Development of Si-Composite Anode for Large-Format Li-ion Batteries

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Hydro-Quebec

June 9, 2016

Project ID : ES222

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Overview

Timeline
• Start date: October 2012
• End date: September 2016
• 81% completed

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

Barriers
• Low energy
• Poor cycle/calendar life

Partners
• LBNL (V. Battaglia)
• PNNL (J. Zhang)
• 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 nano-Si*.

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

Accomplishments

- Production of *nano*-Si powder: Milling process vs. Plasma process.
- Study the effect of precursor composition: Si, SiO$_x$.
- Synthesis of *nano*-Si/Carbon composite using spray-dry process.
- Characterize the gas generated in slurry and cell.

Deliverables to Collaborators

- *nano-Si powder*: ANL, 900g (B. Polzin, July-2015).
- *nano-Si anode electrode*: LBNL, 10m of *nano*-Si electrode (V. Battaglia, Jun-2015).
- *nano-Si/NCM cells*: LBNL, 2 dry cells of 49.5 Ah (V. Battaglia, Sep-2015).
On going:

- Optimize nano-Si/C composite using spray-dry process.
- Continue to study the effect of precursors in Plasma process: Si, SiO$_x$, Si-SiO$_x$.
- Continue to study SEI passivation, fracture of electrode and particles by *in-situ* SEM, dual-beam microscope.
- Increase the loading of Si electrode: development of binder and electrode architecture.
Contents

- Material Development
  - *nano*-Si powder by Milling process
  - *nano*-SiO$_x$ powder by Plasma process
  - *nano*-Si/C composite by Spray dryer process

- Process and Cell Development
  - Gas generation in water-based alginate binder
    - Mixing, Coating and Formation process
  - Cell performance evaluation of the deliverable Y2015

- Post-mortem analysis
Milling Process → Low $ nano-Si Powder

**Milling Process in Y2014**

- **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 I** $d_{50} < 0.2 \mu\text{m}$

**Low process cost**
- Jet mill $< 1$/kg
- Wet mill $< 3\sim4$/kg

**Milling Process in Y2015**

- **Parameter control**
- Milling time (Y15)
- Beads size (Y15)
- Solid contents (Y16)
- Power (Y16)

- **Wet mill II** $d_{50} \sim 0.1 \mu\text{m}$
Milling Process → Bead Size Effect

**Bead Size; 2.0 mm (Y14)**

0 hr

1 hr

3 hrs

5 hrs

21 hrs

**Bead Size; 1.0 mm 4hrs (Y15)**

0 hr

0.5 hr

3 hrs

- Process time was reduced by bead size control; from 5hrs to 30 min to reach the sub-micron size.
# Milling Process → ø 1.0 mm Beads

<table>
<thead>
<tr>
<th>Jet-mill</th>
<th>Wet-mill : 1.0 mm (10 hrs)</th>
<th>Wet-mill : 1.0 mm (24 hrs)</th>
</tr>
</thead>
</table>

- **Jet-mill**
- **Wet-mill : 1.0 mm (10 hrs)**
- **Wet-mill : 1.0 mm (24 hrs)**

- Mean particle size is limited to ~100 nm : Bead size ø1.0 → ø0.3 mm.
Mean particle size measured by PSA remains at ~100 nm.

The 2\textsuperscript{nd} wet-milling using $\varnothing 0.3$ mm generates the nanometric primary particles of < 50 nm with the blunt edges.
**Milling Process → Electrochemical Test**

**Formation C/24**

- nano-Si (Plasma Process)
- Si Powder (Jet-mill)

