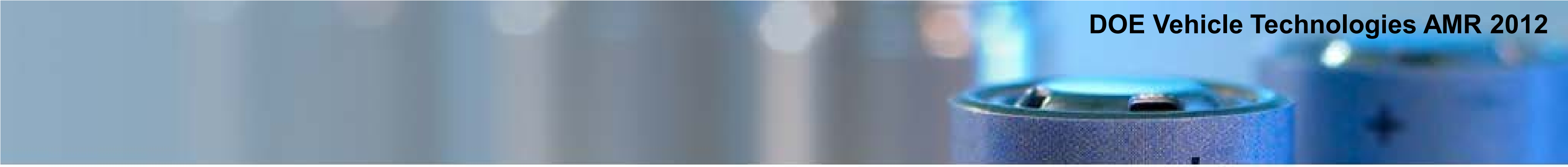

Innovative Cell Materials and Design for 300 Mile Range EVs

Yimin Zhu, PD/PI

Nanosys, Inc, Palo Alto, California

May 14, 2012

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Overview

Timeline

- Start: Oct. 1st, 2011
- End: Sept. 30th, 2014
- 15% complete

Budget

- Total project funding
  - DOE share: $4,840K
  - Contractor share: $3,220K
- Funding received in FY11: $123K
- Funding for FY12: $1,498K

Barriers

- Barriers addressed
  - Performance: Low Wh/kg & Wh/L
  - Life: Poor deep discharge cycles
  - Cost: High $/kWh
- Targets

Anode:	>700 mAh/g ⇨	1,600 mAh/g	>800 cycles
Cathode:	250 mAh/g ⇨	>260 mAh/g	>800 cycle
Cell:	350 Wh/kg	800 Wh/L	<150 $/kWh

Partners

- Interactions/ collaborations

Peidong Yang – UC-Berkeley
Mohamed Alamgir - LG Chem Power (Co-PI)
Geun-Chang Chung - LG Chem
Other DOE National Labs – LBNL, ANL

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Project Objectives

Anode:

To develop a 700~1000 mAh/g Si anode (SiNANOde^{TM}) of >800 cycles, and an eventual 1,600 mAh/g SiNANOde at the end of the program.

Year 1: The project started from Oct. 2011 and the review covers Oct. 2011~Mar. 2012.

- Demonstrate 700~1000 mAh/g SiNANOde with capability to meet a target cycle life of >800
- Demonstrate SiNANOde capability to achieve high electrode loading of 3~5mA/cm2
- Demonstrate an approach to achieve 1600 mAh/g

Cathode:

To develop a 260 mAh/g cathode (Mn-rich) of >800 cycles.

Year 1: The project started from Oct. 2011 and the review cover Oct. 2011~Mar. 2012

- Improve 250 mAh/g cathode with capability to meet a target cycle life of >800
- Demonstrate cathode capability to achieve high electrode loading
- Demonstrate an approach to achieve >260 mAh/g

Cell:

To develop unique large format cell combining SiNANOde with >260 mAh/g cathode to achieve 350 Wh/kg and 800 Wh/L, resulting in driving > 300 miles on a single charge and achieving a cell level cost target of <150 $/kWh.

Year 1: The project related to cell formation will start from May 2012

- Develop cell design with 250 mAh/g cathode and 700~1000 mAh/g (or 1500~1600 mAh/g) anode to achieve 350 Wh/kg
- Demonstrate the feasibility of the cell through single layer pouch cell tests
- Demonstrate 1~2 Ah cell with >250 mAh/g cathode and 700~1000 mAh/g SiNANOde

Project Milestone

Milestones in the period of Oct. 26th, 2011 ~ Mar. 30th, 2012:

- Baseline SiNANOde Cycle Life Demonstration (Achievements shown in this review)
- SiNANOde Specific Capacity Improvement: Increase to 700~1000mAh/g and improve cycle life (Achievements shown in this review)
- Optimization of cathode composition (Achievements shown in this review)
- Scale-up SiNANOde manufacturing process (Pilot line production demonstrated)

Overall Project Milestone Status

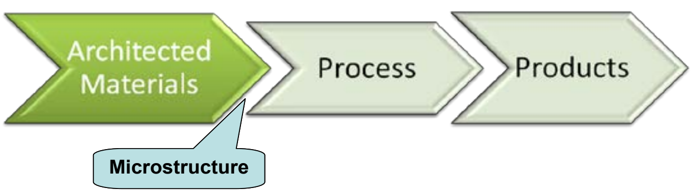
Kick off meeting	**10/26/11**	**Completed**
1st quarterly report	**1/31/12**	**Completed**
Initial Specifications Complete	**10/31/11**	**Completed**
Material Properties Modeled	**12/30/11**	**Completed**
Anode material batch deliveries and characterization	**Multiple**	**On track**
Cathode material batch deliveries and characterization	**Multiple**	**On track**
Test Cell	**Multiple**	**On track**
	(1st deliverable date Nov. 30th, 2012: 18 cells)	
Systems Integration Design Complete	**9/31/12**	**On track**
Test Reports Delivered to DoE	**Multiple**	**On track**

Project Approach

Value Shifting to Novel, Tunable Materials

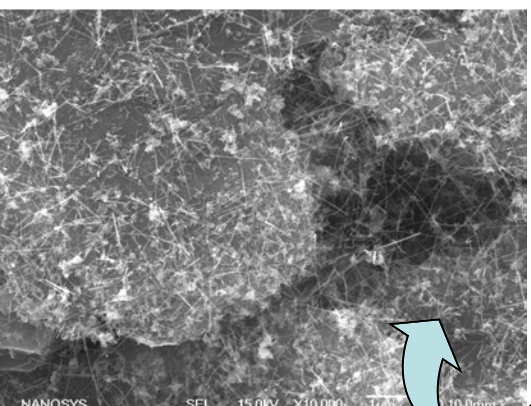
Industrial Revolution Before

Materials Revolution Now - Nanotechnology



Utilize Advantages & Overcome Disadvantages of High Specific Capacity Si Nano-materials

Advantages	Overcome Disadvantages
Better accommodation of strains during cycling	High surface area leads to higher self discharge & poor cycling performance
Unique conversion reactions	
High interfacial charge transfer rates	Low pack density and low volumetric energy density
Short tunneling length for electronic transport	
Short diffusion length for ionic transport within bulk particles and hence high rate capability	Hard to be mass-produced



Solution

High volume production process using battery graphite as substrate for Si nanowire growth

- Cost effective
- Improves dispersion within slurry
- Si-C conductivity improvement
- Si Weight % or anode specific capacity is controllable, focusing on 500 ~ 1600 mAh/g
- High electrode loading
- Good cycling performance

