# *Innovative Cell Materials and Design for 300 Mile Range EVs*

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# Overview

## Timeline

- Start: Oct. 1st, 2011
- End: Sept. 30th, 2014
- 40% complete

## Budget

- Total project funding: $8,060K
  - DOE share: $4,840K
  - Contractor share: $3,220K
- Funding received in FY12: $1,520K
- Funding for FY13: $1,806K

## 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

LGCPI/LG Chem. and other cell manufacturers
US DOE National Laboratories
University of California, Berkeley
Cell components manufacturers

# Project Objectives

## The review covers Apr. 2012 ~ Mar. 2013

**Anode:**

Develop a 700~1600 mAh/g Si anode (SiNANOde™) toward >800 cycles

- Demonstrate 700~1000 mAh/g SiNANOde toward >800 cycles
- Demonstrate SiNANOde with an electrode loading of 3~6mAh/cm2
- Demonstrate SiNANOde with 1600 mAh/g

**Cathode:**

Develop a 260 mAh/g cathode (Mn-rich) toward >800 cycles

- Improve 250~260 mAh/g cathode with capability to meet >800 cycles
- Improve cathode electrode loading and power

**Cell:**

Develop unique cell combining SiNANOde with >250 mAh/g cathode to eventually achieve 350 Wh/kg and 800 Wh/L, resulting in <150 \$/kWh (cell).

- Cell design toward 350 Wh/kg
- Feasibility test using single layer pouch cells
- Demonstrate real pouch cells with increased energy densities (delivered 18x cells for testing at DOE INL)

# Project Milestone

**Milestones in the period of Apr. 2012 ~ Mar. 2013:**

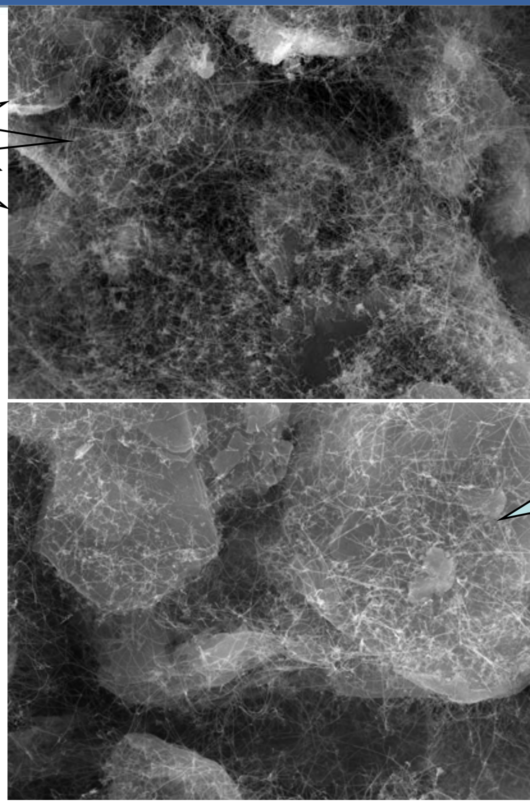
- Baseline SiNANOde Cycle Life Demonstration
- SiNANOde Specific Capacity Improvement: Increase to 700~1600mAh/g and improve cycle life
- Optimization of cathode composition
- Scale-up SiNANOde manufacturing process

## 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** |
| **Delivered 18 cells with high energy density on Nov. 30$^{th}$, 2012 On track** | | |
| **Systems Integration Design** | **9/31/12** | **On track** |
| **Test Reports Delivered to DoE** | **Multiple** | **On track** |

# SES Drop-In Anode Solution

High Capacity



Similar feel to graphite, e.g. tap density similar to graphite powder substrate

Volume production process using graphite as direct substrate for Si nanowire growth

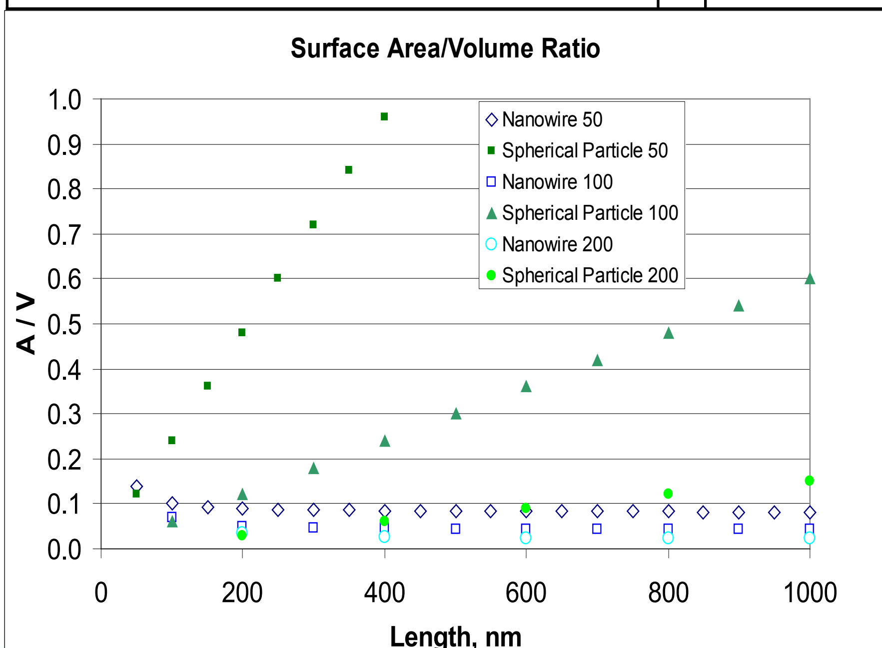
- Cost effective and high Si utilization
- Improves dispersion within slurry and drop in process
- Si-C conductivity improvement
- Si% or anode specific capacity is controllable, focusing on **500 ~ 1600 mAh/g**
- High electrode loading, i.e. 1.5g/cm$^3$
- Good cycling performance, cycled >1000 times

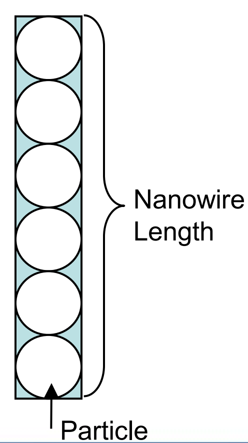
# SES SiNANOde Approach
## vs. Hollow/Porous Approach

### SES Exploit Advantages & Defeat Potential Problems of Si Nano-materials

| Advantages |
|---|
| Better accommodation of cycling strain |
| Unique conversion reactions |
| High interfacial charge transfer rates |
| Short tunneling length for electronic transport |
| Short diffusion length for ionic transport |

| Overcome Potential Disadvantages | SES SiNANOde | Hollow/Porous |
|---|---|---|
| High surface area leads to higher self discharge & poor cycling performance | Low A/V & Intact NW after cycling | High A/V; defects |
| Low pack density and low volumetric energy density | Pack density similar to graphite | Pack density lower than graphite |
| Hard to be mass-produced | Mass-produced with a competing cost * high Si utilization | Difficult and expensive to commercialize |




**The nanowire has lower surface area/volume ratio, A/V, and hence less side-reaction with electrolyte and better cycle life**

# Cathode Approach

## *Cathode Development*

Cathode materials currently being used in PHEVs and EVs have a maximum capacity of ~ 150 mAh g-1 or less.

Mn-rich composite cathode, can deliver an initial capacity >250 mAh g−1, expected to be significantly stable in non-aqueous electrolytes.

