Electrode Architecture-Assembly of Battery Materials and Electrodes

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DOE-BATT Review Meeting

ID # ES222

This presentation does not contain any proprietary or confidential information
Overview

Timeline
- Start date: March 2013
- End date: December 2016
- 35% completed

Budget
- Total Project Funding: $2.92M

<table>
<thead>
<tr>
<th></th>
<th>DOE</th>
<th>HQ</th>
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<tbody>
<tr>
<td>FY13 funding</td>
<td>$365K</td>
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<td>FY14 funding</td>
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<td>FY16 funding</td>
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Barriers
- Low energy
- Poor cycle/calendar life

Partners
- V. Battaglia, V. Srinivasan and R. Kostecki (LBNL)
- J. Goodenough (U. Texas)
- C. Julien, A. Mauger (U. Paris 6)
- X.Q. Yang (BNL)
Objectives

➢ Develop high-capacity, low-cost electrodes with good cycle stability and rate capability.

➢ Identify a low-cost method to produce Si nano-powder.

➢ Identify the mechanism of electrode degradation by using *in-situ* tools to improve the electrode composition and architecture.
Approach

- Design of electrode architecture by controlling tortuosity and porosity and maintaining high ionic conductivity.

- Develop an improved electrode architecture of Si nano-particles with carbon and water-based binders.

- Metallurgical Si is used to produce a low cost Si nano-powder.

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

- **Completed:**
  - Identify Si-based anode materials that can achieve a capacity of 1200 mAh/g.
  - Supply Si powder (1 Kg) from an alternative supplier as a baseline material for BATT PIs.

- **On going:**
  - **Go/No-Go:** Terminate production of Si powder in anode tests that show more than 20% capacity fade in the initial 100 cycles.
  - **Criteria:** Supply laminates Si-based electrodes to BATT PIs.
  - Supply a 20-Ah Li-ion flat cell based on Si and LiMNO materials to BATT PIs.
Plan to Achieve Milestones

Si-Anode Fabrication

- Powder Mixing
  - Carbon type (Fiber vs. particles)
  - Carbon ratio

- Slurry Preparation
  - Binder type (water vs. solvent)
  - Slurry composition
  - Mixing method

- Film Coating
  - Drying conditions control on pilot line machine: (T, speed)
  - Environmental binder

- New Current Collector
  - Metal with embossed surface

Tortuosity & Porosity Optimization

Improve interface adhesion
Powder Dispersion

**Step 1**
Premix step prevents the agglomeration (macrophase separation) of carbon and active materials.

Si + C or graphene →  
VGCF or CNT

**Step 2**
Then, carbon fibers will be added to improve the electric contact between Si particles even after volume expansion.

+ VGCF or CNT →

VGCF: vapor growth carbon fiber  
CNT: carbon nanotube
Effect of Mixing Method on Cycling & Impedance

The jar-mill alone is not effective as a mixing method.

<table>
<thead>
<tr>
<th>Mixing methods</th>
<th>Reversible cap. (mAh/g)</th>
<th>Cap. fade After 70 cycles (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jar mill</td>
<td>3300</td>
<td>65</td>
</tr>
<tr>
<td>Jar mill + Ball mill</td>
<td>4280</td>
<td>48</td>
</tr>
<tr>
<td>Jar mill + Planetary mix</td>
<td>3710</td>
<td>34</td>
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</table>

Hydro Québec

Institut de recherche
- High loading affects the performance by inducing a large accumulation of stress in the anode.
- Carbon improved electric contact between particles, even after cracking.

The Si particle suffers more at high rate (1C), which induces a fade of 85% of the initial capacity compared to 56% at C/6.
Effect of Depth of Discharge on Cycling

The stress level was controlled by varying DoD, at low DoD, the Si particles in the anode will experience minimum stress.

At 40% DoD, a very stable reversible capacity of around 1670 mAh/g with very good coulombic efficiency is obtained.
In-Situ SEM Analysis

The results of the *in-situ* analysis revealed an increase in the electrode thickness during discharge to 5 mV, and the average electrode expansion was about 58%.

An increase in the primary particle size was noted, with an important morphology change in the electrode.
- High reversible capacity was obtained with Hydro-Quebec nano-Si with 3050 mAh/g and high efficiency (~100%).
- Cycling at C/6, Si-HQ shows a capacity fade of 39%.
New TEM Microscope (HF-3300)

Features

- New Cold field emission gun
  - High brightness & high energy resolution
  - Low tip noise and emission decay
  - Long life

- High performance of FE-TEM/STEM
  - High contrast/resolution
  - Low voltage capability*

- High sensitive EDX analysis*
  - The widest solid angle (0.24 sr) in this class

- EELS performance*
  - High energy resolution (<0.5 eV)
  - Chemical analysis (<0.2 eV)

- Advanced analytical approach*
  - Nano beam diffraction
  - Spatially resolved EELS
  - In-situ observation

*Option

First TEM of this class in the world was installed at IREQ
In-Situ SEM: 1st Discharge of Si-Based Anode

- *In-situ* SEM shows the volume expansion of several Si-based particles.
- No evidence of cracking was observed with any of the Si-particle morphologies.
Summary

- Improved silicon anode was developed that utilized nano-Si and water-based binder (alginate).
- A high-carbon content and low-Si ratio in the anode composition yielded a significantly better performance.
- The stress on the Si particles was limited by controlling depth of discharge (DoD); when the anode is cycled at a deep DoD, the capacity fade is severe, which is believed to be due to high stress and cracking.
- This result indicates that sacrificing some capacity may be an acceptable compromise for achieving longer cycle life while maintaining adequate capacity.

- The results of the *in-situ* analysis revealed an increase in the electrode thickness during discharge to 5 mV, and the average electrode expansion was about 58%.
- The volume expansion was dependent on the electrode composition.
Future Activities

Remainder of this year

- Produce 10 m length of Si-anode by using the HQ pilot coating machine for BATT PIs.
- Fabricate 20Ah Li-ion stacking battery by using Si-anode and LiMNO.
- Increase the Si-loading in the anode.
- Study the DoD effect on the performance of the 20 Ah Li-ion battery.