Overview

Timeline
• Start date: October 2012
• End date: September 2016
• 68% completed

Barriers
• Low energy
• Poor cycle/calendar life

Budget
• Total project funding: $1460K
• FY13 funding: $365K
• FY14 funding: $365K
• FY15 funding: $365K
• FY16 funding: $365K

Partners
• LBNL (L. Gao, V. Battaglia)
• PNNL (J. Zhang, C. Wang)
• UT (J. Goodenough)
Objectives

- Develop *high-capacity, low-cost electrodes* with good cycle stability and rate capability.
- Identify a method to produce *new sources of Si*.
- Understand the *mechanism of electrode degradation* by using *in-situ tools* to improve the electrode composition and architecture.
Approach

- Design of *electrode architectures* by controlling tortuosity and porosity to achieve high ionic/electronic conductivity.

- Identify a method to produce *new sources of Si*.

- Utilize *in-situ and ex-situ SEM and TEM* to investigate the failure mode and SEI layer on the anode and cathode.
Milestones

- **Completed:**
  - Production of Si nanopowder: capacity fade < 20% @100 cycles
  - In-situ TEM analysis for Si nanopowder
  - Deliverables:
    - *Si powder* to LBNL (1kg), Stanford Univ. (1kg), Penn State Univ. (0.5kg)
    - *Electrolyte*: Sep-2014, Dec-2014
    - *Cell*: 20 Ah cells (ver.1 _Sep-2014), 60 Ah cells – 250 Wh/kg (ver.2_Dec-2014)

- **On going:**
  - Optimize particle size (200 ~ 50 nm) and process conditions of Si-nano-powder.
  - Study the effect of precursors: Si, SiH₄, SiOₓ, Si-SiOₓ
  - Continue to study SEI passivation, fracture of electrode and particles by in-situ SEM, TEM, dual-beam microscope.
  - Increase the energy density to meet the requirement of the BMR program
  - Increase the loading of Si electrode: development of binder and electrode architecture
  - Characterize the gas generation in slurry and cell.
Si Production – Metallurgical Process

Typical furnace power ~ 20 MW

Carbothermal reduction:

\[ \text{SiO}_2 + 2C \rightarrow \text{Si} + 2\text{CO} \]

Price of MG-Si : ~ $3/kg
Si nano powder - 1. Metallurgical Process

- Large Si chunk
- Jaw crusher $d_{50} < 13 \text{ mm}$
- Roll crusher $d_{50} < 1 \text{ mm}$
- Jet mill $d_{50} < 10 \mu\text{m}$
- Wet mill $d_{50} < 1 \mu\text{m}$

- Low process cost
  - Jet mill $< $1/kg
  - Wet mill $< $3~4/kg
Jet Mill_Particle Size Distribution

- **Homogeneous particle size**: $D_{50} \sim 700 \, \mu m \rightarrow D_{50} \sim 7 \, \mu m$
- **Cleavage of crystalline particles**
Jet Mill_Checmical Analysis

- Oxygen content increases from 0.049% to 0.84% due to the higher surface area (formation of surface oxide).

<table>
<thead>
<tr>
<th>Element</th>
<th>Large Chunks (%)</th>
<th>After Jet mill (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>0.0030</td>
<td>0.00029</td>
</tr>
<tr>
<td>Mg</td>
<td>0.0004</td>
<td>0.0004</td>
</tr>
<tr>
<td>Al</td>
<td>0.057</td>
<td>0.075</td>
</tr>
<tr>
<td>P</td>
<td>0.0034</td>
<td>0.0034</td>
</tr>
<tr>
<td>Ca</td>
<td>0.022</td>
<td>0.023</td>
</tr>
<tr>
<td>Ti</td>
<td>0.069</td>
<td>0.077</td>
</tr>
<tr>
<td>V</td>
<td>0.0019</td>
<td>0.0021</td>
</tr>
<tr>
<td>Cr</td>
<td>0.0012</td>
<td>0.0023</td>
</tr>
<tr>
<td>Mn</td>
<td>0.015</td>
<td>0.017</td>
</tr>
<tr>
<td>Fe</td>
<td>0.31</td>
<td>0.35</td>
</tr>
<tr>
<td>Ni</td>
<td>0.0015</td>
<td>0.0022</td>
</tr>
<tr>
<td>Cu</td>
<td>0.0018</td>
<td>0.0018</td>
</tr>
<tr>
<td>Zn</td>
<td>0.0006</td>
<td>0.0004</td>
</tr>
<tr>
<td>Zr</td>
<td>0.016</td>
<td>0.0180</td>
</tr>
<tr>
<td>C</td>
<td>0.011</td>
<td>0.015</td>
</tr>
<tr>
<td>O</td>
<td>0.049</td>
<td>0.84</td>
</tr>
</tbody>
</table>
Jet Mill_Electrochemical Performance

