New High-Energy Nanofiber Anode Materials

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Subcontractor:

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Project ID # ES010

Overview

Timeline

- Project start date: 09/16/2009
- Project end date: 08/15/2012
- Percent complete: 55%

Barriers

- Barriers Addressed
  - Capacity
  - Cycle Life
  - Cost

Budget

- Total project funding
  - DOE share: $1,349,752
  - Contractor share: $1,350,699

Partners

- American Lithium Energy Corp
  - Jiang Fan
  - 18650 Cells
- Tec-Cel Inc
  - Albert Bender
  - Pilot Production

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

- **FY11 Objectives**
  - **Capacity:** At least twice the specific capacity of conventional graphite electrodes
  - **Cycle life:** 750 cycles of ~70% state of charge swing with less than 20% capacity fade

Relevance:

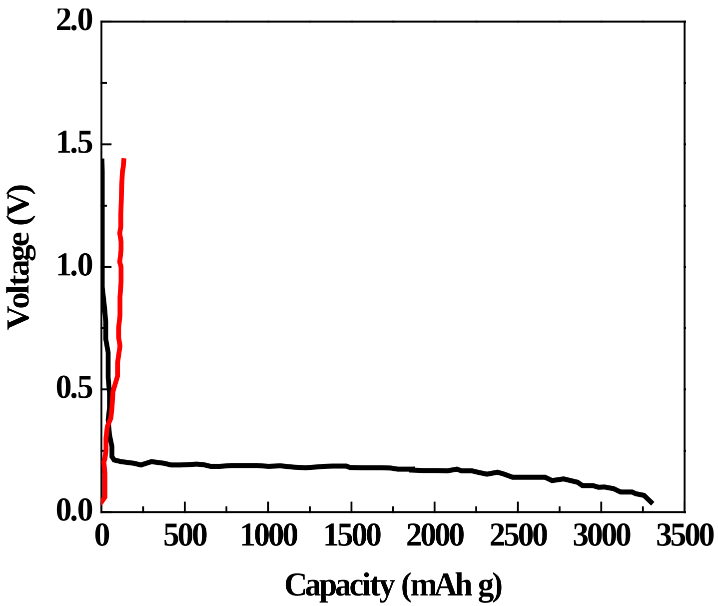
Milestones

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
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
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)

Approach:

Background (1)

Silicon Anodes

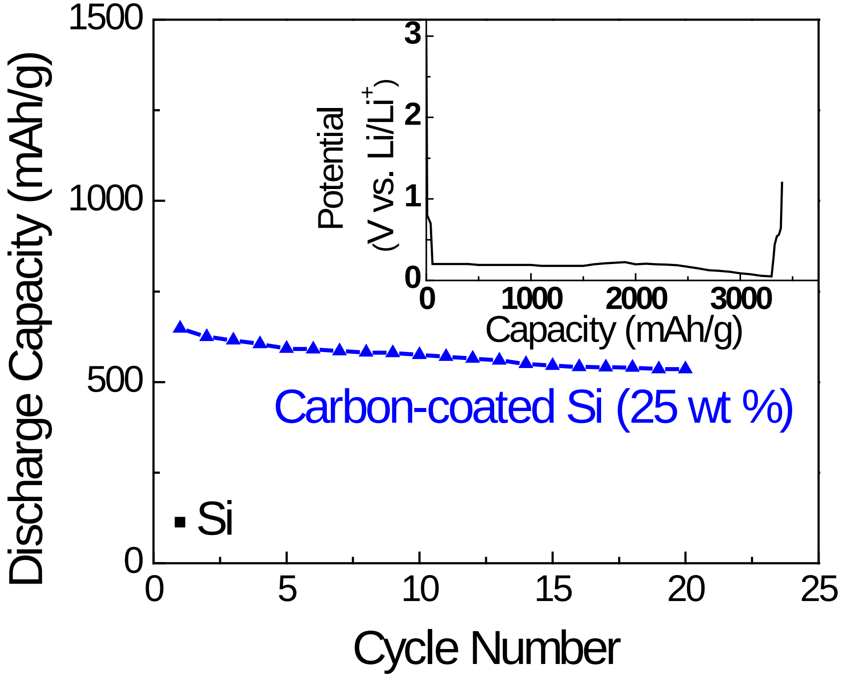


- Silicon – Extremely high theoretical specific capacity of 4200 mAh g^{-1}
- Challenge – 400% expansion and contraction causes early failures

