# High Energy High Power Battery Exceeding PHEV-40 Requirements

**Dr. Jane Rempel (PI)**

**TIAX LLC**

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**2016 DOE VTP Merit Review**

Project ID# ES209

**TIAX LLC**
35 Hartwell Avenue
Lexington, MA 02421

Tel 781-879-1200
Fax 781-879-1201
www.TIAXLLC.com

# Overview

**TIAX is working to develop a lithium-ion battery technology that meets and exceeds the PHEV-40 performance and life goals.**

## Timeline

- Project start date: October 1st, 2013
- Project end date: March 30th, 2016
- Percent complete: 100%

## Budget

- Total project funding: $2,184,733
  - DOE share: $1,747,787
  - Contractor share: $436,946
- Funding received in FY15: $794,241
- Funding received in FY16: $67,206

## Barriers

- Gravimetric and volumetric energy density
- Gravimetric and volumetric power density
- Cycle life and calendar life
- Temperature range

## Partners

- Multiple materials suppliers

# Objectives/Relevance

**The objective for this project was to develop a lithium-ion battery technology that meets and exceeds the PHEV-40 performance and life goals.**

- Implement CAM-7$^{TM}$cathode, Si-based anode chemistry in Li-ion cells designed to achieve >200Wh/kg and >400Wh/L energy and >800W/kg and >1600W/L 10s pulse power targets under USABC PHEV battery testing procedures.
- Demonstrate that these Li-ion cells have higher energy and power capability than CAM-7/graphite baseline cell design, and deliver these cells to DOE for independent performance verification.
- Demonstrate that these Li-ion cells have cycle life and calendar life that project to meeting PHEV-40 targets.

# Milestones

**Program milestones have been completed. Program deliverable 18650 cells are scheduled for shipment.**

| Milestone | Status |
|---|---|
| Down-select silicon active material and inactive materials and formulations | Complete |
| Down-select cathode formulation and implement cathode active material synthesis scale-up | Complete |
| Optimize electrode design in coin cells and select separator, electrolyte, cathode and anode formulations | Complete |
| Finalize design of high capacity cells | Complete |
| Fabricate demonstration cells for delivery to DOE | Complete |
| Confirm performance and cycle life of Li-ion cells | Ongoing* |

*Performance testing was completed. Extended life testing is ongoing.

# Technical Approach

**We employed an iterative system-level approach to cell design to develop Li-ion cells that will exceed the PHEV-40 performance and life goals.**

## CAM-7$^{TM}$ High Energy, High Power Cathode

- Active material ideally suited for PHEV performance and life targets
- Electrodes optimized for energy and power density

## Blended Si/Carbon Anode

- Si-based materials – provide high energy, with state-of-the-art materials sourced from leading suppliers
- Carbon – excellent power delivery but lower volumetric capacity
- Blend and electrode formulations optimized for energy, power, and life

## Cell Design

- High performance separators
- Life-extending electrolyte additives and binders

# Summary

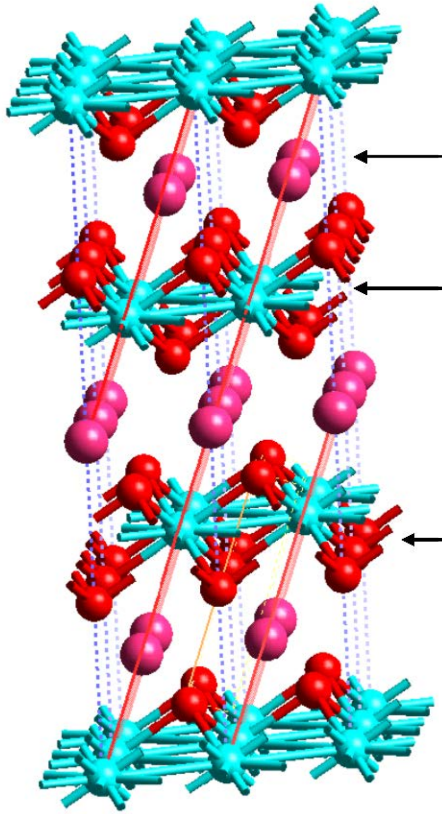
**Key activities completed are summarized below.**

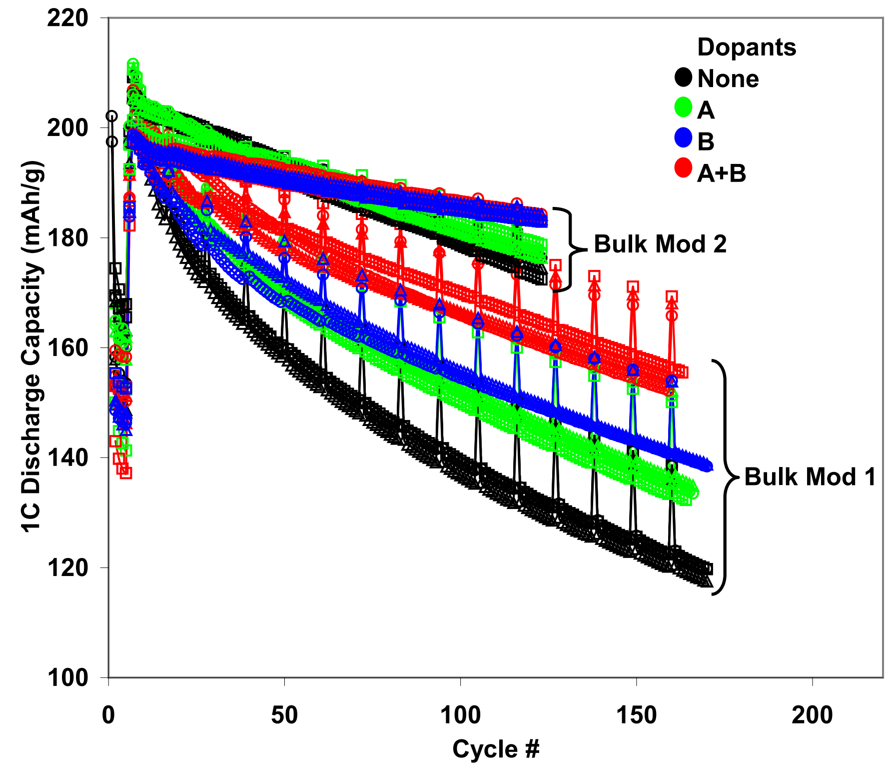
- ♦ Selected, synthesized and scaled-up a higher capacity CAM-7 cathode material that exhibits good cycle life for use in program deliverable cells.
- ♦ Screened and down-selected Si-based active materials from several domestic and international suppliers and test different Si-based anode/graphite blends.
- ♦ Optimized electrodes for power delivery and specific energy required for PHEV-40 batteries.
- ♦ Designed, assembled, and tested CAM-7/Si-based anode 18650 cells that meet energy and power targets.
- ♦ Demonstrated CAM-7/Si-based 18650 cells with 198Wh/kg total energy and 845W/kg at 10% SOC (projected to 250Wh/kg total and 225Wh/kg usable specific energy in 15Ah pouch cells with equivalent specific power).
- ♦ CAM-7/Si-based anode 18650 deliverable cells are scheduled for shipment for independent performance validation.
- ♦ Validated baseline CAM-7/Graphite 18650 cell performance internally and in independent testing at ANL (successfully carried out >2400 cycles at ANL and >4000 at TIAX).

