Hybrid Nano Carbon Fiber/Graphene Platelet-Based High-Capacity Anodes for Lithium Ion Batteries

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Organization: Angstron Materials, Inc

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Award Number: **DE-EE0001219** DE-PS26-08NT01045-02, Subtopic 1

Overview

Timeline

- Project start: Sept. 15, 2009
- Project end: Sept. 14, 2012
- Percent complete: 30%

Budget

- **Total project funding**
  DOE share: $1,594,303
  Contractor share: $1,603,937
- Funding received in FY09: $130,000
- Funding for FY10: $633,871

Barriers

- Barriers addressed (Current Li-ion cells)
  - **A:** High production cost;
  - **B:** Low capacity and short cycle life;
  - **C:** Si pulverization.
- Targets

	2010	2011	2012
Anode Specific capacity	650 (mAh/g)	1000 (mAh/g)	1000 (mAh/g)
Others	50 cycles (1C), < 20% capacity fade	750 cycles, ~70% SOC swing, < 20% of capacity fade	Demonstration cells
Cell status	Button cell	18650 cell	18650 cell

Partners

- K2 Energy Solutions, Inc.,-- Cell evaluation
- Applied Sciences, Inc.,-- VG-CNFs

Project Objective

To develop and commercialize next generation of high-energy density anode materials for Li-ion batteries (Si-NGP/CNF hybrid materials)

Phase 1: Applied Research (Prior to Proposal Submission):
Demonstrated the technical feasibility of new high-energy anode materials– **Si nano coating/particles supported by a 3-D network (mat) of nano graphene platelets (NGP)/carbon nano-fibers (CNF).**

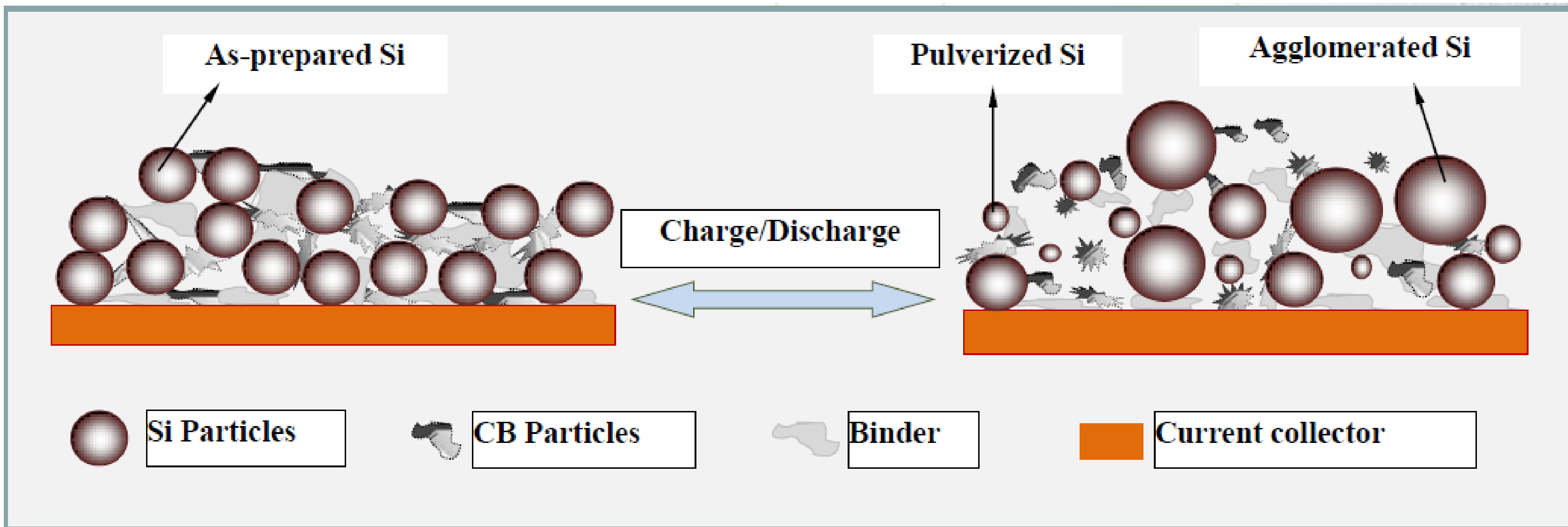
Phase 2: Technology Development (This project)

- Determine the optimized Si-NGP/CNF blends (hybrids) that exhibit the best performance/cost ratios.
- Develop the process technology for cost-effective production of Si-NGP/CNF blends

Phase 3: Technology Validation
Produce high-energy anode materials and initiate a marketing program for their distribution.

Approach

Prevent Si pulverization ?



Conventional Approaches:

- **Reducing the size of active materials:**
  - **Ultra-thin film;**
  - **Using nano particles to reduce the volume change-induced strain energy during cycling;**
- **Adding a cushioning material to offset the volume change of the active material.**

