New High-Energy Nanofiber Anode Materials

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Subcontractor:
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American Lithium Energy Corp, San Marcos, CA

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Project ID # ES010

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

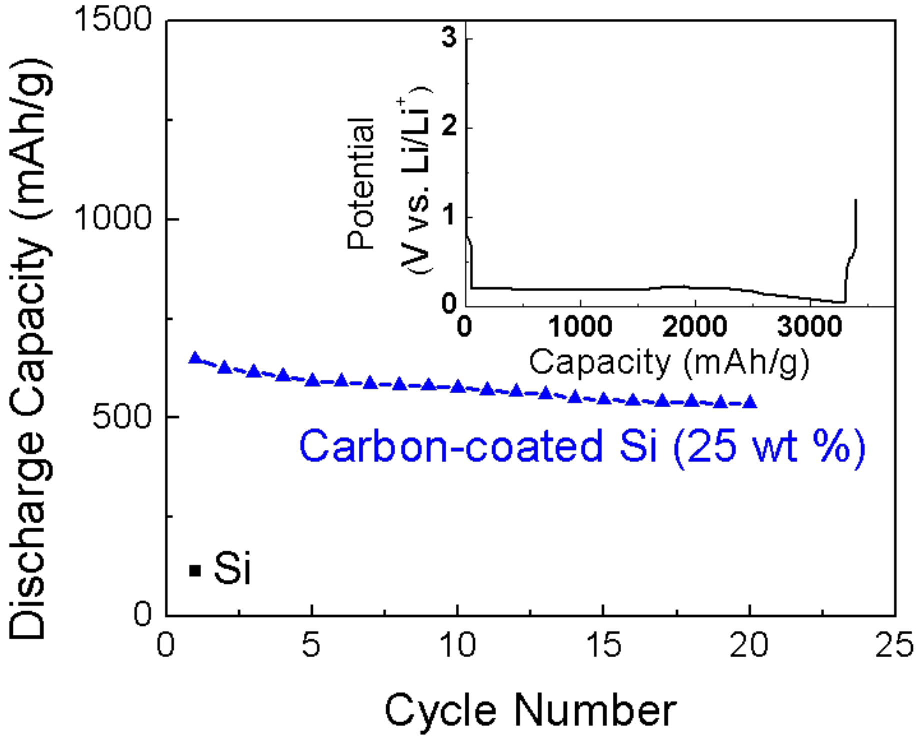
- Overall Objective
  - Use electrospinning technology to integrate dissimilar materials (lithium alloy and carbon) into novel composite nanofiber anodes, which simultaneously have high energy density, reduced cost, and improved abuse tolerance
- FY09 Objectives
  - **Anodes:** Fabricate nanofiber anodes 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

Milestones

Month/Year	Milestone or Go/No-Go Decision
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)

Background

Si/C Anodes



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

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

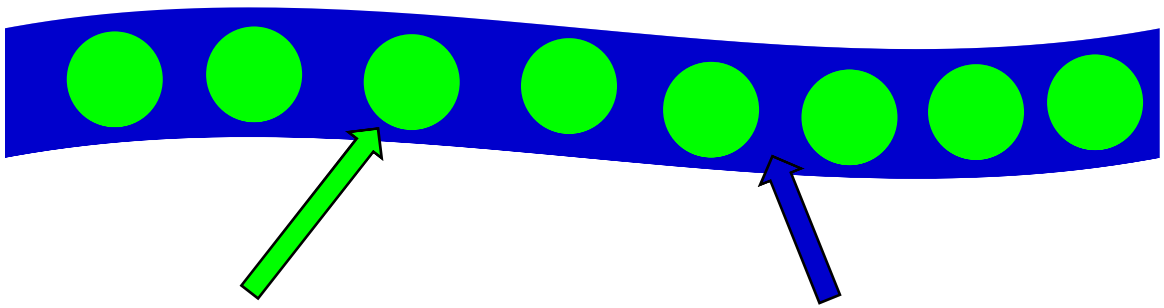
- To achieve high capacity and long cycle life *simultaneously*, a new processing technique must be developed to coat Si with a uniform carbon layer