# Technical Accomplishments and Progress

**CAM-7 is a stabilized, high-nickel cathode material with a doping strategy rationally designed for optimal material performance and stability.***

***We use minimum quantities of purpose-driven dopants located exactly where they are needed in the structure, enabling the highest (stable) nickel content and the highest capacity among LNO-class materials.***




**Accelerated cycle life testing at 45ºC allows for rapid screening of synthetic modifications.**

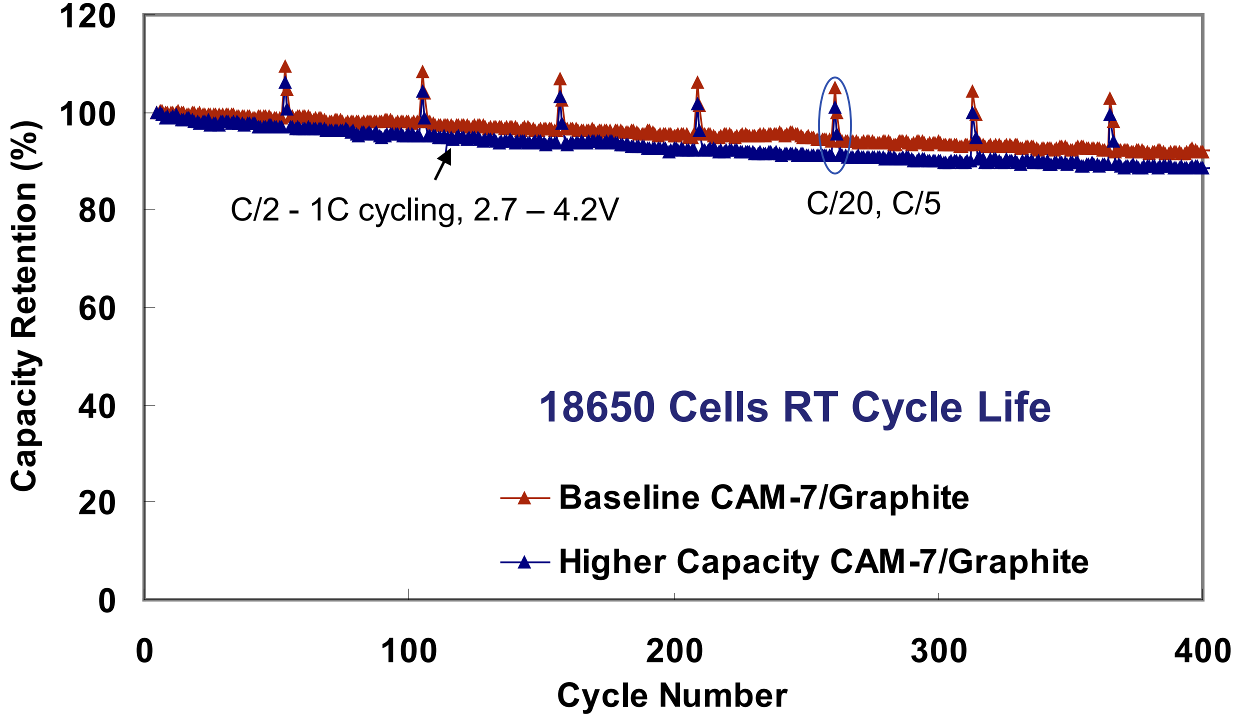


*Under development at TIAX since 2002

# Technical Accomplishments and Progress

**We have selected, synthesized and scaled-up a higher capacity CAM-7 cathode material that exhibits good cycle life for use in program deliverable cells.**

| Half Cells vs. Li metal | Discharge Capacity (mAh/g) | | | |
|---|---|---|---|---|
| | C/20 | C/10 | C/5 | 1C |
| **Baseline CAM-7 (2013)** | 212 | 205 | 199 | 185 |
| **Higher Capacity CAM-7** | 223 | 217 | 210 | 196 |




18650 cell design with equal electrode lengths, ~2 mAh/cm² cathode active material loading, graphite anode, carbonate electrolyte. C/2 Charge – 1C Discharge.

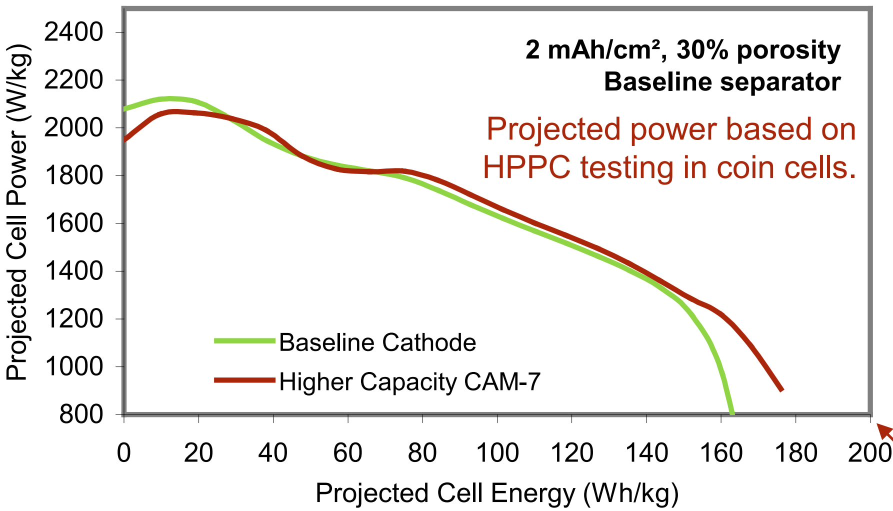
# Technical Accomplishments and Progress

**Cell-level specific energy and power can be increased by implementing higher capacity CAM-7 cathode and improved cell components.**

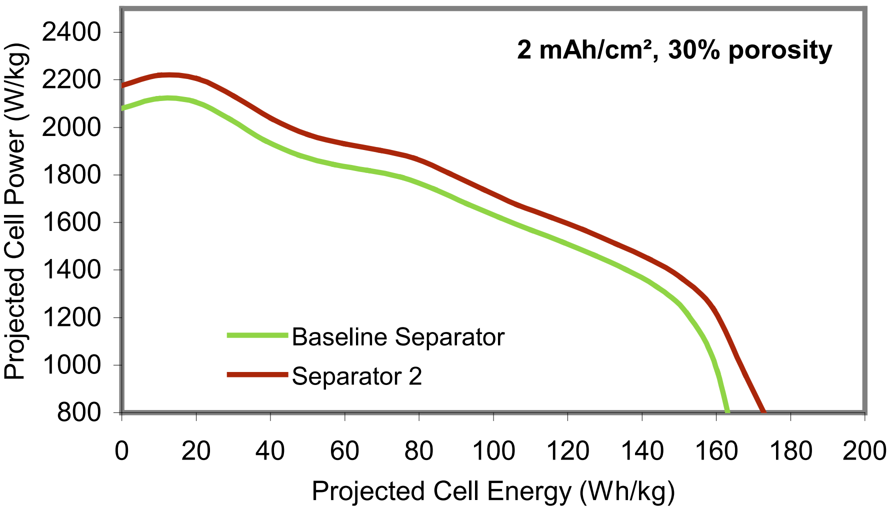
**Using coin cell tests along with 18650 cell design models we are able to assess the impact of active and inactive material components on cell specific energy and power.**

***Illustrative Examples***

**Impact of Cathode Material**




**Impact of Separator**




**200Wh/kg & 800W/kg Target**

Cathode: 94:3:3 formulation, Graphite anode: 96:0:4 formulation. 1M $LiPF_6$ in EC:DMC:EMC (1:1:1) + 1%VC electrolyte. HPPC test with 3C 10s discharge pulse to obtain ASI vs. SOC. Engineering model for 18650 used to project specific energy and power. $V_{min}$ = 2.6V used for power calculations. Additional 20mΩ resistance assumed for cell hardware. Average of 2-3 coin cells.