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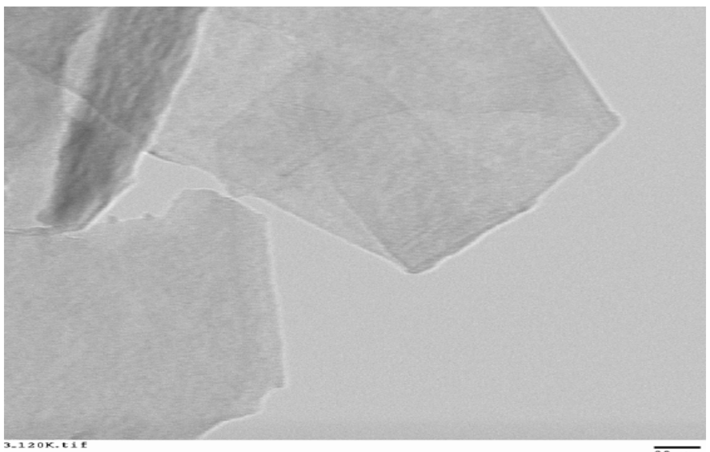
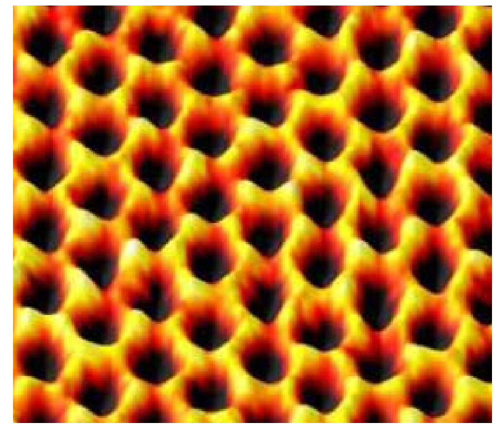
Approach:
Using NGP as a supportive/protective substrate
Nano graphene platelets (NGPs)

A 2-D honeycomb structure of carbon atoms as thin as one carbon atom (< 0.34 nm)





(Image courtesy of DOE/Lawrence Berkeley National Laboratory)

- **Ultra-high Young's modulus (1,000 GPa)**
- **Highest intrinsic strength (up to ~ 130 GPa).**
- **Exceptional in-plane electrical conductivity (up to ~ 20,000 S/cm).**
- **Highest thermal conductivity (up to ~ 5,300 W/(mK)).**
- **High specific surface area (up to ~ 2,675 m^2/g).**

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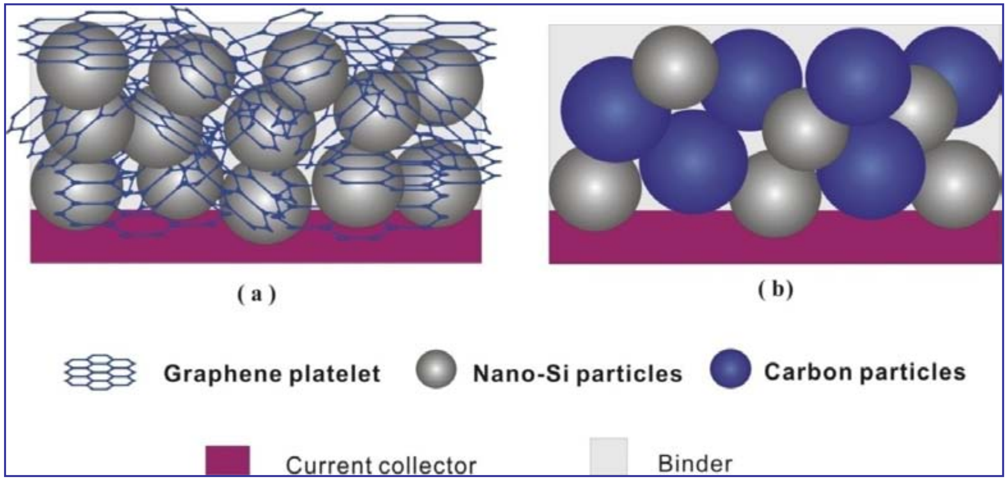
Approach

Functions of NGPs?

- Increased electrode conductivity due to a percolated **graphene** network;
- Dimensional confinement of Si by the surrounding graphene sheets limits the volume expansion upon lithium insertion;
- Si/graphene or SnO_2 /graphene form a stable 3D architecture.
- Graphene sheets prevent aggregation of nanoparticles during the charge/discharge process.



