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

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Overview

Timeline

- Project start: Sept. 15, 2009
- Project end: Sept. 14, 2012
- Percent complete: 60%

Budget

- **Total project funding**
  DOE share: $1,594,303
  Contractor share: $1,603,937
- Funding received in FY10: $671,057
- Funding for FY11: $485,103

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
- Nanotek Instruments, Inc.,-- CNFs

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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.

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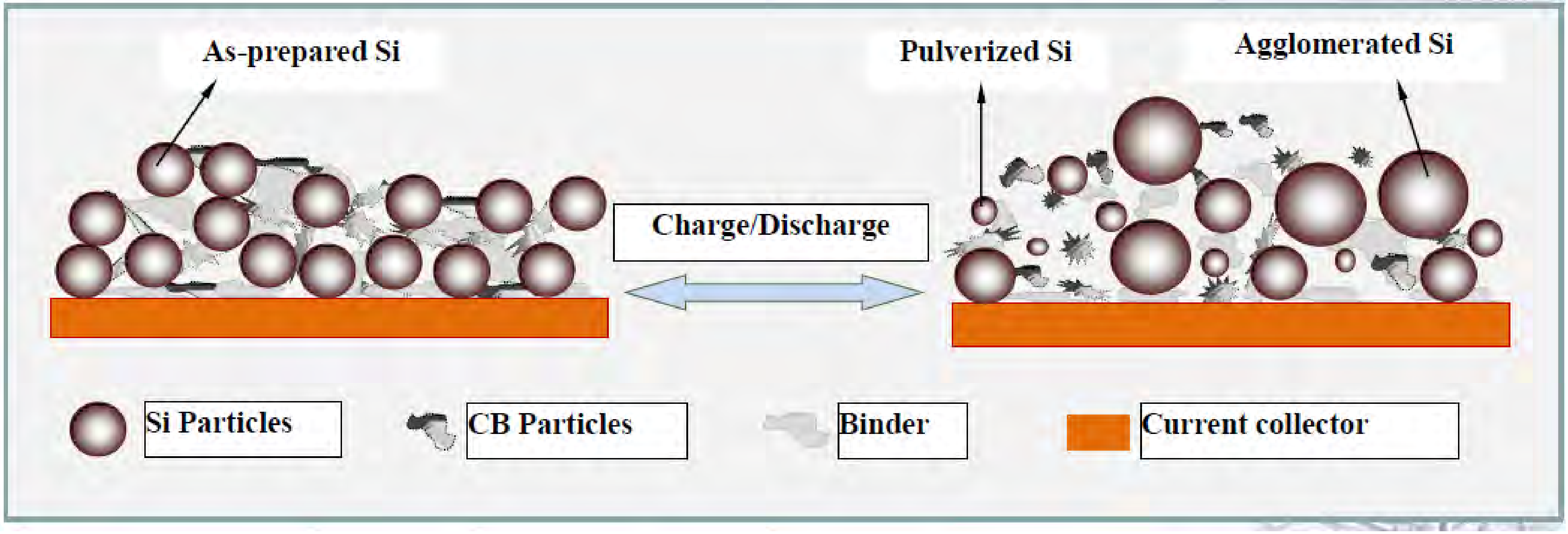
Approach