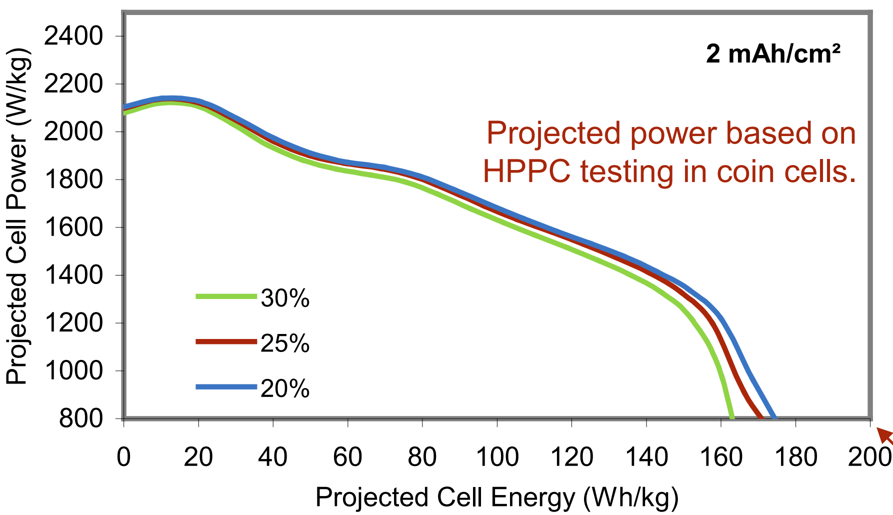
# Technical Accomplishments and Progress

**Cell specific energy can be increased by reducing cathode electrode porosity and increasing electrode loading without loss in specific power.**

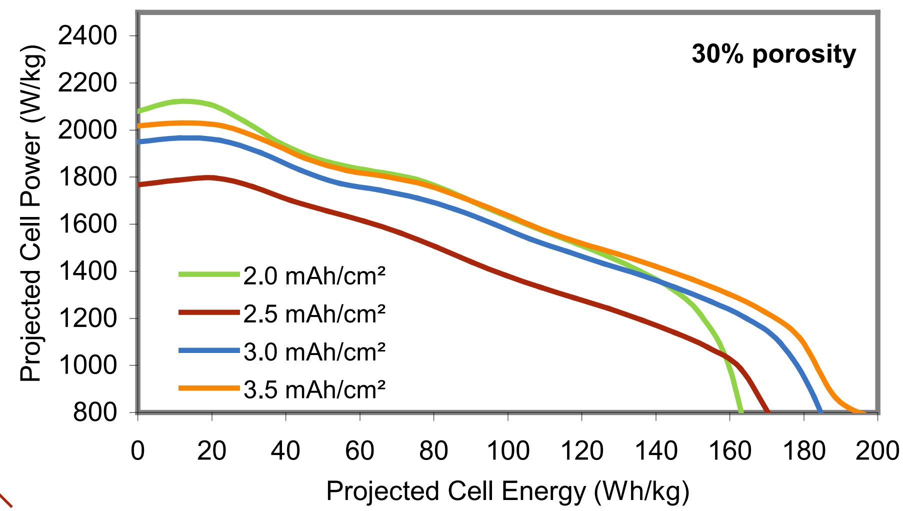
**Using coin cell tests along with 18650 cell design models we are able to assess the impact of electrode design on cell specific energy and power.**

***Illustrative Examples***

## Impact of Electrode Porosity




## Impact of Loading

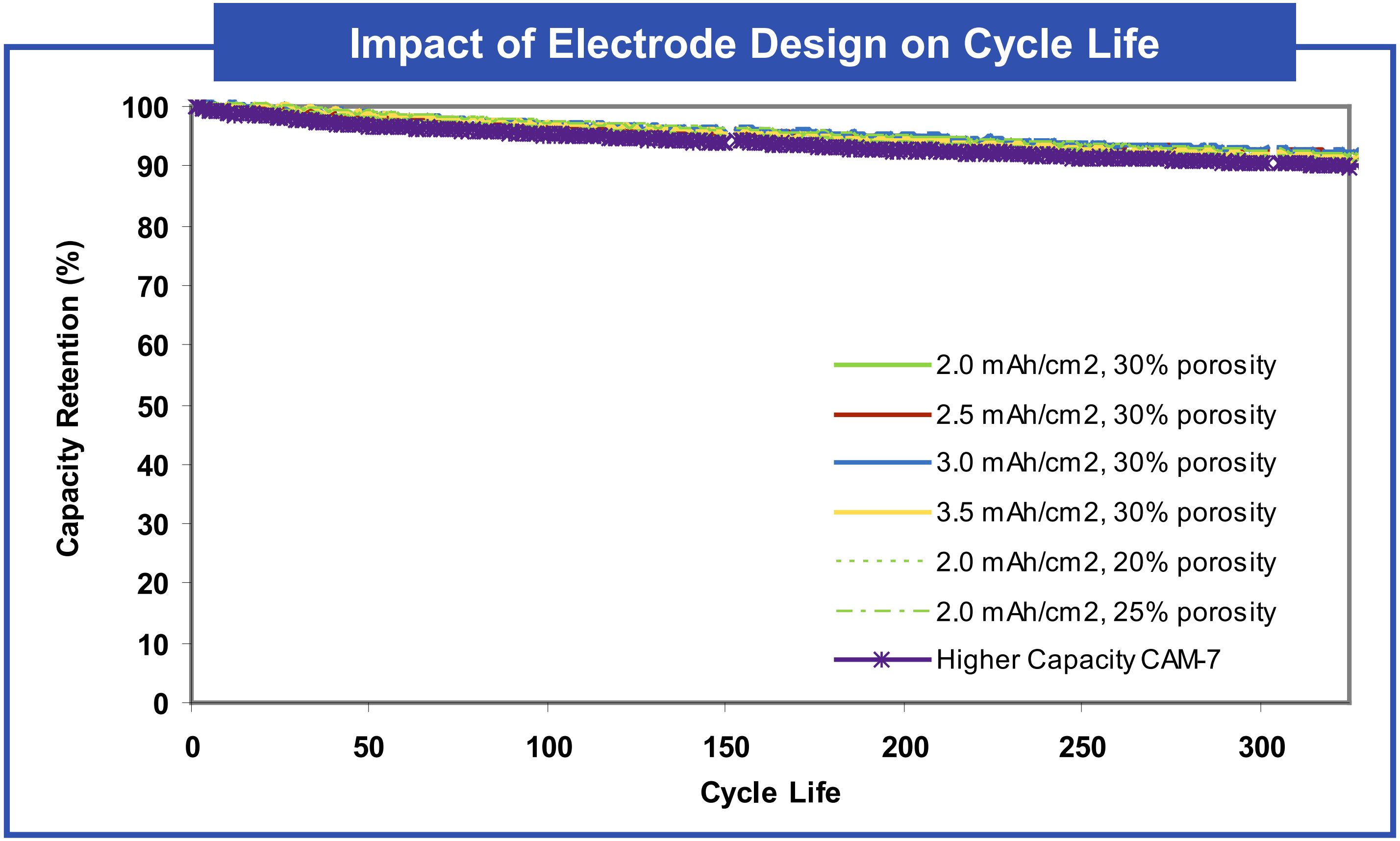



**200Wh/kg & 800W/kg Target**

Cathode: 94:3:3 formulation, Graphite anode: 96:0:4 formulation. 1M $LiPF_6$ in EC:DMC:EMC (1:1:1) + 1%VC electrolyte. HPPC test with 3C 10s discharge pulse to obtain ASI vs. SOC. Engineering model for 18650 used to project specific energy and power. $V_{min}$ = 2.6V used for power calculations. Additional 20mΩ resistance assumed for cell hardware. Average of 2-3 coin cells.

# Technical Accomplishments and Progress

**Modifying cathode electrode loading, porosity, and active material composition did not have a significant impact on cycle life when tested opposite graphite anodes.**

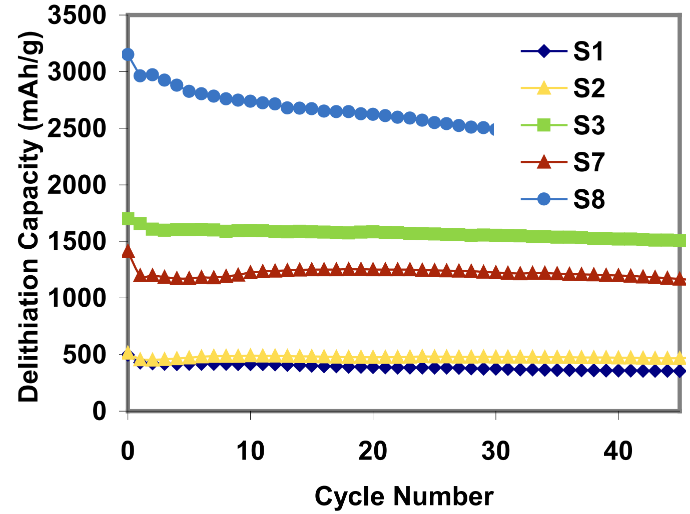



Cathode: 94:3:3 formulation, Graphite anode: 96:0:4 formulation. 1M LiPF6 in EC:DMC:EMC (1:1:1) + 1%VC electrolyte. Cycle life with C/2 charge, 1C discharge 2.7-4.1V cycling. HPPC test every 150 cycles. Average of 2-3 coin cells.