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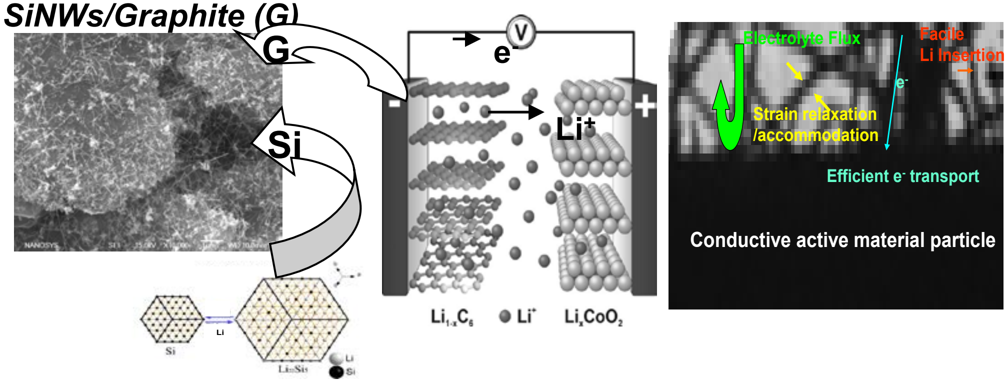
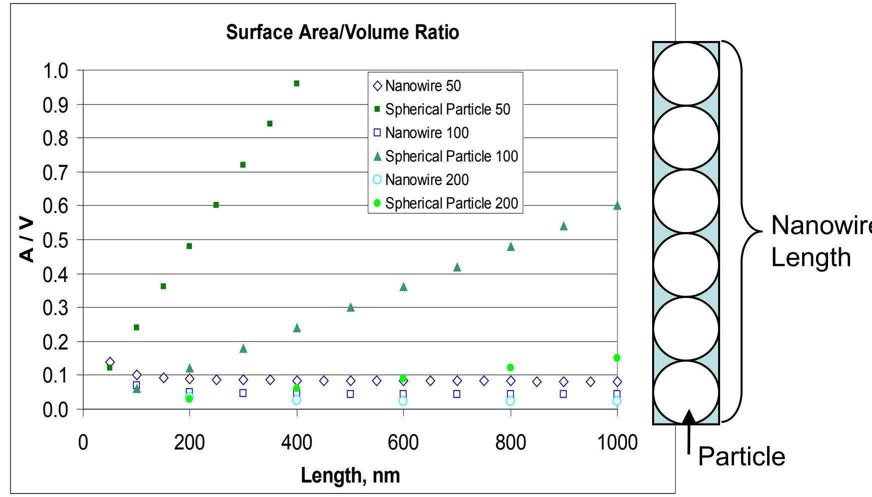
Project Approach

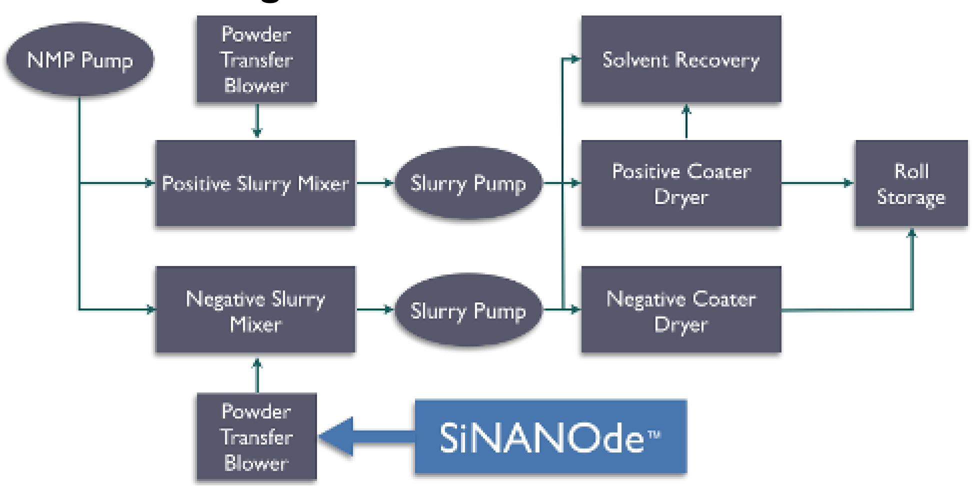
SiNANOde Illustration

SiNWs/Graphite (G)





Integrates into Existing Battery Manufacturing Processes



Lithium-ion Manufacturing Process

- Nanomaterials are generally not stable due to high surface reactivity.
- The nanowire has lower surface area/volume ratio, A/V, compared to the spherical nano-particle with the same diameter.
- Reduction in particle size or diameter results in the A/V ratio much lower for nanowire vs. spherical particle, and hence the nanowires intrinsically have lower surface reactivity and better cycle life, as well nano-material feature in radial direction.

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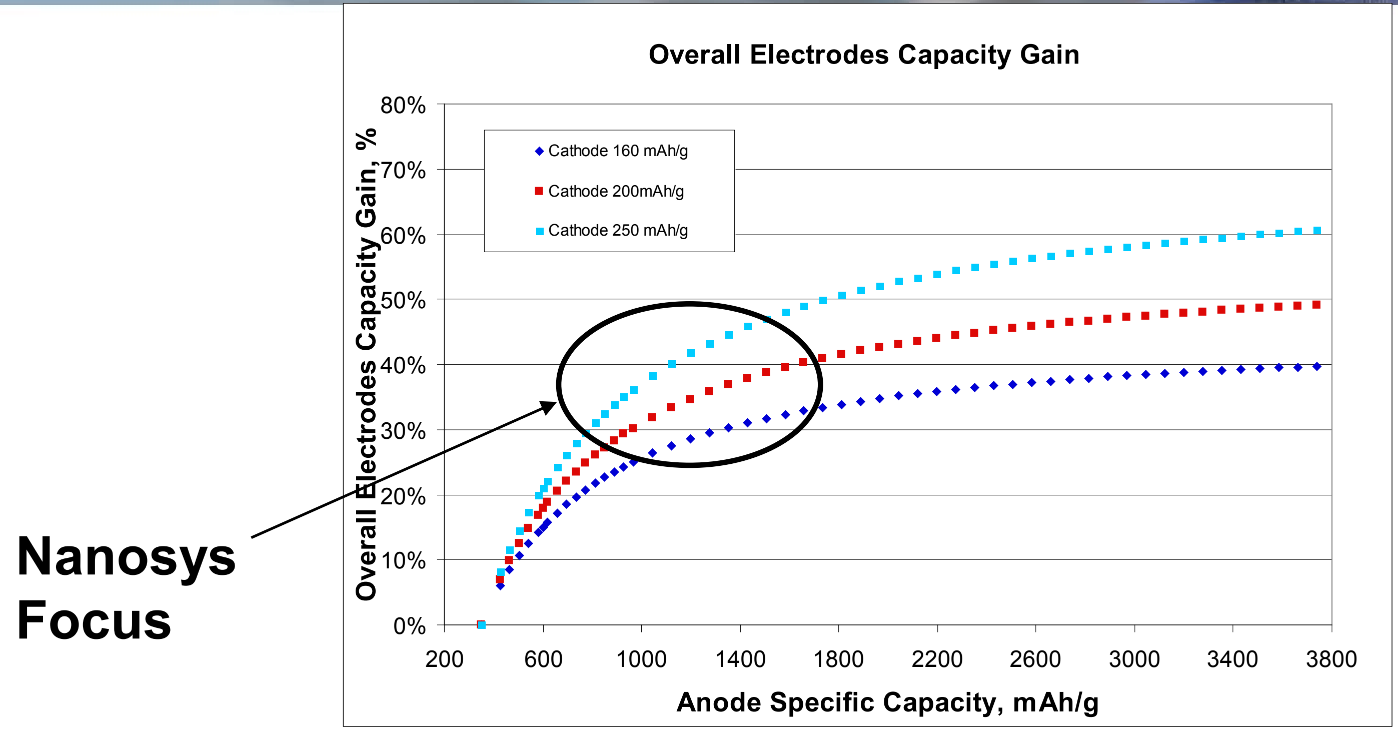
Project Approach
- SiNANOde Production Focus



