**Overview**

### Timeline
- Project start date: 09/16/2009
- Project end date: 08/15/2012
- Percent complete: 20%

### Barriers
- Barriers Addressed
  - Capacity
  - Cycle Life
  - Cost

### Budget
- Total project funding
  - DOE share: $1,349,752
  - Contractor share: $1,350,699
- Funding received in FY09
  - $452,376
- Funding for FY10
  - $442,054

### Partners
- American Lithium Energy Corp
- Jiang Fan
Objective

• Overall Objective
  – Use electrospinning technology to integrate dissimilar materials (lithium alloy and carbon) into novel composite nanofiber anodes, which simultaneously have high energy density, reduced cost, and improved abuse tolerance

• FY09 Objectives
  – **Anodes:** Fabricate nanofiber anodes and understand how to control their structure and performance
  – **Coin cells:** Assemble nanofiber anodes into laboratory-scale coin cells, achieving initial specific capacities of 650 mAh/g and ~50 full charge/discharge cycles
  – **18650 cells:** Initiate the assembling of 18650 cells using nanofiber anodes
<table>
<thead>
<tr>
<th>Month/Year</th>
<th>Milestone or Go/No-Go Decision</th>
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</table>
| August-10  | • Establish guidelines for controlling the anode performance by selectively adjusting the processing and structures of the nanofiber anodes  
• Assemble, cycle, and evaluate laboratory-scale coin cells  
• Determine baseline performance of anodes in 18650 cells  
**Go/No-Go Decision:** Achieve initial specific capacities of 650 mAh/g and ~50 full charge/discharge cycles for nanofiber anodes in laboratory scale **coin cells** |
| August-11  | • Fabricate nanofiber anodes that have improved performance  
• Assemble, cycle, and evaluate 18650 cells  
**Go/No-Go Decision:** Achieve capacity (at least twice the specific capacity of graphite) and cycle life (750 cycles of ~70% state-of-charge swing with less than 20% capacity fade) for nanofiber anodes in **18650 cells** |
| August-12  | • Fabricate and deliver nanofiber anodes with specific capacities greater than 1200 mAh/g  
• Fabricate and deliver 18650 cells  
**Target:** Deliver 18650 cells, in which nanofiber anodes have specific capacities greater than 1200 mAh/g, with cell cycle life longer than 5000 cycles (~70% state-of-charge swing with less than 20% capacity fade) |
To achieve high capacity and long cycle life simultaneously, a new processing technique must be developed to coat Si with a uniform carbon layer.

PVC-based carbon-coated Si composite anode made by ball-milling.

The inset shows the first charge-discharge curve of a typical Si anode.

- To achieve high capacity and long cycle life simultaneously, a new processing technique must be developed to coat Si with a uniform carbon layer.

* PVC: polyvinyl chloride
Our Approach

Electrospun Si/C Nanofibers

- Silicon nanoparticle
  - High Capacity
- Carbon nanofiber
  - Long Cycle Life

- The nanofiber structure will allow the anode to withstand repeated cycles of expansion and contraction

Barriers
- Capacity
- Cycle Life
- Cost
Approach - Electrospinning

- Electrospinning is a simple, yet versatile technique that can produce large quantities of nanofibers with controllable structures.

- Parameters affecting electrospinning:
  - Solution viscosity
  - Solution conductivity
  - Solution surface tension
  - Applied voltage
  - Needle tip-collector distance
  - etc.
Nanofibers of Various Materials

**Approach**

- **Polymer**
- **Carbon**
- **Ceramic**
- **Metal**
- **Composite**
Nanofibers with Various Structures

Approach

<table>
<thead>
<tr>
<th>Aggregates</th>
<th>Particle-in-Fiber</th>
<th>Particle-on-Fiber</th>
</tr>
</thead>
<tbody>
<tr>
<td>Large Particles</td>
<td>Smooth Particles</td>
<td>Rough Particles</td>
</tr>
<tr>
<td>Thin-Film Coating</td>
<td>Pea-Shape Coating</td>
<td>Plates</td>
</tr>
</tbody>
</table>