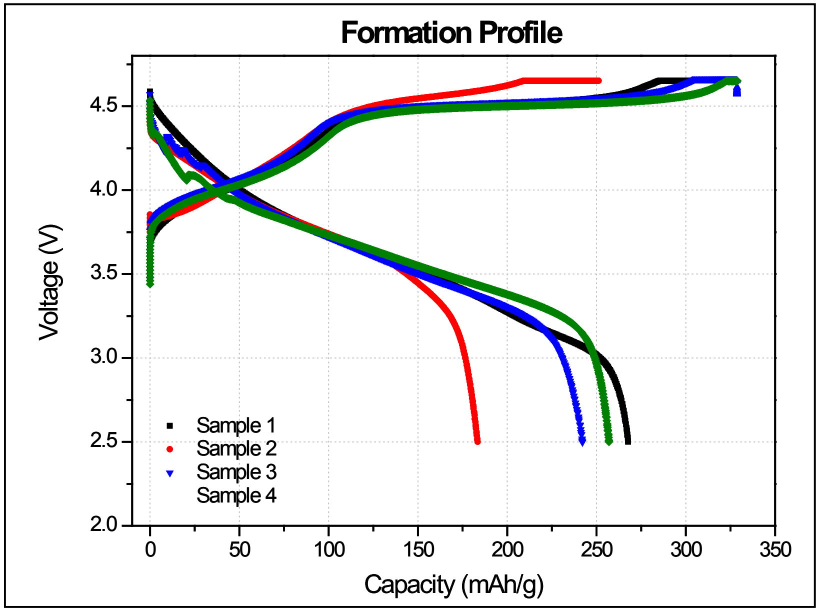
**The high operation voltage electrolyte is being developed**

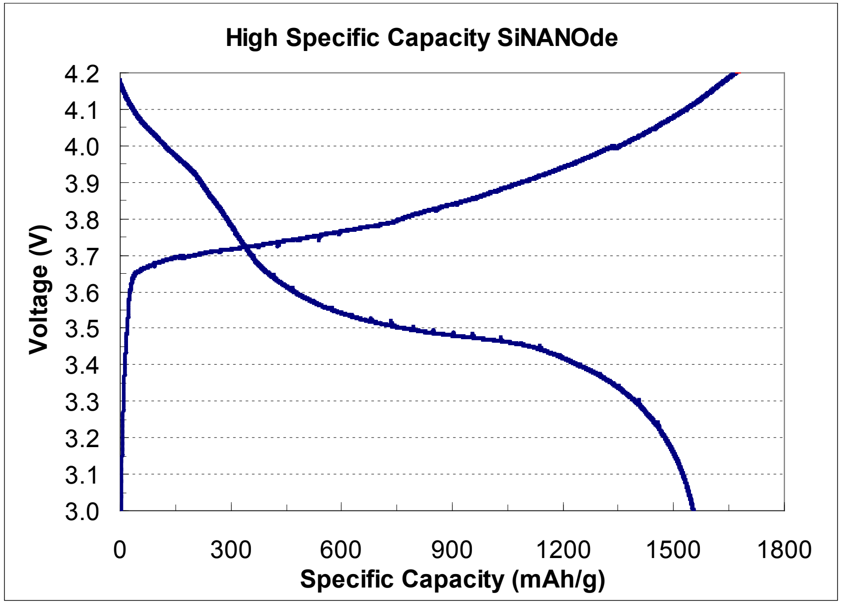
- **Mn-rich cathode materials (>250 mAh/g) are screened to have an attractive cathode and combine with SiNANOde**

- **Mn-rich cathode material surface is modified by oxide or other components to improve its electrochemical performance and stability**

# Cell Development Approach

**Combining the attractive cathode feature with a high-capacity SiNANOde to accomplish our cell development objectives**

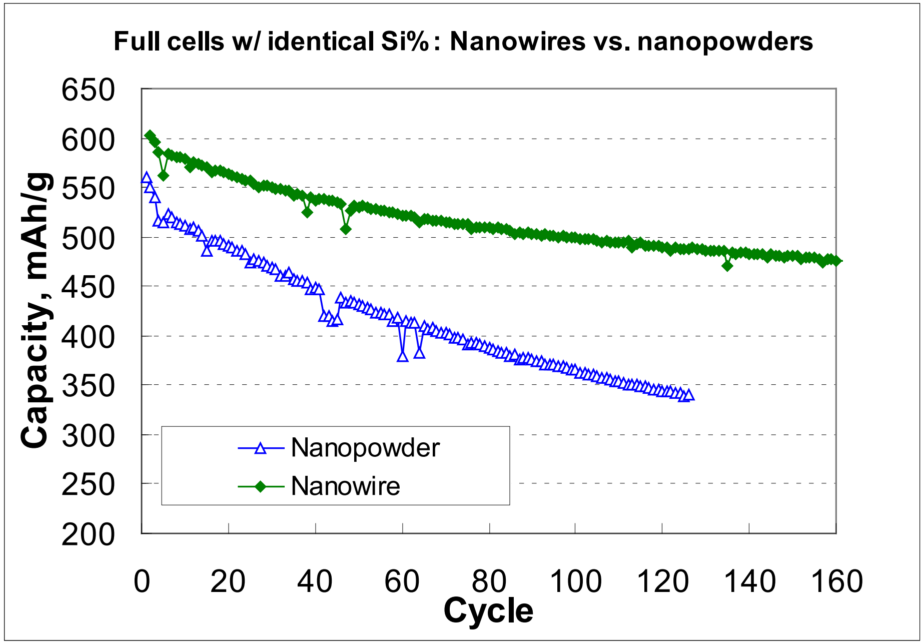


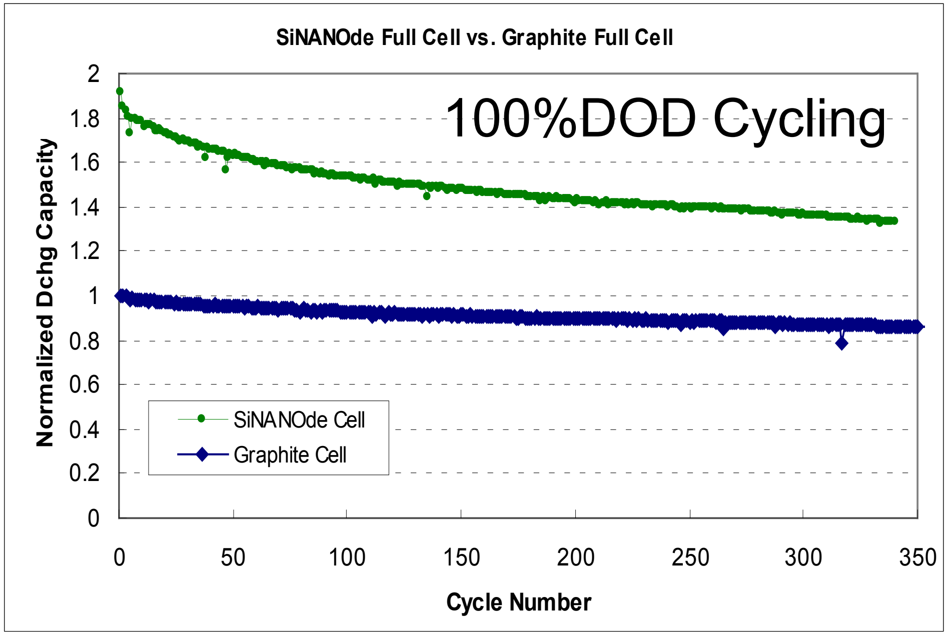




**Mn-rich cathode materials showed a reversible specific capacity as high as 268mAh/g**

**Full cell with high specific capacity SiNANOde showed an ICE of >91% and anode's reversible specific capacity of 1600mAh/g**