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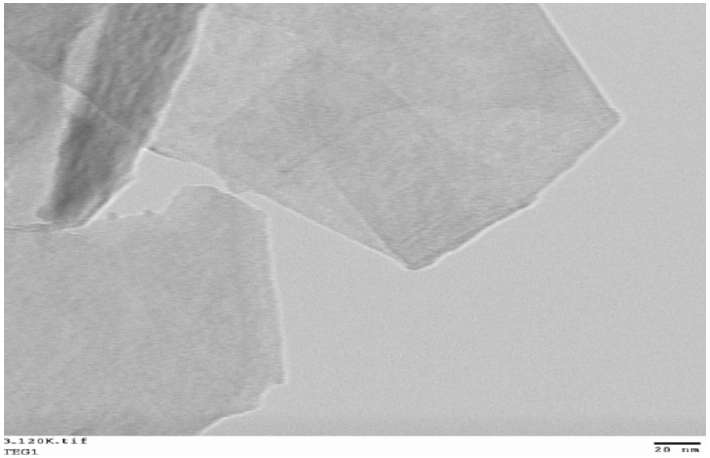
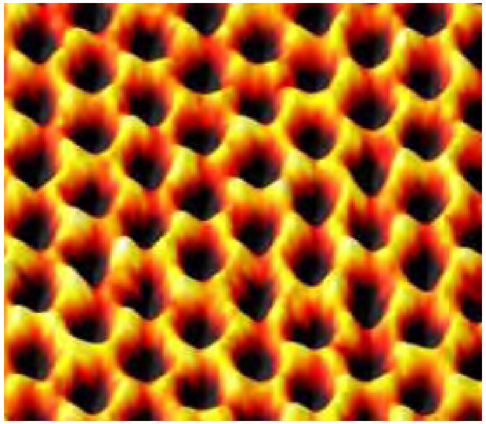
Approach:
Using NGP as a supportive/protective substrate
Nano graphene platelets (NGPs)

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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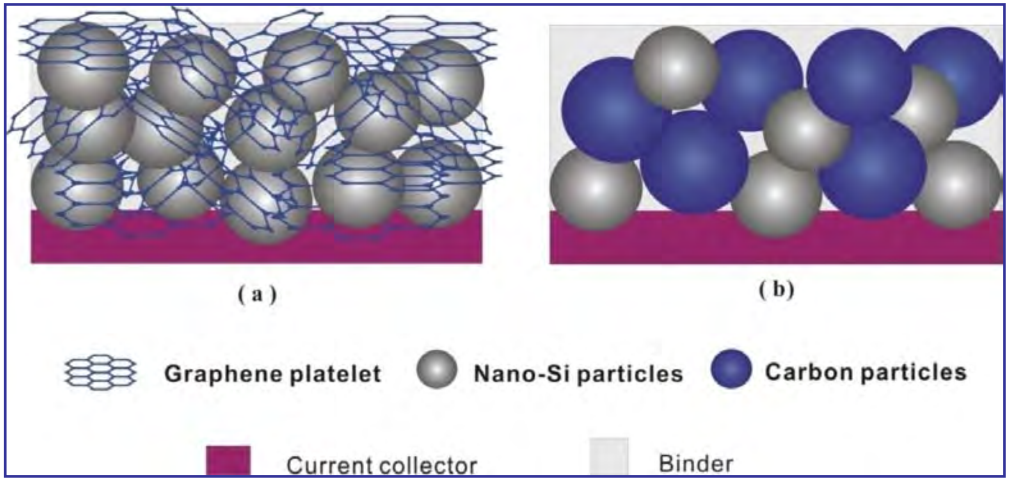
Approach