Formation C/24

Cycle life, C/6 at RT

<table>
<thead>
<tr>
<th>Sample</th>
<th>Charge (mAh/g)</th>
<th>Discharge (mAh/g)</th>
<th>Efficiency (%)</th>
<th>Charge (mAh/g)</th>
<th>Discharge (mAh/g)</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BC4196A</td>
<td>4840</td>
<td>4283</td>
<td>88.5%</td>
<td>4300</td>
<td>4205</td>
<td>97.8%</td>
</tr>
<tr>
<td>BC4196B</td>
<td>5423</td>
<td>4802</td>
<td>88.6%</td>
<td>4847</td>
<td>4741</td>
<td>97.8%</td>
</tr>
<tr>
<td>BC4196C</td>
<td>4976</td>
<td>4406</td>
<td>88.5%</td>
<td>4438</td>
<td>4351</td>
<td>98.0%</td>
</tr>
<tr>
<td>BC4196D</td>
<td>5440</td>
<td>4836</td>
<td>88.9%</td>
<td>4872</td>
<td>4789</td>
<td>98.3%</td>
</tr>
</tbody>
</table>

Cycle life test @ SOC/DOD 100%
- Charge: CC(C/6)/CV(5mV for 15min)
- Discharge: CC(C/6) to 1.0V

- Capacity: > 4200 mAh/g with C/24 at RT
- Initial Coulombic efficiency: > 88%
- Capacity retention: ~50% at 50th cycle
Wet Mill_ Particle Distribution

- Crystalline particles without impurity
- Particle size: $D_{50} \approx 100 \text{ nm}$
- Particle size can be controlled by ball size and process time

Ball diameter: 2 mm
Wet Mill Electrochemical Performance

**Formation C/24**

- **BC4223G**
- **BC4223H**

**Cycle life, C/6 at RT**

- **Efficiency (%)**
- **Capacity (mAh/g)**

**Cycle test @ 100% SOC/DOD**
- **Charge**: CC(C/6)/CV(0.005V for 15min)
- **Discharge**: CC(C/6) to 1.0V

<table>
<thead>
<tr>
<th>Cell#</th>
<th>Charge (mAh/g)</th>
<th>Discharge (mAh/g)</th>
<th>Efficiency (%)</th>
<th>Charge (mAh/g)</th>
<th>Discharge (mAh/g)</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BC4223G</td>
<td>3509</td>
<td>2408</td>
<td>68.6%</td>
<td>2610</td>
<td>2469</td>
<td>94.6%</td>
</tr>
<tr>
<td>BC4223H</td>
<td>3917</td>
<td>2699</td>
<td>68.9%</td>
<td>2863</td>
<td>2716</td>
<td>94.9%</td>
</tr>
</tbody>
</table>

- **Capacity**: ~2500 mAh/g with C/24 at RT
- **Initial Coulombic efficiency**: < 67%
- **Capacity retention**: ~73% at 200th cycle
Si nano powder - 2. Plasma Process

- Silicone powder (µm size, 99.999wt%)
  - Heat vapor
  - Quenching
  - Si nanopowder

- High process cost > $50/kg
Characterization of Plasma-Nano Si

SEM
 ✓ Spherical shape
 ✓ Dia. 50 to 200 nm

TEM
 ✓ Crystalline lattice in the silicon nanoparticles
 ✓ Contamination-free atomic surface

XRD
 ✓ c-Si with diamond cubic lattice
   \(a = 5.43 \text{ Å}\)
 ✓ No impurity phase detected

PSD: \(D_{50} = 85 \text{ nm}\)

BET: 30 \(\text{m}^2/\text{g}\)
Micro-Si (electrode)

- In-situ evolution of micron-sized Si particles on real time cycling
- Cracking of particles leading to the loss of electrode integrity
Nano-Si (electrode)

- No cracking for nano-sized particles.
- Even the biggest particles (200 nm) did not crack.
- Advanced electrode architecture with nano Si is needed for commercialization.
Nano-Si (electrode)

- **In-situ** evolution of nano-sized Si particles on real time cycling
- Electrode densification after lithiation
Silicon nanoparticles were loaded on a platinum electrode.