# Technical Achievement - Anode



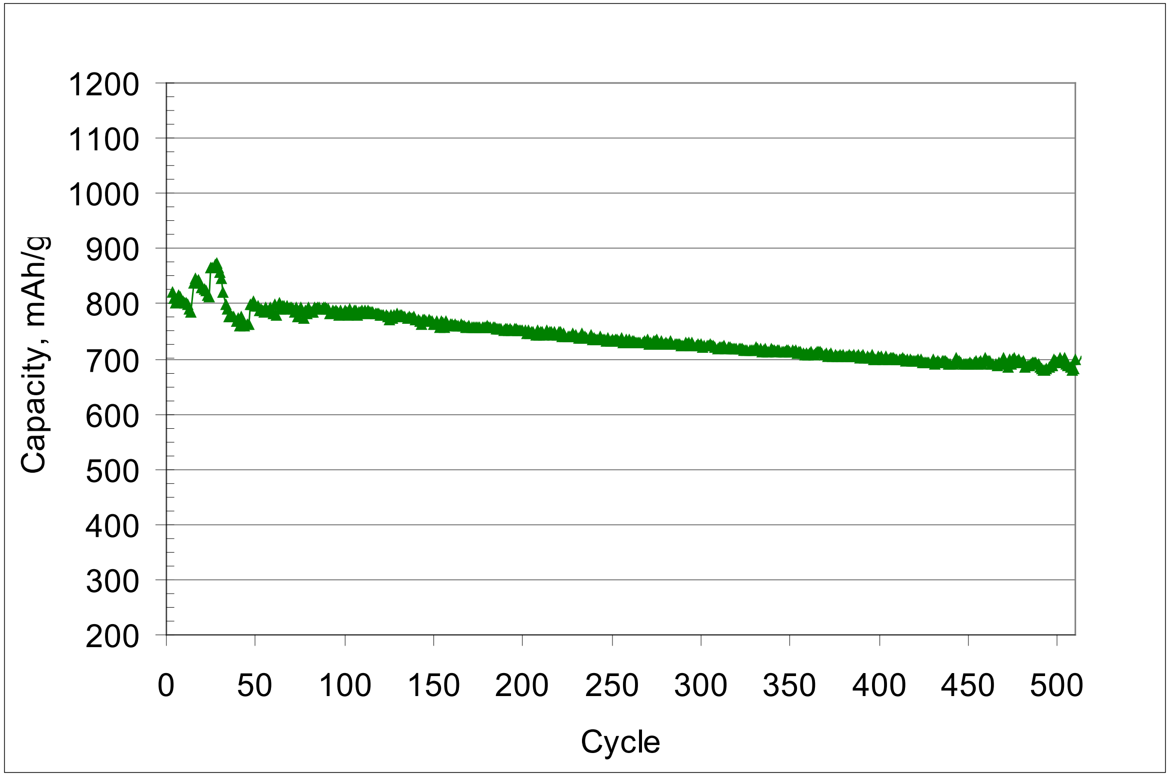




**SiNANOde (Green) OUTPERFORM commercial Si nanopowder (Blue) with identical diameter due to its much lower surface area/volume ratio, better dispersion in slurry and conductivity**

**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.**

**An improved LCO cathode is showing better full cell performance (ongoing)**

# Technical Achievement
# - High Capacity Anode: Cycle Life



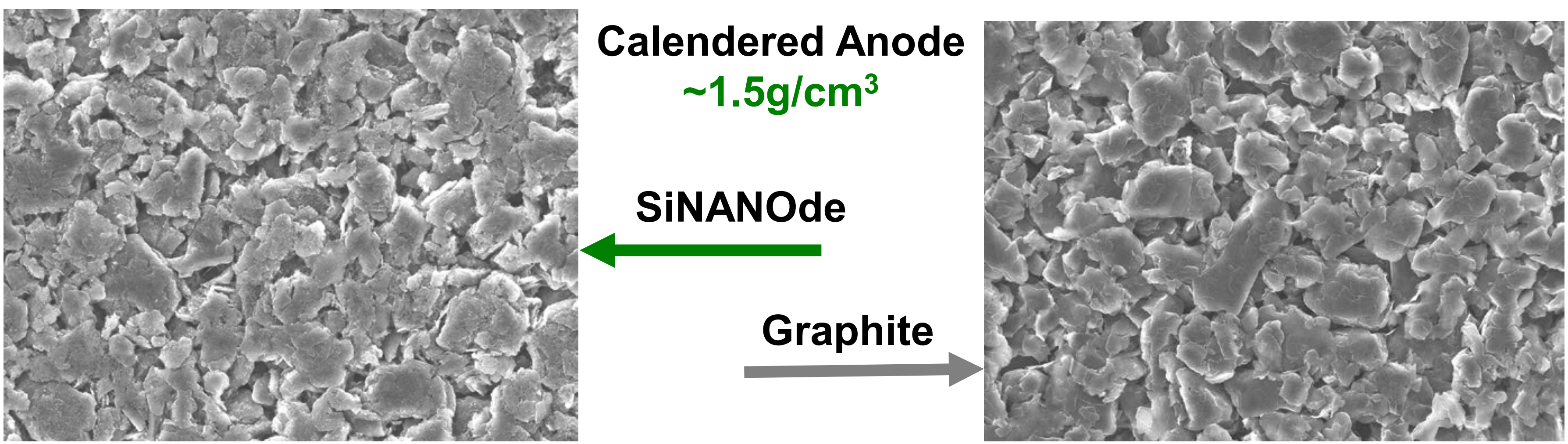

**- Increased the specific capacity of SiNANOde up to 850mAh/g by controlling Si nanowire content.**
**- Continuously improving the conductivity of SiNANOde and further optimizing the SiNANOde material, which has showed longer anode cycling life of ~510 cycles at 83% capacity retention at 0.3C.**
**- At beginning the cell has been used for various C-rate testing.**

# Technical Achievement

## - High Energy Density Pouch Cell Performance

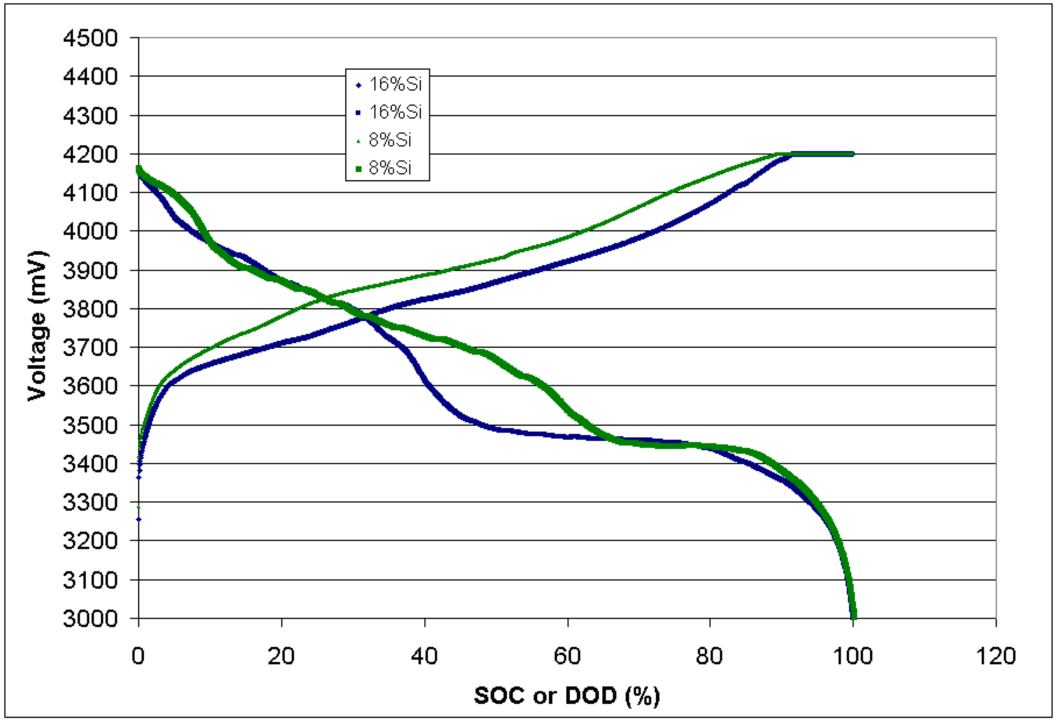
| Discharge C-rate | Energy Density Wh/L |
|---|---|
| C/10 | 627 |
| C/5 | 616 |
| C/3 | 582 |

- The 8%SiNANOde pouch cell has already showed the volumetric energy density **>620Wh/L** in conventional 4.2 ~3.0V.
- The mid-voltage is ~3.7V.