New high-capacity anode compositions: 500-2,000 mAh/g

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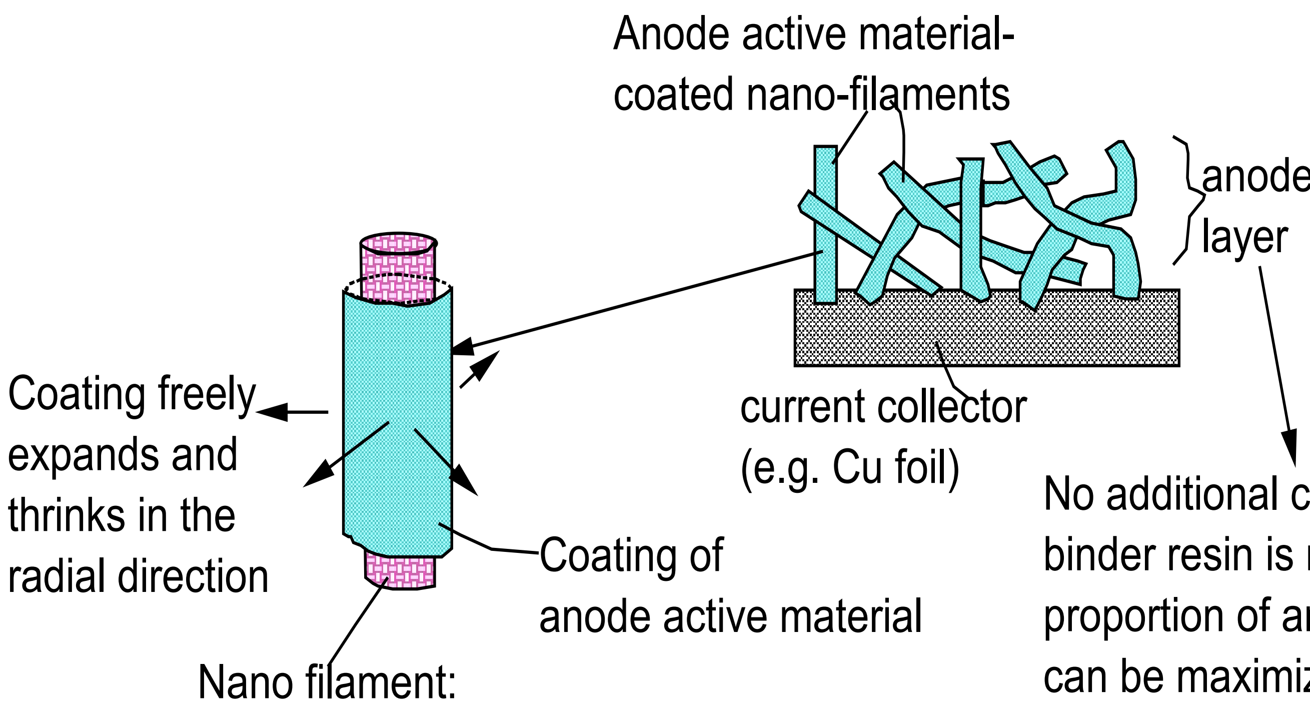
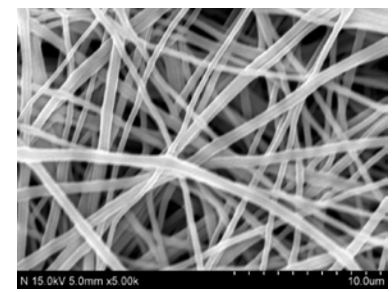
Approach

Functions of CNFs?

- **Impart structural integrity to the 3-D net (mat or paper)**
- **Provide a geometry that enables Si to freely expand and shrink in the radial direction**





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Major Milestones Reached

Phase I	Task 1: Project Management & Planning	M1: (10/28/2009) Project plan
Task 2: Development and Optimization of Anode Materials		
Phase II	2.1 Development & optimization of Si-supporting CNF-NGP blend compositions	M2: (1) (02/28/2010) Provide a window of desired anode material properties: porosity or density of CNF/NGP preforms, electrical conductivity, mechanical strength, surface area, affinity to silicon deposition, and cost; M2: (2) (02/28/2010) Small laboratory scale cells with an anode specific capacity of 650 mAh/g, Charge/discharge cycles 50;

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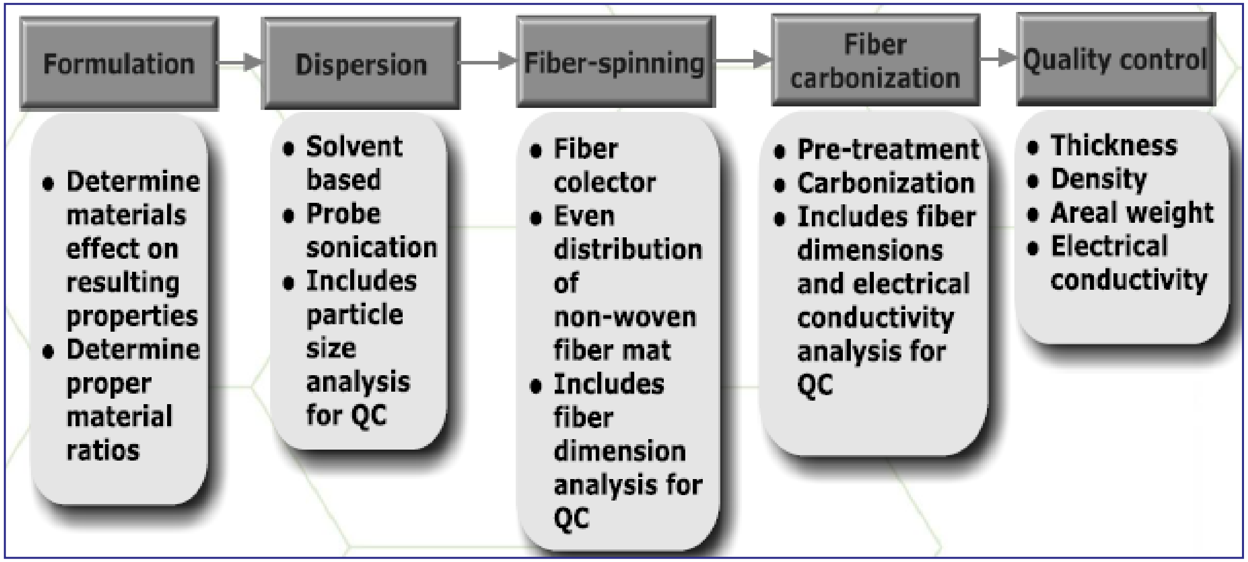
Accomplishments _ Developed the processes for producing electro-spun CNF-based conductive web



Electro-spun CNFs Vs. VG-CNFs:

* Less expensive (can be mass-produced);
* no thermal overcoat (better Si bonding

Conductive mat	Desired Conductivity (S/cm)	Conductivity achieved (S/cm)	Density (g/cm^3)	Surface Area (m^2 /g)	Modulus (MPa)
Aligned CNF mat	> 1	~ 9.15	0.4 ~ 0.8	3 ~ 10	80 ~ 180
Random CNF mat	> 1	~ 11.7	0.4 ~ 0.8	3 ~ 10	80 ~ 180
CNFs/CNT mat	> 1	~ 1.8	0.15 ~ 0.3	10 ~ 20	60 ~ 150