Lithium metal was loaded on a tungsten tip, which was fixed to a piezosystem, with lithium oxide surface layer serving as a solid electrolyte.

Insertion of lithium into Si particles was controlled by application of bias voltage of -2 to -5 V.

Titan 80-300 with a probe corrector was operated at 300 kV for imaging.

Dominic Leblanc, Chongmin Wang, Yang He, Daniel Bélanger, Karim Zaghib
In situ TEM : Si/Li$_2$O/Lithium
a) **Particles in discharged state**: 50 – 200 nm spheres

b) **Initiation of lithium insertion**: rapid reaction from the surface forms a core-shell structure.

c) **Growth of amorphous Li\textsubscript{x}Si alloy**: particle expansion without collapsing
Discharge capacity of 3500 mAh/g was achieved at 100% SOC/DOD.

SOC should be limited to < 40% in order to reach the cycle life > 100 cycles.

Useable capacity at 40% SOC : ~1670 mAh/g.

Cycle life > 200 cycles
Effect of Electrode Loading

- Electrode chemical performance of Si electrode is highly dependent on the electrode loading.
- Cycle life > 700 cycles at the low loading of 0.45 mg/cm².

### Table: Coating Gap, Loading Level, C-rate, and Cycle Life

<table>
<thead>
<tr>
<th>Coating Gap (mil)</th>
<th>Loading Level (mg/cm²)</th>
<th>C-rate</th>
<th>Cycle</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.45</td>
<td>O</td>
<td>&gt;700</td>
</tr>
<tr>
<td>3</td>
<td>0.75</td>
<td>O</td>
<td>&gt;400</td>
</tr>
<tr>
<td>5</td>
<td>0.99</td>
<td>Δ</td>
<td>&gt;250</td>
</tr>
<tr>
<td>6</td>
<td>1.26</td>
<td>X</td>
<td>&gt;100</td>
</tr>
<tr>
<td>10</td>
<td>1.96</td>
<td>XX</td>
<td>&lt;50</td>
</tr>
</tbody>
</table>
Design of Large Format Cell (ver.1)

- **Cathode**: HV LMNO
- **Anode**: nano Si
- **Cathode determining design with limited utilization (40%) of anode**
Process Flow (Automatic Pilot Line)

LMNO  Carbon  PVDF/NMP  Si-nano  Carbon  Alginate/Water

Mixing  Coating  Pressing  Cutting  Drying

Mixing  Coating  Pressing  Cutting  Drying

Separator

Stacking  EL Injection  Formation  Grading

Electrolyte
Test Condition
- Charge : CC(6.7A)/CV(4.9V to 1A) at RT
- Discharge : CC(6.7A) to 3.5V at RT
Issues in Manufacturing Process (ver.1)

LMNO  Carbon  PVDF/NMP  Si-nano  Carbon  Alginate/Water

Mixing  Coating  Pressing  Cutting  Drying

Mixing  Coating  Pressing  Cutting  Drying

Separator

Stacking  EL Injection

Formation  Grading

Electrolyte

Deliverable w/o EL  Main-formation  Pre-formation  Pressing
Severe Gas Generation (ver.1)

NCM vs. Graphite

LMNO vs. Si-nano

EL Injection
Pre-formation
Degassing
Main formation
2nd-degassing
3rd-degassing
4th-degassing
5th-degassing
Grading
3 cycles
3rd-grading
3 cycles
2nd-grading
3 cycles
4th-degassing
3 cycles
5th-degassing
1 step
Discharge
1 step
6th-degassing
1 step
Charge
1 step
Discharge

SOC
0%
100%
40%
30%
100%
30%
30%
100%
100%

Gas
Gas
Gas
Gas
Gas
Gas
Gas
Gas
Gas

https://www.liv.ac.uk/chemistry/research/hardwick-group/research/
Cycle Test : Coin-type Full Cell (ver.1)

- **Cycle life** : *<70% at 50th cycle*
- **Coulombic efficiency** : *98.6 ± 0.2 %*
  - Continuous lithium consumption

- **Post mortem analysis after 80 cycles**
  1. Complete discharge to 3.5V with floating for 12hrs
  2. Open the full cell and collect the electrodes
  3. Re-assemble the half cells using the cathode and anode respectively
Post Mortem Analysis Cathode Half Cell

Cathode performance is completely recovered in the half cell.

Capacity decay in full cell is due to the mismatch of anode-cathode balance, caused by the irreversible loss of lithium.