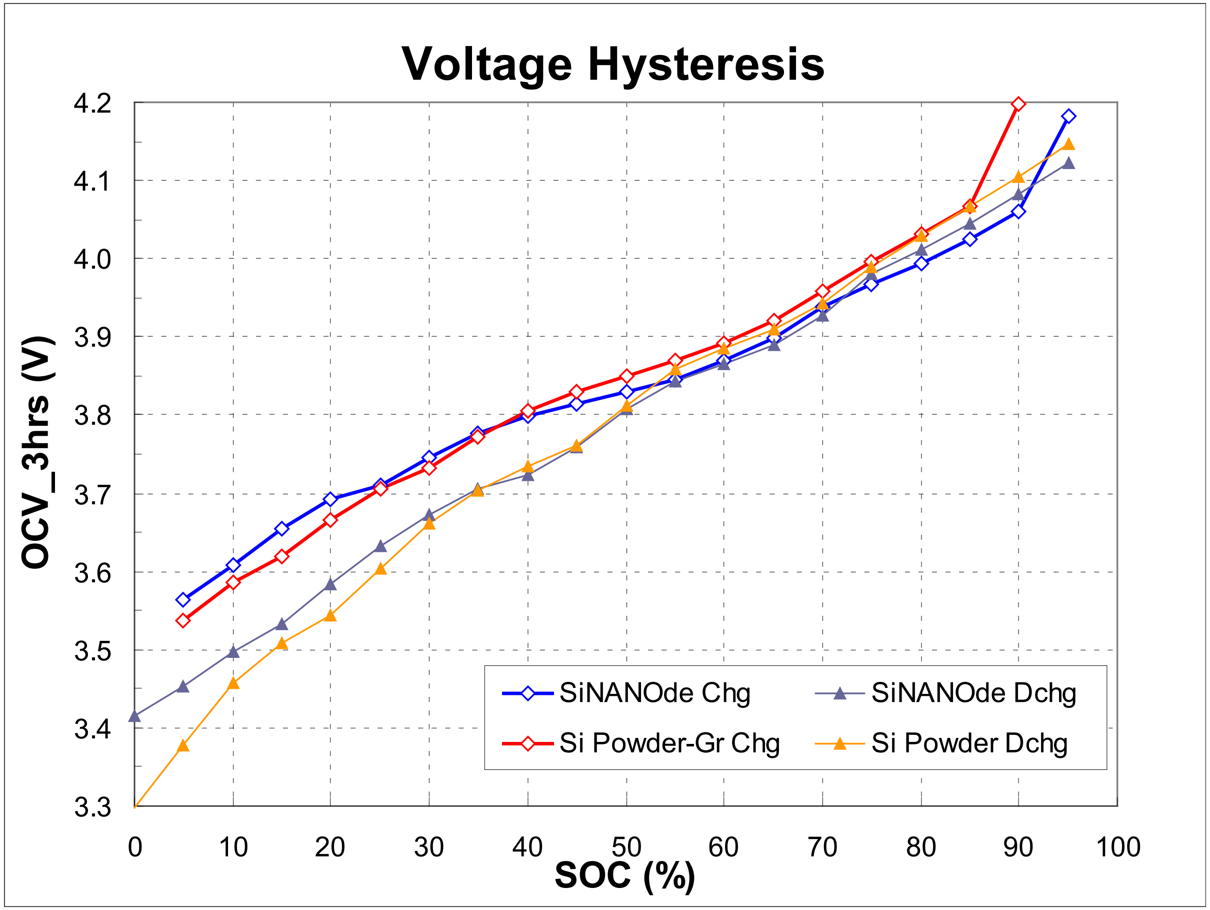
# Technical Achievement

## - 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

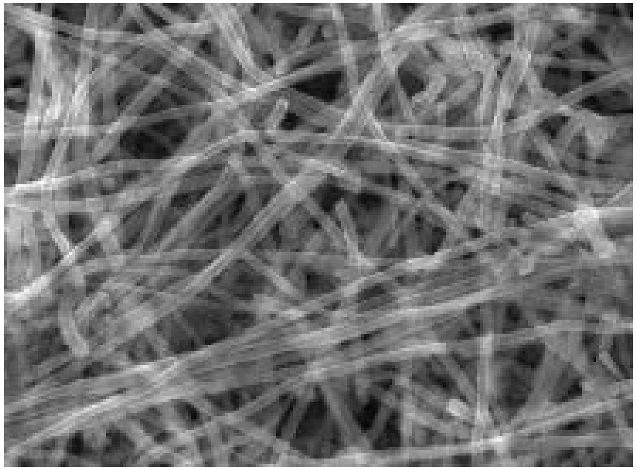
# *Technical Achievement*
# *- Less Voltage Hysteresis for SiNANOde*



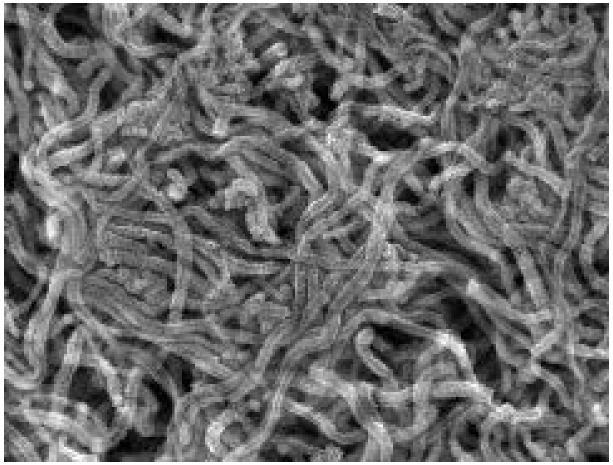

**The hysteresis effect is less pronounced for 8%SiNANOde/LCO full cell in comparison with 8%Si power-graphite/LCO full cell**

# Technical Achievement

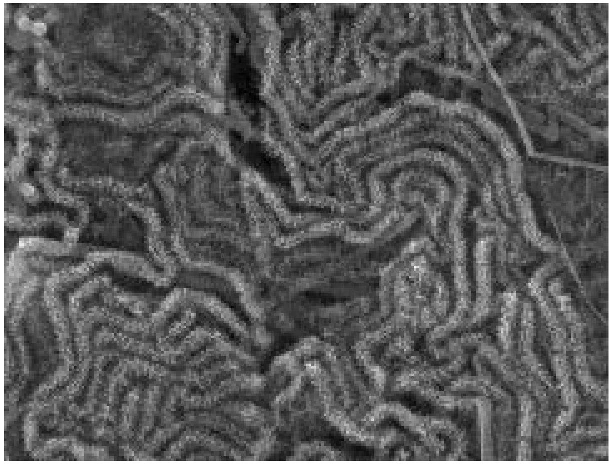
## - SEM Characterization of Si Nanowires/Current Collector Post Cycling