Process window for making conductive CNF web

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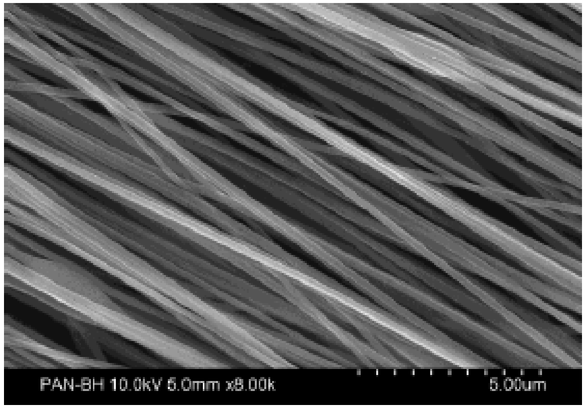
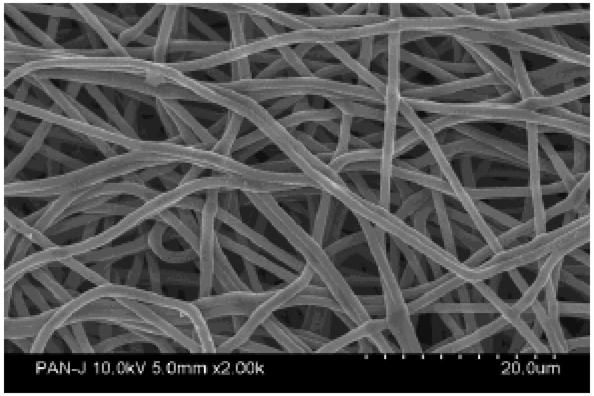
Accomplishments ___ Electrically conductive CNF web

Conductive web	Conductivity (S/cm)
Highly aligned carbon nanofiber web	9.15
Randomly arranged carbon nanofiber web	11.7
CNFs/CNTs web	1.8



Highly aligned carbon nanofibers

Compared to the VG-CNFs/CNTs mat prepared by a conventional paper-making process, the electrical conductivity of this new conductive mat is 6.5 times higher, and the density is also higher (0.40g/cm^3, as opposed to 0.25g/cm^3 for VG-CNF/CNT mats).



Randomly oriented carbon nanofibers

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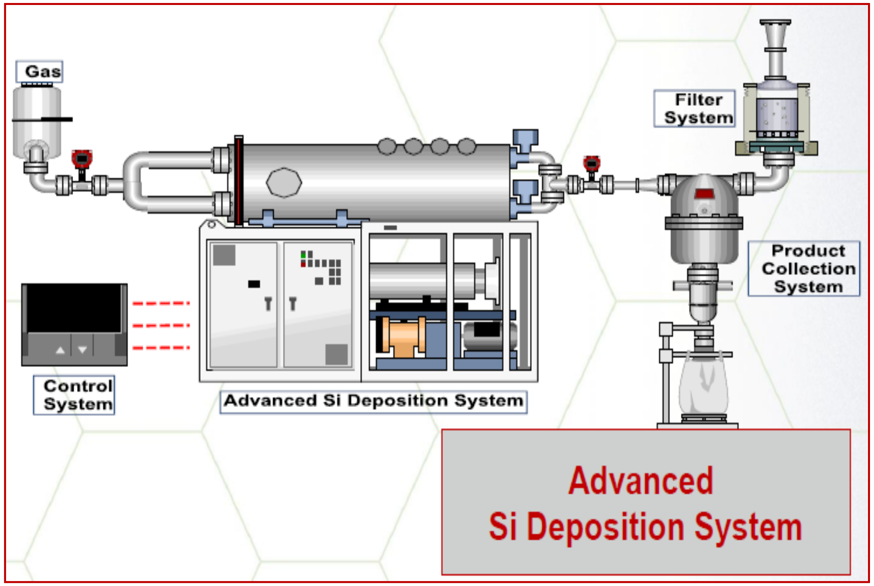
Accomplishments ___ Si coated conductive CNF web

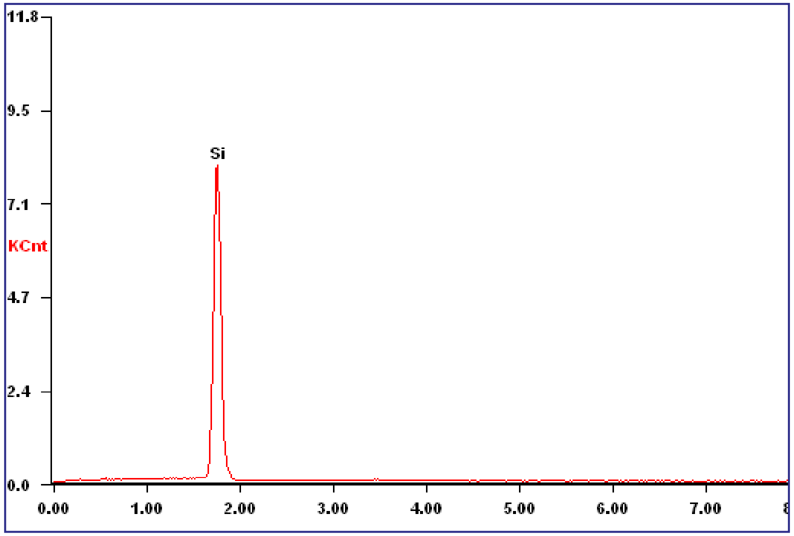
Designed a CVD system for mass-producing Si-coated conductive web

