Overview

Timeline

- Start: Jan 1, 2011
- End: Dec. 31, 2014
- Percent complete: 85%

Budget

- Total project funding $1,200k from DOE
- Funding received in FY12 $300k
- Funding for FY13 $300k
- Funding for FY14 $300k

Barriers

Barriers of batteries
- Low energy density
- High cost
- Cycle and calendar life

Targets: high energy electrode materials and cells

Partners

- Collaboration
  - BATT program PI’s
  - PNNL: In-situ TEM
  - SLAC: In-situ X-ray
  - UT Austin: Prof. Korgel, materials
  - Stanford: Prof. Nix, mechanics; Prof. Bao, materials.
  - Amprius Inc.
Project Objective and Relevance

Objective
- To develop Si anodes with 10x specific charge capacity to replace the existing C anodes for high energy Li ion batteries for transportation, relevant to VT Program.
- To Understand and design nanostructure Si can address the challenging issues caused by the large volumetric expansion and provide a good cycle life.
- To Develop scalable low-cost methods for nanostructured Si anodes.

Si: 4200 mAh/g, 10X of carbon

For Si: volume expansion by 4 times

Si ← Li$_{4.4}$Si → Break

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<table>
<thead>
<tr>
<th>Month/year</th>
<th>Milestones</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/2013</td>
<td>Develop low cost and scalable Si yolk-shell nanostructures with stable cycle life (completed)</td>
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<tr>
<td>4/2013</td>
<td>Develop low-cost synthesis of Si nanoparticles from renewable sources (completed)</td>
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<tr>
<td>7/2013</td>
<td>Optimize nano/micro particle electrodes for high capacity, &gt;1000 cycles, &gt;99.7% CE (completed)</td>
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<tr>
<td>10/2012</td>
<td>Use in-situ TEM and ex-situ SEM to test critical size and rate for fracture for crystalline, polycrystalline, and amorphous Si nanostructures (completed)</td>
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<tr>
<td>1/2014</td>
<td>Utilize Si micro-sized particles as an anode with capacity &gt; 1500 mAh/g, and cycle life &gt;100 cycles. (completed)</td>
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<tr>
<td>4/2014</td>
<td>Stop Layer-by-layer deposition method for assembling hierarchical electrode structure if the assembly can not provide areal capacity higher than 2 mAh/cm² (completed)</td>
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<td>Go-no go</td>
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<tr>
<td>7/2014</td>
<td>Complete In-situ TEM and ex-situ SEM studies of two or multiple Si nanostructures during lithiation/delithiation to understand how neighboring particles affect each other and volume changes. (on schedule)</td>
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</tbody>
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Approach/Strategy

Advanced nanostructured Si materials design and synthesis

Structure and property characterization
- Ex-situ transmission electron microscopy
- In-situ transmission electron microscopy
- Ex-situ scanning electron microscopy

Electrochemical testing
- Coin cells and pouch cells.
- A set of electrochemical techniques.
Previous Results on Silicon Nanowire Anodes

Gen 1: Nanowire  Gen 2: Core-Shell Nanowire  Gen 3: Hollow


Gen 4: Double-walled hollow

Nature Nanotechnology, 7, 310 (2012)

Gen 5: Yolk-shell

Nano Letters, 11, 2949 (2011)

Nano Letters, 12, 3315 (2012)
Accomplishment

In-situ TEM for amorphous Si nanoparticles

- No fracture up to 800 nm

Cui group, Nano Letters, 13, 758 (2013)
Accomplishment

Si nanoparticles from abundant and cheap Source: rice husk

1.2X10^8 tons/y

Cui group, Scientific Reports, DOI: 10.1038/srep01919 (2013)
Accomplishment

Incorporation of conducting hydrogel into Si nanoparticle anodes
- Preparation and morphology

Cui group, Nature Communications, DOI: 10.1038/ncomms2941 (2013)
Accomplishment

- Battery performance

*In-situ* polymerized PANi-Si
pomegranate-inspired design for Si anode

Cui group, Nature Nanotechnology, 9, 187 (2014)
Accomplishment

- Preparation and morphology

**Si nanoparticle**

80 nm

**Si@SiO₂**

**Oil phase**

**Water phase**

**Microemulsion droplet**

**Evaporation-driven self-assembly**

**Si@SiO₂ cluster**

**Si@SiO₂@C cluster**

**Si pomegranate**

1~10 μm
Accomplishment

- Void space control

- Carbon thickness: ~5-10 nm

Etch away Si
Accomplishment

-Battery performance
Accomplishment

- High areal mass loading
Accomplishment

- Morphology change after cycling

![Before cycling](image1.png)

![After cycling](image2.png)

With SEI

Without SEI

SEI thickness: 

~150 nm

![Histogram](image3.png)

Pristine

After cycling (with SEI)

3.1 µm

3.4 µm
Collaboration and Coordination

- PNNL: In-situ TEM, Dr. C. Wang
- SLAC: In-situ X-ray, Dr. M. Toney
- UT Austin: Prof. Korgel, a-Si materials
- Stanford: Prof. Nix, mechanics; Prof. Bao, polymer materials
- Companies: Amprius Inc.
Proposed Future Work

- Understand how neighboring particles affect each other and volume changes
- Develop micro-sized Si anodes with long cycle life
- Further understand the nanoscale design to optimize Si anodes, for example, the ratio of Si material dimension vs porosity/hollow space.
- Further develop scalable and low-cost method for synthesizing nano-Si with desired performance.
- Test the Si electrodes with high areal mass loading up to 2-3mg/cm².
- Develop surface modification to increase the first cycle coulombic efficiency >90% and improve the later cycle coulombic efficiency.
Summary

- **Objective and Relevance:** The goal of this project is to develop high capacity Si anodes with nanomaterials design to enable high energy batteries, highly relevant to the VT Program goal.

- **Approach/Strategy:** This project combines advanced nanosynthesis, characterization and battery testing, which has been demonstrated to be highly effective.

- **Technical Accomplishments and Progress:** The project has produced many significant results, meeting milestones. They include identifying the fundamental materials design principles, synthesizing and testing, and developing low-cost and scalable methods. The results have been published in top scientific journal. The PI has received numerous invitations to speak in national and international conferences.

- **Collaborations and Coordination:** The PI has established a number of highly effective collaboration.

- **Proposed Future Work:** Rational and exciting future has been planned.