# Technical Accomplishments and Progress

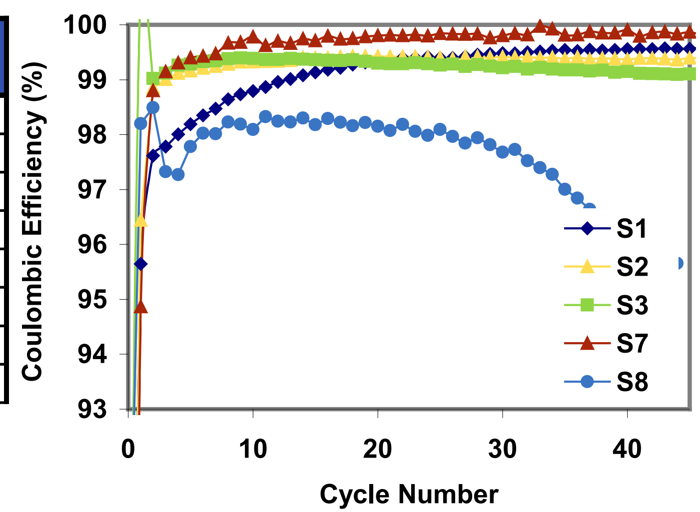
**We have evaluated many Si-based anode materials that show promising performance and have down-selected one of these materials for program demonstration cells.**

- Sourced several state-of-the-art silicon-based anode materials.
- Focused on materials that are available in multi-kg quantities essential for 18650 cell production.
- Evaluated materials for capacity, first cycle efficiency, cycle life, and cycle-to-cycle columbic efficiency vs. Li-metal in coin cells.
- Best performing materials were also evaluated in blends with graphite.




| Range of Materials | | Capacity (mAh/g) | 1st Cycle Efficiency | Cycle Life | Columbic Efficiency |
|---|---|---|---|---|---|
| S1 | Si/Carbon composite | 500 | 82% | Good | OK |
| S2 | Si/Carbon composite | 600 | 84% | Good | OK |
| S3 | Si/Carbon composite | 1650 | 86% | OK | OK |
| S4 | Si/Carbon composite | 1850 | 86% | OK | OK |
| S5 | Micron-scale Si | 3800 | 90% | Poor then good | Good |
| S6 | Micron-scale Si | 3400 | 89% | Poor then good | Good |
| S7 | SiOx | 1400 | 71% | Good | Good |
| S8 | Nano-Si | 3100 | 88% | Good | Poor |

Coin cells with Li metal counter electrode. 1M $LiPF_6$ in EC:DMC:EMC 1:1:1 + 1%VC + 10%FEC electrolyte. C/10 delithiation, then C/2 – C/2 cycling.

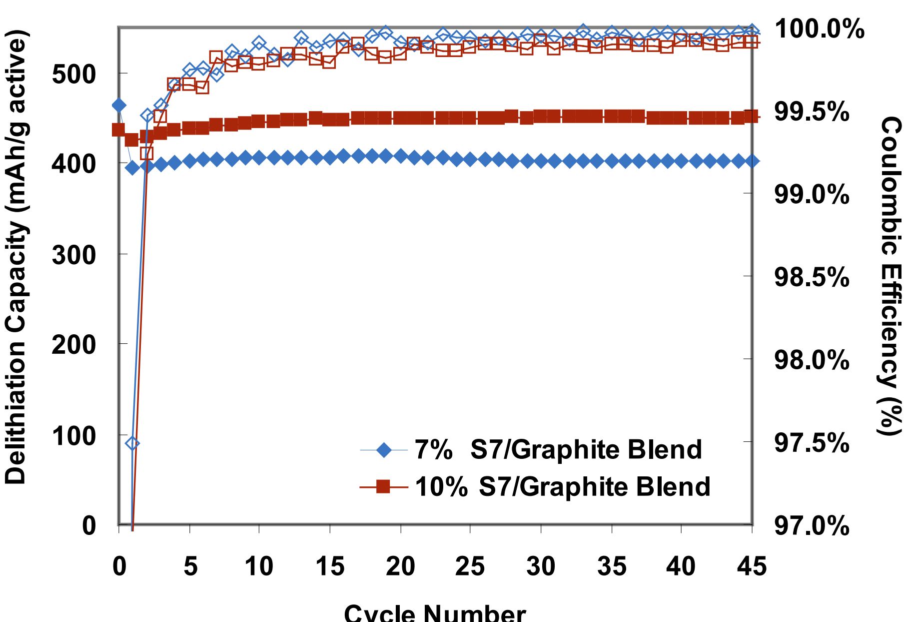



*all materials obtained under NDA

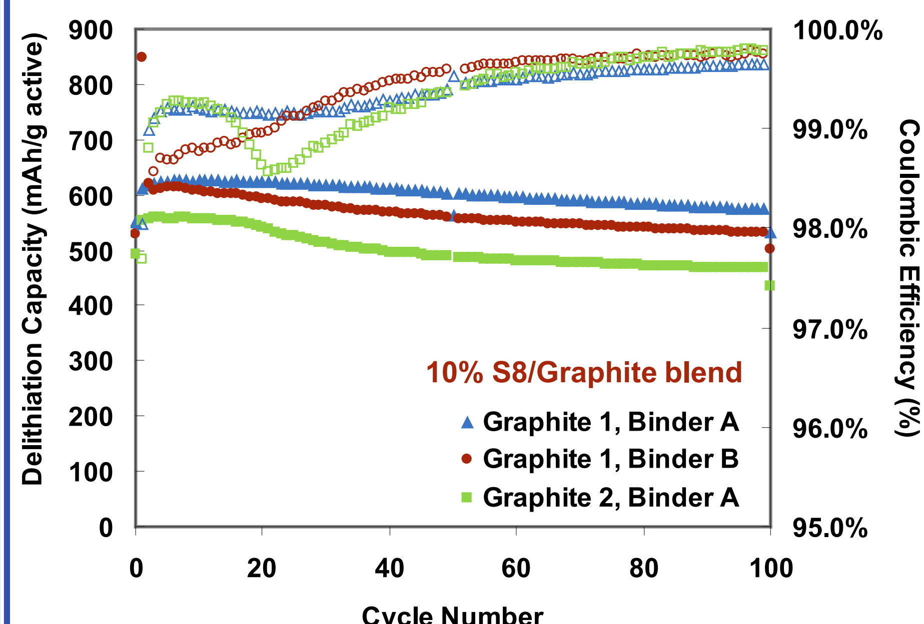
# Technical Accomplishments and Progress

**Best-performing Si-based materials were evaluated in blends with graphite, leading to increased first cycle efficiency, capacity retention, and coulombic efficiency.**