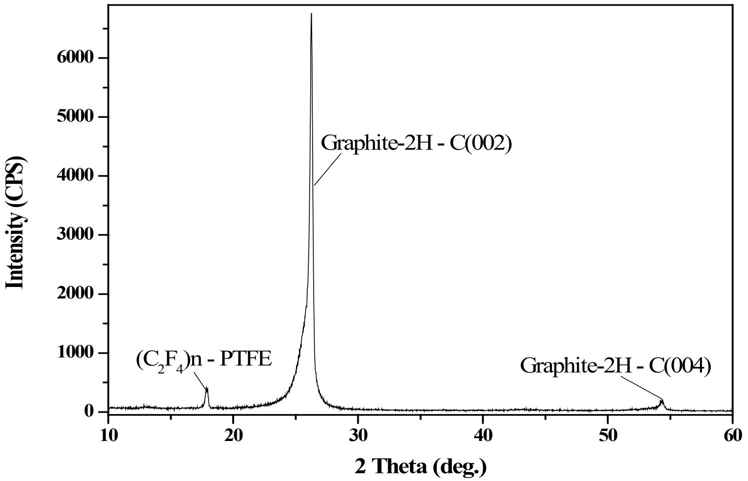


- **Significantly higher deposition rate.**
- **Allows for more flexible chamber design.**
- **More conducive to roll-to-roll manufacturing.**

Composition analysis of Si coatings

- Chemical composition of Si coated CNF web analyzed by EDS & XRD
- The XRD spectra of Si coated carbon fiber





- ➢ EDS results: coating prepared is pure silicon
- ➢ XRD results: deposited silicon coating is amorphous

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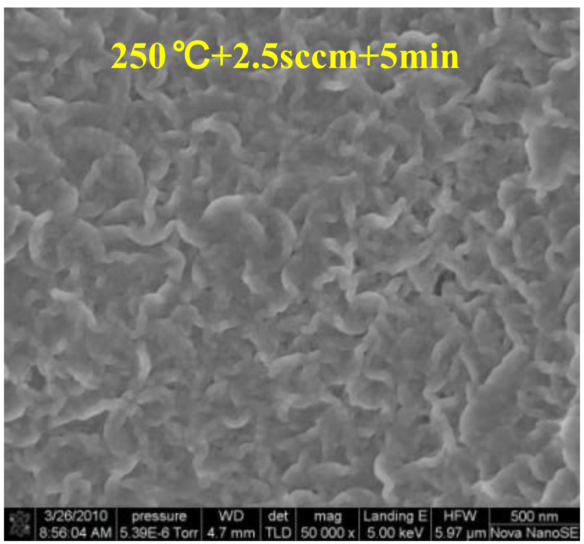
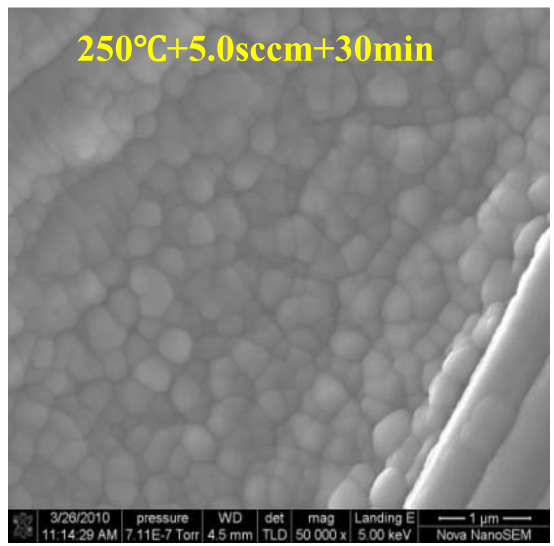
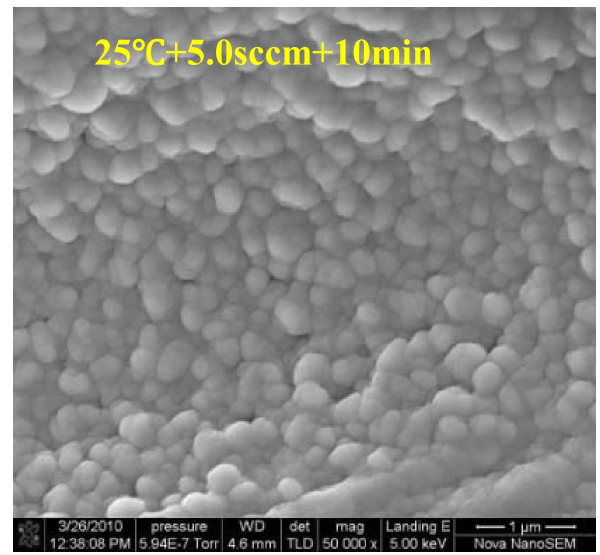
Microstructural analysis of Si films

- Effects of deposition time on the Si morphology
- Effects of SiH_4 flow rate on the Si morphology
- Effects of deposition temperature on the Si morphology