* PVC: polyvinyl chloride

Our Approach

Barriers
- Capacity
- Cycle Life
- Cost

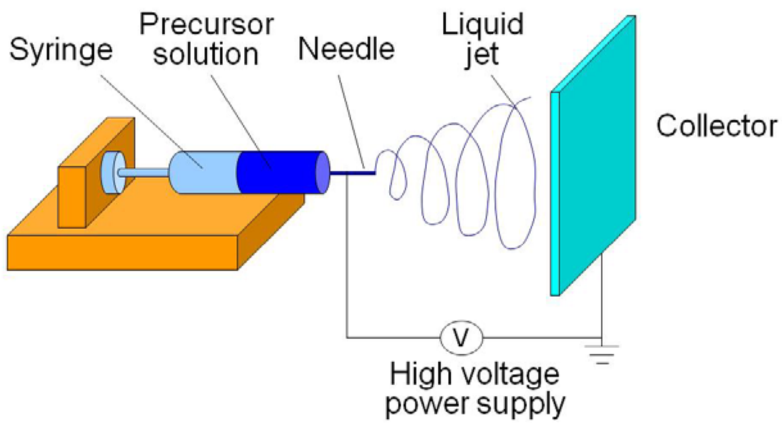
Electrospun Si/C Nanofibers

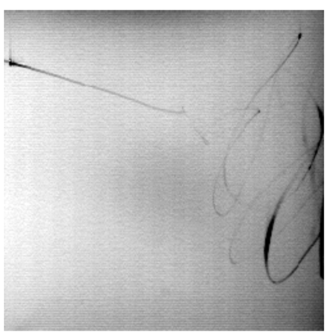


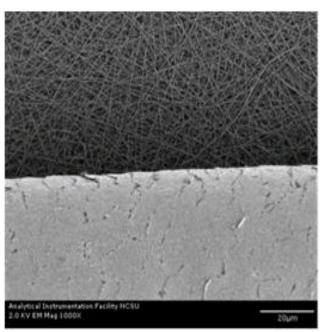
- Silicon nanoparticle
  - High Capacity
- Carbon nanofiber
  - Long Cycle Life

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

Approach - Electrospinning







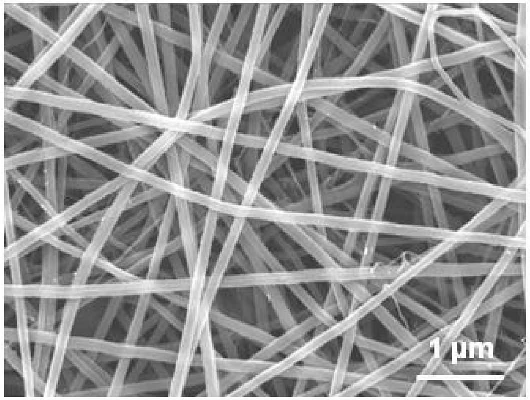
Human hair with electrospun nanofibers in the background

www.mecc.co.jp

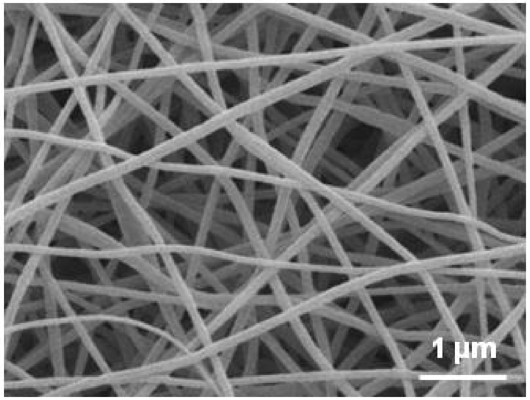
- Electrospinning is a simple, yet versatile technique that can produce large quantities of nanofibers with controllable structures
- Parameters affecting electrospinning:
  - Solution viscosity
  - Solution conductivity
  - Solution surface tension
  - Applied voltage
  - Needle tip-collector distance
  - etc.