## Impact of Blend Composition – $SiO_x$




## Impact of Graphite and Binder – Nano Si

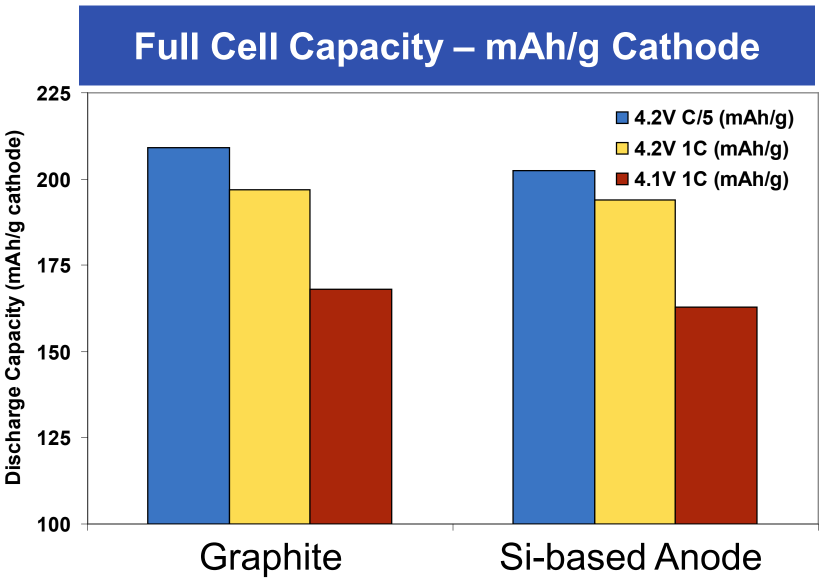


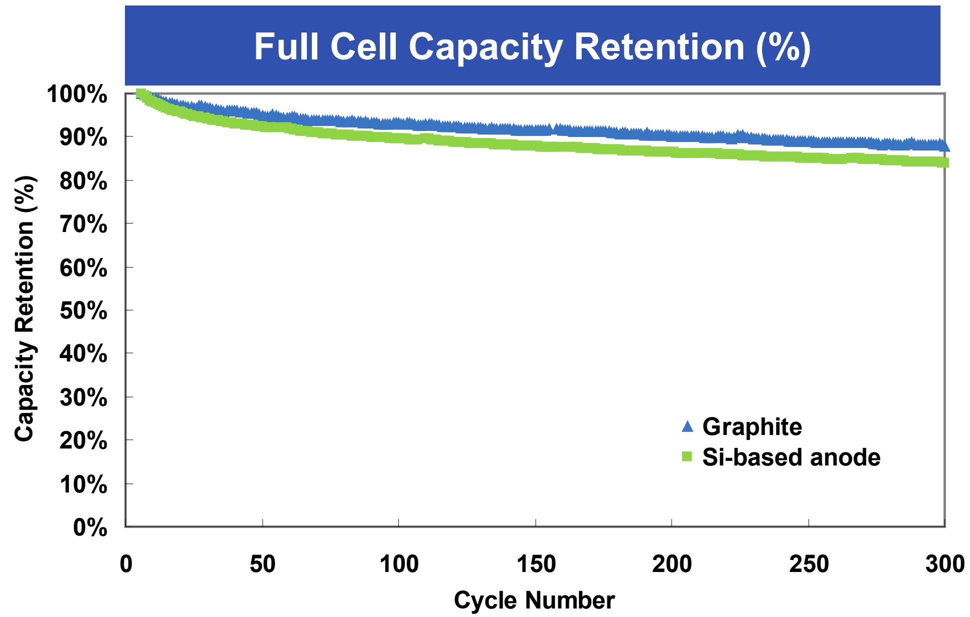

**High coulombic efficiency is required to achieve high capacity retention opposite a fixed Li content cathode electrode.**

Si material/Graphite blend. 90:10 formulation active:binder. 1.3-1.5g/cc density, 1.8-2.4mg/cm² active loading. Cycling C/2 – C/2 5mV to 1.2V; 1C = 400mAh/g nominal.

# Technical Accomplishments and Progress

**Full cells with blended Si-based anodes show excellent cathode utilization with comparable cycle life to graphite-only cells.**



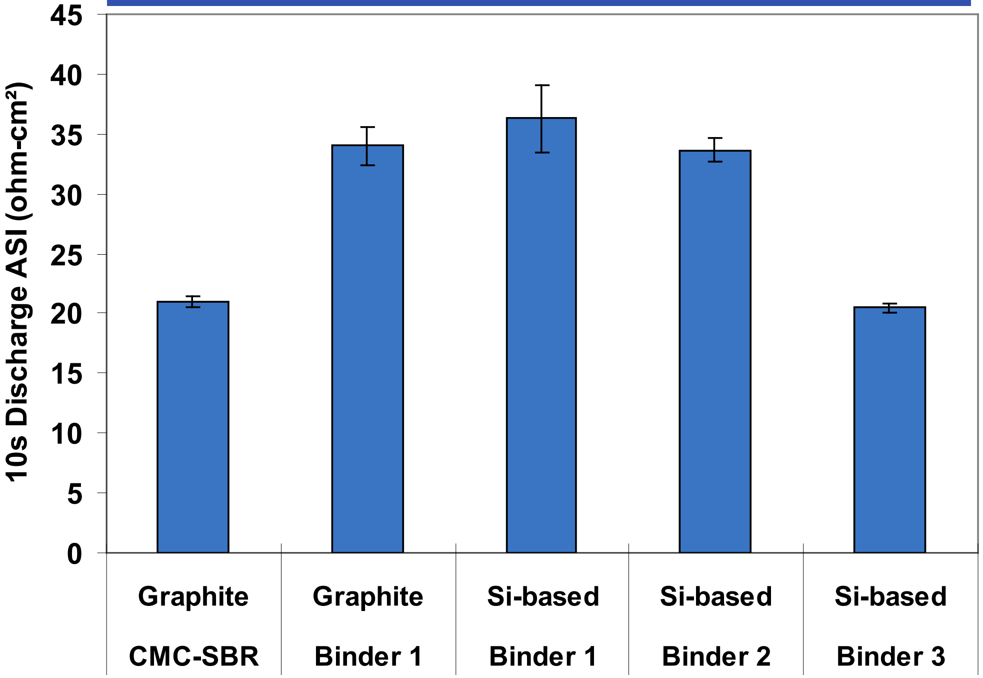

**High cathode utilization is critical for maximizing specific energy at the cell level.**

Blended anode: 95:5 active:binder formulation, ~3mAh/cm² active cathode loading. Coin cell tests average of 2-3cells. Cycling C/2 – 1C 2.7 – 4.1V; HPPC – 3C 10s discharge pulse every 50 cycles.

# Technical Accomplishments and Progress

**We identified a binder for the high loading Si-based blended electrodes that provides good anode adhesion and low ASI in HPPC testing.**

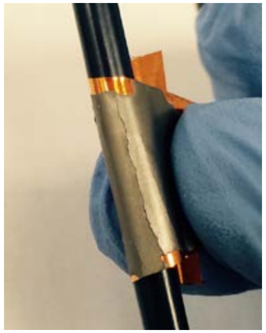
## Binder Selection – ASI @ 50% SOC



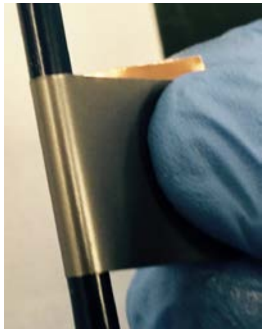

## Adhesion Test

Si-based Binder 1

Si-based Binder 2



Si-based Binder 3



Bar test used to mimic electrode durability during 18650 cell winding (4mm diameter bar).

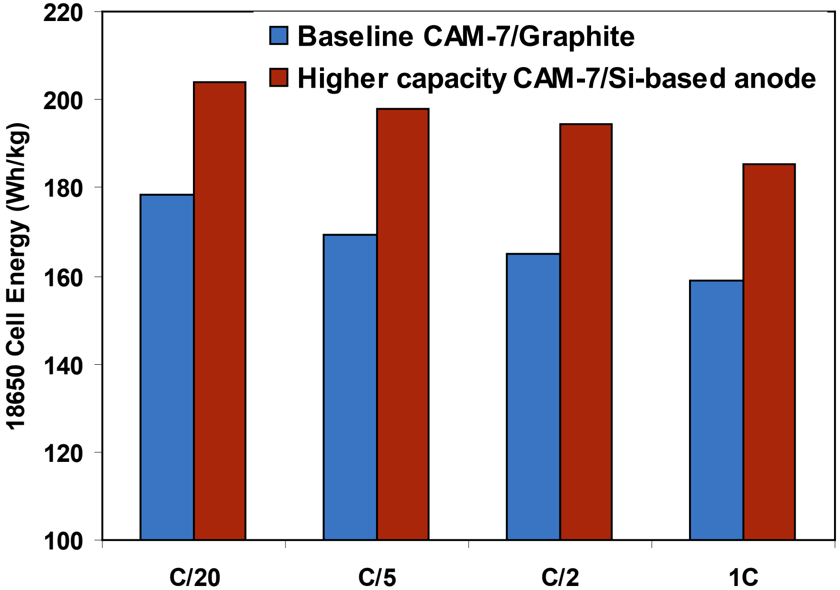
**Typical binder used for Si anodes (Binder 1) has poor adhesion with high loading blended Si-based electrodes leading to higher impedance in HPPC testing.**

95:5 active:binder formulation, ~3mAh/cm² active cathode loading.  Coin cell tests average of 2-3cells.
HPPC Test with 3C 10s discharge and 2C 10s charge pulse as a function of SOC. 1M $LiPF_6$ in EC:DMC:EMC (1:1:1) + 1%VC + 10%FEC electrolyte.