- Overall cell electrodes capacity can be effectively improved between 30% ~50% when used 900~1600mAh/g SiNANOde and 160~250mAh/g cathode.

- SiNANOde production are both process ready and to meet the cost/production scale requirements for the LiB industry
- Extensive materials metrology capability on site (SEM/TEM/XRD/etc.) and ~1300 channels battery testing

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Cathode Approach

Cathode Development

Cathode materials currently being used in PHEVs and EVs have a maximum capacity of ~ 150 mAh or less. ANL composite cathode (LGCPI licensed this technology) contains a layered component, such as Li_2MnO_3, which is inter-grown with another, such as $LiMn_{0.5}Ni_{0.5}O_2$ or $LiMn_{0.33}Ni_{0.33}Co_{0.33}O_2$, can deliver an initial capacity >250 mAh g^{-1}.

These materials are expected to be significantly stable in non-aqueous electrolytes at elevated temperatures, and potentially less expensive.

The high operation voltage electrolyte is being developed

- **Screening the cathode candidate materials (>250 mAh/g)**

  - In-house and commercial Mn-rich cathode materials are being evaluated to search for an attractive cathode for combining with SiNANOde

- **Surface modification of cathode materials**

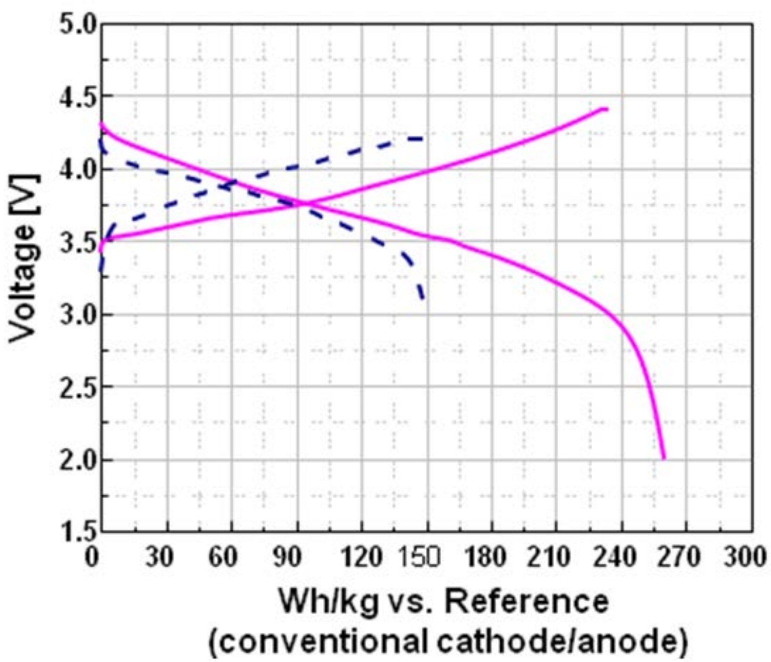
  - Mn-rich cathode materials are trying to be modified on their surface by oxide or other components so that their electrochemical performance and stability can be improved in a cell system.

Cell Development Approach

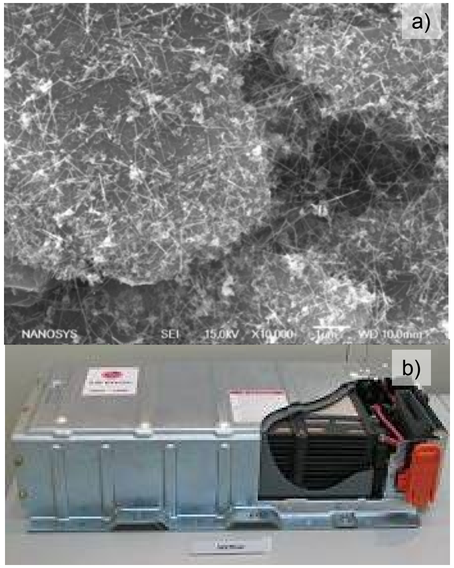
Combing the attractive cathode feature with a high-capacity SiNANOde, we are designing our cells to accomplish our objectives.

Current data shows that LGCPI's proprietary cell fabrication technology (stack-and-fold in a laminated packaging) is suitable for scaling to a larger cell.