Nanofibers of Various Materials

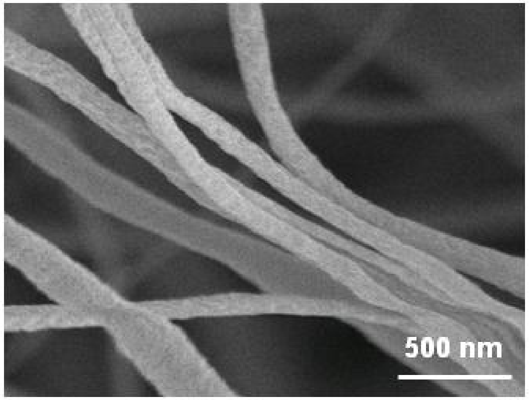
Polymer



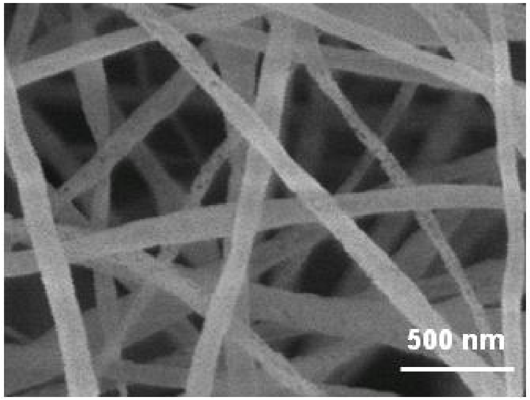
Carbon



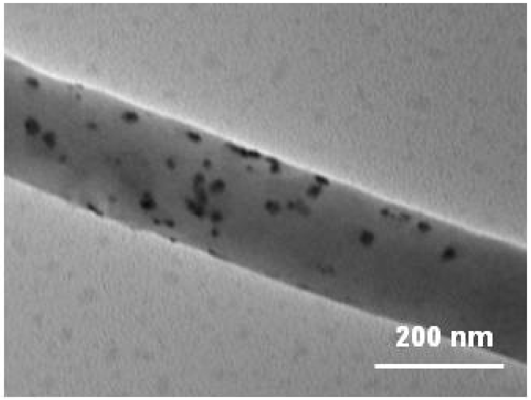
Ceramic



Metal



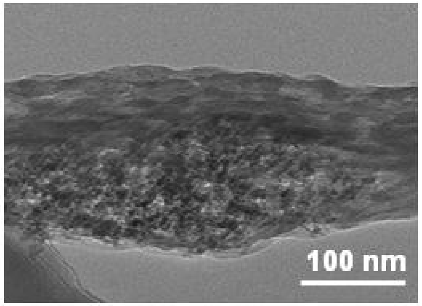
Composite



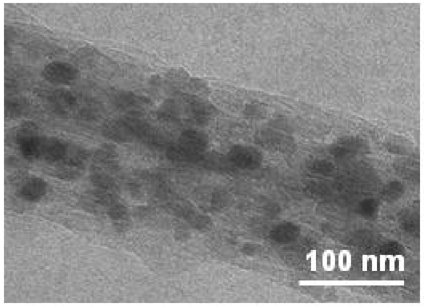
Approach

Nanofibers with Various Structures

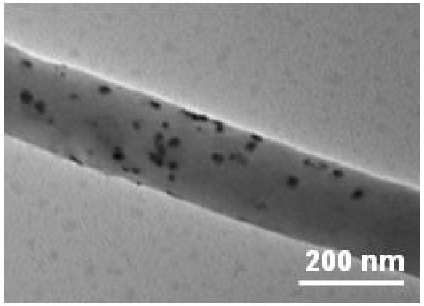
Aggregates



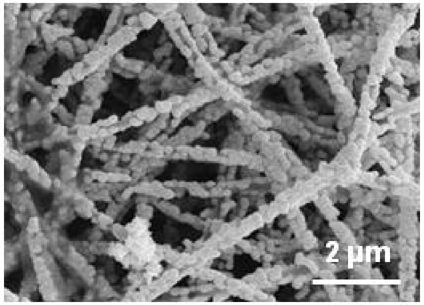
Particle-in-Fiber



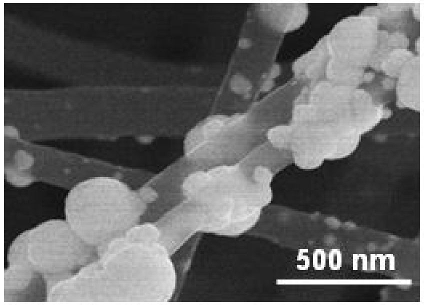
Particle-on-Fiber



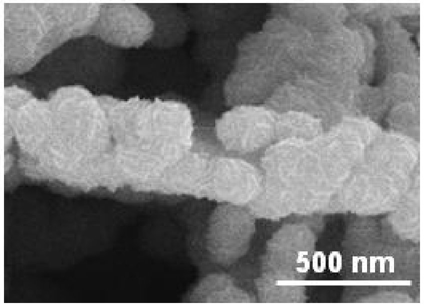
Large Particles



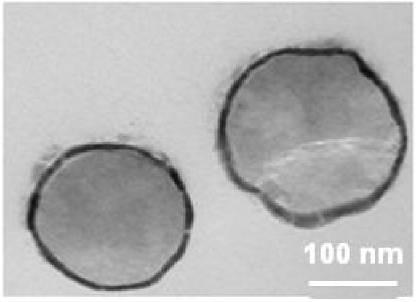
Smooth Particles



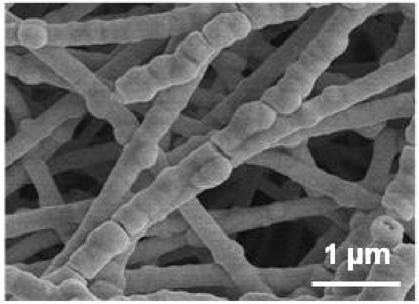
Rough Particles



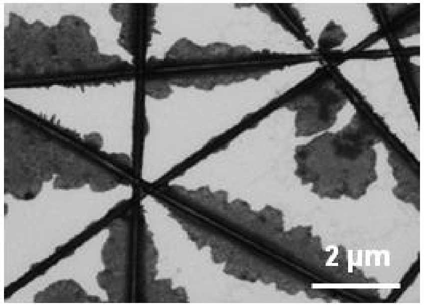
Thin-Film Coating



Pea-Shape Coating



Plates



Industry-Scale Electrospinning Machines

Elmarco: Nanospider™

ANSTCO: eSpinner

MECC: EDEN

Fuence: High-Speed Production Unit

Yflow: eSpinning Unit 1.2.S-300

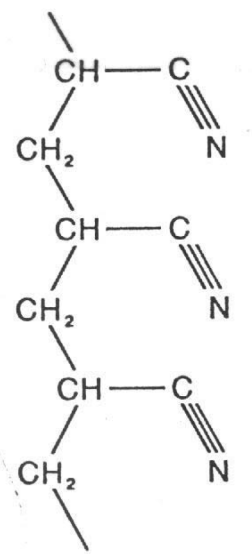
Kato Tech: Nanofiber Electrospinning Unit

Technical Accomplishments and Progress

- Anodes
- Coin cells
- 18650 cells

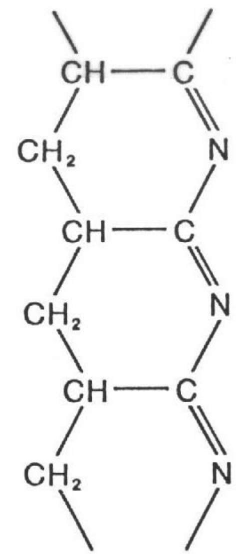
Preparation of Carbon Nanofibers

Polyacrylonitrile (PAN)