[Images of various structures shown]
Industry-Scale Electrospinning Machines

Approach

Elmarco: Nanospider™

ANSTCO: eSpinner

MECC: EDEN

Fuence: High-Speed Production Unit

Yflow: eSpinning Unit 1.2.S-300

Kato Tech: Nanofiber Electrospinning Unit
Technical Accomplishments and Progress

- Anodes
- Coin cells
- 18650 cells
Preparation of Carbon Nanofibers

- Widely used as a precursor for carbon fibers
- Desirable for electrospinning
Carbon Nanofibers

- Fiber diameter decreases after carbonization

Stabilization Temperature: 280 °C
Carbonization Temperature: 700 °C

Technical Accomplishments – Anodes
Preparation of Si/C Nanofibers

Si/C nanofibers were prepared by the electrospinning and carbonization of Si/PAN precursor nanofibers.
Structure of Si/C Nanofibers

Si/C nanofibers produced from 15 wt % Si/PAN precursor

- XRD pattern indicates crystalline Si nanoparticles exist in a face-centered cubic structure
- Ramen spectrum shows the predominantly amorphous/disordered nature of the carbon matrix
Technical Accomplishments – Coin Cells

Charge/Discharge Performance

2032 coin-type half cells
Anode: Si/C nanofibers from 15 wt % Si/PAN
Electrolyte: 1 M LiPF$_6$ in EC/EMC
Current density: 100 mA g$^{-1}$

- **Year 1 Go/No-Go Decision**: initial specific capacities of 650 mAh/g and ~50 full charge/discharge cycles in lab-scale coin cells.
Technical Accomplishments – Anodes

Improvement of Structure and Performance

- Establish guidelines for controlling the anode performance by selectively adjusting the processing and structures of the nanofiber anodes:
  - Si content and dispersion*
  - Solution properties: viscosity, surface tension, and conductivity
  - Spinning conditions: voltage, flow rate, and needle-collector distance
  - Carbonization conditions: temperature, time, and heating rate
Improvement of Structure and Performance

- The addition of 0.01 mol/L NaD surfactant improves the Si dispersion

* NaD: Sodium dodecanoate, $\text{CH}_3(\text{CH}_2)_{10}\text{COONa}$
Si/C nanofibers from 10 wt % Si/PAN + 0.01 mol/L NaD*

• The addition of 0.01 mol/L NaD surfactant improves the charge and discharge capacities

Current density: 100 mA g\(^{-1}\)
The cycling tests are still in progress.
Assembling of 18650 Cells Using Nanofiber Anodes

- **Year 1 Target**: Determine baseline performance of anodes in 18650 cells
• Decent processing condition for Si/C nanofiber anodes has been identified

* capacity was calculated on Si/C nanofiber anodes
Stability of Si/C Nanofiber Anodes

Anode: Si/C nanofibers from 12 wt % Si/PAN nanofibers
Electrolyte: LiPF$_6$ in EC/DMC/EMC
Cathode: LiNiCoAlO$_2$

- Si/C nanofiber anodes are stable in contact with electrolyte upto 150 °C
Collaboration

• Partner:
  – American Lithium Energy Corp - The assembling and testing of 18650 cells

• Technology Transfer:
  – Tec-Cel Inc: A start-up company was founded
Proposed Future Work

• Establish guidelines for controlling the anode performance by selectively adjusting the processing and structures of the nanofiber anodes:
  – Si content and dispersion
  – Solution properties: viscosity, surface tension, and conductivity
  – Spinning conditions: voltage, flow rate, and needle-collector distance
  – Carbonization conditions: temperature, time, and heating rate

FY10:
• Anodes: Fabricate nanofiber anodes that have improved performance
• Coin cells: Fabricate and evaluate coin cells with improved nanofiber anodes
• 18650 cells: demonstrate practical and useful cycle life (750 cycles of ~70% state-of-charge swing with less than 20% capacity fade) with at least twice the specific capacity of graphite
• **Anodes:** Si/C nanofiber anodes have been prepared using the electrospinning technique

• **Coin cells:** Si/C nanofiber anodes have demonstrated a capacity of about 800 mAh/g, which exceeds the Year 1 Target of 650 mAh/g

• **18650 cells:** Si/C nanofibers have been incorporated into 18650 cells