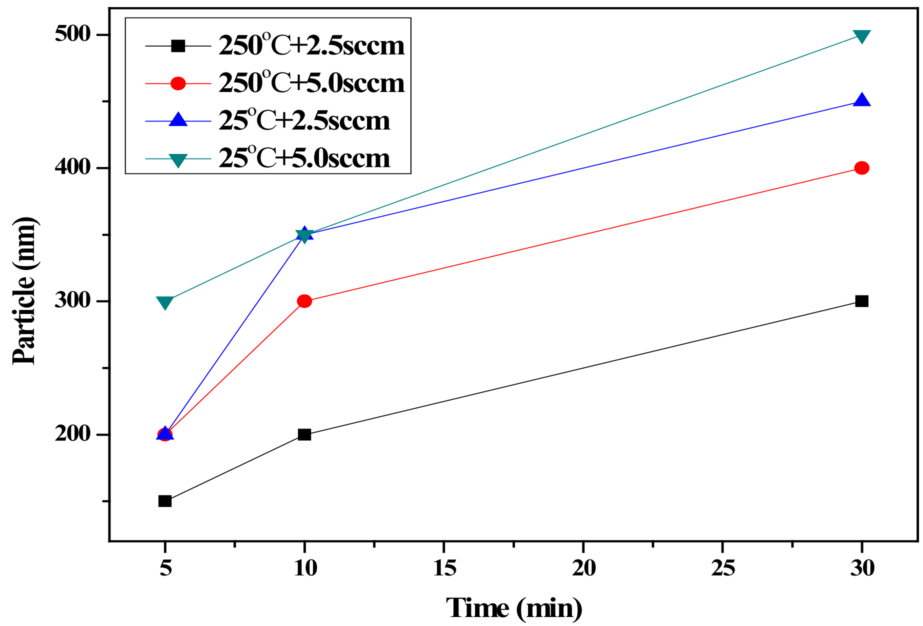






Accomplishments __ Characterization of Si coating

Effects of process parameters on the Si grain size



- Silicon film has been successfully fabricated by CVD; grain size from 100 nm to 500 nm.
- The Si coated conductive web is comprised of about 60.76 wt% Si element.
- Silicon film is amorphous

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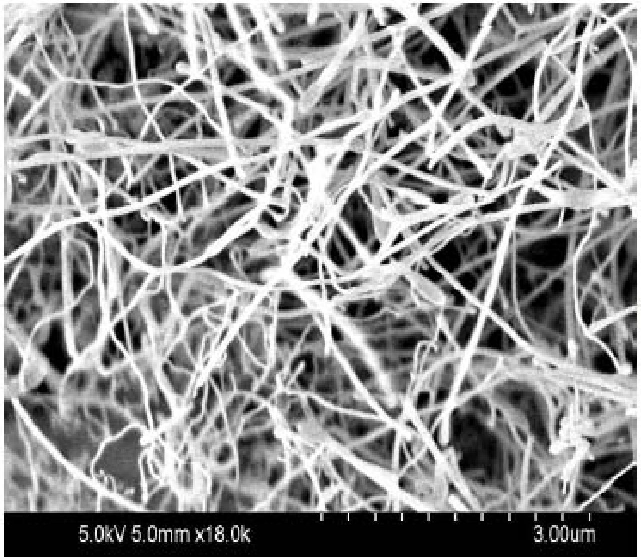
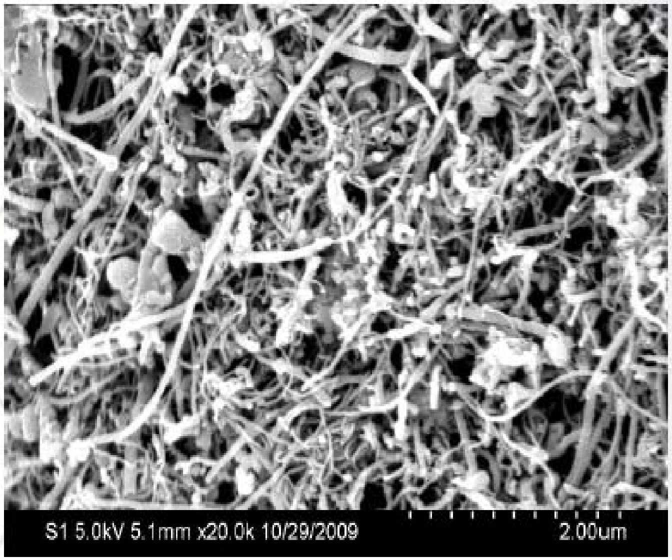
Accomplishments __ (Si nanowire/conductive web)



SEM image of Silicon nanowires grown by a chemical process



SEM image of Silicon nanowires grown within CNTs

- Low-cost process: Chemical solution process
- Tailorable Si loading: 5 wt% ~ 50 wt%

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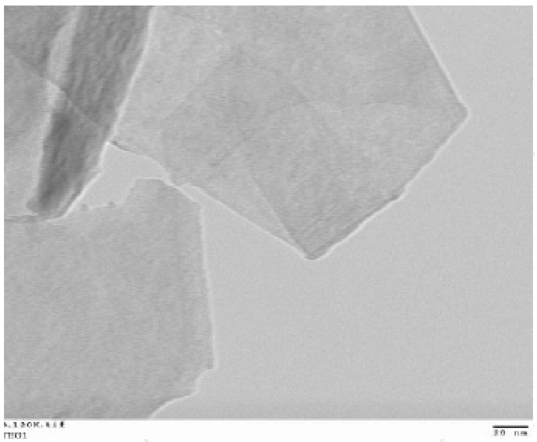
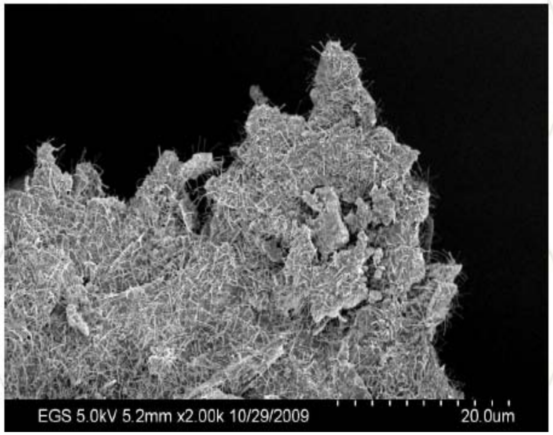
Accomplishments _ (Si nanowire/NGP conductive web)