**Test Condition**

- **Charge**: CC(C/3)/CV(4.9V for 15 min)
- **Discharge**: CC(C/3) to 3.5V

<table>
<thead>
<tr>
<th>C-rate</th>
<th>Charge (mAh/g)</th>
<th>Discharge (mAh/g)</th>
<th>Charge (mAh/g)</th>
<th>Discharge (mAh/g)</th>
<th>Unused Capacity</th>
<th>Capacity Retention in Full Cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>BC4307A</td>
<td>101</td>
<td>125</td>
<td>142</td>
<td>129</td>
<td>28.9%</td>
<td>63%</td>
</tr>
<tr>
<td>BC4307C</td>
<td>-</td>
<td>66</td>
<td>141</td>
<td>129</td>
<td>51.1%</td>
<td>49%</td>
</tr>
</tbody>
</table>
Anode Half Cell, C/24

<table>
<thead>
<tr>
<th>C-rate</th>
<th>Discharge (mAh/g)</th>
<th>Charge (mAh/g)</th>
<th>Discharge (mAh/g)</th>
<th>Charge (mAh/g)</th>
<th>Capacity Loss (mAh/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BC4307A</td>
<td>4</td>
<td>3284</td>
<td>2828</td>
<td>2888</td>
<td>-</td>
</tr>
<tr>
<td>BC4307C</td>
<td>-</td>
<td>3221</td>
<td>2724</td>
<td>2613</td>
<td>-</td>
</tr>
</tbody>
</table>

Test Condition
- Charge: CC(C/6)/CV(5mV for 15 min, or SOC40% at RT
- Discharge: CC(C/6) to 1.0V at RT

- Anode performance is **completely recovered** in the half cell.
- Capacity decay in full cell is due to the mismatch of anode-cathode balance, caused by the **irreversible loss of lithium**.
Design of Large Format Cell (ver.2)

- **Target**: specific energy >250 Wh/kg
- **Cathode- limited design**: HE NCM
- **Anode utilization**: 90% of usable capacity
Voltage Profile

Ver. 1
- Charge: CC(6.7A)/CV(4.9V to 1A) at RT
- Discharge: CC(6.7A) to 3.5V at RT

Ver. 2
- Charge: CC(20A)/CV(4.4V to 3A) at RT
- Discharge: CC(20A) to 2.5V at RT

- No gas generation in ver. 2
- Cell thickness change: ~7.4% (SOC 100% vs. 0%)
## Rate Capability (ver.2)

**Discharge C-rate at RT, 2.5~4.4V**

<table>
<thead>
<tr>
<th>C-rate</th>
<th>Capacity (Ah)</th>
<th>Retention (%)</th>
<th>Average. V (V)</th>
<th>Energy (Wh)</th>
<th>Energy Density (Wh/kg)</th>
<th>Energy Density (Wh/L)</th>
<th>Max. Temp. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C/3_20A</td>
<td>59.9</td>
<td>100%</td>
<td>3.481</td>
<td>209</td>
<td>237</td>
<td>445</td>
<td>27</td>
</tr>
<tr>
<td>C/2_30A</td>
<td>56.6</td>
<td>95%</td>
<td>3.494</td>
<td>198</td>
<td>225</td>
<td>423</td>
<td>29</td>
</tr>
<tr>
<td>1C_60A</td>
<td>53.8</td>
<td>90%</td>
<td>3.467</td>
<td>187</td>
<td>212</td>
<td>399</td>
<td>33</td>
</tr>
<tr>
<td>1.3C_80A</td>
<td>52.3</td>
<td>87%</td>
<td>3.446</td>
<td>180</td>
<td>205</td>
<td>385</td>
<td>38</td>
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<tr>
<td>1.7C_100A</td>
<td>50.9</td>
<td>85%</td>
<td>3.422</td>
<td>174</td>
<td>198</td>
<td>372</td>
<td>42</td>
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</tbody>
</table>

**Test Condition**
- Charge: CC(C/3)/CV(4.4V to 3A) at RT
- Discharge: CC to 2.5V at RT
## Specification: ver.1 vs. ver.2