It enables to achieve $150/kWh cell level within this program



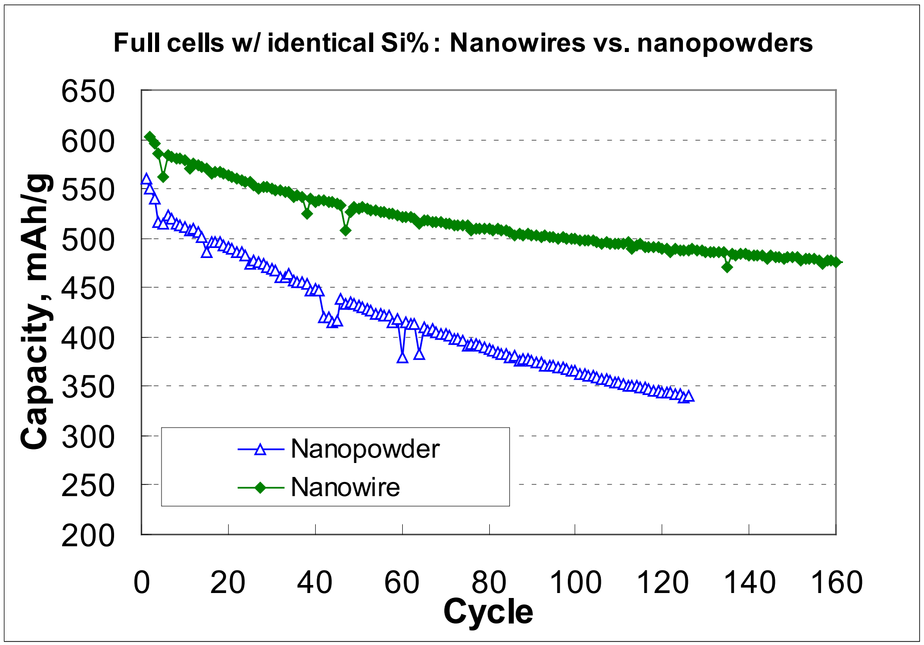
Energy density comparison of a cell made with a conventional cathode/anode with that made using a Mn-rich cathode/Si anode.

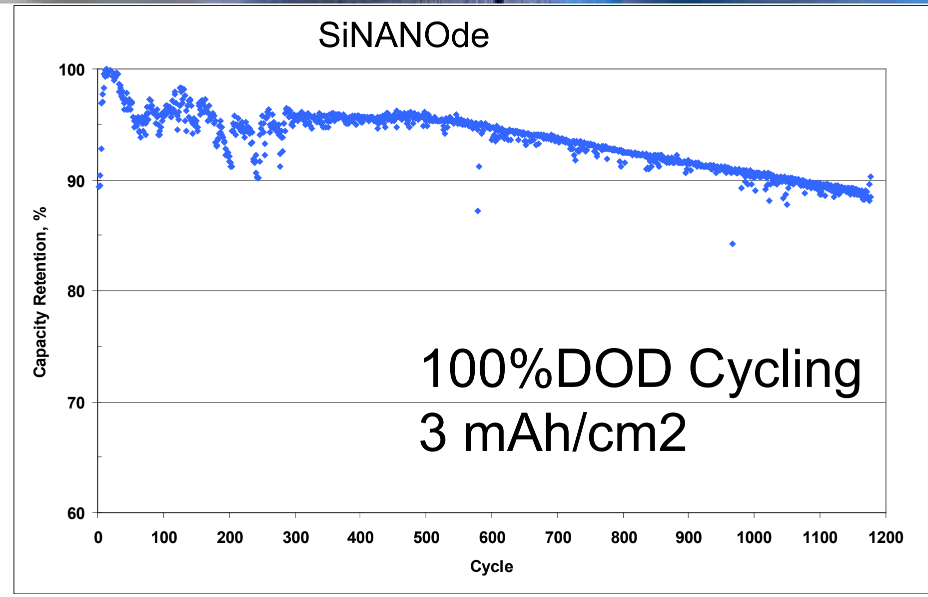


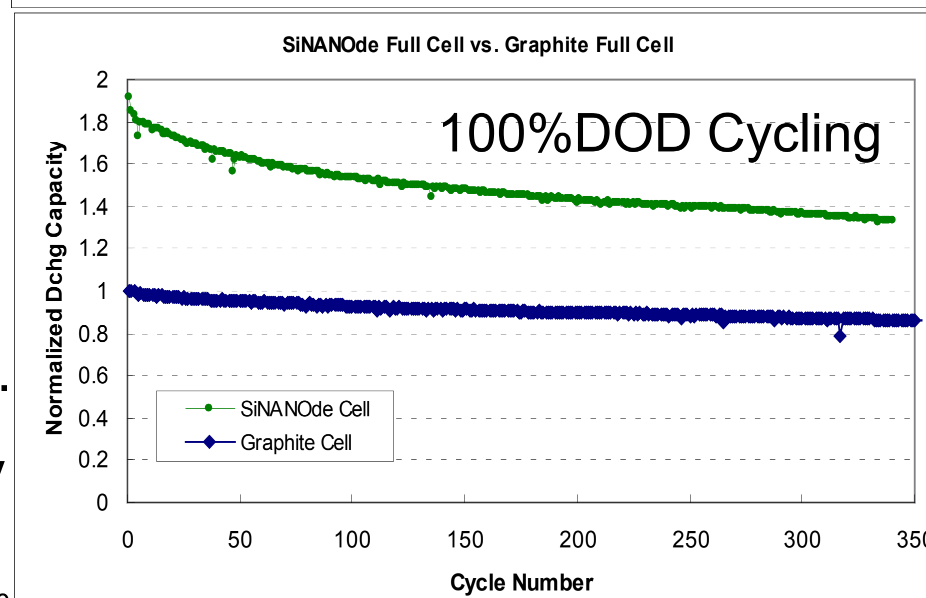
a) Existing SiNANOde™ silicon/graphite composite material
b) CPI/LG Chem horizontal pack baseline

Technical Achievement - Anode

SiNANOde (Green) OUTPERFORM commercial Si nanopowder (Blue) with identical diameter due to its much lower surface area/volume ratio, better dispersion in slurry and conductivity







- SiNANOde half cells have been cycled for more than 1200 times with a capacity retention of > 87%.
- Full cells with a baseline cathode (LCO) & a SiNANOde exhibited ~350 cycles at ~76% capacity retention, which still showed much higher anode-specific capacity over graphite anode.

