Li Batteries Using Nanowire Electrodes

Candace K. Chan[1], Hailin Peng[2], Robert A. Huggins[2], and Yi Cui[2]

Global Climate & Energy Project

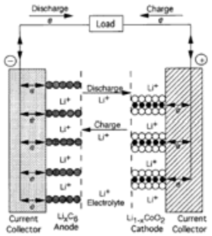
(1) Department of Chemistry
(2) Department of Materials Science and Engineering

STANFORD UNIVERSITY

Geballe Laboratory for Advanced Materials

Motivation

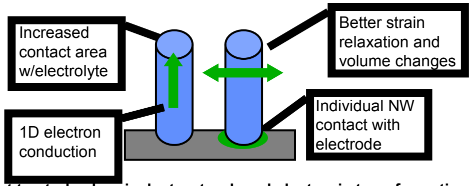
- **Want improved Li batteries for portable electronic devices and electric vehicles**



Need:

- **High energy density: Store more Li, higher capacity**
- **High power density: Discharge and charge faster**
- **Long cycle life: Durable materials**

- **Nanowire electrodes may be better than bulk electrodes**



Increased contact area w/electrolyte

Better strain relaxation and volume changes

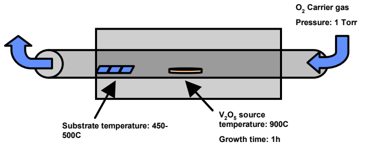
1D electron conduction

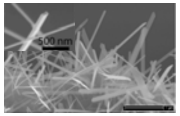
Individual NW contact with electrode

- **Want to study chemical, structural, and electronic transformations in nanostructures during Li insertion/deinsertion and determine if they would improve battery performance**

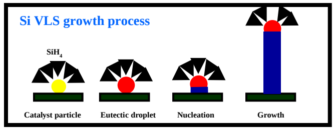
Nanowire Synthesis

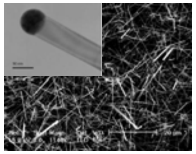
1. V_2O_5 nanoribbons (NR) as cathode: Chemical vapor transport



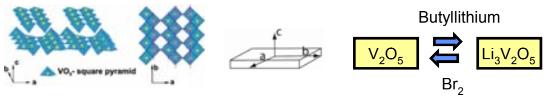


2. Si nanowires (NW) as anode: Vapor-liquid-solid (VLS) growth

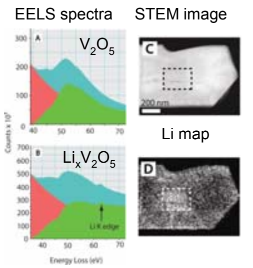




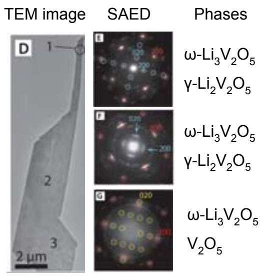
Improved Li Intercalation and Phase Transformation at the Nanoscale



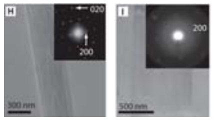
Li intercalates into layers of V_2O_5, corresponding to width and length of V_2O_5 NR. Lithiation/delithiation were performed chemically.



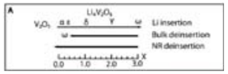
Electron-energy loss spectroscopy (EELS) was used to detect Li in $Li_xV_2O_5$ NRs. The Li signal was extracted and spatially mapped. Higher Li content (bright regions) were observed near the edges and at the crack (boxed region) indicating more Li insertion due to increased contact area and shorter insertion lengths.



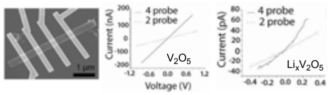
Looking at a NR with different widths along its long axis, electron diffraction in the TEM determined different lithiated phases. Less Li insertion was observed at the wider distance and phase transformation to the fully lithiated phases was more difficult in the micron vs. nanometer distance.



10 sec lithiation gave $Li_3V_2O_5$ in 20 nm thick/ 740 nm wide NR (I) but not 100 nm thick/ 400 nm wide NR (H). Layer stacking direction thickness is important for facile phase transformation. 10 sec lithiation is a very high power density.



Full delithiation back to V_2O_5 observed in NRs but not bulk, indicating 30% increased energy density by nanostructuring.



Electronic conduction in NR sufficient to charge a single NR in < 5 sec.

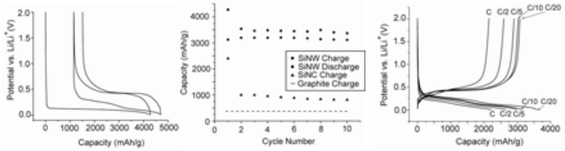
Results

- **Facile phase transformation in nanoscale width and thickness**
- **Lithiation fully reversible in NRs – Increased energy density by 30%**
- **Full lithiation in 10 sec in thin NRs – Faster Li diffusion by 3 orders of magnitude in NRs and increased power density**

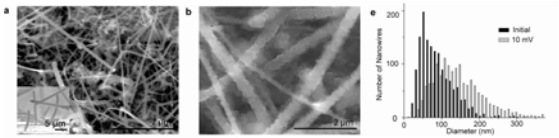
SiNWs for High Capacity Anodes

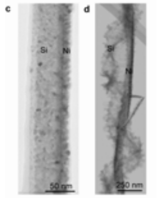
- **Si is an attractive material to replace graphite as anode**
- **Durability problems due to huge volume change during Li insertion/deinsertion**

Starting Material	C	Si
Lithiated Phase	LiC_6	$Li_{22}Si_5$
Theoretical Specific Capacity (mAh/g)	372	4200
Theoretical Volumetric Capacity (Ah/L)	833	9340
Packing Density (mol/mL)	0.0279	0.0851
Volume Changes (%)	12	400



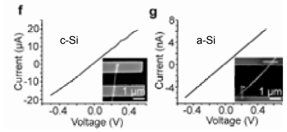
Constant current measurements at C/20 rate. Long voltage plateau at < 0.2 V indicates Li_xSi is a suitable replacement for Li or Li_6C. Capacity was ~ an order of magnitude higher than graphite's (372 mAh/g) at fast power rates and stable for many cycles.





SEM and TEM images of SiNWs before (a,c) and after (b,d) lithiation to 10 mV revealed structural changes. SiNWs were observed to increase in diameter (from 89 nm to 141 nm) and length after lithiation. Length expansion was observed by evaporating Ni film to act as inert backbone (c). After lithiation, Ni was unchanged and crystalline in TEM while SiNW was amorphous and buckled, indicating length expansion (d). Electrochemical cycling causes SiNWs to become amorphous.

Single NW devices showed SiNWs remain conducting after amorphization. The resistivity changes from 0.02 Ω-cm (f) to 3 Ω-cm (g) after one cycle.



Results

- **SiNWs show promise as high capacity anode materials**
- **SiNWs can easily accommodate large volume changes and show good cycling life better than bulk or thin film Si**

Acknowledgements

This work was supported by NSF and SGF Graduate Fellowships, CPN seed fund, and GCEP.

Characterization was done in the Stanford Nanocharacterization Laboratory. EELS and STEM work was performed by K. Jarausch and X. F. Zhang from Hitachi High Technologies and R. D. Twesten from Gatan, Inc.