**Plasma 3108 2527 2651 2501 81.3 94.2**

**Bio-mill**

<table>
<thead>
<tr>
<th>Process</th>
<th>Charge 1 (mAh/g)</th>
<th>Discharge 1 (mAh/g)</th>
<th>Charge 2 (mAh/g)</th>
<th>Discharge 2 (mAh/g)</th>
<th>Efficiency 1 (%)</th>
<th>Efficiency 2 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plasma</td>
<td>3108</td>
<td>2527</td>
<td>2651</td>
<td>2501</td>
<td>81.3</td>
<td>94.2</td>
</tr>
<tr>
<td>Jet-mill</td>
<td>3937</td>
<td>3401</td>
<td>3351</td>
<td>3065</td>
<td>86.4</td>
<td>91.5</td>
</tr>
<tr>
<td>Wet-mill (φ1.0 mm)</td>
<td>3513</td>
<td>2879</td>
<td>2954</td>
<td>2835</td>
<td>81.9</td>
<td>96.0</td>
</tr>
<tr>
<td>Wet-mill (φ0.3 mm)</td>
<td>3220</td>
<td>2495</td>
<td>2625</td>
<td>2512</td>
<td>77.5</td>
<td>95.7</td>
</tr>
</tbody>
</table>

- The cumbolic efficiency and capacity are lowered with more grinding.
  - Jet-mill > Wet-mill φ1.0 mm > Wet-mill φ0.3 mm
Milling Process → Electrochemical Test

Nano-Si made by milling process shows better cycle performance than that of nano-Si obtained by Plasma process.

![Graph showing cycle life and capacity for different nano-Si and Si Powder samples.](image-url)

**Electrode** | **Nano-Si (1.0mm)** | **Nano-Si (0.3mm)**
--- | --- | ---
**TOTAL Loading (mg/cm²)** | 2.75 | 2.1

½ cell (Lithium 200µm) at RT
Electrolyte: 1M LiPF6 EC DEC + 10% FEC
Voltage cut-off: 0.005 ~ 1.0 V
Plasma Process $\rightarrow$ nano-$\text{SiO}_x$ Powder

**Plasma Process in Y2014**

- Micrometric powder $\rightarrow$ Plasma gas
  - RF electrical supply (MHz)
  - Magnetic coupling
  - Nucleation zone
  - Nanopowder

- Cloud of metal vapor

**Silicone powder** (µm size, 99.999wt%)

**Heat** $\rightarrow$ **Metal vapor** $\rightarrow$ **Quenching** $\rightarrow$ **nano-Si Powder**

- High process cost $>50$/kg

**Plasma Process in Y2015**

- New precursor
  - $\text{SiO}_x$
- Operation parameter
  - Quench condition (Y15)
  - Feeding rate (Y15)
Plasma Process → Process Control

Raw Material

SiOₓ Ver.1

SiOₓ Ver.2; Quenching Speed ↓

- SiOₓ with primary particle size <100 nm was obtained by plasma process
Plasma Process → Electrochemical Test

### Formation C/24

<table>
<thead>
<tr>
<th></th>
<th>Charge 1 (mAh/g)</th>
<th>Discharge 1 (mAh/g)</th>
<th>Charge 2 (mAh/g)</th>
<th>Discharge 2 (mAh/g)</th>
<th>Efficiency 1 (%)</th>
<th>Efficiency 2 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference</td>
<td>2280</td>
<td>1383</td>
<td>1430</td>
<td>1379</td>
<td>60.6</td>
<td>96.5</td>
</tr>
<tr>
<td>Version 1-A</td>
<td>2432</td>
<td>1057</td>
<td>1164</td>
<td>1067</td>
<td>43.5</td>
<td>91.7</td>
</tr>
<tr>
<td>Version 1-B</td>
<td>2095</td>
<td>1008</td>
<td>1091</td>
<td>1024</td>
<td>48.1</td>
<td>93.8</td>
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<tr>
<td>Version 2-A</td>
<td>2757</td>
<td>1205</td>
<td>1316</td>
<td>-</td>
<td>43.7</td>
<td>-</td>
</tr>
<tr>
<td>Version 2-B</td>
<td>2237</td>
<td>1187</td>
<td>1277</td>
<td>-</td>
<td>53.0</td>
<td>-</td>
</tr>
</tbody>
</table>

> **Lower quenching speed in the plasma process leads to better capacity.**
Nano-SiO_x shows improved cycle life compared to the pristine SiO_x.

