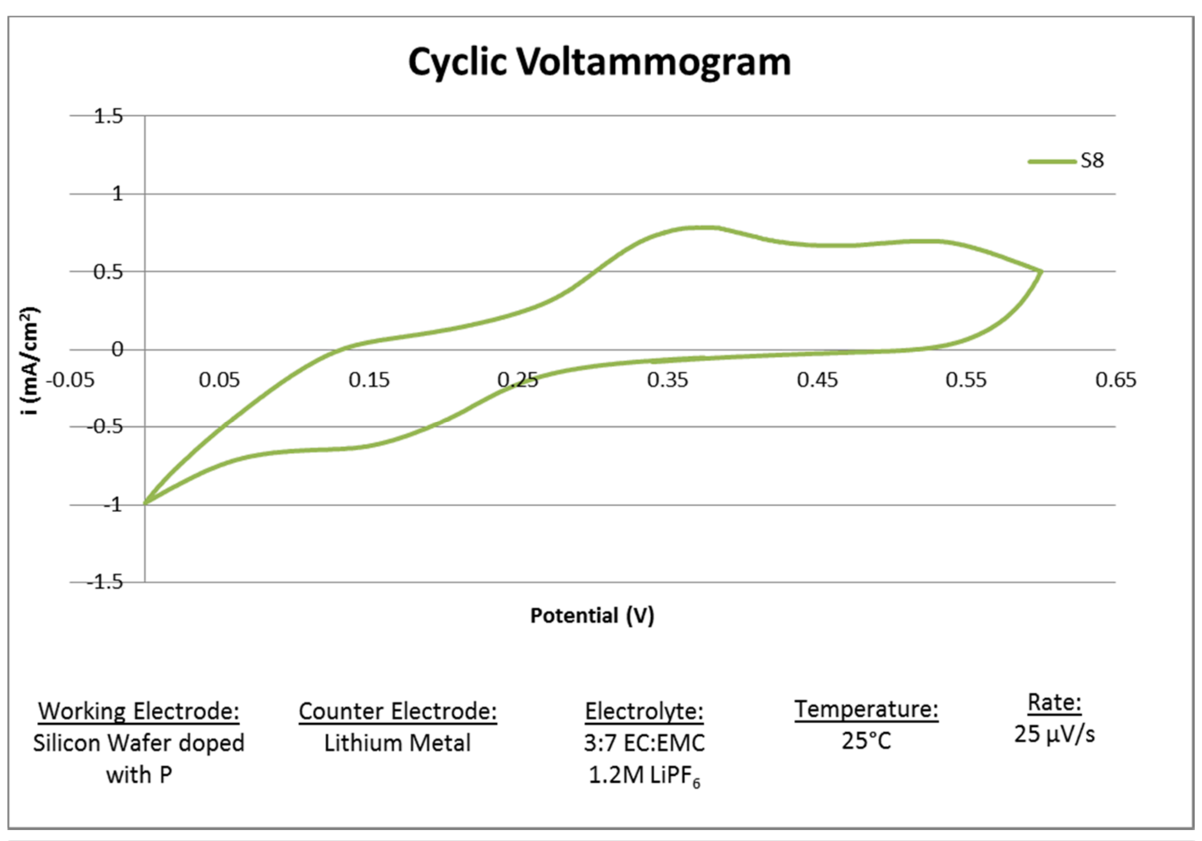
# Methods

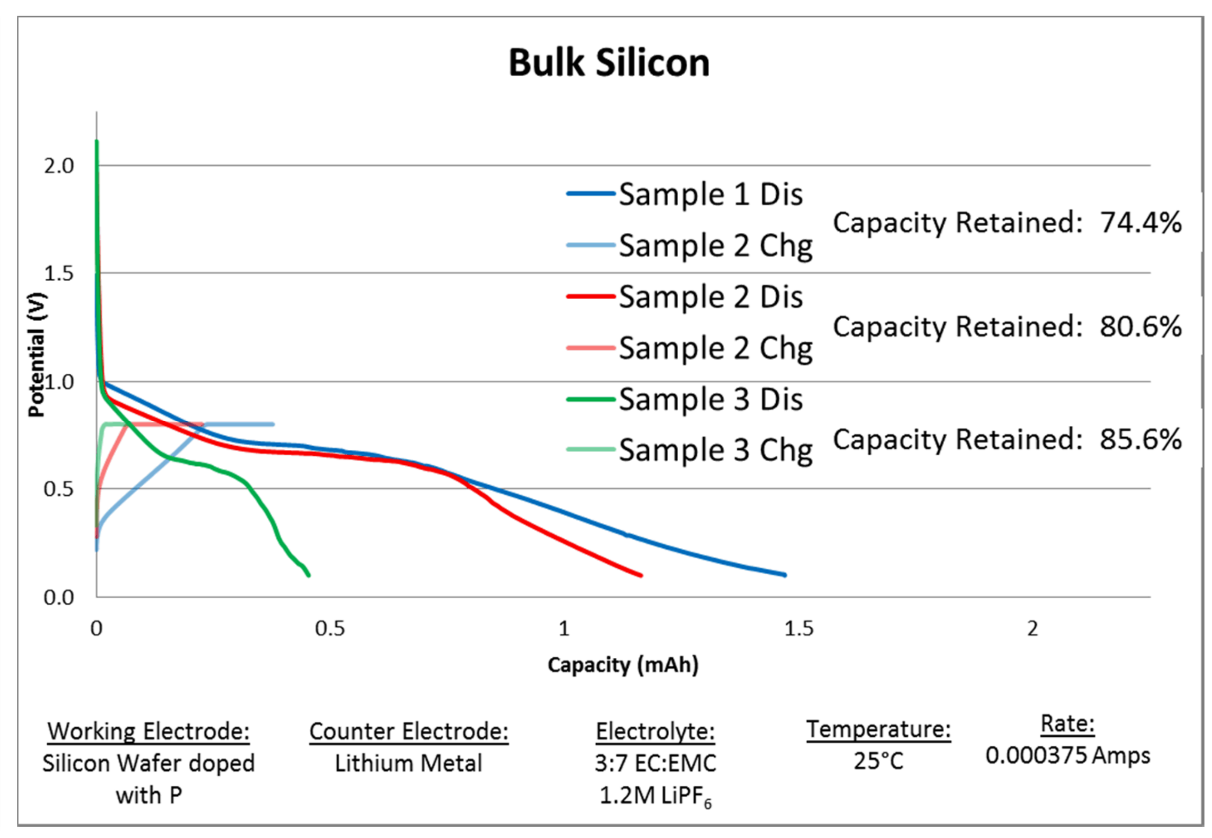
The silicon samples of interest are built into electrochemical half-cells consisting of a silicon anode and a lithium metal cathode. A schematic of the coin cell configuration is shown in Figure 3. The silicon material is secured to the case using a carbon black and PVDF “glue”, which provides enough conductivity to pass charge. The