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: 500-1,000 mAh/g

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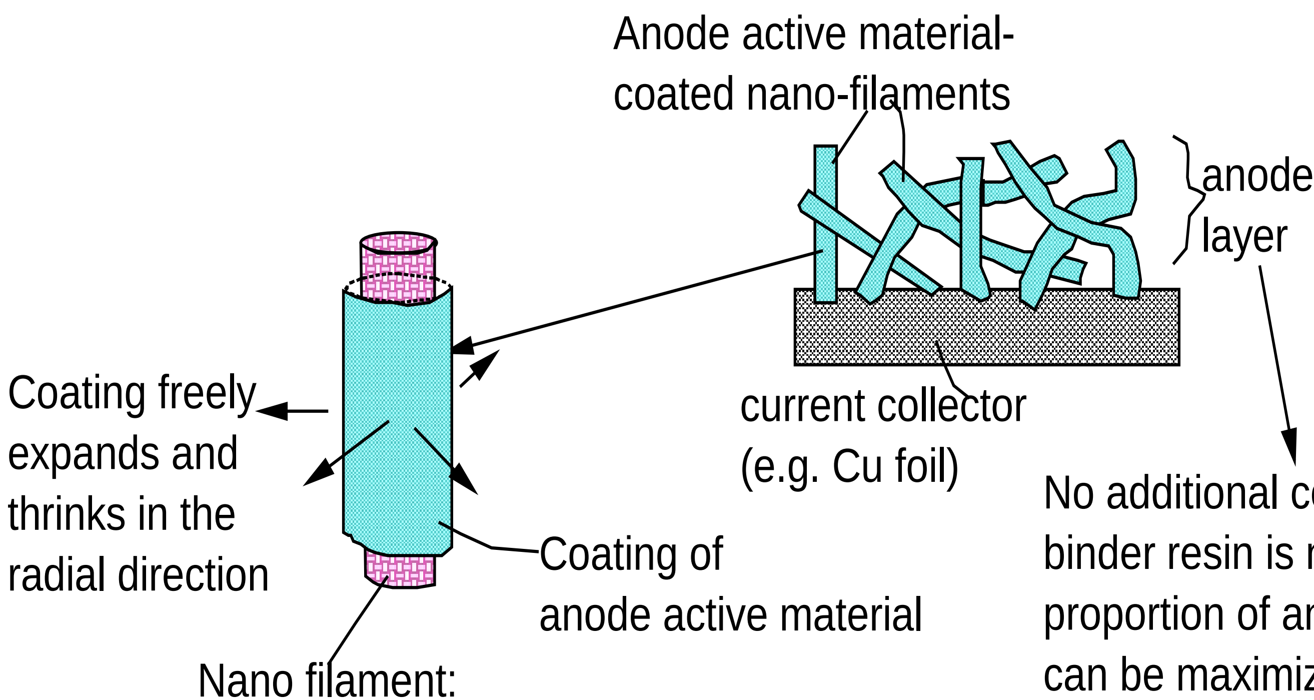
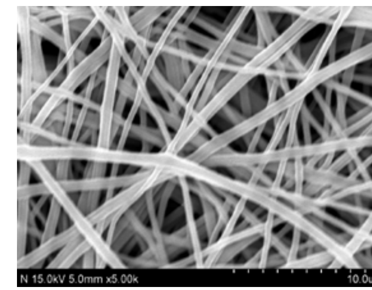
Approach

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**





No additional conductive additive or binder resin is needed. The proportion of anode active material can be maximized.

Major Milestones Reached

Table 2: Tasks and Milestones. Notes:

Tasks	Metrics
Task 2.0: Project Management & Planning	M1: Project plan finalized
Phase II Task 2: Development and Optimization of Anode Materials • 100% completed • >50% completed	M2: (1) Optimal anode material properties identified; (2) For the small cells (75 mAh), achieve specific capacities of 650mAh/g, 50 cycles at the 1C rate with < 20% capacity fade, Si coating weigh percentage ~ 15; (3) For the 18650 or larger format cells, achieve specific capacities of 1000 mAh/g, 750 cycles of ~70% state of charge (SOC) swing with less than 20% capacity fade; Si coating weight fraction ~ 30%. M3: Ability to cost-effectively & consistently manufacture Si-coated nano filaments: (1) scaled up slurry molding technique for mass-producing preforms; (2) a uniform Si coating with thickness 50nm ~500nm, produced by CVD; (3) Optimized parameters of dynimic-CVD, including wire temperature, total pressure, gas flow rates, and substrate temperature. (4) A new nano material platform technology for Li-ion battery anode. M4: (1) Evaluate performance of both lab- and large format cells, and provide feedback for re-design of anode materials; (2) Install production line for 18650-format cylindrical wound cells (capacity of 1000 cells/day).
Phase III, Task 3: Commercialization of Next Generation of Li-ion Batteries • 100% completed • >50% completed	M5: (1) Prototype Li-ion battery for vehicle applications constructed and tested; (2) Progress reports (p) and final report (f)

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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 .