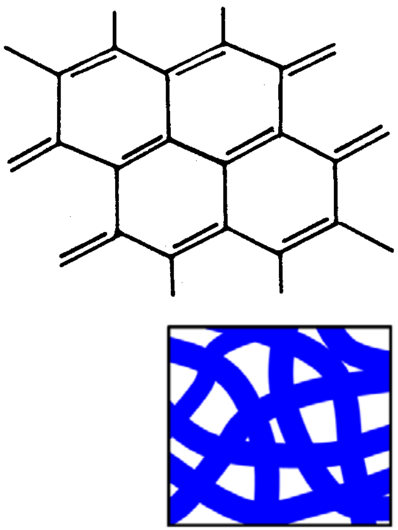
Stabilized in air

Cyclic or ladder structure



Carbonized in inert gas

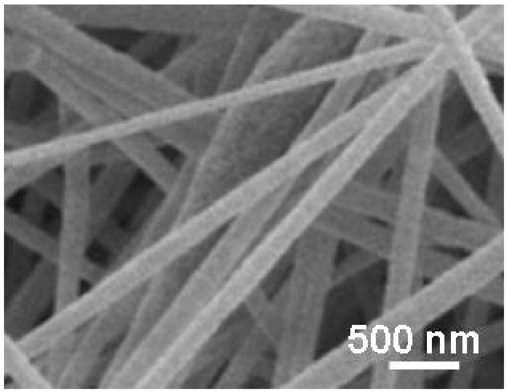
Carbon nanofibers

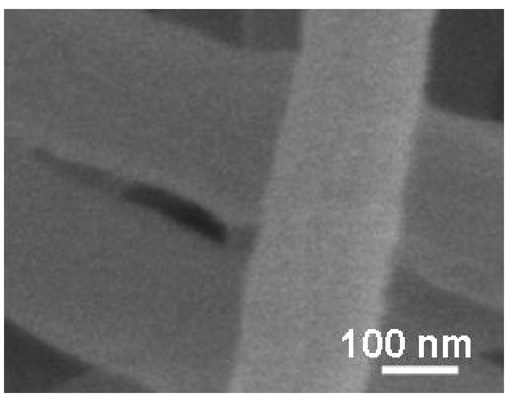


- Widely used as a precursor for carbon fibers
- Desirable for electrospinning

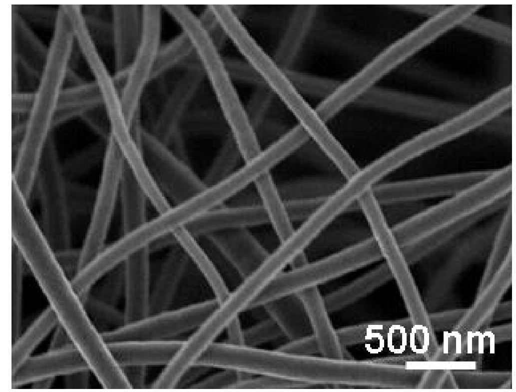
Carbon Nanofibers

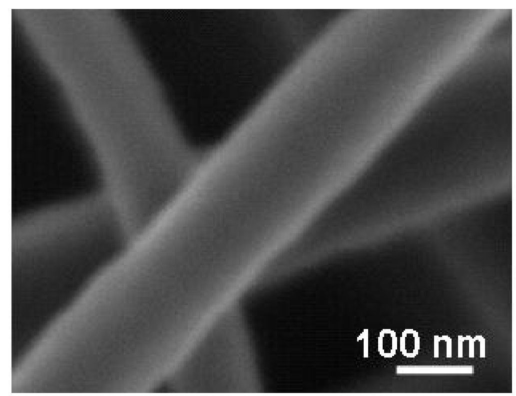
PAN Precursor Nanofibers





Carbon Nanofibers





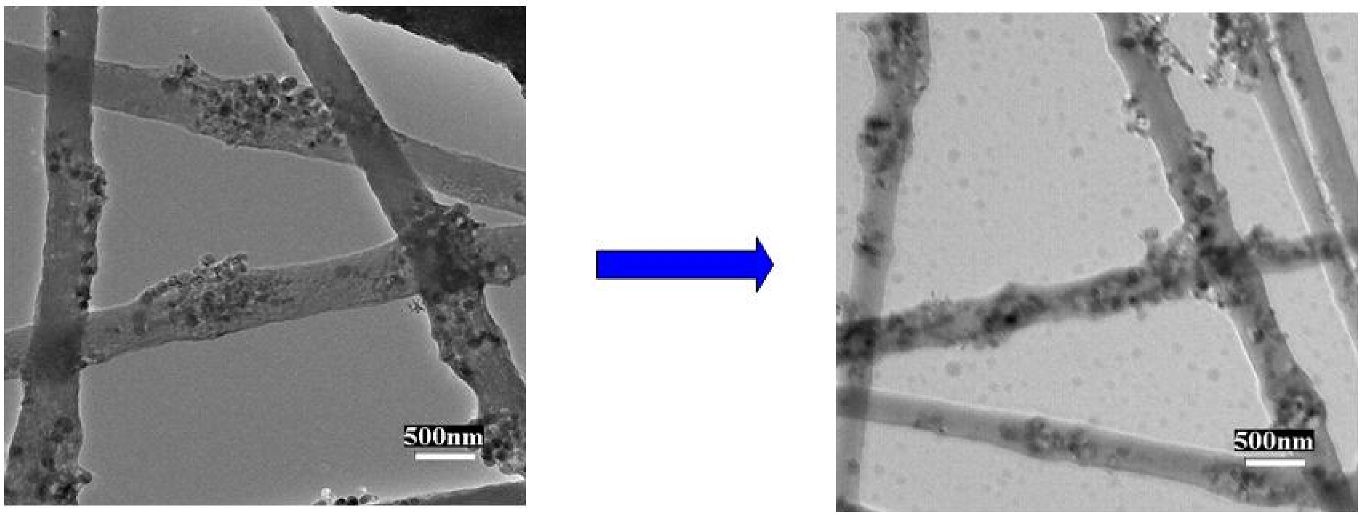
Stabilization Temperature: 280 °C
Carbonization Temperature: 700 °C