cells are then tested using cyclic voltammetry or charge/discharge cycling. After cycling the cells are disassembled and the Si electrode is analyzed with a scanning electron microscope (SEM) and the chemical composition is determined by energy-dispersive X-ray spectroscopy (EDS).

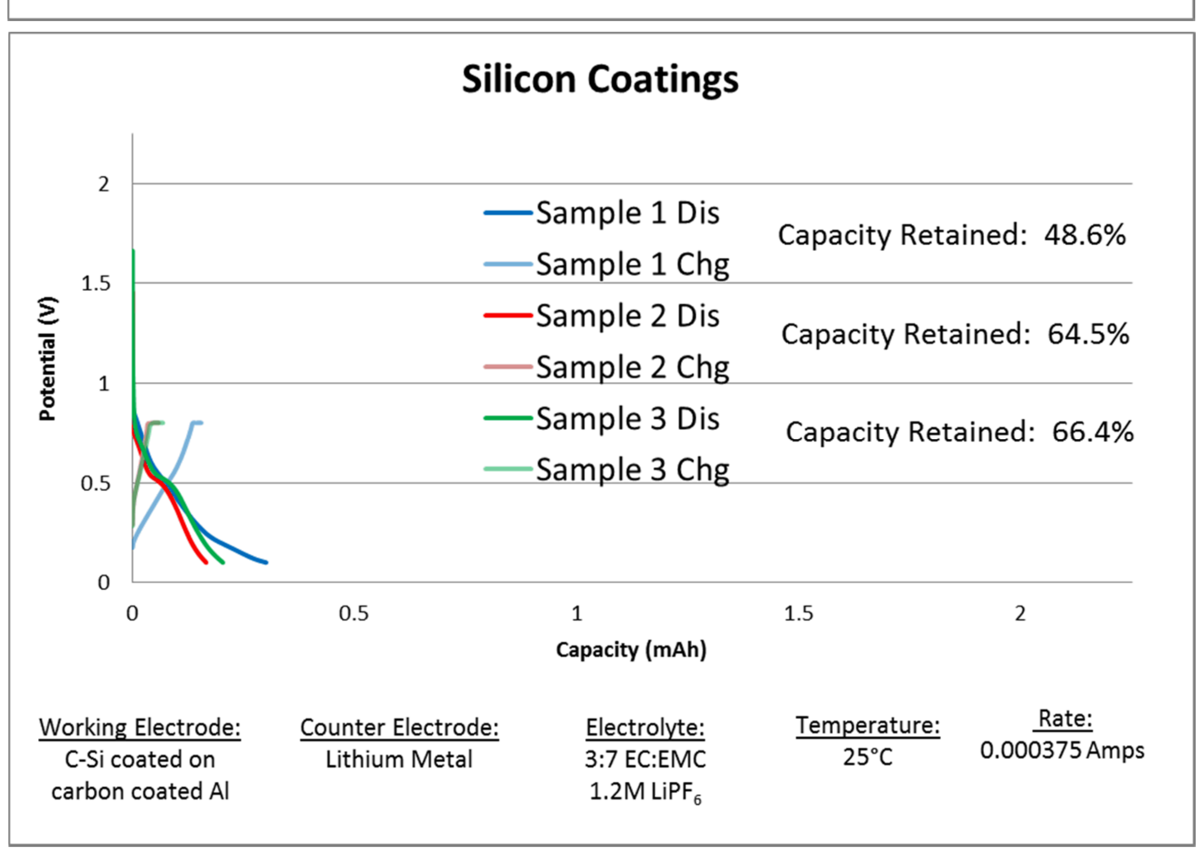
**Figure 3.** Electrochemical cell and its components. The separator is saturated with electrolyte.