Lower quenching speed leads to better cycle life.
Plasma Process $\rightarrow$ Electrochemical Test

**Formation C/24**

- nanos-$\text{SiO}_x$ Version 2-B

**Stability +/- C/6**

- nanos-$\text{SiO}_x$ Version 2-B $\rightarrow$ ~1.2 mAh/cm$^2$

### Project Outline

- Material Development
- Cell and Process Development
- Post-Mortem Analysis

### Electrode Version 2-B

| Thickness (µm) | 39 |
| Vol. Density (g/cm$^3$) | 0.68 |
| Loading Total (mg/cm$^2$) | ~1.82 |

### Performance Metrics

<table>
<thead>
<tr>
<th>Version 2-B</th>
<th>Discharge 1 (mAh/g)</th>
<th>Charge 1 (mAh/g)</th>
<th>Discharge 2 (mAh/g)</th>
<th>Charge 2 (mAh/g)</th>
<th>Efficiency 1 (%)</th>
<th>Efficiency 2 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Discharge 1</td>
<td>2464</td>
<td>1340</td>
<td>1439</td>
<td>1362</td>
<td>54.4</td>
<td>94.7</td>
</tr>
</tbody>
</table>

- **Nano-$\text{SiO}_x$ shows very stable cycle life even with high electrode loading.**
Micro-sized Si/C composite was prepared by Spray-drying process, using the nano-Si primary particles.
Nano-Si/C composite shows comparable cycle performance to that of original nano-Si (plasma).
With polyimide binder, adhesion strength of electrode was improved, which permits higher loading: 2.9 mg/cm².
Gas generation → In Mixing Process

# Possible cause; Hydrolysis

$$2Si + 2H_2O \rightarrow 2SiOH + H_2(g)$$

# Approaches

1. Surface coating of nano-Si powder; Spray dryer
2. pH control with additives
3. Surface oxidation by low temperature heat-treatment; 24hrs, 80~150°C
4. Aging the slurry more than 24hrs

<table>
<thead>
<tr>
<th>Aging</th>
<th>Mixing Condition</th>
<th>Vials</th>
<th>Slurry</th>
<th>Sample Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>24 hrs</td>
<td>Si+Water</td>
<td>20 ml</td>
<td>5 ml</td>
<td>5 ml</td>
</tr>
<tr>
<td></td>
<td>Si+Water+Add.</td>
<td>20 ml</td>
<td>5 ml</td>
<td>5 ml</td>
</tr>
<tr>
<td></td>
<td>Si+Water+HT</td>
<td>20 ml</td>
<td>5 ml</td>
<td>5 ml</td>
</tr>
<tr>
<td></td>
<td>Si+Water+HT+Add.</td>
<td>20 ml</td>
<td>5 ml</td>
<td>5 ml</td>
</tr>
<tr>
<td>48 hrs</td>
<td>Si+Water</td>
<td>20 ml</td>
<td>5 ml</td>
<td>5 ml</td>
</tr>
<tr>
<td></td>
<td>Si+Water+Add.</td>
<td>20 ml</td>
<td>5 ml</td>
<td>5 ml</td>
</tr>
<tr>
<td></td>
<td>Si+Water+HT</td>
<td>20 ml</td>
<td>5 ml</td>
<td>5 ml</td>
</tr>
<tr>
<td></td>
<td>Si+Water+HT+Add.</td>
<td>20 ml</td>
<td>5 ml</td>
<td>5 ml</td>
</tr>
</tbody>
</table>

(Add. ; Additive for pH control, HT ; Heat-treatment)

- **H₂** is the main component in the generated gas from the water-based slurry.
- Gas generation can be suppressed by pH control of slurry and heat-treatment of Si.
Gas generation $\rightarrow$ PAA Coating on nano-Si

**Surface Coating of nano-Si Powder**

Methanol + PAA + Si

Si + Poly(acrylic acid)

nano-Si in H$_2$O

10 min after MX

24 hrs

pH 7.14

Surface coated nano-Si in H$_2$O

10 min after MX

24 hrs

pH 4.7

➢ Gas generation in water-based slurry is greatly suppressed by PAA coating on Si surface.
Due to the processing issues related with the gas generation, polyimide binder system was selected for the deliverable in Y2015.
Gas generation → In Coating Process

# Possible cause

*Air entrainment* during the coating process; *Fluid mechanics*

→ Approaches

(1) Coating method; Direct-comma, die-coating, gravure coating etc.