- Fiber diameter decreases after carbonization

Preparation of Si/C Nanofibers

15 wt % Si/PAN precursor nanofibers

Si/C nanofibers

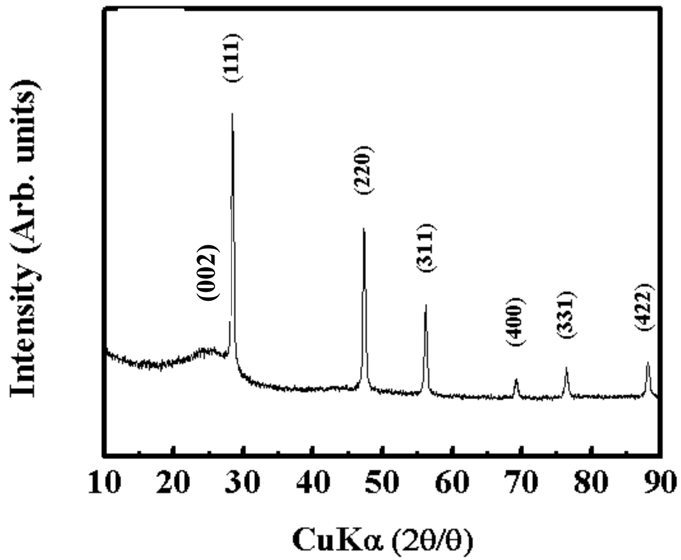


- Si/C nanofibers were prepared by the electrospinning and carbonization of Si/PAN precursor nanofibers