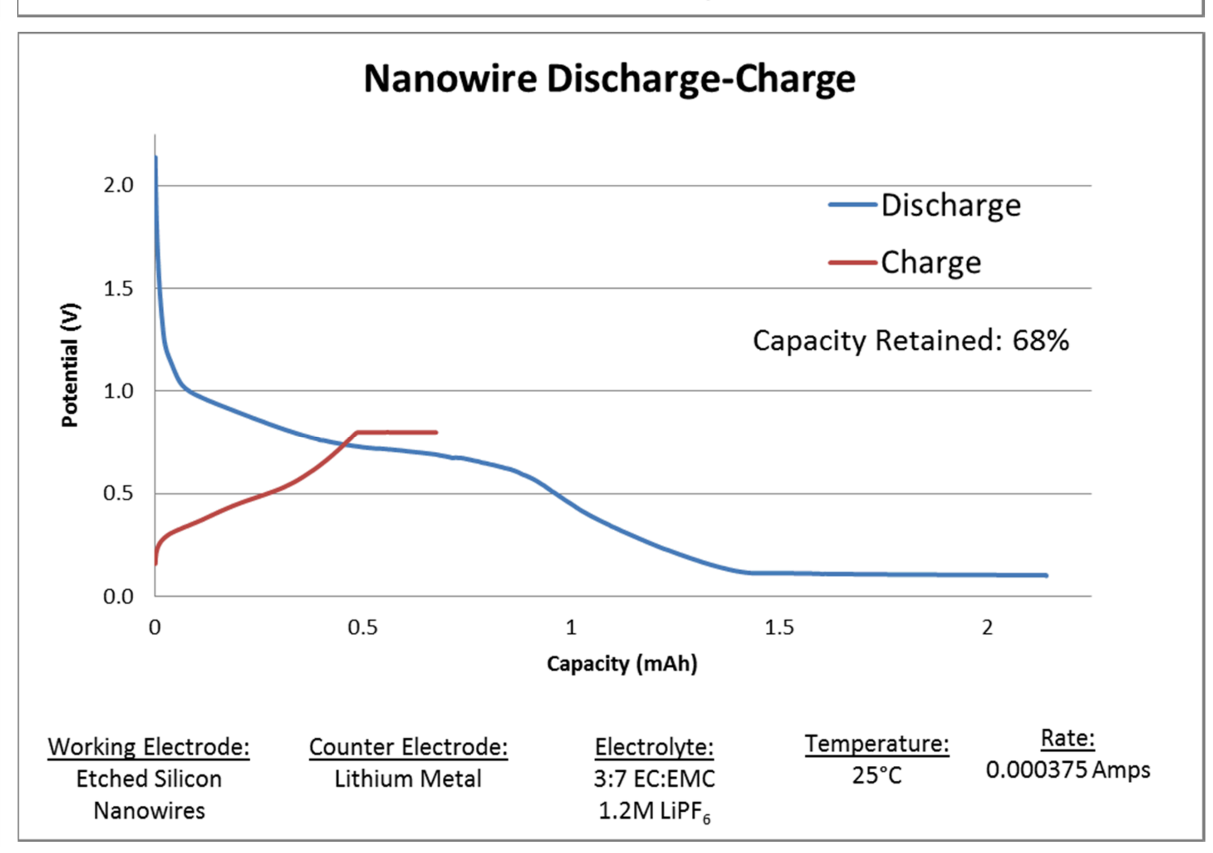
# Results

All three types of silicon samples exhibit similar capacity retention.