Prior to cycling



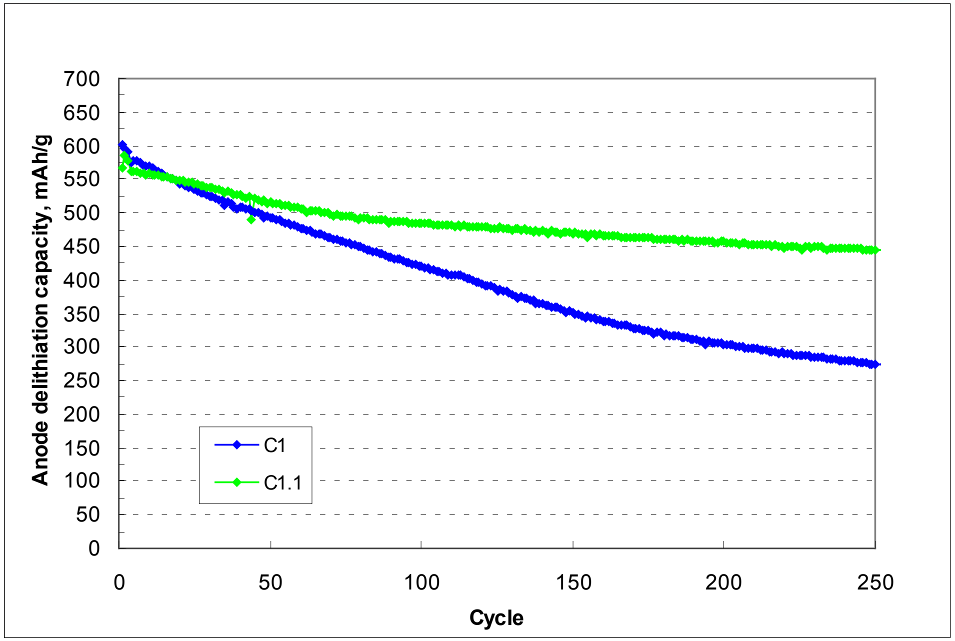
$10^{th}$ cycle

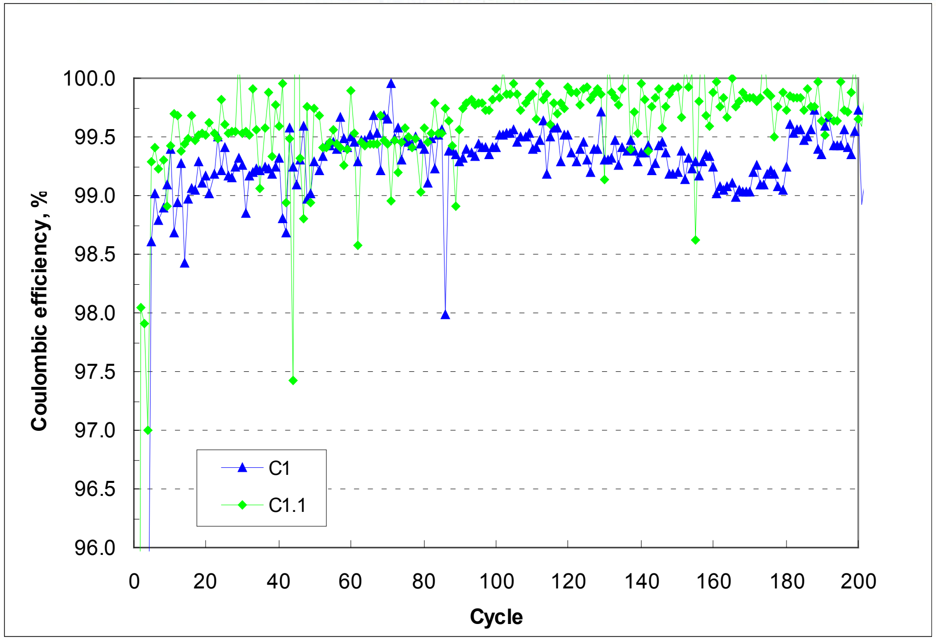


$100^{th}$ cycle

- Si nanowire deforms to fill void areas in carbon anode material matrix
- Si nanowire remains intact and fully functional after 100% DoD cycling
- Thin SEI formed on Si nanowires

# Technical Achievement
## - SiNANOde SEI in SES's C1 & C1.1 Electrolyte

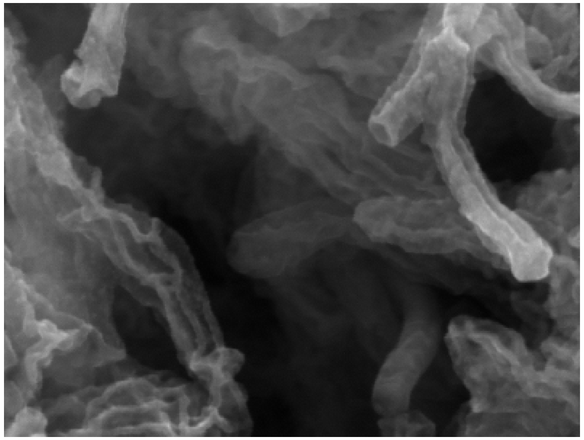


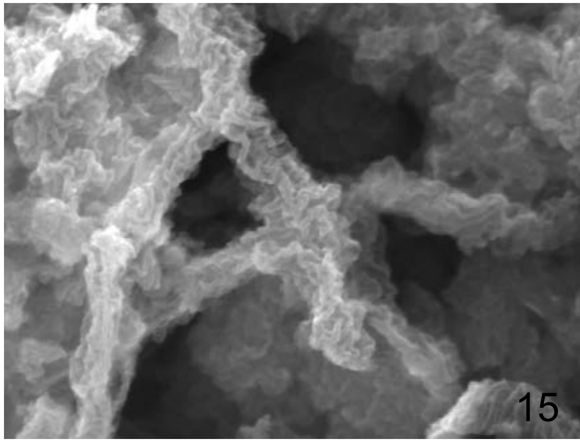

-C1.1 cell showed higher coulombic efficiency and better cycling performance than C1 cell

- In C1: the Si nanowires in the composite can be deteriorated faster and formed thicker SEI
- In C1.1: thin SEI or less decomposed electrolyte buildup on Si nanowires in the composite