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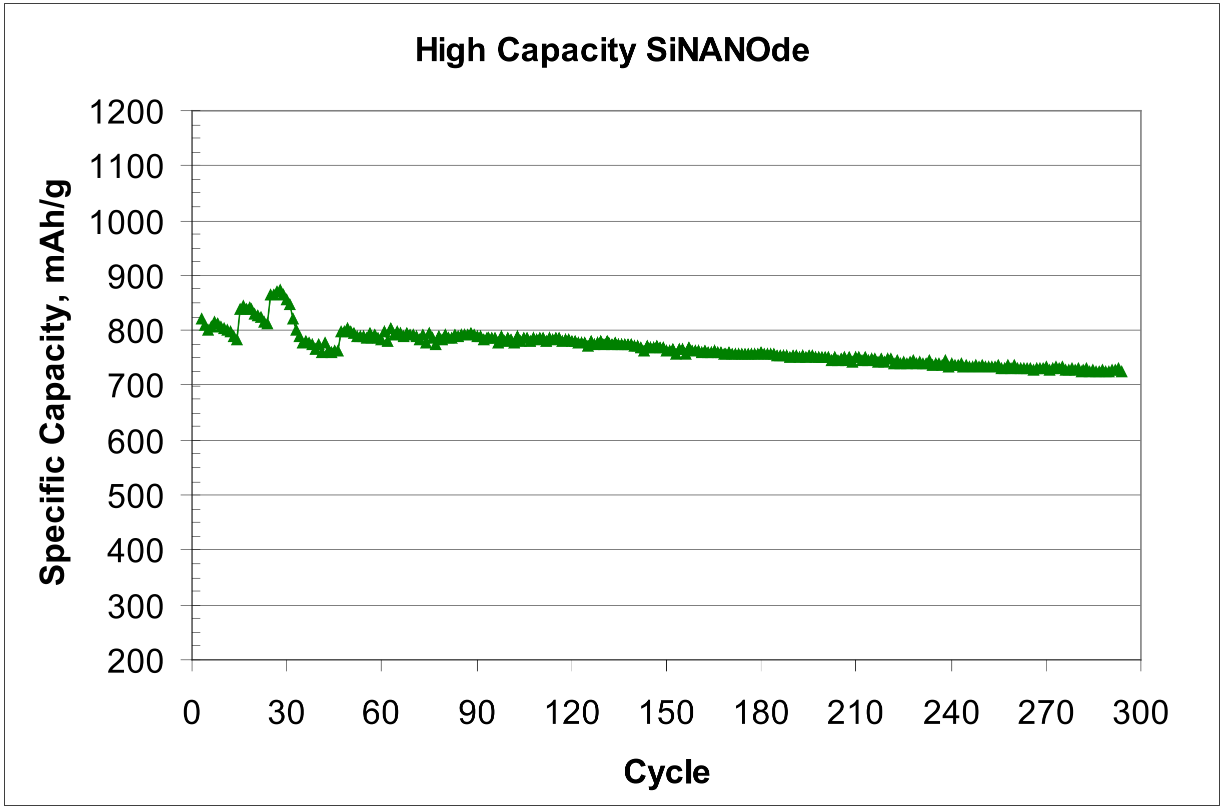
Technical Achievement
- High Capacity Anode: Cycle Life



- Increased the specific capacity of SiNANOde up to 850mAh/g by controlling Si nanowire content.
- Continuously improving the conductivity of SiNANOde to further optimize the SiNANOde material, which has showed longer cycling life of ~300 cycles at 88% capacity retention at 0.3C cycling in the half cells.
- At beginning the cell has been used for various C-rate testing.

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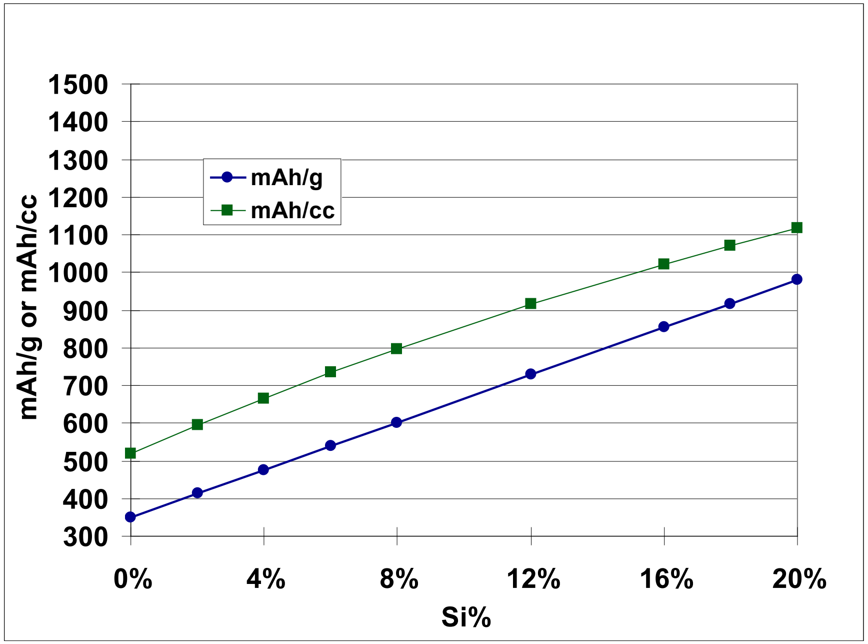
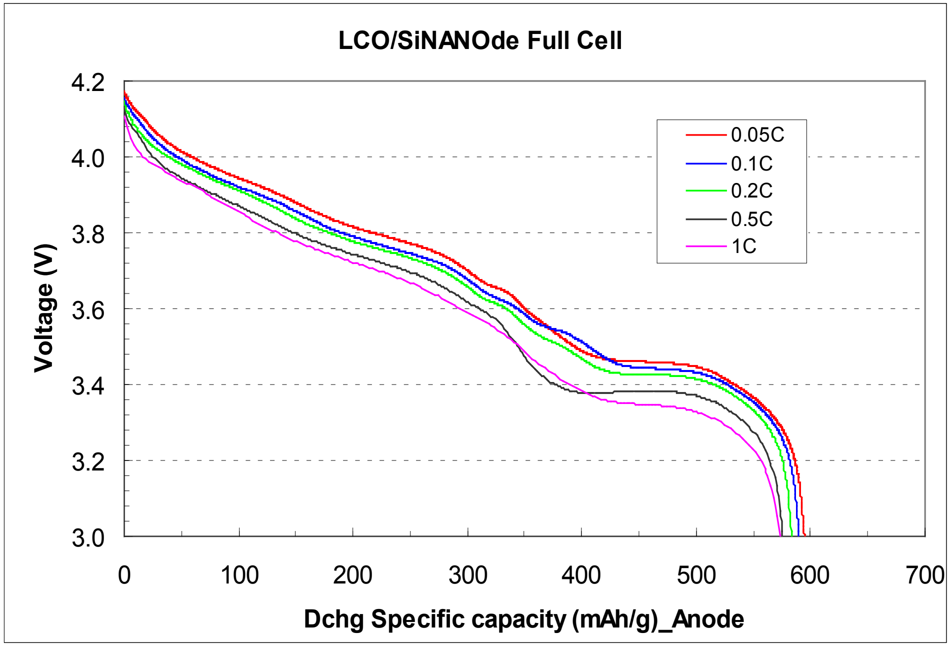
Technical Achievement