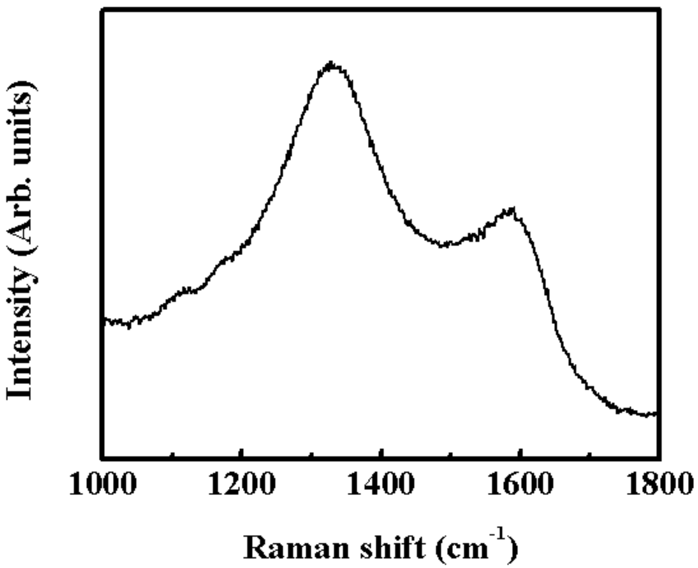
Structure of Si/C Nanofibers

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

XRD



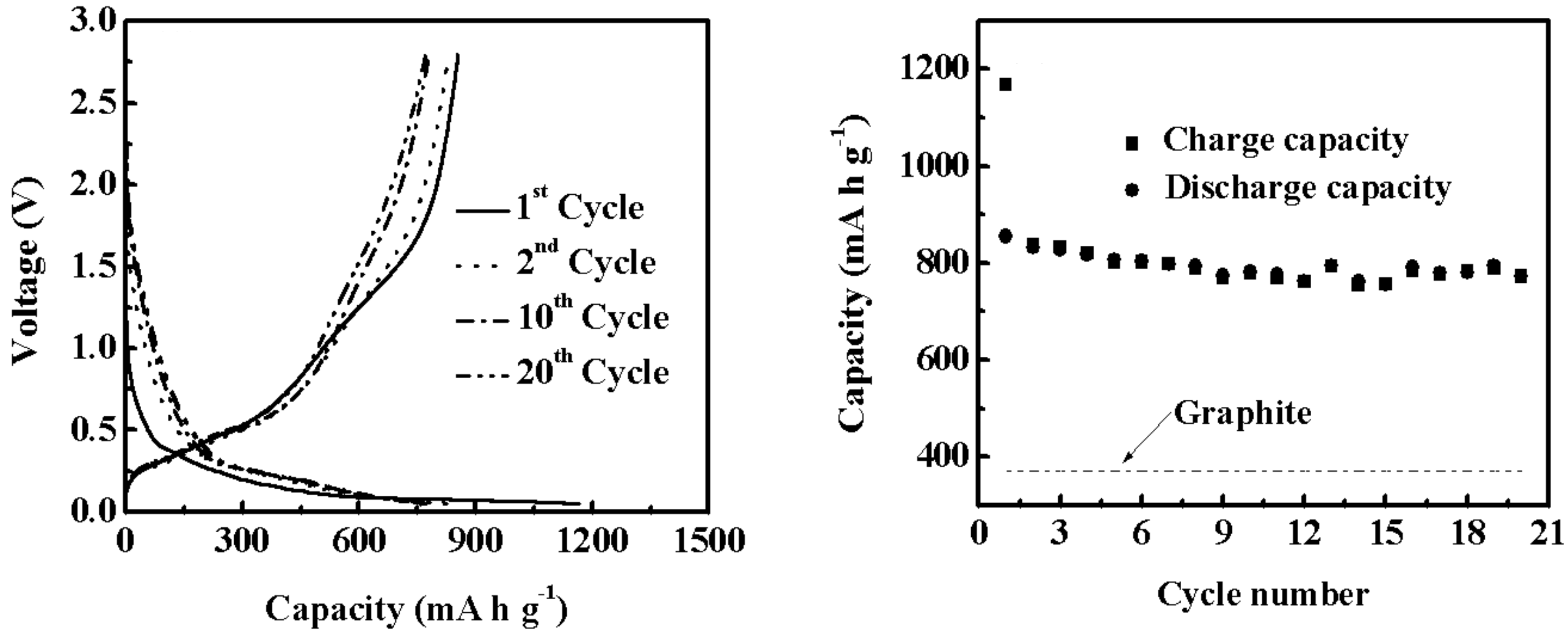
Raman



- 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

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}



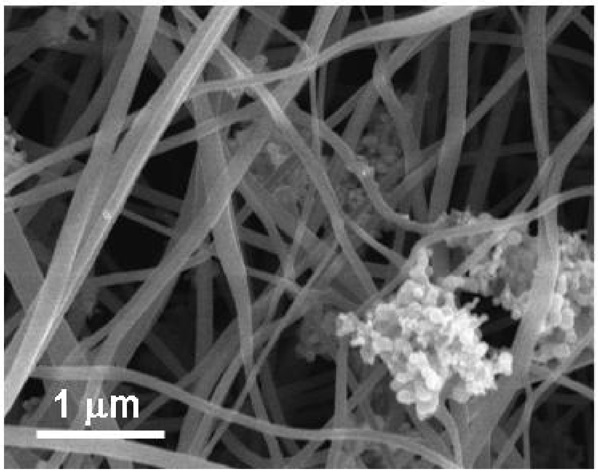
- Year 1 Go/No-Go Decision: initial specific capacities of 650 mAh/g and ~50 full charge/discharge cycles in lab-scale coin cells.

Improvement of Structure and Performance

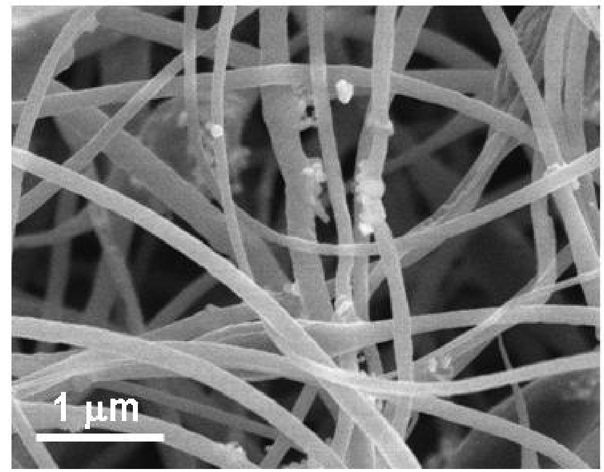
- Establish guidelines for controlling the anode performance by selectively adjusting the processing and structures of the nanofiber anodes:
  - Si content and dispersion*
  - Solution properties: viscosity, surface tension, and conductivity
  - Spinning conditions: voltage, flow rate, and needle-collector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