Approach:

Background (2)

Conventional Si/C Anodes



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

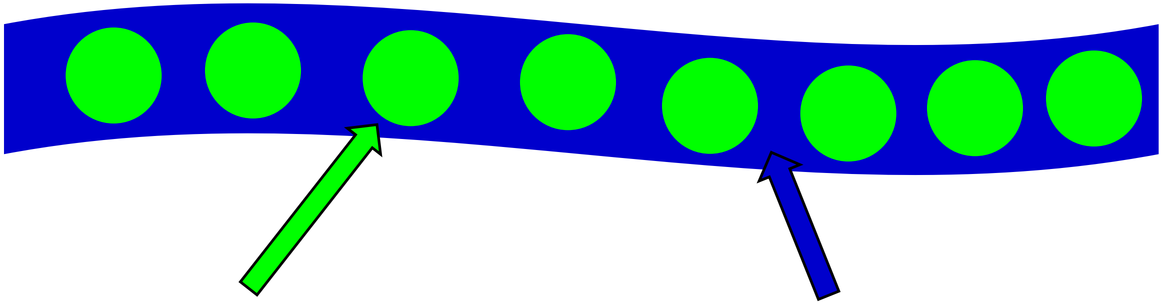
The inset shows the first charge-discharge curve of a typical Si anode.

- Si/C anodes – Cycling life can be improved by preparing Si/C composite anodes, but it is still not sufficient for practical applications
- Challenge – To further increase capacity and 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

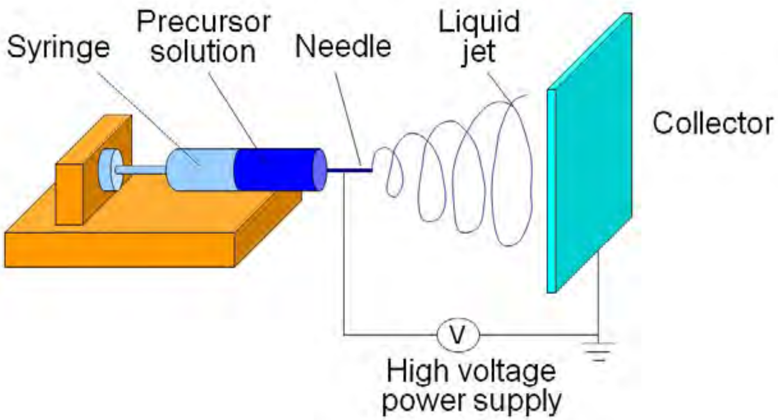
Carbon nanofiber

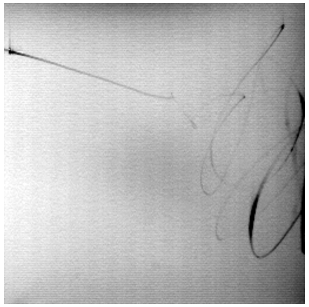
– Long Cycle Life

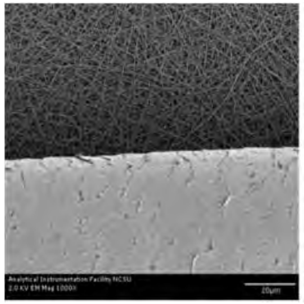
- Si nanoparticles are encapsulated in electrospun carbon nanofibers
- The nanofiber structure will allow the anode to withstand repeated cycles of expansion and contraction

Approach:

Electrospinning







Human hair with electrospun nanofibers in the background

www.mecc.co.jp

- **Production-Scale Machines:**

Elmarco: Nanospider™

ANSTCO: eSpinner

MECC: EDEN

Fuence: High-Speed Production Unit

Yflow: eSpinning Unit 1.2.S-300

Kato Tech: Nanofiber Electrospinning Unit

- **Current commercial applications:**
  - Freudenberg Nonwovens: air filters, acoustic nonwovens, and wound pads
  - Donaldson Company: Ultra-Web® filters for dust collection
  - eSpin Technologies: carbon nanofibers for thermal insulation