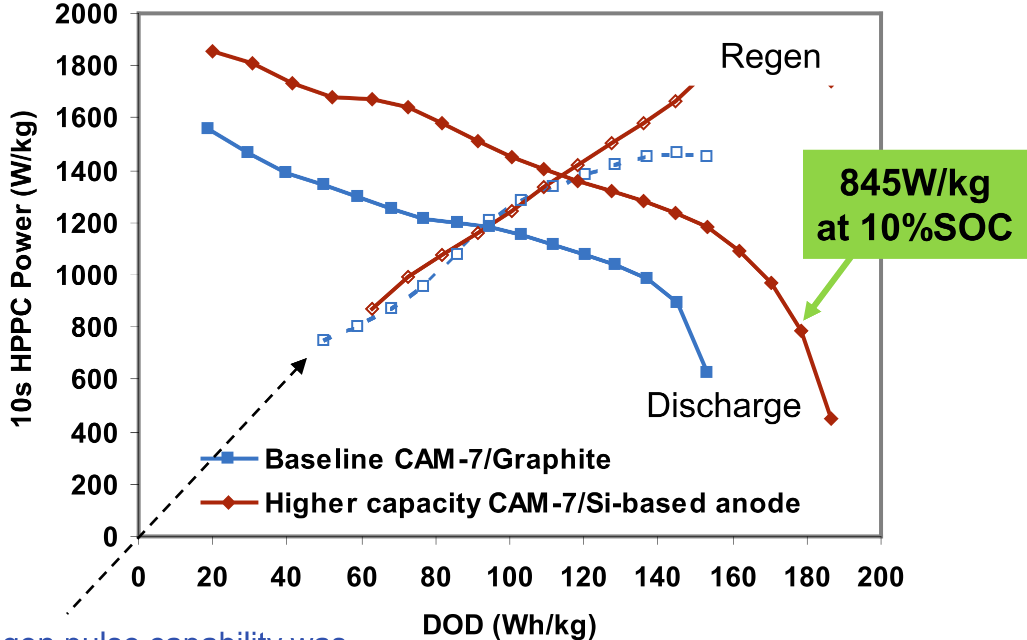
# Technical Accomplishments and Progress

**Implementing higher capacity CAM-7 with a blended Si-based anode and improved cell hardware yields 18650 cells with higher specific energy and power.**

**18650 Specific Energy**




**10s HPPC Projected Power**




Note that regen pulse capability was not tested at < 40Wh/kg DOD.

***18650 hardware circa 2004, ~5-10% higher specific energy and power can be achieved with current 18650 hardware.***

HPPC: 5A 10s Discharge, 3.6A 10s Charge. $V_{min}$ = 2.6V, $V_{max}$ = 4.3V for HPPC power calculation.

# Technical Accomplishments and Progress

**Implementing higher capacity CAM-7 with a blended Si-based anode and improved cell hardware yields 18650 cells with higher specific energy and power.**

| Measured Cell Performance | CAM-7/Graphite Baseline | CAM-7/Blended Si-based Anode |
|---|---|---|
| C/5 Discharge Capacity (Ah) | 1.83 | 2.29 |
| C/5 Discharge Energy (Wh) | 6.70 | 8.38 |
| Total Specific Energy (Wh/kg*)<br>(Wh/kg electrode stack only**) | 167*<br>*(235)***** | 198*<br>*(273)***** |
| 10s Discharge Power at 10% SOC<br>(W/kg* and W/kg electrode stack only**) | 800*<br>*(1110)***** | 845*<br>*(1165)***** |

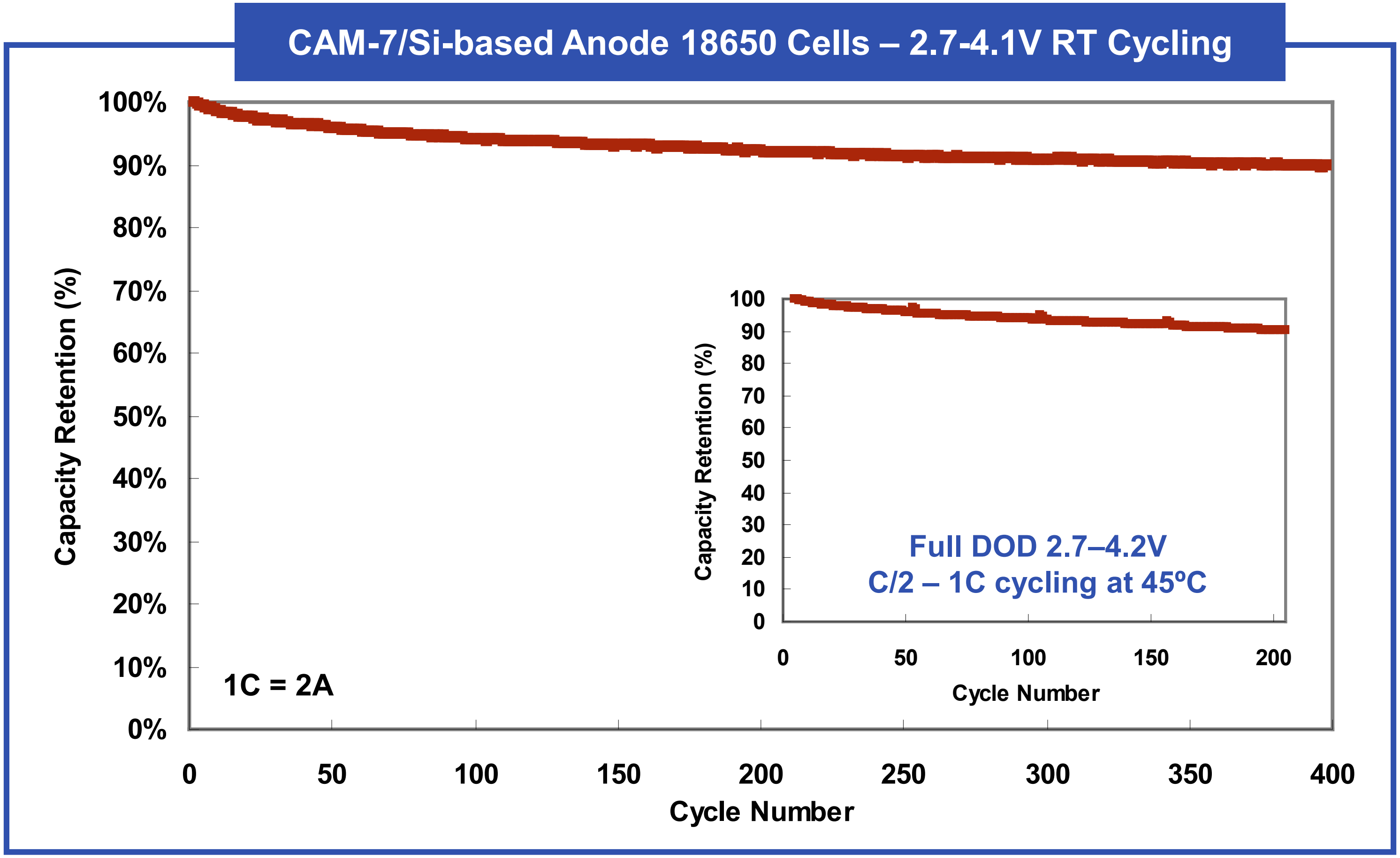
***The CAM-7/Si-based chemistry and electrode design can meet and exceed the 200Wh/kg (available) and 800W/kg targets in mass production 18650 hardware (projected to 250Wh/kg total and 225Wh/kg available energy in 15Ah pouch cells).***