- Anode Reversible Specific/Volumetric Capacity & C-rate Performance

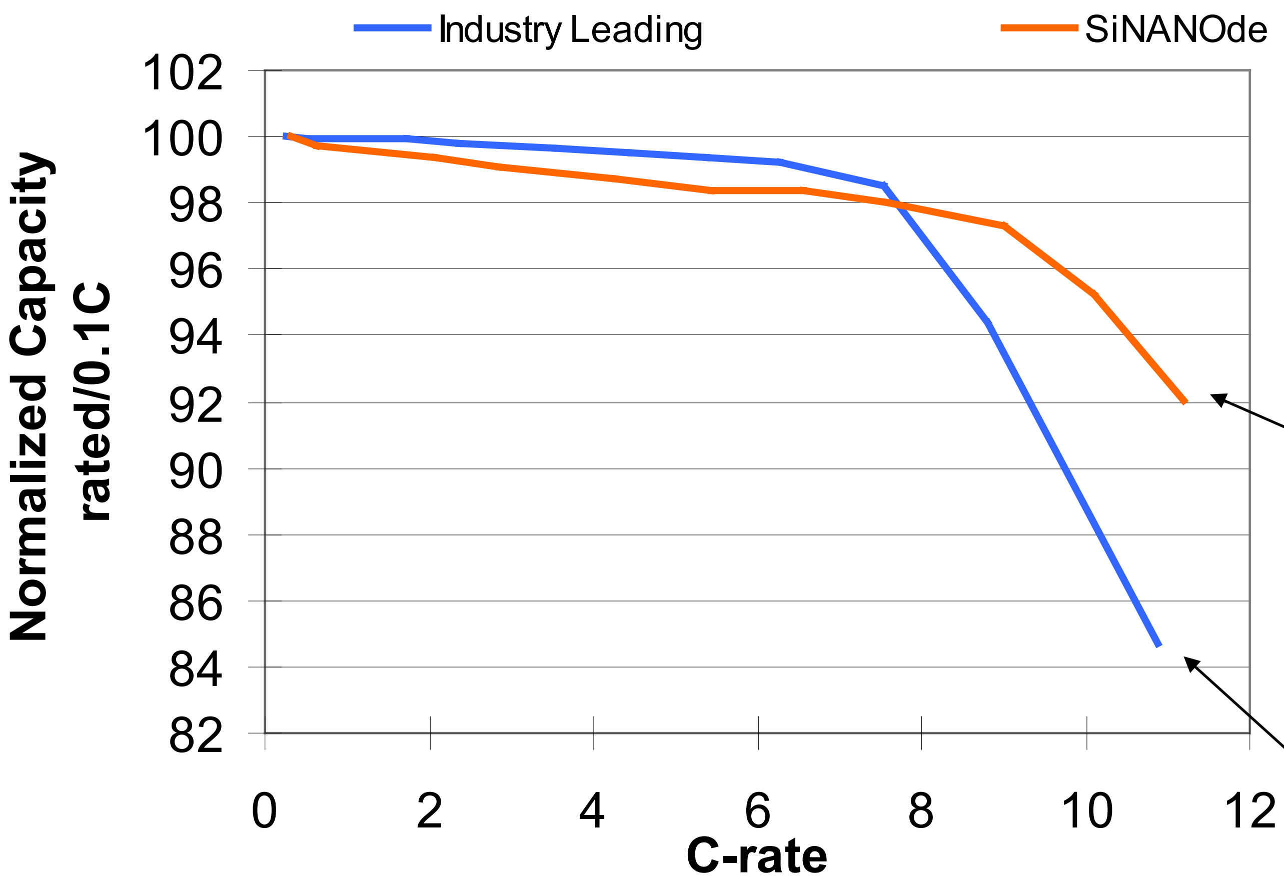


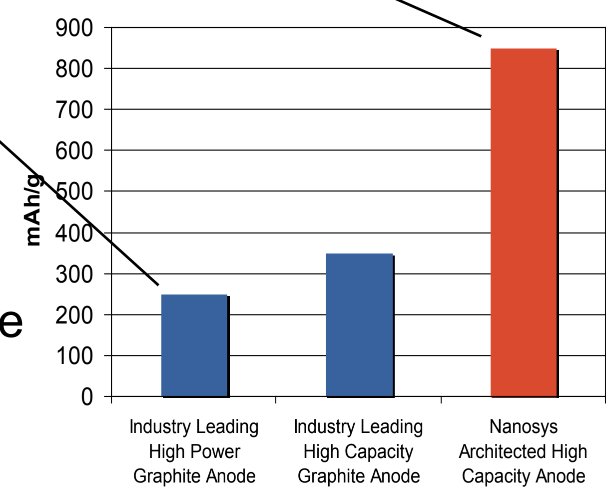


- The reversible specific capacity of SiNANOde linearly increases up to 20% Si, which shows very high Si capacity utilization in SiNANOde composite.
- Up to 12% Si the volumetric capacity of SiNANOde proportionally increases with Si%, then the increasing rate becomes slightly lower.

- In the LCO/SiNANOde full cell SiNANOde exhibits exceptional performance at different C-rates up to 1C.
- There is no difference in the cell discharging between 0.05C and 0.2C.
- Beyond 0.5C the discharging voltage profile is slightly impacted by the electrode polarization.

Technical Achievement
- Normalized Capacity at High C-Rate





- At < 8C SiNANOde shows comparable rate performance to high power graphite
- At > 8C SiNANOde outperforms the graphite due to Si nanowire's intrinsic nano-feature in radial direction

