How Can Nanotechnology Help Solve Problems in Energy Storage?

From Fundamental Studies to Electrode Design

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Nanomaterials for Energy Storage

- Nano-composite Level
- Nanowire Ensemble Level
- Single Nanowire Level

Cycling performance
Electrode design

Phase & structural transformations
Chemical & compositional changes
Electrochemical Energy Storage

Electric Cars

HEVs
- Combustion Engine
- Regenerative Braking
- Electric Motor
- Batteries
- Gasoline

~1-2 kWh

PHEVs
- Combustion Engine
- Regenerative Braking
- Electric Motor
- Batteries

~5-15 kWh

BEVs
- Regenerative Braking
- Electric Motor
- Batteries

>40 kWh

http://www.burbankwaterandpower.com/electric-vehicles
DOE cost goals:

- HEV: $20/kWh (by 2010)
- PHEV: $250/kWh (by 2015)

Today PHEV costs are $2000/kWh!
- Stores 56 kWh
- Delivers 185 kW power (~ 248 hp)
- 6800 of 18650 cells wired in series
- Weighs 450 kg (990 lbs)
- Full charge time 3.5h at 240V
- Costs $25,000

Tesla Roadster battery pack
It’s clear that the main problems are:

- Cost
- Weight (volume)

How can nanotechnology help?

Nanotechnology can:

1. Enable better performance – more “efficient” materials mean less material is needed
2. Allow for new types of chemistry and reactions
3. Be designed and assembled to exploit these properties
What is a Battery?

**Anode** oxidation reaction

**Cathode** reduction reaction
Key Characteristics

- Capacity – how much charge (Li) can you store? [mAh/g]
- Voltage – at what potential does the electrochemical rxn occur? [V vs. Li]
- Energy density = capacity x voltage [Wh/kg]
- Power density
Graphite

Li metal

Capacity (mAh/g)

Potential vs. Li (V)

Cathodes

Oxygen evolution

Electrolyte oxidation

Solvent reduction

Graphite

Li metal

Lithium plating

Anodes

Capacity (mAh/g)
Cathodes

- Li$_{1-x}$Mn$_{2-y}$M$_y$O$_4$
- Li$_{1-x}$Co$_{1-y}$M$_y$O$_2$
- Li$_{1-x}$Ni$_{1-y}$Co$_y$M$_2$O$_4$ [M=Mg, Al,...]

Polyanionic compounds [Li$_{1-x}$VOPO$_4$, Li$_x$FePO$_4$]

Vanadium oxides [V$_2$O$_5$, LiV$_3$O$_8$]

Anodes

- Composite alloys [Sn(O)-based]
- Carbons
- Graphite

Electrolyte oxidation

Silicon

Potential vs. Li (V)

Capacity (mAh/g)
Example 1: V$_2$O$_5$ nanoribbons

![Image](image)

![Graph](graph)

**Chem. Mater., 2008, 20 (22), 7044-7051**
Example 1: V$_2$O$_5$ nanoribbons

Key science questions:

- How does nanostructuring affect physical & chemical transformations?
- What implications in device performance?

Substrate temperature: 450-500°C

Source temperature: 900°C

Growth time: 1h

O$_2$ Carrier gas
Pressure: 1 Torr

Chan, C.K. et. al Nano Lett. 2007, 7, 490-495
Example 1: $V_2O_5$ nanoribbons

$V_2O_5$: Layered structure

Li$^+$

$V_2O_5$ nanoribbons

Lithiation

$V_2O_5$$\rightarrow$$Li_xV_2O_5$

Delithiation

$Li_xV_2O_5$$\rightarrow$$V_2O_5$

Chan, C.K. et. al Nano Lett. 2007, 7, 490-495
Example 1: $\text{V}_2\text{O}_5$ nanoribbons

Chemical transformation

In collaboration with Hitachi High Technologies and Gatan, Inc.