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

Technical Accomplishments and Progress

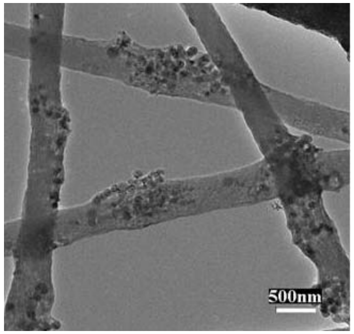
1. Preparation and performance of Si/C nanofiber anodes
2. Performance improvement of Si/C nanofiber anodes
3. Scale-up of Si/C nanofiber anodes
4. *Progress by March 11th*

1. Preparation and Performance
— Preparation of Si/C Nanofibers

Si + PAN* solution

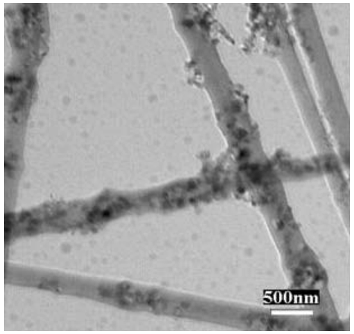
Electrospinning →

Si/PAN precursor nanofibers



Carbonization →

Si/C anode nanofibers



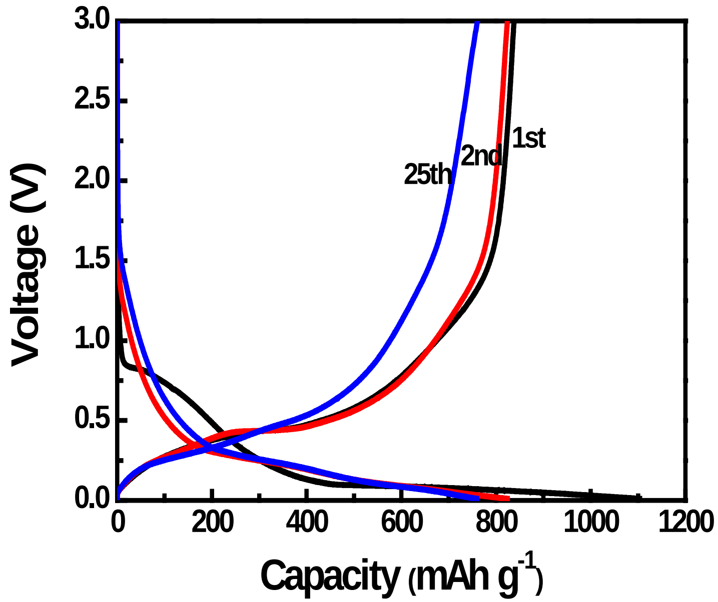
- Si/C nanofibers were prepared by electrospinning Si + PAN solutions in N,N-dimethylformamide, following by carbonization in Argon

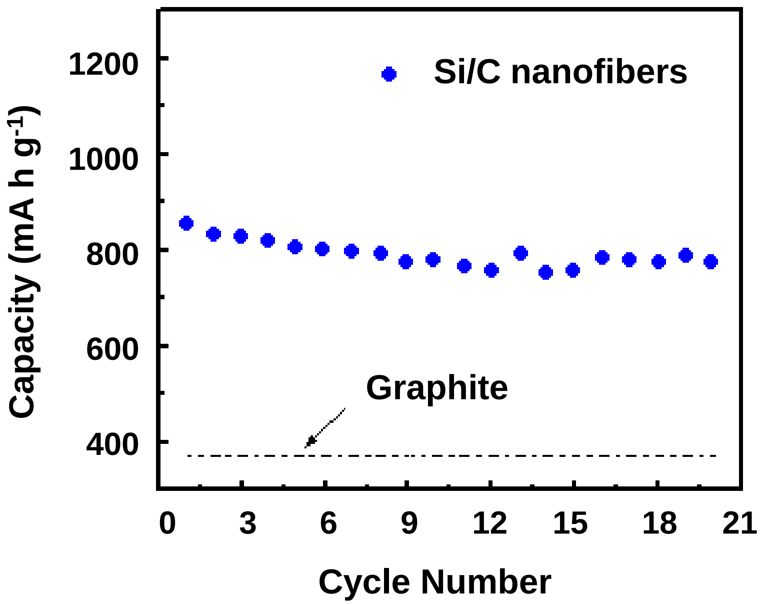
* PAN: Polyacrylonitrile

Technical Accomplishments and Progress:

1. Preparation and Performance — Baseline Performance of Si/C Nanofibers

Anode: Si/C nanofibers from 15 wt % Si/PAN
Electrolyte: 1 M $LiPF_6$ in EC/EMC
Current density: 100 mA g^{-1}





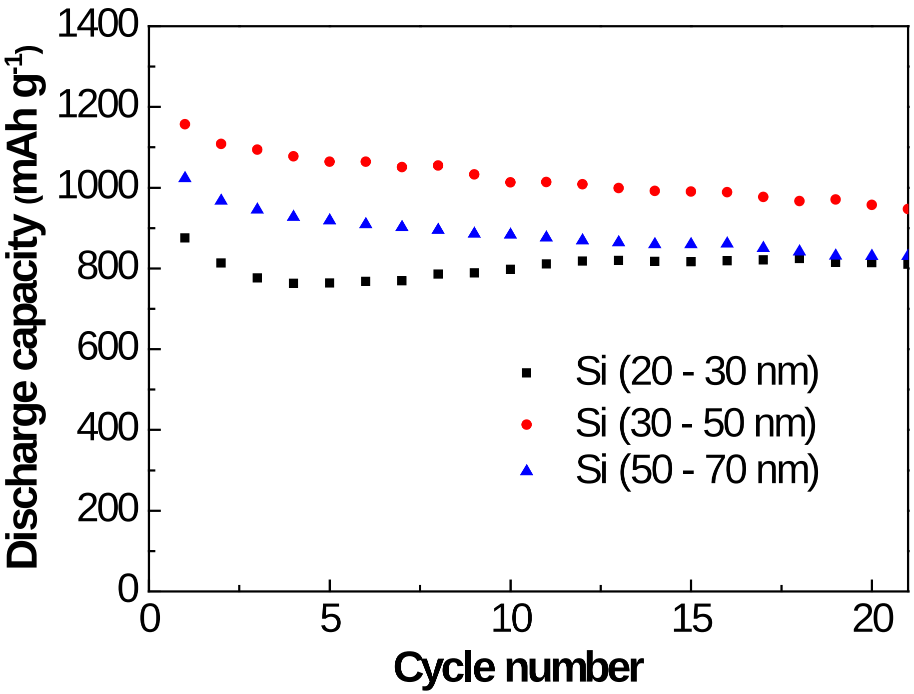
- Si/C nanofibers have significantly higher capacities than graphite

2. Performance Improvement

- Improve the anode performance by selectively adjusting the processing and structures of the nanofiber anodes:
  - Si type, size*, 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

2. Performance Improvement — by Changing Si Particle Size

Anode: Si/C nanofibers from 15 wt % Si/PAN
Electrolyte: 1 M $LiPF_6$ in EC/EMC
Current density: 50 mA g^{-1}

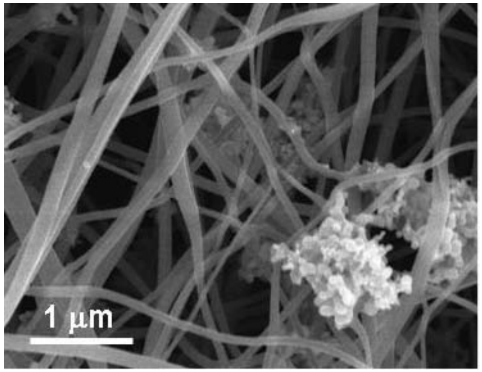


- Nanofiber anodes containing Si nanoparticles (30-50 nm) give the highest capacities

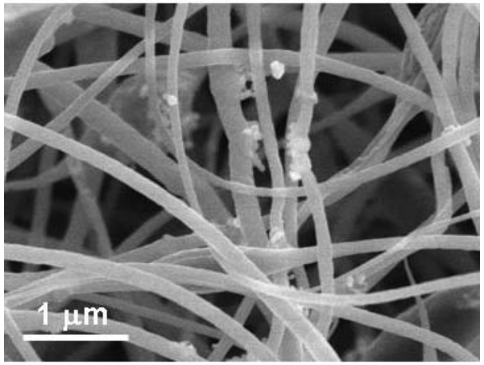
Technical Accomplishments and Progress:

2. Performance Improvement — by Enhancing Si Dispersion

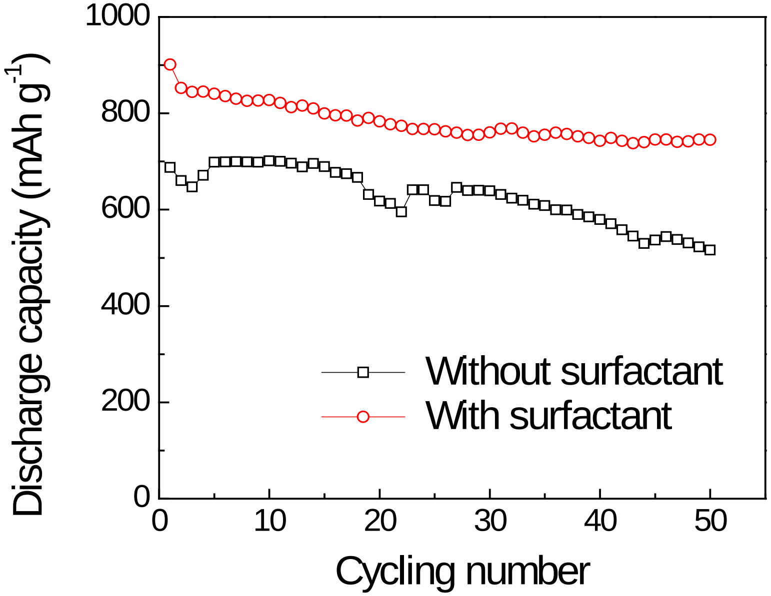
Si/C nanofibers from
10 wt% Si/PAN



Si/C nanofibers from
10 wt% Si/PAN + 0.1 mol/L NaD*



Current density: 100 mA g^{-1}



- The addition of surfactant enhances Si particle dispersion, increases discharge capacity, and improves cycling performance

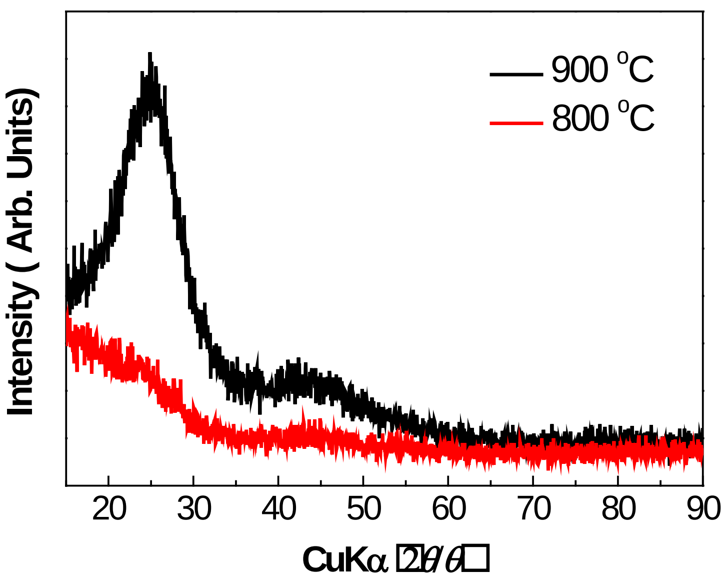
* NaD: Sodium dodecanoate
$CH_3(CH_2)_{10}COONa$

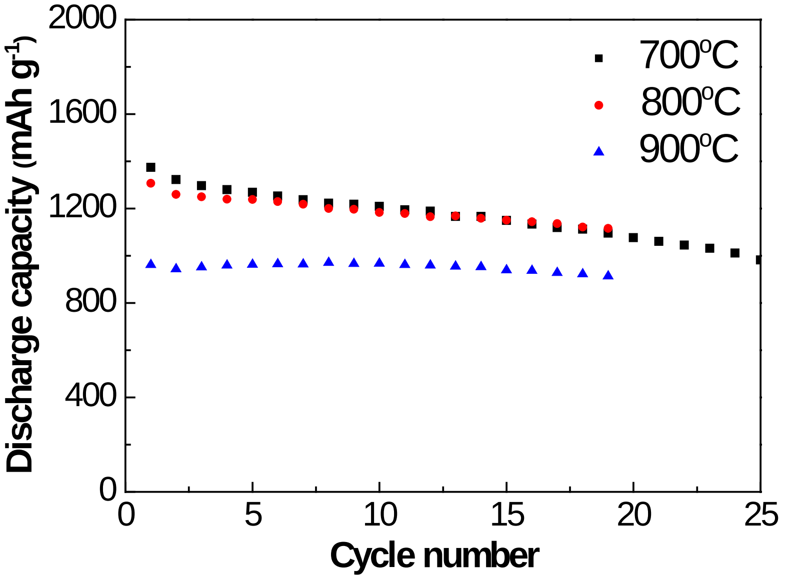
Technical Accomplishments and Progress:

2. Performance Improvement
— by Changing Carbonization Temperature

Anode: Si/C nanofibers from 20 wt % Si/PAN
Electrolyte: 1 M $LiPF_6$ in EC/EMC
Current density: 50 mA g^{-1}

XRD of carbon matrix





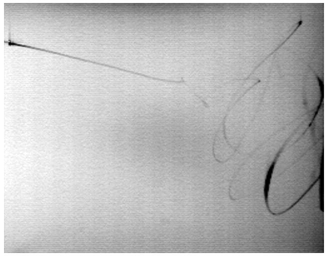
- Increasing carbonization temperature leads to the formation of more ordered carbon matrix, which is beneficial in improving the anode cycling stability although the discharge capacity decreases

3. Scale-Up — Lab Scale *vs.* Production Scale

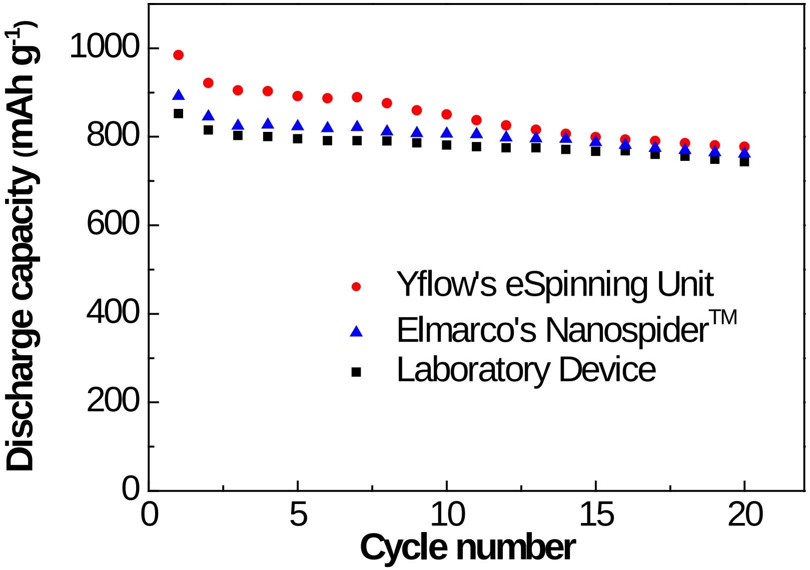
Yflow's eSpinning Unit:

Elmarco's Nanospider™:

Laboratory Device:



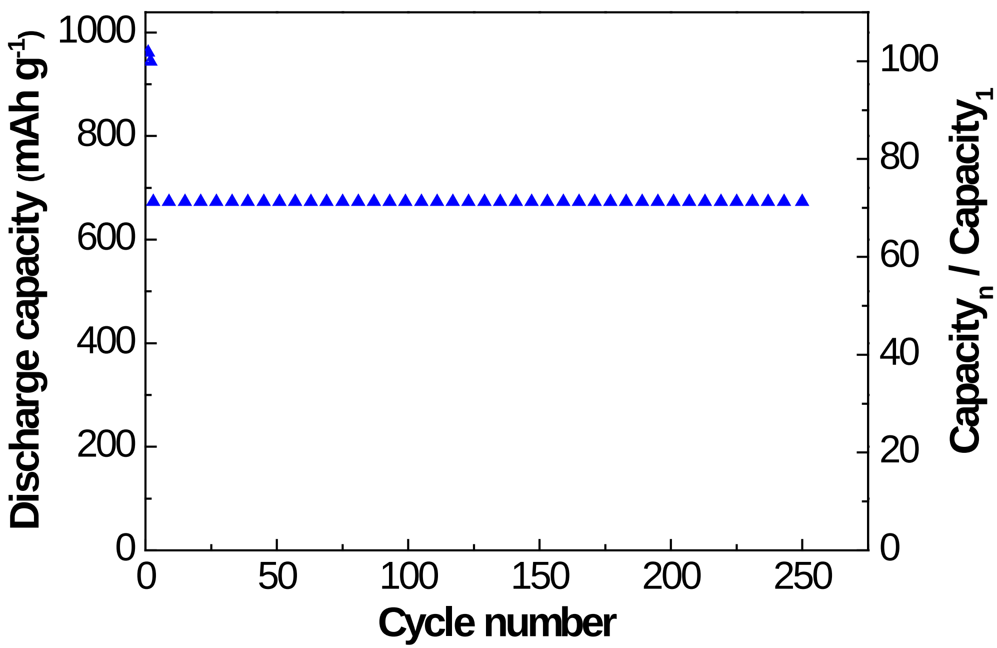
Anode: Si/C nanofibers from 10 wt % Si/PAN
Electrolyte: 1 M $LiPF_6$ in EC/EMC
Current density: 100 mA g^{-1}