***18650 hardware circa 2004, ~5-10% higher specific energy and power can be achieved with current 18650 hardware.***

*** Electrode stack includes cathode and anode electrodes, current collector foils, separator, and electrolyte filling the electrode and separator pores. It does not include any cell packaging.*

# Technical Accomplishments and Progress

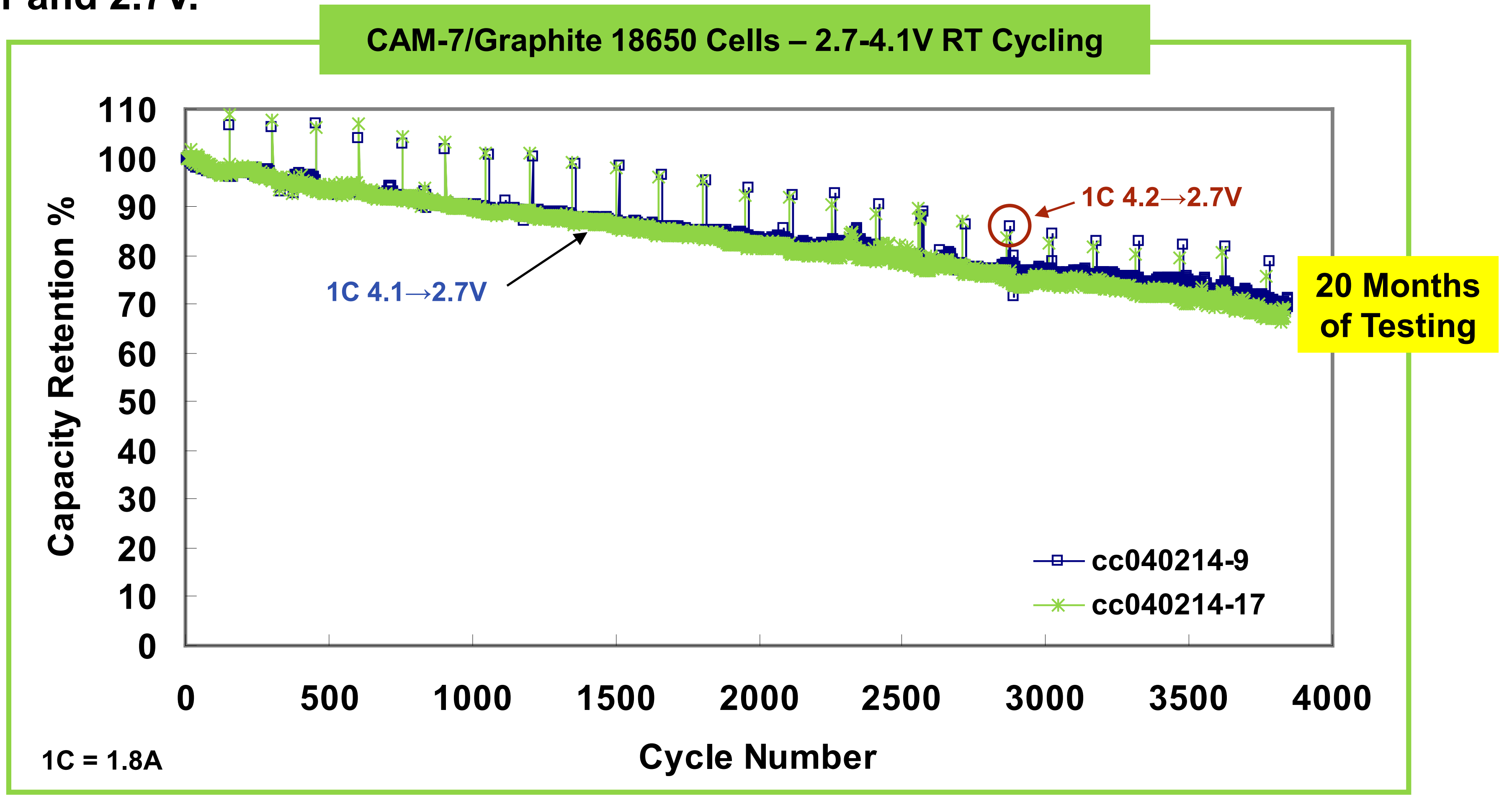
## 18650 cells with higher capacity CAM-7 and blended Si-based anode showed good capacity retention during cycle life testing.




18650 cells with higher capacity CAM-7/Blended Si-based anode.
C/2 charge - 1C discharge, 4.1 to 2.7V; 1C 4.2 to 2.7V discharge every 150 cycles.

# Technical Accomplishments and Progress

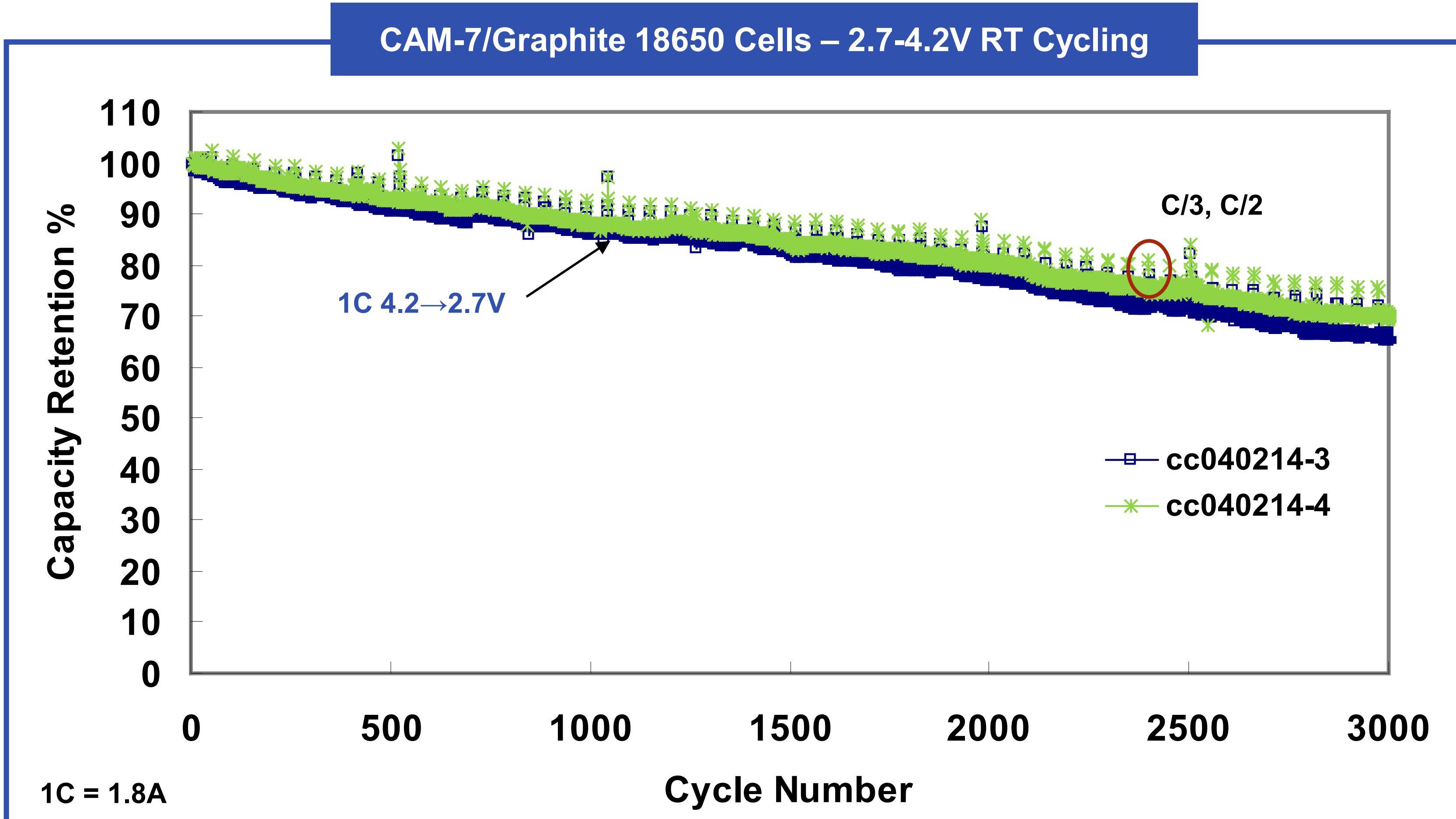
**Continuing cycle life testing of the baseline CAM-7/Graphite 18650 cells fabricated in 2014 shows 70% capacity retention after ~4000 cycles between 4.1 and 2.7V.**