- Increased interfacial contact area
- Decreased Li insertion distance

Electron Energy Loss Spectroscopy (EELS)

- STEM image
- Li map

Chan, C.K. et. al Nano Lett. 2007, 7, 490-495
Example 1: $V_2O_5$ nanoribbons

Structural transformation

$V_2O_5$ $\xrightarrow{Li}$ $\omega$-$Li_3V_2O_5$

Chan, C.K. et. al Nano Lett. 2007, 7, 490-495
What is the width dependence on Li insertion?

- Red: $\omega$-Li$_3$V$_2$O$_5$
- Blue: $\gamma$-Li$_2$V$_2$O$_5$
- Yellow: V$_2$O$_5$

- More lithiation at shorter insertion lengths
- Facile phase transformation at nano vs micron scales

Chan, C.K. et. al Nano Lett. 2007, 7, 490-495
Example 1: V$_2$O$_5$ nanoribbons

Is there a thickness dependence on Li insertion?

100 nm thick and 400 nm wide remains V$_2$O$_5$

20 nm thick and 740 nm wide transforms to Li$_3$V$_2$O$_5$

- Li intercalation also depends on THICKNESS of nanoribbon
- Need facile phase transformation in all 3 axes for full lithiation

*Chan, C.K. et. al Nano Lett. 2007, 7, 490-495*
Conclusions

- How are the chemical and structural transformations different in nano vs. bulk?
  - Nanoscale dependence on change in width AND thickness
  - Fully reversible process

Example 1: \( \text{V}_2\text{O}_5 \) nanoribbons

- How can they improve device performance?
  - Higher energy density by 30%
  - Higher power density

*Chan, C.K. et. al Nano Lett. 2007, 7, 490-495*
Key science questions:

• How does nanostructuring affect physical & chemical transformations?

• What implications in device performance?
Beyond Graphite: Silicon as a Lithium Alloy Material

Example 2: Si nanowires

<table>
<thead>
<tr>
<th>Starting Material</th>
<th>C</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithiated Phase</td>
<td>LiC₆</td>
<td>Li₂₂Si₅</td>
</tr>
<tr>
<td>Theoretical Specific Capacity (mAh/g)</td>
<td>372</td>
<td>4200</td>
</tr>
<tr>
<td>Theoretical Volumetric Capacity (Ah/L)</td>
<td>833</td>
<td>9340</td>
</tr>
<tr>
<td>Packing Density (mol/mL)</td>
<td>0.0279</td>
<td>0.0851</td>
</tr>
<tr>
<td>Volume Changes (%)</td>
<td>12</td>
<td>400</td>
</tr>
</tbody>
</table>

Graphite

LiC₆

Silicon

Li₂₂Si₅ (Li₄.4 Si)
Poor Cycling Performance of Bulk Si Anodes

Example 2: Si nanowires

Lower capacity than expected
Capacity fades over time

Charge storage capacity (mAh/g)
Cycle number

10 µm Si particles (15% carbon)

Example 2: Si nanowires

Si Morphology Changes with Lithiation

Initial

After electrochemical cycling (400% volume change)

Sputtering  Electron Beam  Slurry (Si powder)

Before cycle

After 1st cycle

State of charge (S.O.C.): 0%

Sanyo
Terminal Particle Size Phenomenon

If the particle size is small enough, it will not fracture!

Example 2: Si nanowires

Critical size (µm)

Terminal particle size

Volume mismatch (strain)

Dilation strain parameter

The Problem with (Nano)particles

Initial state needed for “ideal” final state – not practical

Why Use Nanowires?