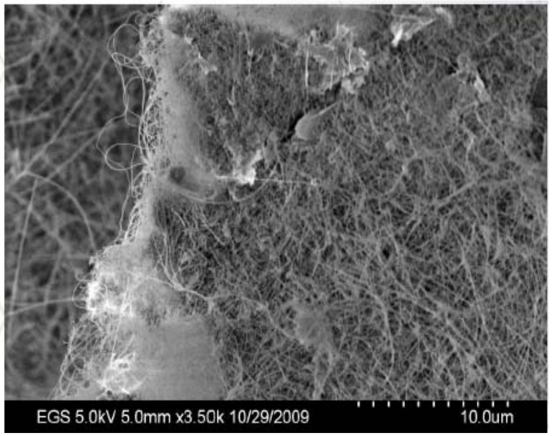
Silane-less Deposition of Si on Nano Graphene Platelets (NGPs)



Nano Graphene Platelets



SEM image of Silicon nanowires grown on NGPs by chemical process



SEM image of Silicon nanowires grown on NGPs

- Low-cost process: Chemical solution process
- Tailorable Si loading: 5wt% ~ 50wt%
- Highly conductive substrate: NGPs

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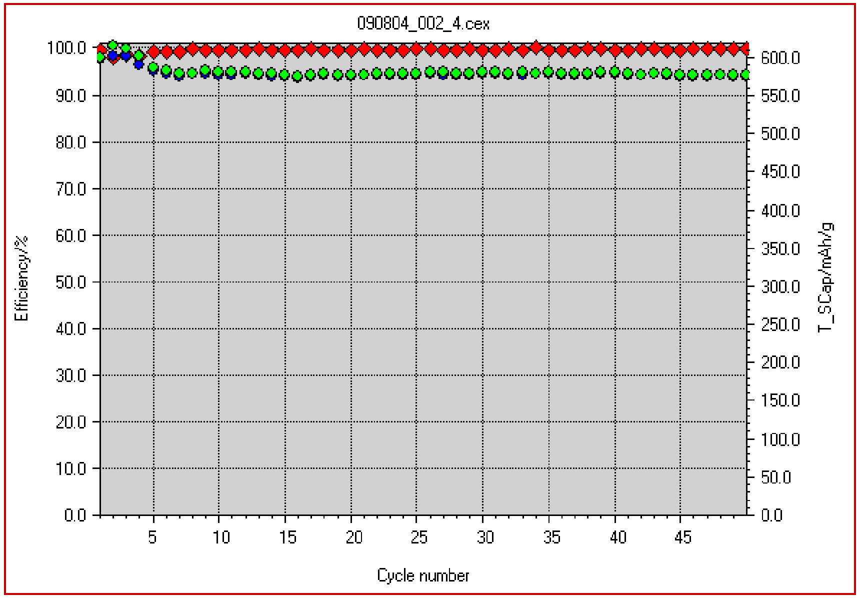
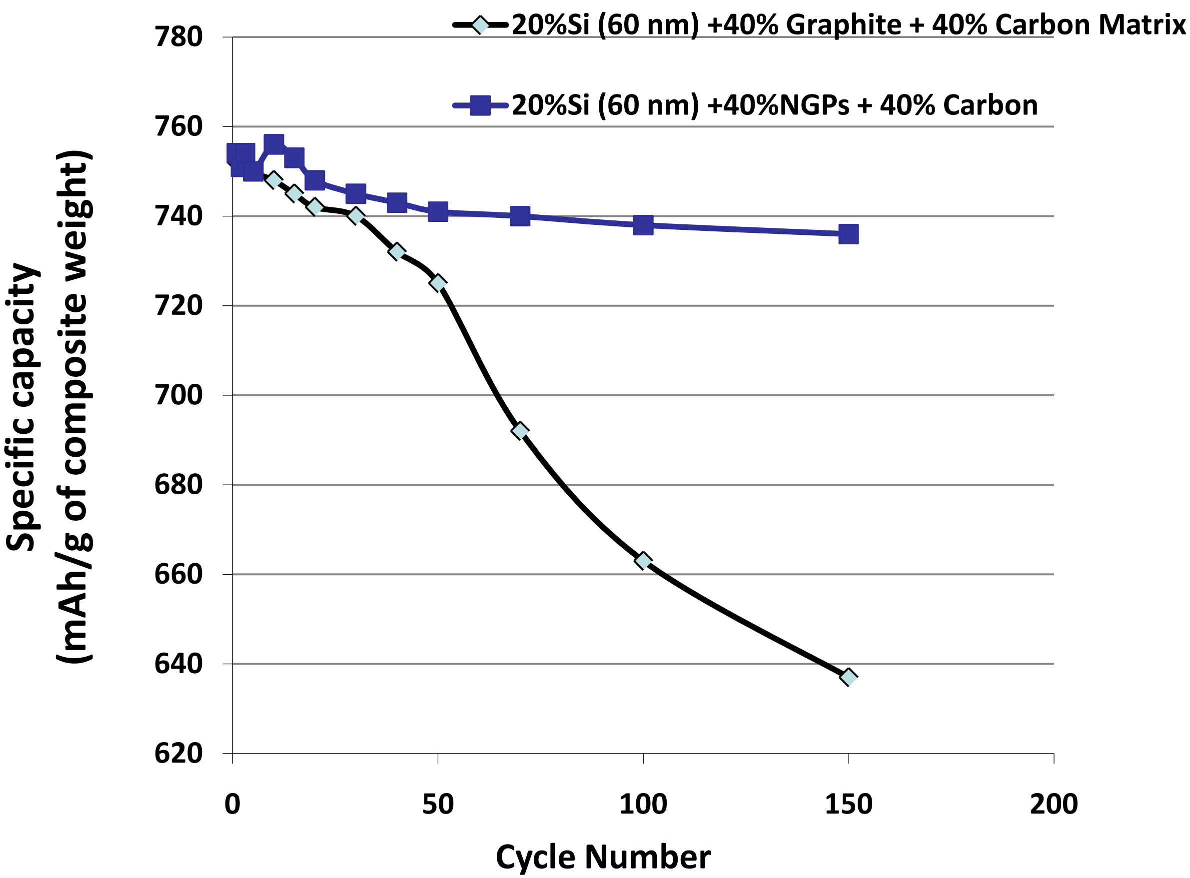
Accomplishments