(2) Use additives; defoamer, air release additive

(3) Control process parameters; viscosity, speed, loading level etc.

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**Reverse-comma roll method**

**Direct-comma roll method**

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Post-Mortem Analysis

Cell and Process Development

Material Development

Project Outline
Gas generation → In Formation cycle

# Possible cause; Electrolyte decomposition at high voltage of LMNO (>4.9V)
1.0M LiPF₆ in EC/DEC 3/7 + 10wt% FEC

→ Approaches

(1) Change the cathode; LMNO (~5.0V) → NCM (~4.5V)
(2) Develop new electrolytes/additives for high voltage application
(3) Surface treatment of LMNO powder to stabilize SEI

- H₂, O₂ and CO₂ are main components.
- CH₄ and C₂H₄ are also detected.

- No gas generation during the formation step from the cell using NCM cathode.
Cathode-limited design: HE NCM (Ni 70%)  
Anode utilization: 90% of usable capacity  
Lowered anode efficiency: 76% vs. 88%
Voltage Profile (Y2015 vs. Y2014)

**Y2015**

- **Average Voltage**: 3.4 V
- **Charge**: CC(20A)/CV(4.4V to 3A) at RT
- **Discharge**: CC(20A) to 2.5V at RT

**Y2014_Ver.1**

- **Average Voltage**: 3.3 V
- **Charge**: CC(20A)/CV(4.4V to 3A) at RT
- **Discharge**: CC(20A) to 2.5V at RT

**Y2014_Ver.2**

- **Average Voltage**: 4.2 V
- **Charge**: CC(6.7A)/CV(4.9V to 1A) at RT
- **Discharge**: CC(6.7A) to 3.5V at RT

- **No gas generation during cycle**
- **Rated capacity**: 45Ah
- **Energy density**: 193 Wh/kg
Rate Capability (Y2015)

**Current** | **Capacity** | **Retention** | **Average. V** | **Max. Temp.**
---|---|---|---|---
C/10_5A | 43,8 | 100% | 3,489 | 24
C/5_10A | 40,1 | 92% | 3,505 | 27
C/3_16,7A | 37,0 | 85% | 3,508 | 30
C/2_25A | 34,1 | 78% | 3,507 | 32
1C_50A | 30,3 | 69% | 3,477 | 39
2C_100A | 26,5 | 60% | 3,409 | 48

High power capability enables 100A discharge

**Test Condition**
- Charge: CC(C/3)/CV(4.4V to 2.5A) at RT
- Discharge: CC to 2.5V at RT
Full cell shows limited cycle life due to the low coulombic efficiency.

Half cells show much stable cycle life for both cathode and anode.
# Specification (Y2015 vs. Y2014)