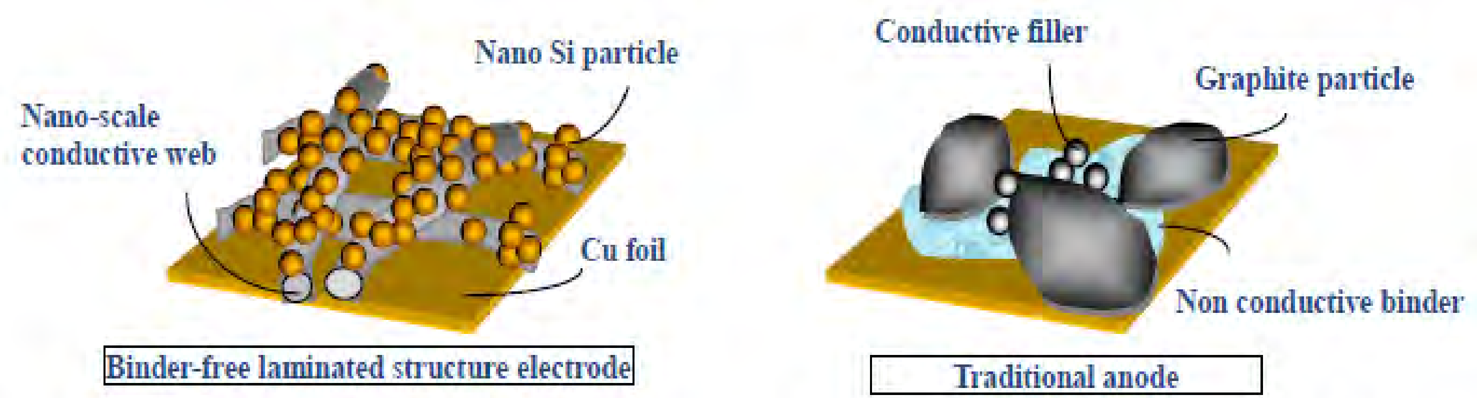

Figure 1. A comparison of a binder-free laminated structure anode and a traditional anode.

- A conductive web of nano-fibers was directly electro-spun onto the copper foil current collector without any binder.
- The electrical conductivity of this laminated electrode is about 7 times higher than that of the electrode made by traditional coating processes.

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Accomplishments _ Prepared the large-size NGP/CNF web

Figure 2. Optical images of a laminated structure anode electrode during different stages of the heat treatment process: (a) as-made, (b) pre-oxidized, (c) after carbonization.