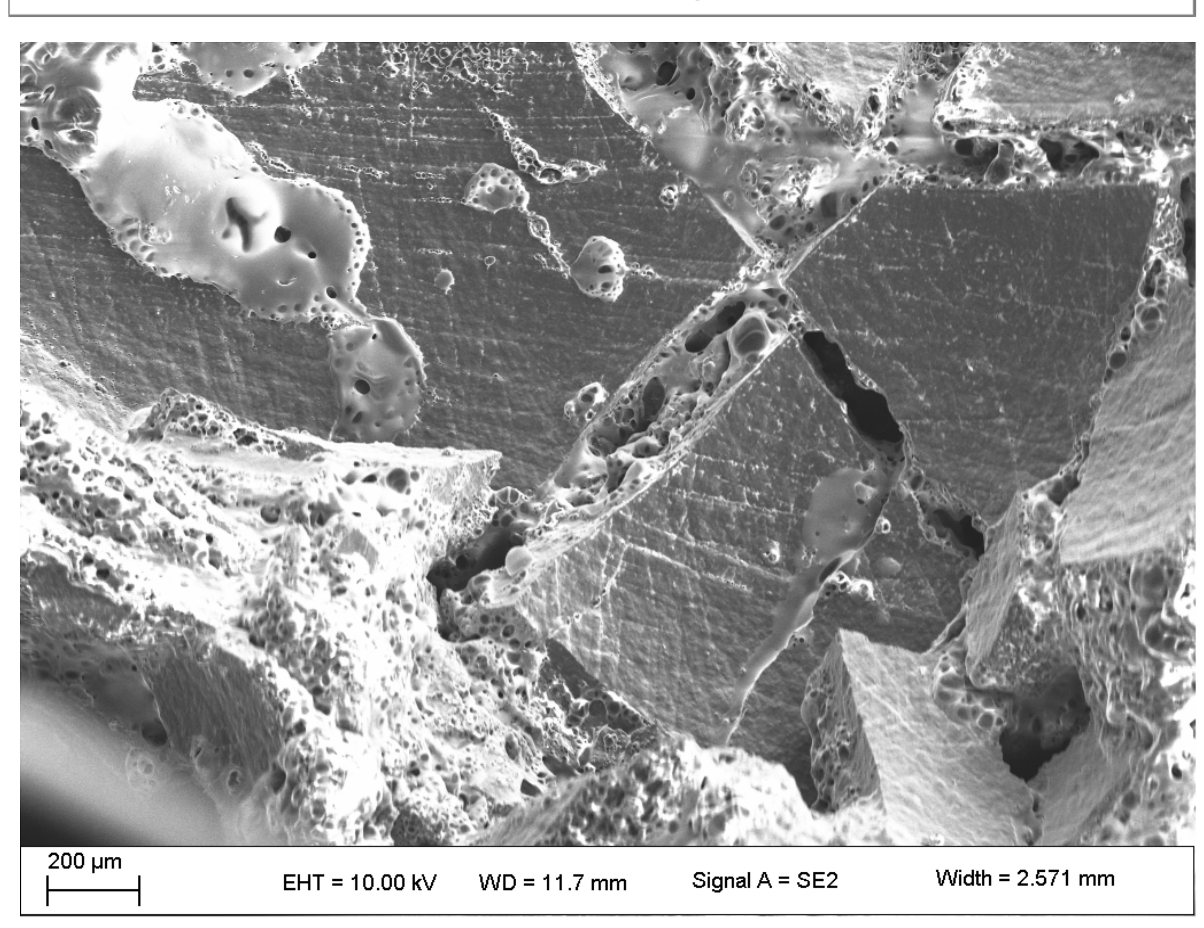





SEM of silicon wafer before cycling




SEM of silicon wafer after 5 charge-discharge cycles

# Future Work

- Analyze current sample structure with SEM/EDS.
- Try using a commercially produced silicon powder to incorporate into the silicon coating.
- Work with samples of different nanowire lengths and densities to correlate current to nanowire density.

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The authors would like to acknowledge Dr. Scott D. Collins from the University of Maine for the fabrication of the silicon nanowire samples.