Improvement of Structure and Performance

Si/C nanofibers from 10 wt % Si/PAN



Si/C nanofibers from 10 wt % Si/PAN + <u>0.01mol/L NaD*</u>



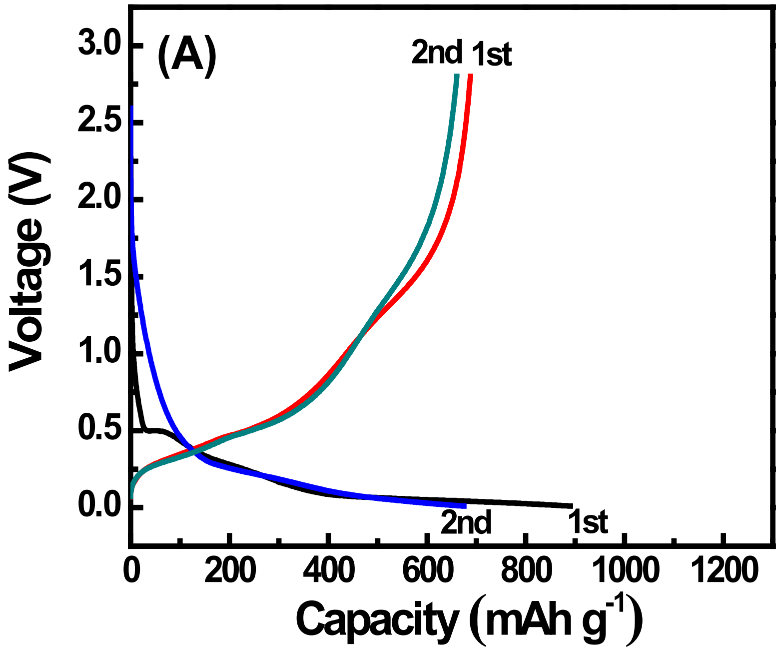
- The addition of 0.01 mol/L NaD surfactant improves the Si dispersion

* NaD: Sodium dodecanoate, $CH_3(CH_2)_{10}COONa$

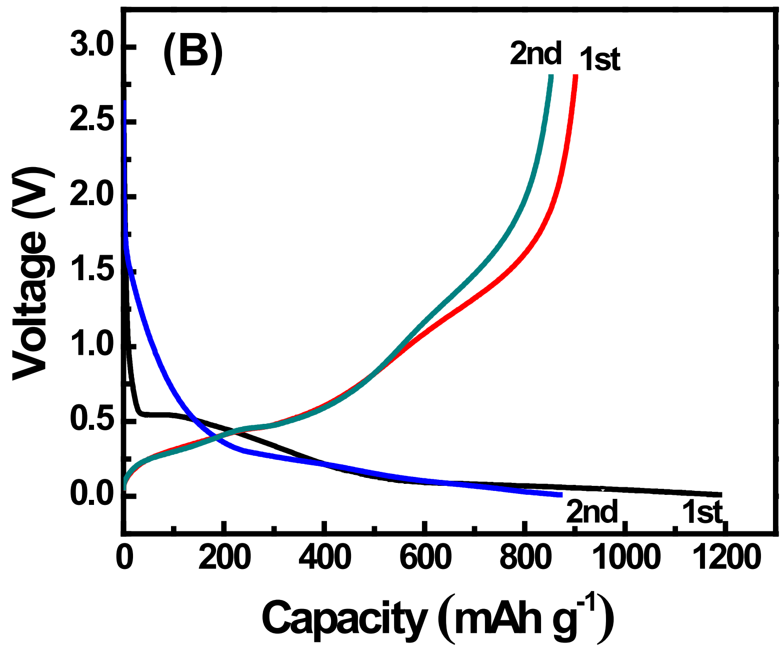
Improvement of Structure and Performance

Current density: 100 mA g^{-1}

Si/C nanofibers from 10 wt % Si/PAN



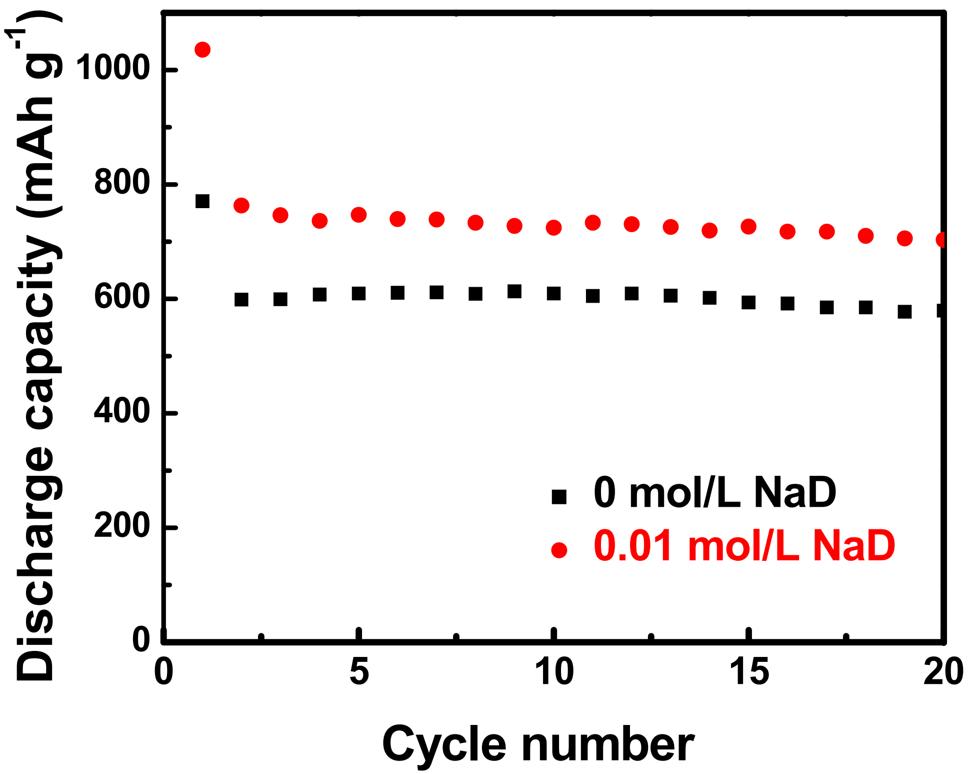
Si/C nanofibers from 10 wt % Si/PAN + <u>0.01 mol/L NaD*</u>