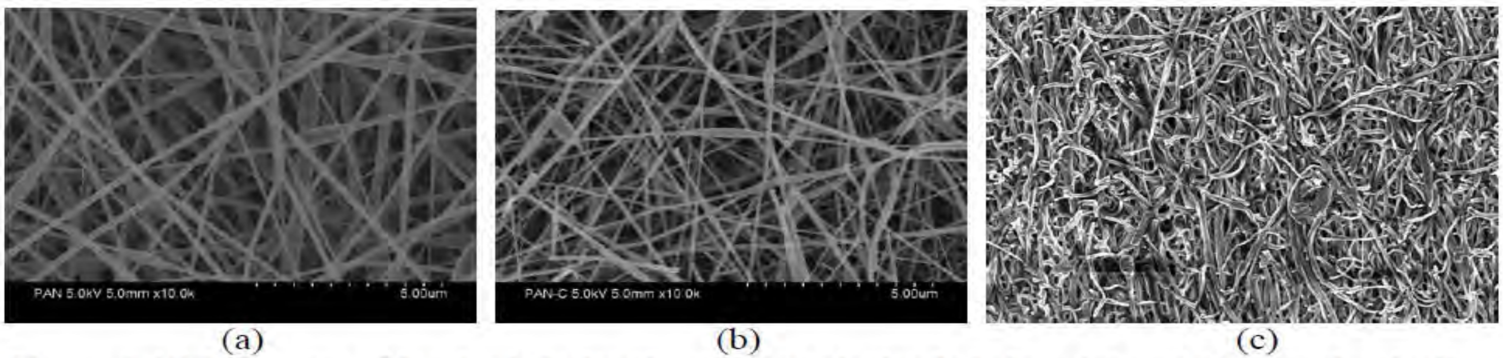
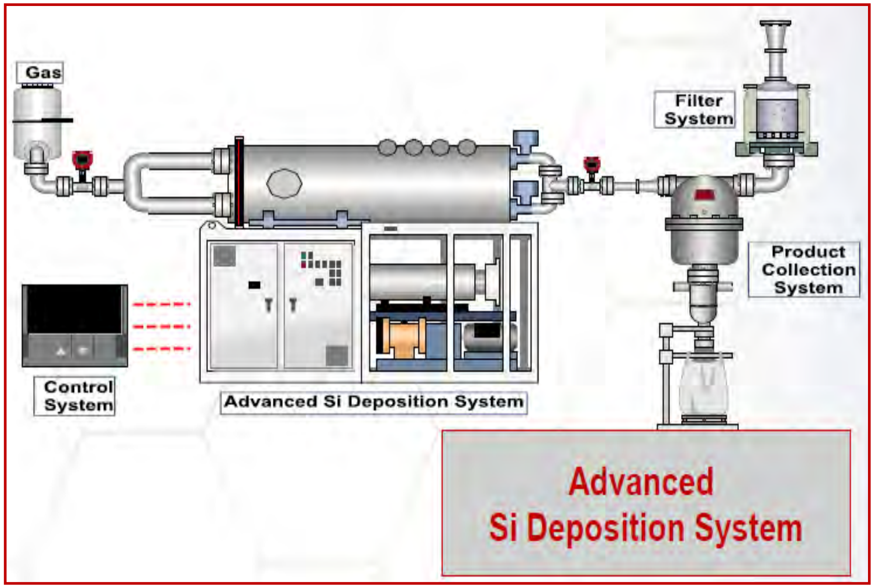


Figure 3. SEM images of laminated-structure anode electrode before (a) and after carbonization (b). An image of previously prepared structure (c) is also shown for comparison.

This large-size conductive web can be used in a roll-to-roll process to make the anode electrode in a cost-effective manner, further reducing the total cost of a battery.