<table>
<thead>
<tr>
<th>Item</th>
<th>Unit</th>
<th>2015</th>
<th>2014</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td><strong>Version1</strong></td>
<td><strong>Version2</strong></td>
<td></td>
</tr>
<tr>
<td><strong>Material</strong></td>
<td></td>
<td><strong>Remark</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cathode</td>
<td>-</td>
<td>HE NCM (Ni 70%)</td>
<td>HV LMN</td>
<td>HE NCM (Ni 60%)</td>
</tr>
<tr>
<td>Anode</td>
<td>-</td>
<td>Nano Si</td>
<td>Nano Si</td>
<td>Nano Si</td>
</tr>
<tr>
<td>Anode Binder</td>
<td>-</td>
<td>Polyimide</td>
<td>Alginate</td>
<td>Alginate</td>
</tr>
<tr>
<td>Separator</td>
<td>-</td>
<td>Ceramic</td>
<td>Ceramic</td>
<td>Ceramic</td>
</tr>
<tr>
<td>Electrolyte</td>
<td>-</td>
<td>EC/DEC/FEC</td>
<td>EC/DEC/FEC</td>
<td>EC/DEC/FEC</td>
</tr>
<tr>
<td><strong>Capacity</strong></td>
<td>(Ah)</td>
<td>46.7</td>
<td>19</td>
<td>64</td>
</tr>
<tr>
<td><strong>Average Voltage</strong></td>
<td>(V)</td>
<td>3.427</td>
<td>4.246</td>
<td>3.433</td>
</tr>
<tr>
<td><strong>Specific Energy</strong></td>
<td>(Wh/kg)</td>
<td>193</td>
<td>124</td>
<td>250</td>
</tr>
<tr>
<td><strong>Energy Density</strong></td>
<td>(Wh/L)</td>
<td>398</td>
<td>204</td>
<td>437</td>
</tr>
<tr>
<td><strong>Thickness</strong></td>
<td>(mm)</td>
<td>11.5</td>
<td>-</td>
<td>9.13</td>
</tr>
<tr>
<td><strong>Width</strong></td>
<td>(mm)</td>
<td>216</td>
<td>216</td>
<td>216</td>
</tr>
<tr>
<td><strong>Length</strong></td>
<td>(mm)</td>
<td>255</td>
<td>255</td>
<td>255</td>
</tr>
<tr>
<td><strong>Weight</strong></td>
<td>(g)</td>
<td>830</td>
<td>653</td>
<td>880</td>
</tr>
<tr>
<td><strong>Thickness increase at 1st charge</strong></td>
<td>-</td>
<td>Gas</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- **Polyimide binder leads to significant increase of cell thickness with lowered columbic efficiency.**
Thickness Increase Issue

**Photos after cycle life test (large format)**

- Significant deformation during the 1st charge, leading to the thickness increase of the cell; more than 60%. Part of anode electrode is transformed to separator surface.
- Thickness increase is more dominant at high SOC (>80%) → SOC control is required for longer cycle life.
- Alginate binder shows less thickness increase at <SOC60%.

**Thickness evolution with SOC (small format)**

- Alginate binder shows less thickness increase at <SOC60%.
Post mortem analysis was conducted after 1st cycle, 10th cycles and 50th cycles: SEM, 3D optical microscope, TOF-SIMS and Dual Beam Microscope were used.

The electrode deformation appears even after the 1st cycle.
Roughness of nano-Si anode increases more than 600% after 50th cycles.
Significant fractures are developed from the 1st cycle and getting worse with cycles.
SEM → Cross-Section

- Significant thickness increase and electrode deformation with cycles.
- The electrodes are partly detached from the current collector.
**TOF-SIMS Analysis → After 10th cycles**

- HQ is capable of analyzing the Li distribution using its unique microscopy.
- Li distribution varies with the morphology change.
Local X-ray Analysis (FIB X-section)

- Fresh Electrode
- After 10th cycles

> Increase of oxygen content after cycle, especially at the surface.
Local Chemical Analysis Comparison

Spectra taken in the Nano-Si agglomerates phase (3 µm x 3µm area)

- Si intensity decreases with enhanced O K intensity over cycles; Si K intensity is only half of the fresh electrode after 10 cycles.
- SEI layer is regenerated continuously on cycling.
Summary

- Cycle life of metallurgical Si was greatly improved by optimizing the milling conditions and the particle size.
- SiO_x obtained by plasma process showed improved capacity retention at cycle life test.
- Nano-Si/C composite was developed using a spray-dry technique to suppress the gas generation in the water-based slurry.
- The gas generated during the slurry mixing process was identified as H_2, which was effectively suppressed by using a polyimide binder.
- Post-mortem analysis using dual beam SEM and TOF-SIMS revealed significant electrode deformation along with the accumulation of electrolyte decomposition products.
- HQ has delivered the large-format cells (46.5 Ah) using the developed material, as well as Si-powder (0.9kg) and Si-electrode (10m).
Future Activities (Y2016)

- Optimize nano-Si/C composite
  - 1st Deliverable; Si/C Powder → End of March, 2016

- Develop high loading electrode using nano-Si/C composite with optimized electrode architecture.
  - 2nd Deliverable; Si Electrode → End of June, 2016

- Verify the performance of developed electrode using 2Ah pouch cells
  - 3rd Deliverable; 2Ah Cells → End of September, 2016

- Study the evolution of SEI passivation and electrode morphology by using in-situ SEM and dual-beam microscope.