- **Large contact area w/electrolyte**
- **1D conduction pathway**
- **Short Li⁺ diffusion distances**
- **Volume expansion w/o pulverization**
- **Electrical contact**

Example 2: Si nanowires

- **Initial Nanowires**
- **After electrochemical cycling**
Example 2: Si nanowires

Vapor-Liquid-Solid (VLS) Growth of Si Nanowires

Metal nanoparticles → Metal substrate

SiH₄ 400-500 °C
CVD

Metal Nanoparticles → Si Nanowires

Scale: 10 μm
Example 2: Si nanowires

**Electrode Fabrication**

- **Cu current collector**
- **Li metal**
- **Separator soaked with electrolyte**
- **Si Nanowires**
- **Stainless steel**

Electrolyte: 1M LiPF$_6$ in ethylene carbonate/diethyl carbonate

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Example 2: Si nanowires

Structural Changes in SiNWs During Lithiation

Initial

Lithiation

Example 2: Si nanowires

Morphology Changes in SiNWs During Lithiation

Example 2: Si nanowires

Increase in length during lithiation

Example 2: Si nanowires

Step-wise Pore Evolution

Summary of Morphology Changes in SiNWs

Initial

Lithiation

Many cycles

~400% increased volume

~400% increased surface area

Observed in bulk Si

Pulverization

Example 2: Si nanowires

Electrochemical Cycling Performance

VLS SiNWs

Graphite

Example 2: Si nanowires

Role of Electrode Architecture / Scale Up

Good electron transport
Room for volume change
Large interfacial area with electrolyte

VS

Conducting carbon
Polymer binder

Compatible with roll-to-roll deposition
Example 2: Si nanowires

Electron Transport Pathways

Micron/Bulk Particles

Rigid Nanowires/Nanorods

High Aspect Ratio Nanowires

5 µm

500 nm
Example 2: Si nanowires

Silicon Nanowire Synthesis

Vapor-Liquid-Solid (VLS)

NWs tethered to substrate
Low yield (~200 ug/cm²)
Clean surfaces

Supercritical Fluid-Liquid Solid (SFLS)

Korgel Group (UT Austin)

Flow-through reactor
Higher yields (~1mg/mL, 20-40 mg/batch)
Pressurized organic solvents (400-600 °C)
Example 2: Si nanowires

Carbon Coating of Si Nanowires

A. Uncoated SiNWs

B. Carbon coated

39

Example 2: Si nanowires

SiNW/MWNT Composite

SiNW:MWNT:CMC ratio %wt of 78:12:8.5 with carbon coating 1.5%

Electronic transport improved by using MWNTs
CMC not sufficient binder for large volume changes
Possibly problems with ionic charge transfer into SiNWs

Example 2: Si nanowires

SiNWs

SiNWs/C composite

SiNCs

Graphite


Conclusions

• Fundamental studies on chemical, structural, and morphology changes in nanomaterials during electrochemical reactions can help understanding and direct design of better devices

• A nanowire-based electrode architecture was developed and led to significant improvement in electrochemical performance for the Li-Si system compared to bulk/traditional electrodes
  – Nanoscale dimension for relaxation of strain/stress
  – Space for volume expansion
  – Efficient electronic and ionic transport

• Integrating nanomaterials into conventional composites while retaining the desired properties needs improvement
Stanford Scientists Design New 40 Hour Laptop Battery

By Charlie Sorrel  
January 16, 2008 | 4:49 am | Categories: Uncategorized

Stanford Tech researchers hope to have a new kind of lithium ion battery available in a few years. The tech could boost battery life to ten times the current capacity.

Professor Yi Cui and his team resurrection an old but abandoned method for charging the batteries: Silicon anodes. These have a theoretical capacity ten times larger than that of the graphite anodes currently used, but were left for dead, as they expand up to 400 times when charged, smashing themselves in the process.

If the silicon is made into nanowires, however, the problem goes away. The silicon still expands, but doesn't pulverise the battery. Instead the nanowires jostle closer together, but don't break, and still transfer charge into the lithium. The diagram shows this best.

What does this mean for gadget lovers? It means we can quit whining about non user-replaceable batteries.
Future Work: Next Generation Cathode

Cathodes

Anodes

SiNWs
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