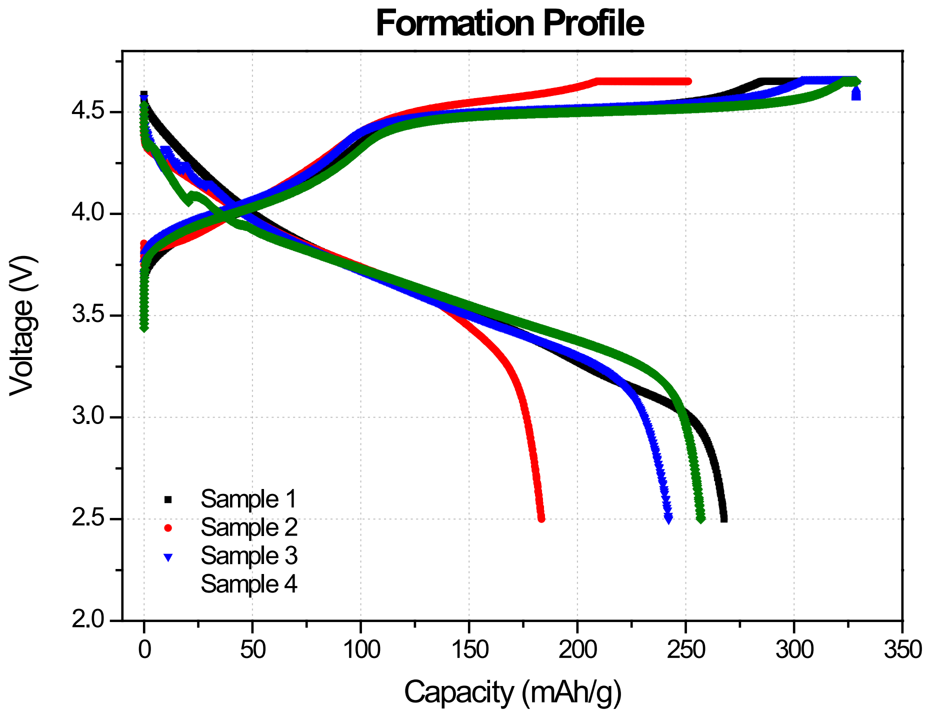
C1.1

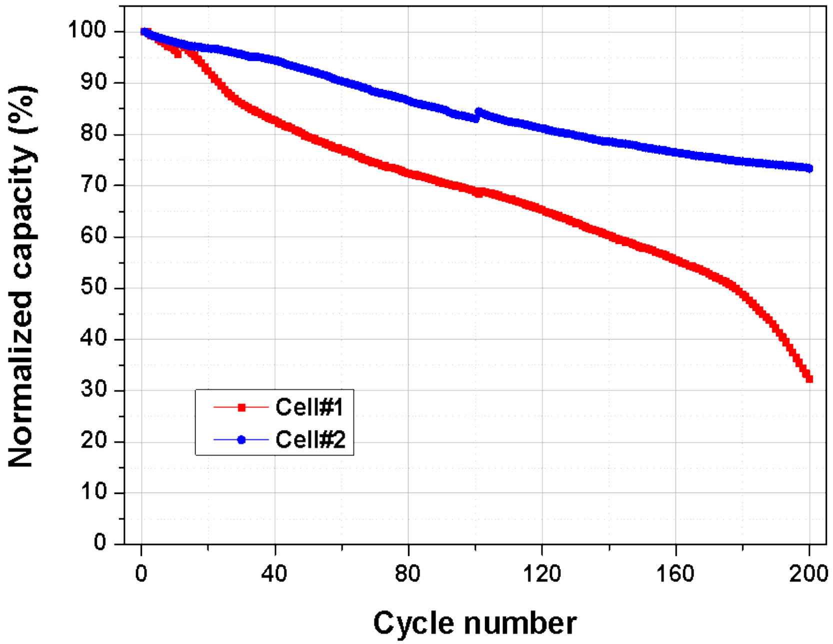


C1



# Technical Achievement
## - Cathode



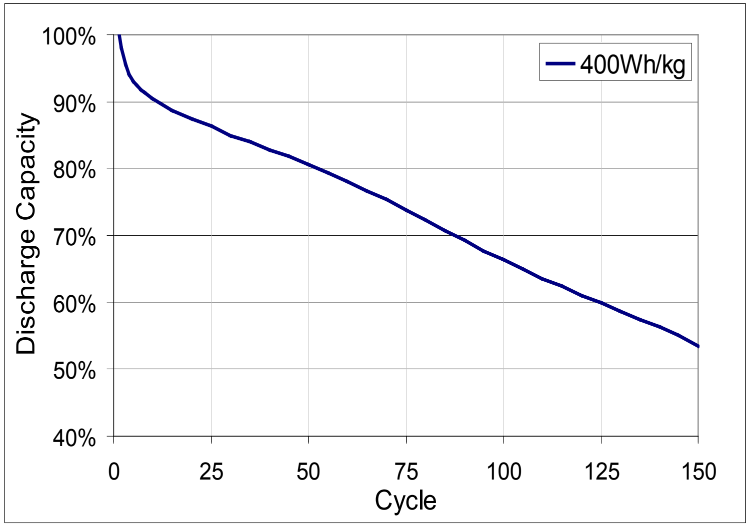

- Mn-rich cathode materials, in-house and commercial ones, were screened for an optimal one (>250 mAh/g) to be combined with SiNANOde.
- Charge/discharge of the Li/Mn-rich cathode half cell in 4.6-2.5V at room temperature
- Surface modification has been tried to improve the cathode materials.

- 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.

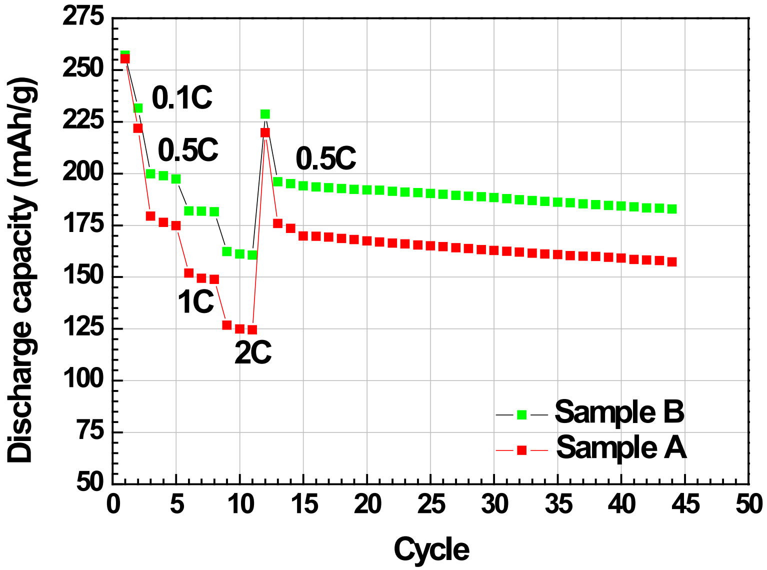
# Technical Achievement
## - Cell Development

**To make pouch cells of SiNANOde/Mn-rich cathode in plant, the cell fabrication has been developing to achieve high energy densities and improve its processablity (ongoing)**

| SiNANOde | 600 mAh/g | 800 mAh/g | 1200 mAh/g |
|---|---|---|---|
| Processable in plant 4.4 V | 225 Wh/kg | 240 Wh/kg | 255 Wh/kg |
| Unprocessable in plant 4.4 V (~1300 mg/25 cm$^2$) | 255 Wh/kg | 275 Wh/kg | 300 Wh/kg |



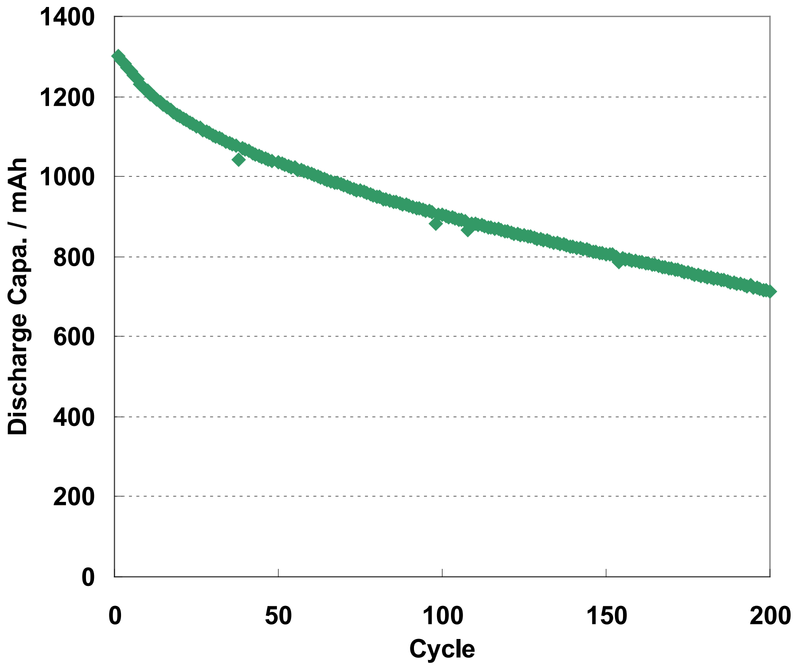

**The 400 Wh/kg-designed cell made manually is cycled at 0.3C.**
**The capacity is initially fading faster, showing 55% retention at 150th cycle**