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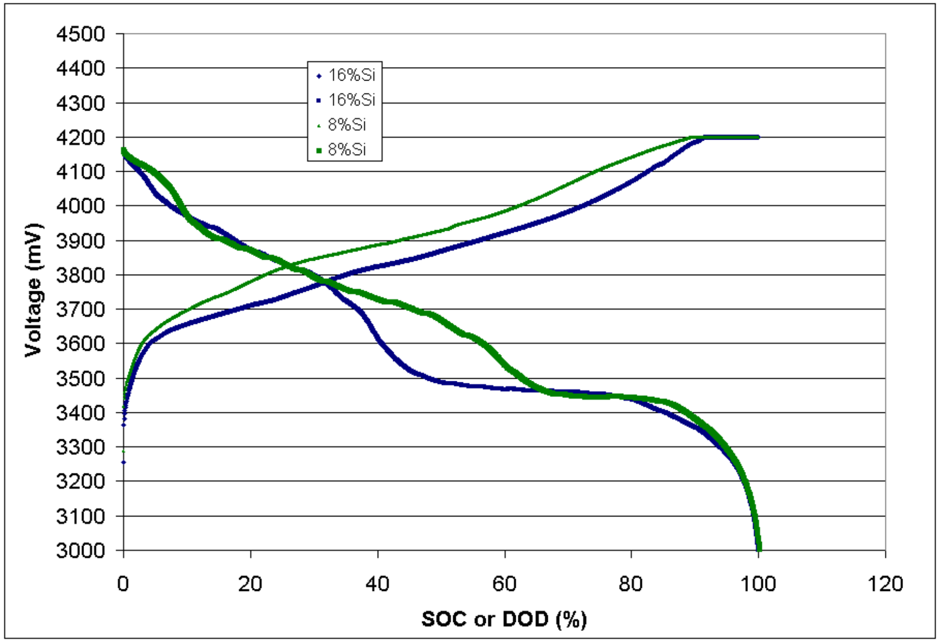
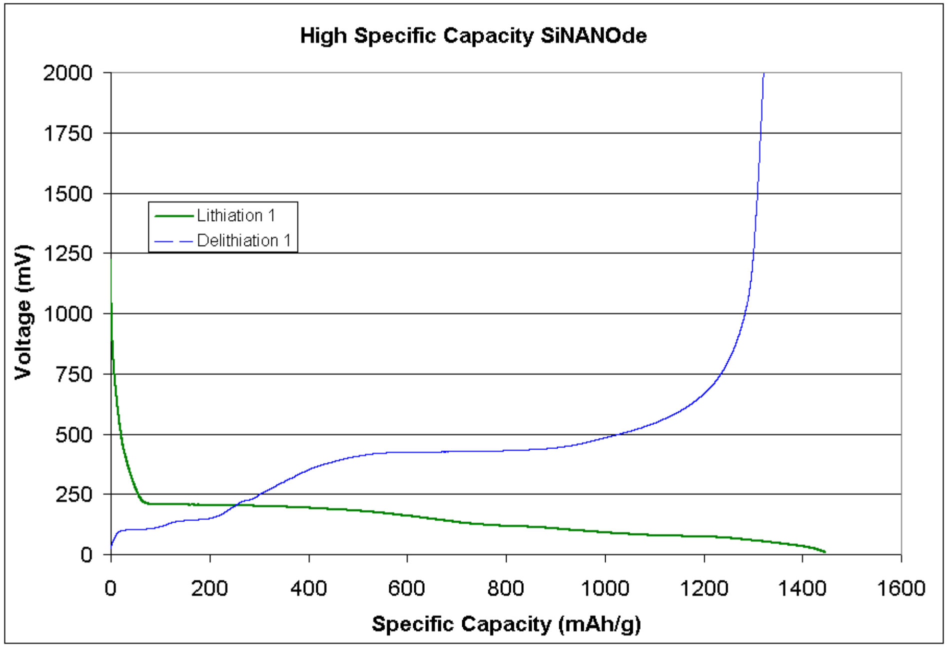
Technical Achievement
- SiNANOde Full Cell Voltage Profile





- The voltage profile for the full cells showed a typical slope-like charging behavior between 3.0 and 4.2V though there is a shoulder between 3.8 and 3.9V.
- During discharging a clear plateau around 3.4~3.5V can be attributed to Si capacity contribution
- The full cells can be used in a typical voltage range of 3 ~ 4.2V

Enhanced SiNANOde Capacity

- Achieved even higher specific capacity of SiNANOde and obtained a reversible capacity of ca. 1450mAh/g.

-The first coulombic efficiency was more than 91%.

- Further improve it up to 1600mAh/g, ongoing

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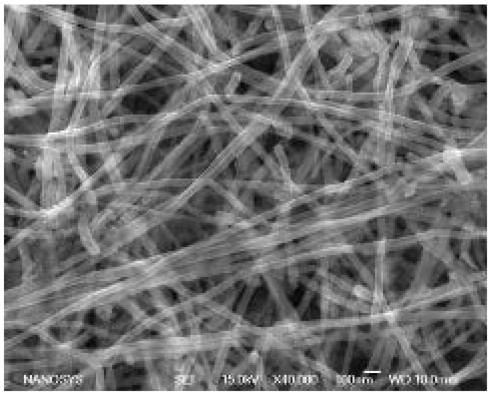
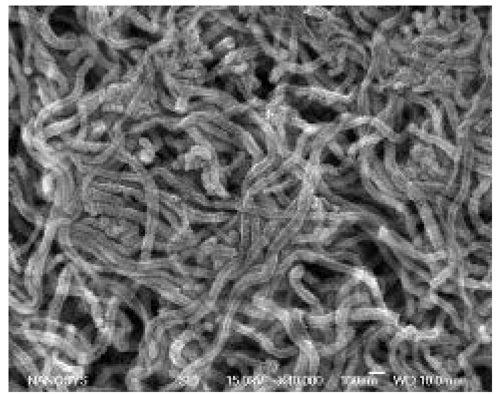
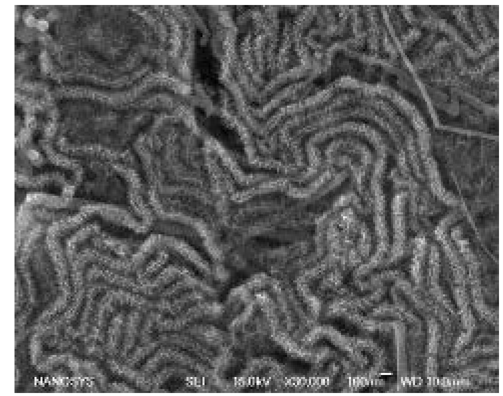
Technical Achievement
- SEM Characterization of SiNANOde Post Cycling