18650 cells with CAM-7/Graphite. 2mAh/cm² active material loading, carbonate electrolyte.
C/2 charge - 1C discharge, 4.1 to 2.7V; 1C 4.2 to 2.7V discharge every 150 cycles.

# Technical Accomplishments and Progress

**Baseline CAM-7/Graphite 18650 cells also show stable capacity cycling with 4.2V charging at room temperature.**



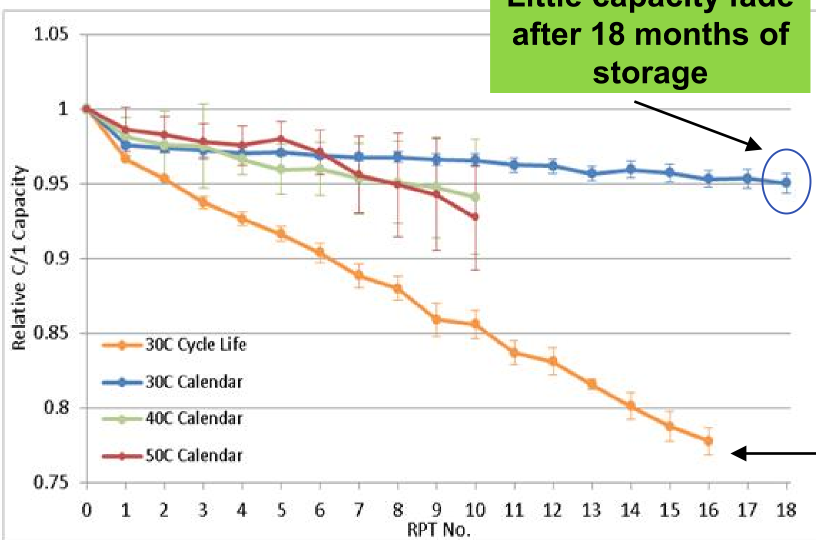

18650 cells with CAM-7/Graphite. 2mAh/cm² active material loading, carbonate electrolyte.
C/2 charge - 1C discharge, 4.2 to 2.7V; C/3 and C/2 discharge every 50 cycles.

# Technical Accomplishments and Progress

**Baseline CAM-7/Graphite 18650 cell performance has been validated in independent testing by Argonne National Laboratory.**

## Capacity Aging Data - Tiax Baseline ABR-IC3P PHEV

**Little capacity fade after 18 months of storage**




| Tiax IC3P Baseline | |
|---|---|
| Vmin | 2.6 V |
| Vmax (continuous/pulse) | 4.2/4.2 V |
| $I_{HPPC}$ | 5.4 A |
| BSF | 1 |
| Rated Capacity (C/1) | 1.8 Ah |

**78% retention after 2400 cycles at 30°C**

1RPT = 150 cycles between 2.7 and 4.1V
1RPT = 28 days at temperature

ANL PROTECTED BATTERY INFORMATION

# Summary

- Selected, synthesized and scaled-up a higher capacity CAM-7 cathode material that exhibits good cycle life for use in program deliverable cells.
- Optimized electrode design to maximize cell specific energy and power for PHEV-40 batteries.
- Down-selected Si-based anode material for program deliverable CAM-7/Si-based 18650 cells.
- Optimized anode blend composition and electrode formulation and selected binders and electrolyte to demonstrate excellent cycle life.
- Implemented higher capacity CAM-7 with Si-based blended anode and improved cell hardware yielding 18650 cells that deliver 198Wh/kg total energy and 845W/kg at 10% SOC (projected to 220Wh/kg in mass production 18650 cells and 250Wh/kg in 15Ah pouch cells).
- Achieved >90% capacity retention for 400 cycles in on-going cycle life testing of the CAM-7 cathode and Si-based blended anode in 18650 cells (cells will be independently tested at ANL).
- Achieved 70% capacity retention after ~4000 cycles (20 months of on-going testing) in baseline CAM-7/Graphite 18650 cells fabricated in 2014.
- Validated baseline cell performance and life in independent testing by ANL (78% retention after 2400 cycles at 30ºC).

# Remaining Challenges and Barriers/Proposed Future Work

- Program deliverable CAM-7/Si-based anode 18650 cells for independent performance and life testing are being assembled.
- Extended cycle life and calendar life testing of CAM-7/Si-based anode 18650 cells is on-going.
- Although the program performance period is complete, we are investigating further ways of optimizing and scaling this CAM-7/Si-based lithium-ion battery chemistry.
- Specifically we are working to:
  - Further optimize electrolyte composition to improve capacity retention.
  - Scale-up to larger cylindrical and/or stacked prismatic cell size.
  - Demonstrate scaled-up cells in small modules.

# Responses to Previous Year Reviewers' Comments

| Comments | Response |
| --- | --- |
| Reviewers noted that cycle life of the Gen 1 Si-based 18650 cells was lacking | ♦ Improving cycle life in large-scale cells was our primary focus for FY15 and FY16.<br>♦ For the final program demonstration cells we down-selected a Si-based material with excellent coulombic efficiency and capacity retention. By blending the Si-based material with graphite we were able to improve first cycle efficiency while providing increased capacity relative to graphite-only cells.<br>♦ With the final blended Si/Graphite anode chemistry we have demonstrated cycle life for over 300 cycles first in coin cells and subsequently in 18650 cells. Cycle life testing is on-going. |
| Reviewers expressed concern regarding meeting cycle life requirements with Si-based anode | ♦ We are keenly aware that long term structural stability of the Si-containing anode requires stability of the anode SEI during substantial volume changes occurring on cycling.<br>♦ We have focused on obtaining anode materials that address this fundamental limitation by utilizing nano-sizing, composite formation or carbon coating, or dilution in an inert matrix to minimize volume changes and to prevent electrolyte contact with freshly exposed Si surfaces.<br>♦ In addition, we tested different binders and electrolyte additives that stabilize the SEI for long term cycling stability. |
| Reviewers inquired about the type of collaboration with Si materials suppliers. | ♦ Our general objective for the program was to be Si material-agnostic, to allow for exploration, testing, and down-selection of the best-performing materials for the PHEV cells.<br>♦ During the program, we have worked closely with multiple companies that are commercializing Si-based anode materials.<br>♦ These companies iteratively provided us with their state-of-the art materials. In return, we supplied them with electrochemical test data and feedback that led to improved materials. |

# Collaboration and Coordination

**TIAX has a strong working relationship with our materials suppliers.**

**Active Material Suppliers**

- Si-based materials – domestic and international suppliers have provided us state-of-the-art Si and Si-based composites.

**Inactive Materials Suppliers**

- Electrolytes – access to high purity electrolytes with additives specifically formulated for Si-based anodes.
- Separators – access to production and research grade high-performance separators ideal for energy and power applications.

**We work closely with our materials suppliers and provide them with electrochemical test data and feedback. These close relationships have led to iterative sampling of their state-of-the art materials.**