<table>
<thead>
<tr>
<th>Item</th>
<th>Unit</th>
<th>Version1</th>
<th>Version2</th>
<th>Remark</th>
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<tbody>
<tr>
<td><strong>Material</strong></td>
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</tr>
<tr>
<td>Cathode</td>
<td>-</td>
<td>HV LMN</td>
<td>HE NCM</td>
<td></td>
</tr>
<tr>
<td>Anode</td>
<td>-</td>
<td>Nano Si</td>
<td>Nano Si</td>
<td></td>
</tr>
<tr>
<td>Binder</td>
<td>-</td>
<td>Alginate</td>
<td>Alginate</td>
<td></td>
</tr>
<tr>
<td>Separator</td>
<td>-</td>
<td>Ceramic</td>
<td>Ceramic</td>
<td></td>
</tr>
<tr>
<td>Electrolyte</td>
<td>-</td>
<td>EC/DEC/FEC</td>
<td>EC/DEC/FEC</td>
<td></td>
</tr>
<tr>
<td><strong>Cell</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Capacity</td>
<td>(Ah)</td>
<td>19</td>
<td>64</td>
<td>@ C/3</td>
</tr>
<tr>
<td>Average Voltage</td>
<td>(V)</td>
<td>4.246</td>
<td>3.433</td>
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</tr>
<tr>
<td>Specific Energy</td>
<td>(Wh/kg)</td>
<td>124</td>
<td>250</td>
<td></td>
</tr>
<tr>
<td>Energy Density</td>
<td>(Wh/L)</td>
<td>204</td>
<td>437</td>
<td></td>
</tr>
<tr>
<td>Thickness</td>
<td>(mm)</td>
<td>-</td>
<td>9.13</td>
<td>@ SOC100</td>
</tr>
<tr>
<td>Width</td>
<td>(mm)</td>
<td>216</td>
<td>216</td>
<td></td>
</tr>
<tr>
<td>Length</td>
<td>(mm)</td>
<td>255</td>
<td>255</td>
<td></td>
</tr>
<tr>
<td>Weight</td>
<td>(g)</td>
<td>653</td>
<td>880</td>
<td></td>
</tr>
<tr>
<td>Gas</td>
<td></td>
<td>No Gas</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Summary

- **Completed:**
  - Production of Si nanopowder: capacity fade less than 20% @100 cycles.
  - In-situ TEM analysis for Si nanopowder
  - Sample delivery
    - **Si powder** to LBNL (1kg), Stanford Univ. (1kg) and Penn State Univ. (0.5kg)
    - **Si anode electrode** to LBNL (Jun-2014, Sep-2014, Dec-2014) with Gr electrode (Dec-2014), to Utah Univ.
    - **Cathode electrode**: HV LMN (Sep-2014), HE NCM (Dec-2014), NCM-LMO (Dec-2014) to LBNL
    - Electrolyte (Sep-2014, Dec-2014) to LBNL
    - **20 Ah large format cell**: ver.1 (Sep-2014) to LBNL
    - **60 Ah large format cell** (250 Wh/kg): ver.2 (Dec-2014) to LBNL
Future Activities

- **On going:**
  - Optimize the particle size (200 ~ 50 nm) and process conditions of nano-Si powder.
  - Study the effect of precursor composition: Si, SiO_x, Si-SiO_x.
  - Synthesis of secondary particles using spray-dry process.
  - Continue to study SEI passivation, fracture of electrode and particles by in-situ SEM, TEM, dual-beam microscope.
  - Increase the energy density to meet the requirement of BMR program.
  - Increase the loading Si electrode: further development of binder and electrode architecture.
  - Characterize the gas generation in slurry and cell.
  - Surface treatment of nano-Si powder by using spry dryer.
  - HQ wants to be a provider of baseline nano-Si powder for BMR program and supply it to PI’s without NDA.
Dual-beam(electron+ion) Microscope

- Dual-beam microscope for in-situ specimen preparation and 3D characterization
- ‘One of a kind’ instrument
  - TOF-SIMS (H, Li, …)
  - 2 EDS (Li detectable)
  - 1 EBSD
  - 2 BSE detector
  - 5 gas injections
  - 1 micro-manipulator
New Pouch Cell Assembly Line (1-5Ah)

- Coin Half Cell
  - Coin type

- 1-5 Ah Full Cell
  - Cylindrical type (1~3 Ah)
  - Pouch type (1~5 Ah)

- 10~50 Ah Full Cell
  - Pouch type (10~50 Ah)

Steps:
- Stamping
- Z-Stacking
- Tab Welding
- Pouch Forming
- Side Sealing
- Electrolyte Filling

- Formation
- Degassing
- Pouch Cutting
- Hot Press
- OCV/IR Check
- Pouch Cell

[Image of various assembly line machines]