Prior to cycling



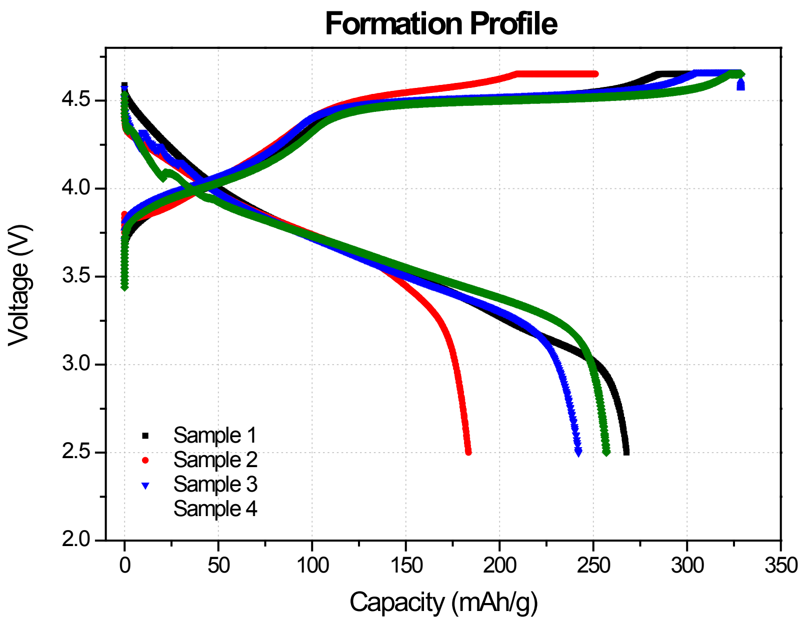
10th cycle

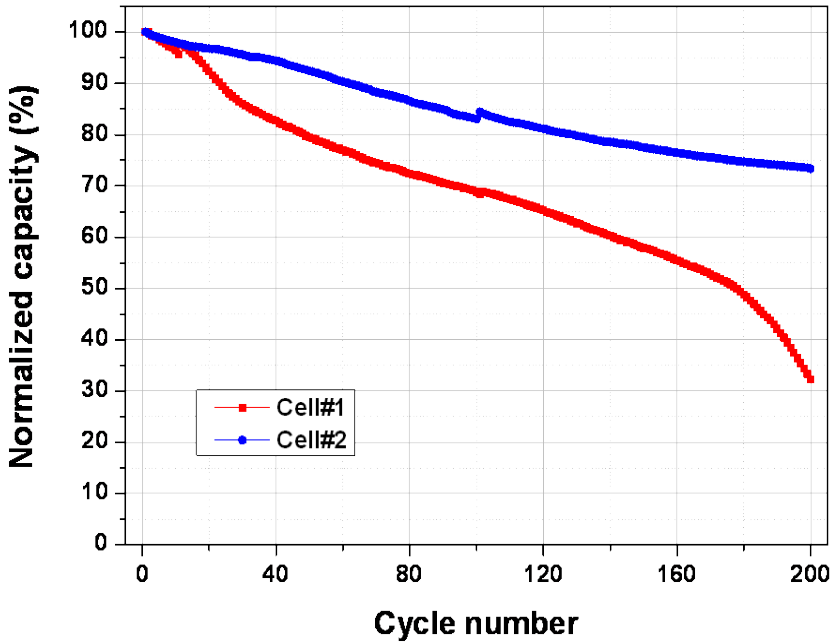


~100th cycle

- SiNANOde material deforms to fill void areas in carbon anode material matrix
- SiNANOde material remains intact and fully functional after 100% DoD cycling

Technical Achievement - Cathode





- Mn-rich cathode materials, in-house and commercial ones, were screened for selection of optimal one (>250 mAh/g) to be combined with Si anode, SiNANOde.
- Charge/discharge of the Li/Mn-rich cathode half cell in 4.6-2.5V at room temperature

- For the improvement of the cathode materials, surface modification have been tried continuously.

- Identification of a high voltage electrolyte is very critical in enhancing its cyclability.
- The effect of electrolyte composition on the cyclability: Cell #2 used an electrolyte tailored to have high voltage stability.

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Technical Achievement
- Cell Development

We are designing cell using Mn-rich cathode (>250 mAh/g) and high capacity anode, SiNANOde (850 and 1600 mAh/g), and trying to demonstrate the feasibility of the cell in order to accomplish our objectives in the well-designed cells.

Using single layer pouch cells with the variation of electrode loading, the feasibility will be demonstrated by Jun. 2012.

Mn-rich Capa. (mAh/g)	CHG. Voltage (V)	Cat./An. Loading (mAh/cm^2)	Cat. AM loading ($g/25\ cm^2$)	Capacity (Ah)/0.5C	Energy Density (Wh/kg)/0.5C
302/268	4.6V/4.6V	7.7/8.2	0.718	50.4	406
302/268	4.6V/4.4V	7.5/8.0	0.699	51.9	352
302/268	4.6V/4.4V	4.35/4.6	0.406	52.7	300

- Anode: 1600 mAh/g SiNANOde

Based on the single layer pouch cell's data, we will have cell built (1~2 Ah) by Nov. 30th, 2012.

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Collaborations

-LG CPI (sub, industry): Within the VT program

-LGC (Industry): Within the VT program

-AMAT (Industry, outside the VT program): collaborations about high loading anode and cathode cell development

-ANL (US DOE Laboratory, outside the VT program): collaborated to obtain independent HPPC testing of SiNANOde.

-LBNL (US DOE Laboratory, outside the VT program): collaborated to build independent SiNANOde baseline for US DOE.

Future Work

The rest of 2012 in first 15-month phase we will focus on achieving high energy density objectives and enhanced cycle life.

Cycle Life Enhancement for 700~1000 mAh/g Anode
- To produce pilot-scale manufacturing quantities of SiNANOde product.
- To optimize the SiNANOde and appropriate binders.
- To evaluate electrolyte additives to improve cycle life.
- Electrochemical analysis.

Enhanced Si Capacity 1,600 mAh/g Anode
- To enhance battery discharge rate performance
- To achieve high electrode loading
- Upon completion of this task, a reversible specific capacity of the new SiNANOde will be 1,600 mAh/g.

Optimization of Cathode Composition
- To optimize the cathode material composition.
- To minimize inactive components in the cell.
- To address cathode electrode activation during cell formation cycles.
- The compatibility of the developed electrolyte will be evaluated in this task.

2013 in second 21-month phase we will focus on manufacturing scale-up, value stream mapping, and cost-sensitivity modeling of the materials developed in 2012.
- The cell design will be further improved to achieve high energy density and long cycle life.
- The integration of new binder and electrolyte and cell formation/testing protocol will be carried out.
- The desired materials and quantity will be delivered from Nanosys to LGCP/LG Chem.
- The effort in this phase will result in functional cells for validation testing.

Summary

- The anode-specific capacity has been increased up to 700~1450 mAh/g as scheduled.
- By optimizing Si coverage and distribution on the graphite surface and optimizing electrolyte and binder chemistry, cycle life is to be greatly extended. We have achieved >300 cycles for the baseline SiNANOde of ~600mAh/g in full cells with >3 mAh/cm2 electrode loading and are to improve it to 500 cycles in 2012. We have also demonstrated ~300 cycles for the high specific capacity of SiNANOde with 700~1000 mAh/g in half cells.
- The cathode-specific capacity has showed >~250 mAh/g. We are optimizing the electrolyte to improve its cycle life
- The electrode density and thickness is being optimized for high energy density cell.

Summarized achievements:

Anode Targets:	700-1000 mAh/g	>800 cycles	
Anode Achievement:	700~1450 mAh/g	~300 cycles	
Cathode Targets:	250 mAh/g	>800 cycle	
Cathode Achievement:	>250 mAh/g	150 cycles	
Battery Targets:	350 Wh/kg	800 Wh/L	<150 $/kWh (cell)
Battery Achievement:	plan to review in 2013		