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.**

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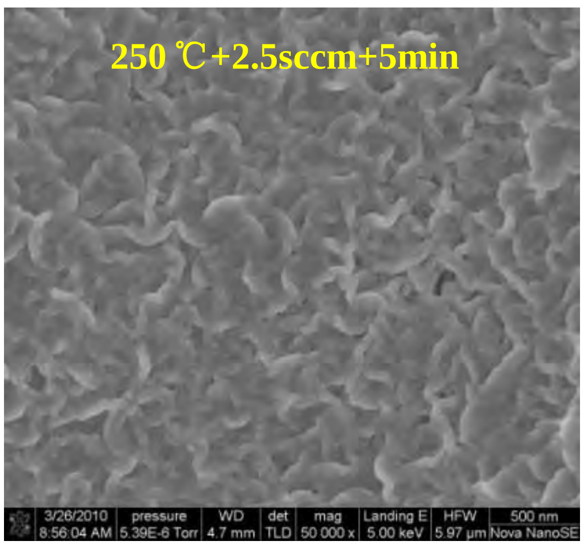
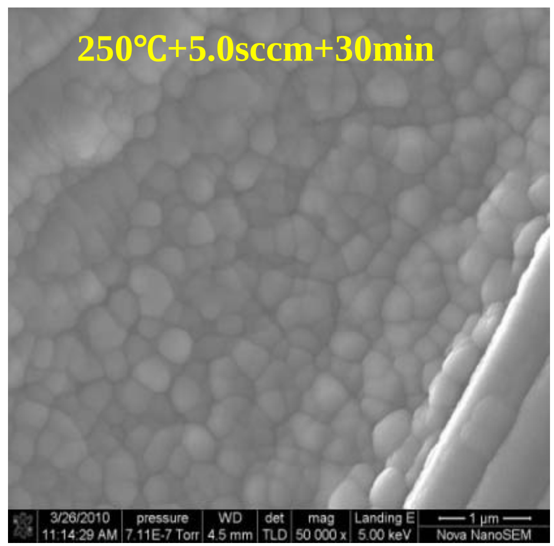
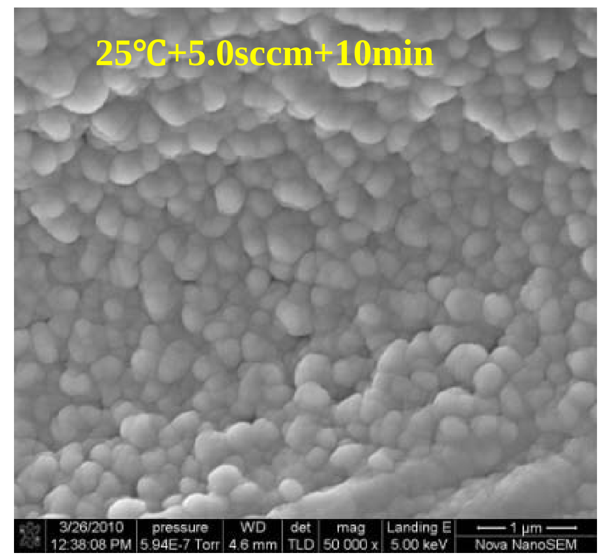
Microstructural analysis of Si films

- 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







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Accomplishments ___ Characterization of Si coating

Microstructure of Si film on NGPs

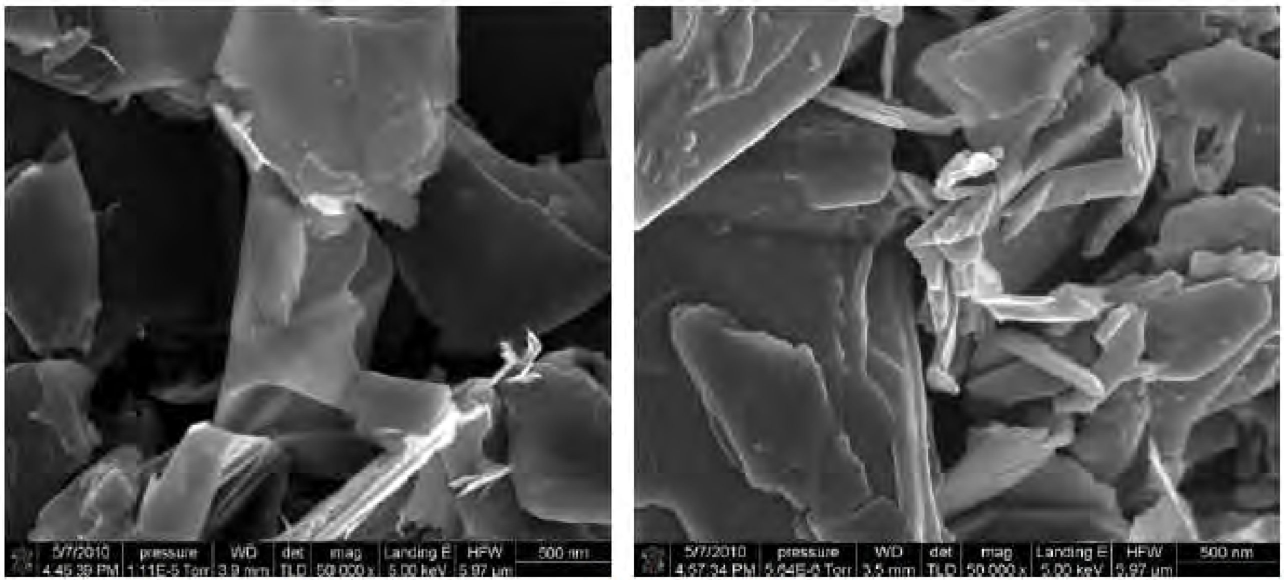

Figure 5. SEM images of uncoated graphene platelets (left) and Si coated graphene platelets (right).