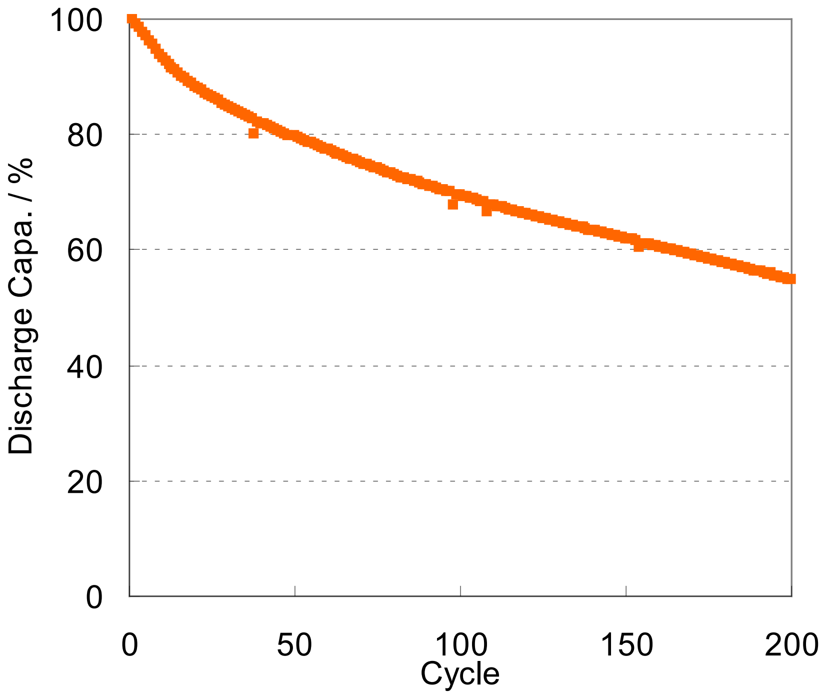



**The cathode material surface has been modified, which has enhanced its C-rate performance.**

# Technical Achievement
## - Cell Development

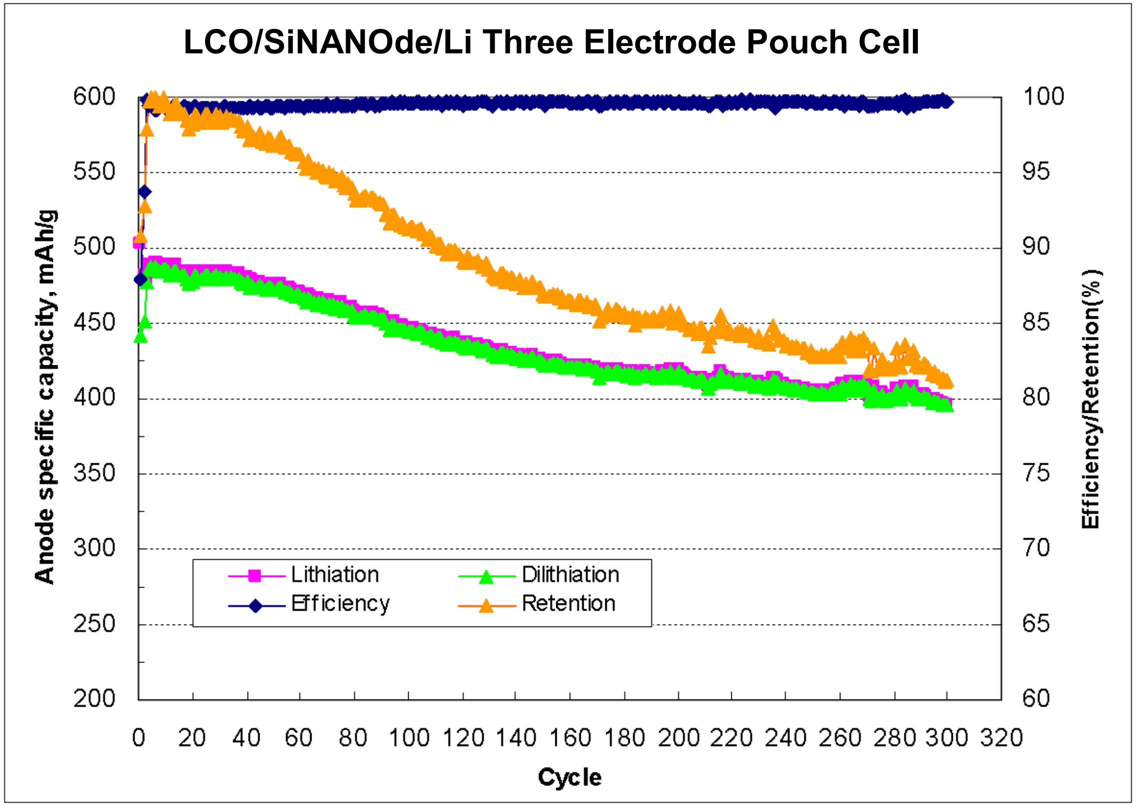
***1.3 Ah Baseline Cell with 500~600 mAh/g Anode and LCO cathode, achieved >260 Wh/kg and >600 Wh/L***




**The cell is Cycled at 0.5C rate (DOD 100%)**

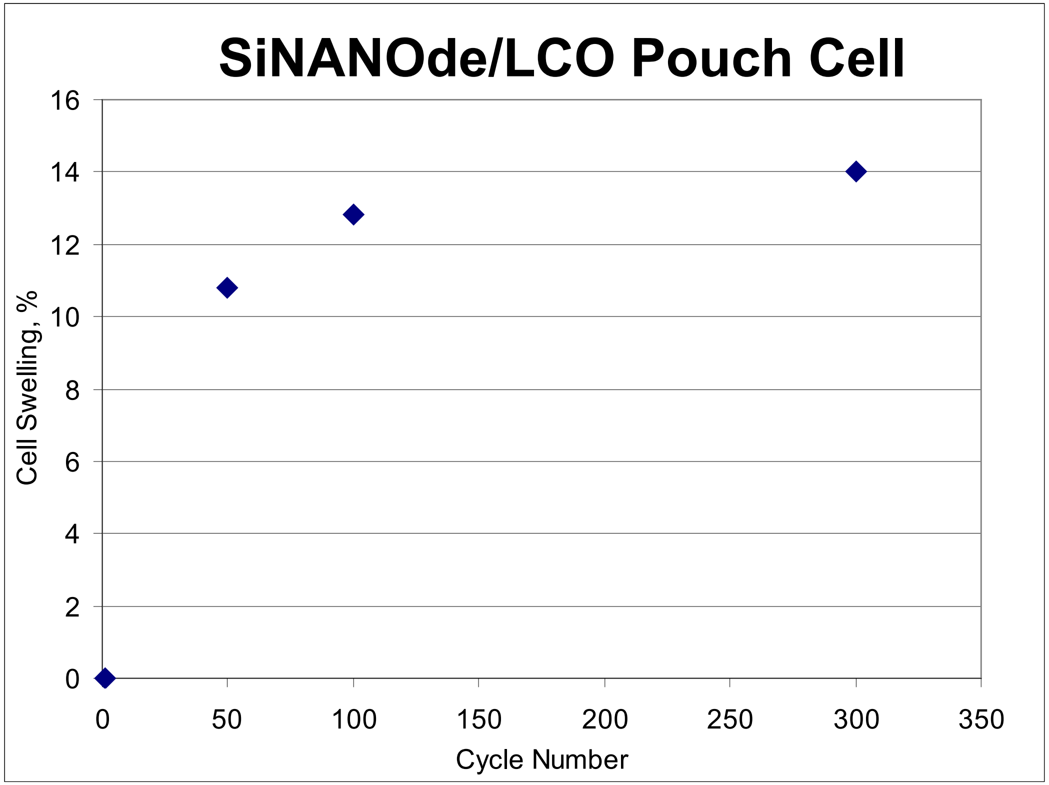
# *Technical Achievement*
## *- Cell Development*




- The lithium is provided by LCO cathode
- Anode potential is controlled by using Lithium metal reference electrode
- The cell shows high coulombic efficiency of 99.5~100%
- The cell gives a beginning capacity of 490mAh/g and stabilizing around 400mAh/g over 300 cycles **if anode potential is in the range of 10~700mV**.