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

Improvement of Structure and Performance

Anode: Si/C nanofibers from 10 wt % Si/PAN
Current density: 100 mA g^{-1}



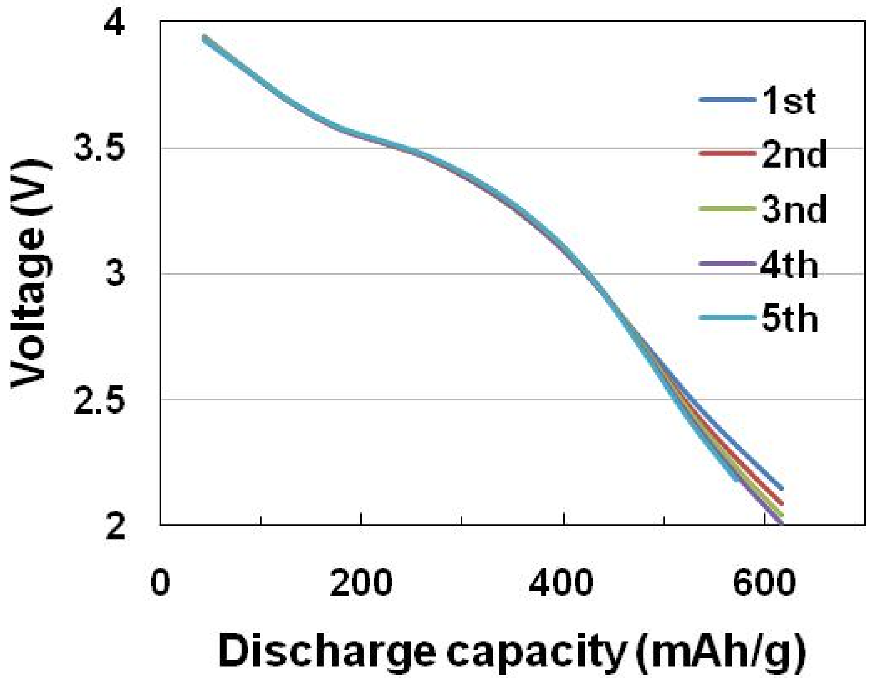
- The cycling tests are still in progress

Assembling of 18650 Cells Using Nanofiber Anodes

- <u>Year 1 Target:</u> Determine baseline performance of anodes in 18650 cells

Charge/Discharge Performance

Anode: Si/C nanofibers from 12 wt % Si/PAN nanofibers
Electrolyte: $LiPF_6$ in EC/DMC/EMC
Cathode: $LiNiCoAlO_2$
Current: 0.2 A

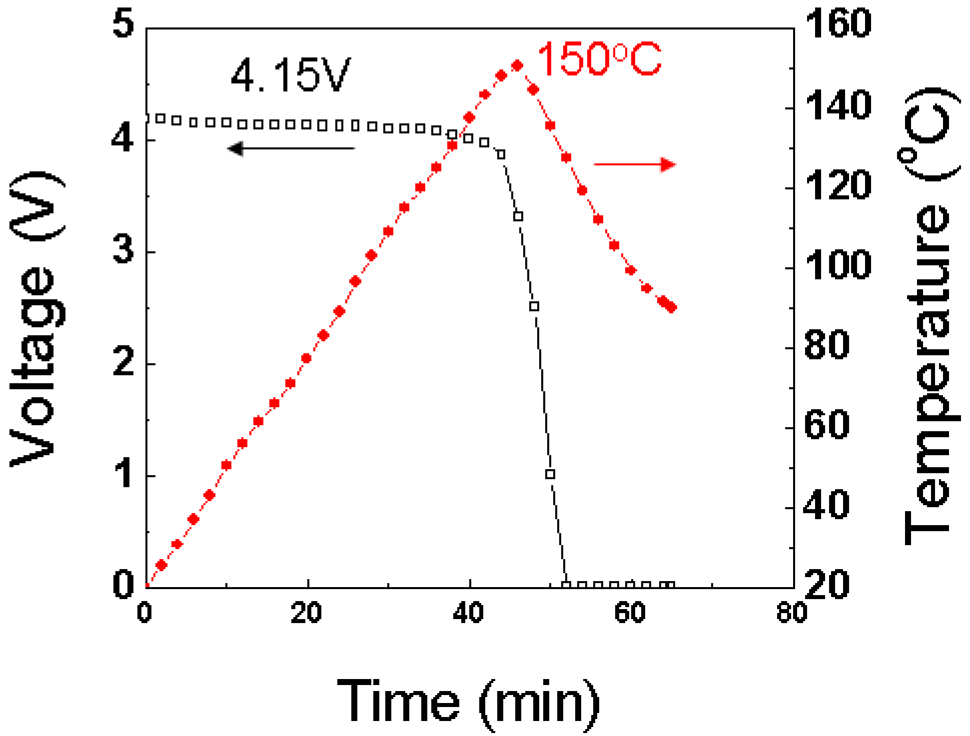


- Decent processing condition for Si/C nanofiber anodes has been identified

* 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 coins 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

Summary

- **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