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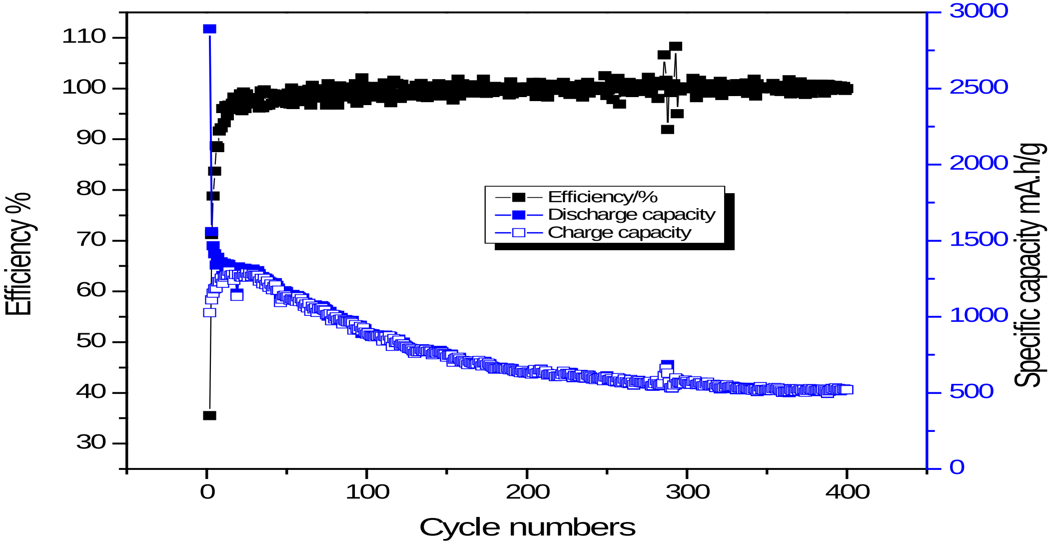
Accomplishments

---- Small lab-scale cell performance



It can be seen that the discharge capacity is still higher than 500 mAh/g after 400 cycles. Similar finding (fast capacity fading after initial 20-30 cycles) has also been reported in some recent literature.

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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

Nanotek - a supplier of electro-spun CNFs.

The technology integrator and battery producer

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

E-One Moli – A leading manufacturer of EV cells

The OEM

Honda America – world's leading producer of automobiles,

Nissan Motor – a leading producer of EVs.

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Proposed Future Work---- FY2011

• Large size (12” x 12”) conductive webs with laminated structures of NGP/CNF and the anode electrodes using Si-coated conductive webs will be prepared at Angstron.

• Further evaluation of Si/conductive web anode materials, Si/graphene powder anode materials, and Si/laminated anode electrode by using button cells will be continued both at Angstron and K2, and pouch cells for full cell performance evaluation will be made and tested.

• Commercialization activities: (1) We will have additional conference meetings and site visits with potential investors and partners. (2) A pilot-scale production line to manufacture alloy anode materials will be set up during the next two quarters.

Summary____2011 DOE Merit Review

- A large-size (12” x 12”) NGP/CNF conductive web has been prepared by using Angstron’s nano-fiber electro-spinning system.
- This large-size conductive web can be directly deposited onto a copper foil current collector in a continuous manner. This technology could enable a roll-to-roll process for making high-performance, low-cost anode electrodes, further reducing the total cost of a battery.

Summary____2011 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 about 500-2,000 mAh/g is routinely achieved at 0.35C-10C)
  - – 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.

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