# Technical Achievement
## - Cell Development

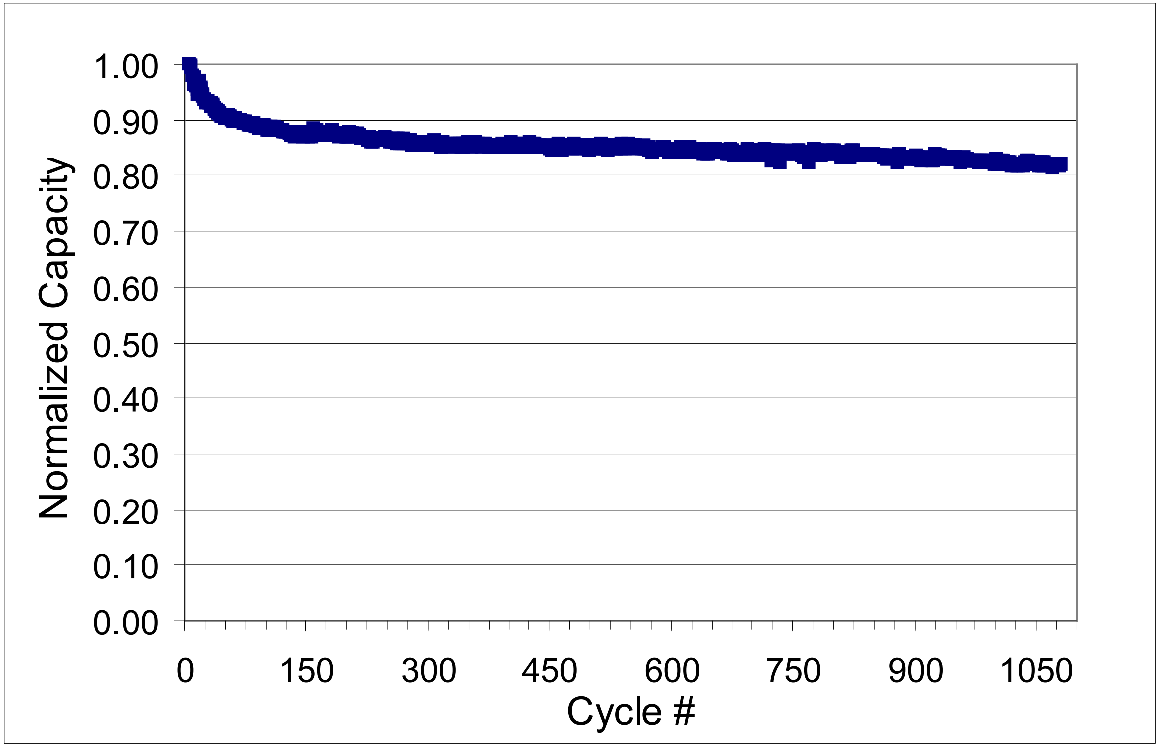
***Thickness change of High Energy Density Pouch Cells:***
***SiNANOde/LCO*** after 300 cycles




**- Pouch cells have showed acceptable cell thickness change, < 14% cell swelling over 300 cycles.**

# Technical Achievement
## - 18650 Cell Development

### *Superior full cell performance at high electrode loading*




- SiNANOde 18650 full cell shows >1000 cycle 80% retention at 0.5C cycling though it fades faster in the first 50 cycles

# Technical Achievement

## - Cell Development

***Self discharge and subsequent recharge is comparable (~1% less) than commercial graphite***

| Condition | 8% Si-Composite /LCO Normalize to Graphite/LCO Control |
|---|---|
| Retention % @20$^{o}$C at end of 1 month | 99.6% |
| Realized capacity upon recharge after discharging at 20$^{o}$C for 1 month | 98.7% |
| Retention % @60$^{o}$C at end of 1 week | 98.7% |
| Realized capacity upon recharge after discharging at 60$^{o}$C for 1 week | 99.3% |

# Collaborations

-LG CPI (Industry, within the VT program)

-LGC (Industry, within the VT program)

-Dow Kokam (Industry, within the VT program)

-EaglePicher (Industry, outside the VT program)

-AMAT (Industry, outside the VT program)

-ANL (US DOE Laboratory, outside the VT program)

-LBNL (US DOE Laboratory, outside the VT program)

-University of California, Berkeley

# Future Work

**Focus on achieving high energy density and enhanced cycle life**

***Cycle Life Enhancement for 700~1000 mAh/g Anode***
- Pilot-scale manufacturing quantities of SiNANOde product
- Cost-sensitivity modeling
- Optimize the SiNANOde and appropriate binders
- Develop electrolyte additives to improve cycle life
- Electrochemical analysis

***Enhanced Si Capacity 1,600 mAh/g Anode***
- Improve battery discharge rate performance
- Achieve high electrode loading
- Achieve a reversible specific capacity of 1,600 mAh/g

***Optimization of Cathode Composition and Cell Components***
- Optimize the cathode material composition
- Minimize inactive components in the cell
- Address cathode electrode activation during cell formation cycles
- Evaluate the compatibility of the developed electrolyte
- Improve the cell design to achieve high energy density and long cycle life
- Integrate the new binder and electrolyte and cell formation/testing protocol

# Summary

## Accomplishments

- The specific capacity of SiNANOde can be controlled in 500 ~ 1800mAh/g with an ICE of > 92%.
- Almost 100% utilization of Si capacity has been realized in the cells.
- We demonstrated > 510 cycles at 83% retention in coin cell using 700~1000 mAh/g SiNANOde.
- We demonstrated good cycling performance of >300 cycles (baseline SiNANOde/LCO) or ~1000 cycles (baseline SiNANOde/NCA).
- We achieved a reversible specific capacity of 255 mAh/g for cathode and improved its C-rate performance from 0.2C to >0.5C even at high loading.
- Pouch cells achieved 300~400Wh/kg with 1200mAh/g SiNANOde and 255mAh/g cathode.
- Pouch cells achieved 260Wh/kg and 600Wh/L with 550mAh/g SiNANOde and LCO cathode. We delivered 18 cells to U.S. DOE for evaluation.
- SiNANOde development has been extensively explored on various graphite, which will lead to a cost effective production.

**Summarized achievements:**

| | | | |
|---|---|---|---|
| **Anode Targets:** | 700-1000 mAh/g | >800 cycles | |
| **Anode Achievement:** | 700~1600 mAh/g | >510 cycles (ongoing) | |
| **Cathode Targets:** | 250 mAh/g | >800 cycle | |
| **Cathode Achievement:** | >250 mAh/g | >200 cycles (ongoing) | |
| **Battery Targets:** | 350 Wh/kg | 800 Wh/L | <150 $/kWh (cell) |
| **Battery Achievement:** | 250~400 Wh/kg | 550~700 Wh/L (up to Si% and cathode) | |

# Acknowledgements


- Team Battery at Nanosys (Silicon Energy Storage) and LGCPI/LG Chem.
- Support from the U.S. Department of Energy