- Si/C nanofiber anodes produced by production-scale machines have higher capacities than those produced using lab-scale device

4. Progress by March 11th — Cycling Performance

Anode: Si/C nanofibers from 20 wt % Si/PAN
Electrolyte: 1 M $LiPF_6$ in EC/EMC
Current density: 50 mA g^{-1}



Test procedure

- First two cycles
  Full charge/discharge (cut-off voltages: 0.05 – 2.5 V)
- Following cycles
  70% state-of-charge swing, i.e., changing the current polarity if:
  1) capacity reaches 70% of first-cycle capacity, or
  2) voltage reaches cut-off values: 0.05 – 2.5 V

- No capacity loss was observed in the first 250 cycles
- The test is still ongoing, and the target for FY11 is 750 cycles of ~70% state-of-charge swing with less than 20% capacity fade

Collaborations

- **American Lithium Energy Corp, San Marcos, CA (Industry)**
  - Jiang Fan, 760-591-0611, jfan@americanlithiumenergy.com
  - The assembling and testing of 18650 cells
- **Tec-Cel Inc, Cary, NC (Industry)**
  - Albert bender, 919-878-8464, abender@tec-cel.com
  - Licensing the technology
  - **Short-term target**: pilot scale production
  - **Longer-term target**: full scale production
- **Argonne National Laboratory, Argonne, IL (Federal)**
  - Wenquan Lu, 630-252-3704, luw@anl.gov
  - Improvement of carbon matrix structure by using ANL's heat-treatment facility
- **Indiana University-Purdue University Indianapolis, IN (University)**
  - Jian Xie, 317-274-8850, jianxie@iupui.edu
  - Improvement of Coulombic efficiency by coating the anodes with graphene or other materials

Proposed Future Work/Proposed Future Activities:

Future Work

- Optimize the anode performance by selectively adjusting the processing and structures of the nanofibers:
  - Si content, type, size, content, and dispersion (increase capacity and improve cycle life)
  - Surface coating using graphene or other materials (increase Coulombic efficiency)
  - Solution properties: viscosity, surface tension, and conductivity
  - Spinning conditions: voltage, flow rate, and needle-collector distance
  - Carbonization conditions: temperature, time, and heating rate

FY12 Targets:

- **Anodes:** Fabricate nanofiber anodes that have optimized performance
- **18650 cells:** Deliver 18650 cells, in which the anode has a specific capacity greater than 1200 mAh/g and cycle life longer than 5000 cycles of ~70% state of charge swing with less than 20% capacity fade

Summary

- Si/C nanofiber anodes have been prepared using the electrospinning technique
- 18650 cells have been assembled using Si/C nanofiber anodes
- The performance of Si/C nanofiber anodes has been improved by selectively adjusting the processing and structures of the nanofibers
- The scale-up production is successful, and the resultant Si/C nanofiber anodes have higher capacities than those produced using lab-scale device
- The Year 2 work is still ongoing, and the current results show the FY11 Targets are achievable

	FY10 Results	FY11 Results (by March 2011)	FY11 Targets (by August 2011)
Capacity	~800 mAh g^{-1}	~950 mAh g^{-1}	Twice the specific capacity of graphite (*i.e.*, 744 mAh g^{-1})
Cycle Life	50 full charge/discharge cycles	250 cycles of ~70% state-of-charge swing without capacity fade	750 cycles of ~70% state-of-charge swing with less than 20% capacity fade