---- Small lab-scale cell performance



- Si Loading: < 15 wt%
- Specific surface area (m^2/g): < 2.0 m^2/g
- First cycle efficiency: > 93%
- Tap density: >1.2 g /cm^3
- Charge / Discharge rate: 0.35C

Accomplishments
- Half-cell performance



- Si Loading: < 21 wt%
- First cycle efficiency: > 93%
- Charge / Discharge rate: 1C

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Accomplishments _ Reporting

- **Reporting (Fedreporting.gov, VIPERS, etc.)**
  - √ Kick-off Meeting
  - √ 1st Quarterly Report
  - √ 2nd Quarterly Report
  - √ Progress Report
  - √ Final Scientific Report
  - √ SF 425 Federal Financial Report- Q1

Collaboration and Coordination

Partners:

- **K2 Energy Solutions, Inc.**

K2 Energy will perform electrochemical testing and provide battery specifications for various market segments, including automotive and non-automotive, and will be one of the first adopters of the technology at the conclusion of the project. A lab scale battery evaluation line has been established at K2' USA facility.

- **Applied Sciences, Inc.**

ASI will provide the VG-CNFs, Angstron will provide NGPs, Angstron will mix NGPs and VG-CNFs to form a porous web of nano filaments that will compare with Angstron's conductive web.

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Collaboration and Coordination

➢ **The proposing team includes companies leading in their respective markets along the entire supply chain**

The suppliers

Angstron – a leading supplier of NGPs and NGP-based anode technology

ASI - a world leading supplier of CNFs and developer of a breakthrough VG-CNF-based anode technology

The technology integrator and battery producer

K2 - a leading manufacturer of the safer lithium iron phosphate batteries

The OEM

GM – world's leading producer of automobiles,

HST Auto – a leading producer of high-performance cars).

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Proposed Future Work---- FY2010

- A larger lab-scale CVD system will be installed and operated at Angstron Materials. The Si coating processes will be optimized by varying the time, pressure, and silane concentration to achieve desired properties.
- A safe operating procedure for the coating process will be established, including MSDS of Silane, and the detailed personnel protection requirements.
- The morphology, thickness, crystal structure (crystalline or amorphous structure), and the weight percentage of Si coating will be characterized during FY 2010.
- The evaluation of Si-coated anode materials by the half cell method will be conducted at Angstron and K2 during FY 2010

Proposed Future Work---- FY2011

- Development and optimization of processes for mass-producing Si-supporting CNF-NGP blends
- Optimized manufacturing parameters of CVD, including temperature, total pressure, gas flow rates, and substrate temperature will be obtained.
- A new nano material platform technology for Li-ion battery anode will be developed and fully evaluated with both button cells and 18650 cells.

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Summary____2010 DOE Merit Review

- **Great progress has been made in developing superior lithium ion battery anode technologies:**
  - High-capacity (depending upon the Si proportion, an electrode capacity of 500-2,000 mAh/g is routinely achieved at 0.35C-3C)
  - High-rate capable
- **Actively seeking strategic partners for accelerated commercialization of our anode technologies.**

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Summary:
Advantages of Si-CNF/NGP Technology

- Nano Si coating provides the highest specific capacity.
- NGP/CNT Web serves as a network of interconnected electron-conducting paths.
- NGPs assist in reducing electrical resistance and dissipating the heat generated during battery operations. No additional conductive additives are needed.
- CNFs impart structural integrity to a NGP web and, hence, improve ease of web handling.
- NGPs and electro-spun CNFs are low-cost nano materials.
- The CNF or NGP geometry enables the supported coating to freely undergo strain relaxation in transverse directions.
- NGPs provide geometric confinement effect and 2-D envelop maintains good contact with Si particles.
- A coating thickness less than 100 nm means an ultra-short lithium ion diffusion distance. → High rate capable !

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Summary: Value Proposition

- At a price of $30-50/Kg, Angstron's high-capacity anode materials will enable an HEV producer to spend an additional $120-$150 (including anode price difference and costs for additional cathode and electrolyte amounts, corresponding 4%-5% of the total cost of a $3000 battery) to double the battery-only operating range of a $30,000 HEV.
  - Doubling this range would dramatically improve the market potential for HEVs.
  - The Chevy Volt (as an example) has a targeted range of 40 miles on its battery pack. Our technology could provide GM Volt with a commanding 80 mile range.