High Energy High Power Battery Exceeding PHEV-40 Requirements

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2015 DOE VTP Merit Review

Project ID# ES209

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Overview

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

Timeline

- Project start date: October 1st, 2013
- Project end date: September 30th, 2015
- Percent complete: 75% (time)
- Percent complete: 69% (budget)

Barriers

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

Budget

- Total project funding: $2,184,733
  - DOE share: $1,747,787
  - Contractor share: $436,946
- Funding received in FY13: $118,534
- Funding received in FY14: $888,649
- Funding for FY15: $740,604

Partners

- Multiple materials suppliers

Objectives/Relevance

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

- Implement CAM-7^{TM}/Si 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 the 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

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

Technical Approach

We are employing 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™ 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
- Hard carbon – excellent power-delivery but lower volumetric capacity
- Blend and electrode formulations optimized for energy, power, and life

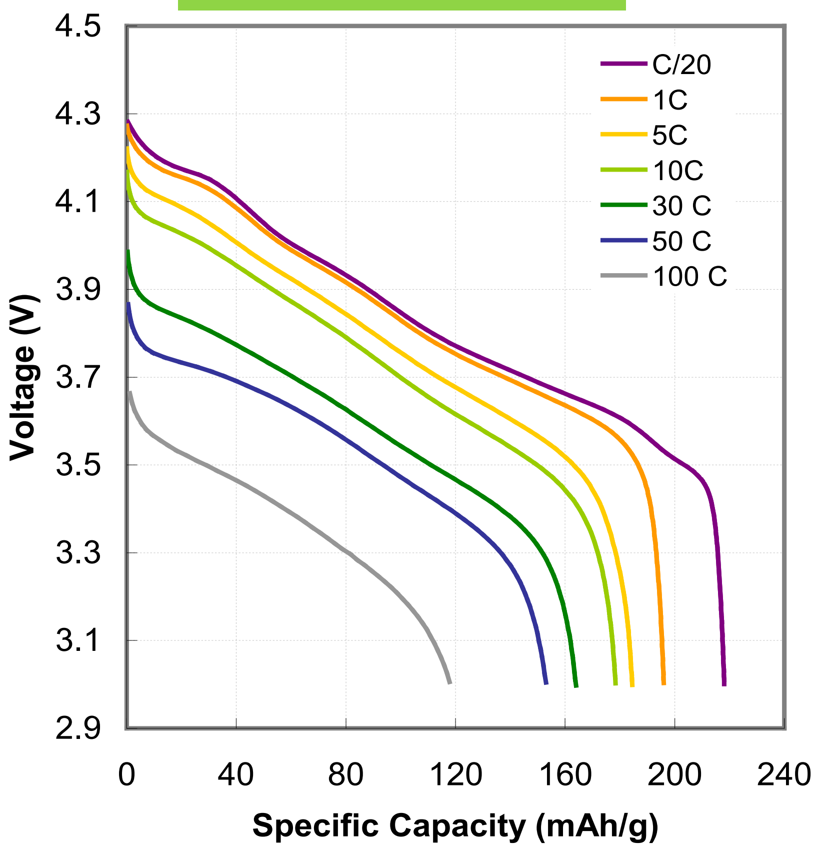
Cell Design

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

Technical Approach

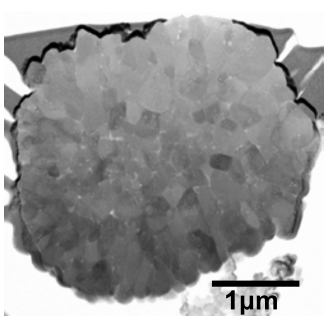
CAM-7 can deliver >200 mAh/g at rates below C/5 and 120 mAh/g at 100C discharge making it attractive for vehicle applications.

Discharge in Half Cells

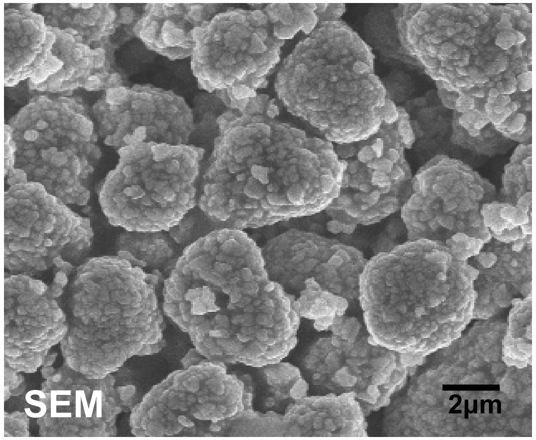


85:10:5, active:cc:PVdF, low-loading electrode,
Li metal anode, 1.0 M $LiPF_6$ in 1:1:1 EC:DMC:EMC + 1%VC electrolyte

- CAM-7 is a stabilized, high-nickel cathode material that combines high energy content with high power capability
- Now in various stages of sampling at major companies in Korea and Japan for both portable electronics and vehicle applications
- CAM-7 has been evaluated in high energy and high power cell designs both at TIAX and by other companies

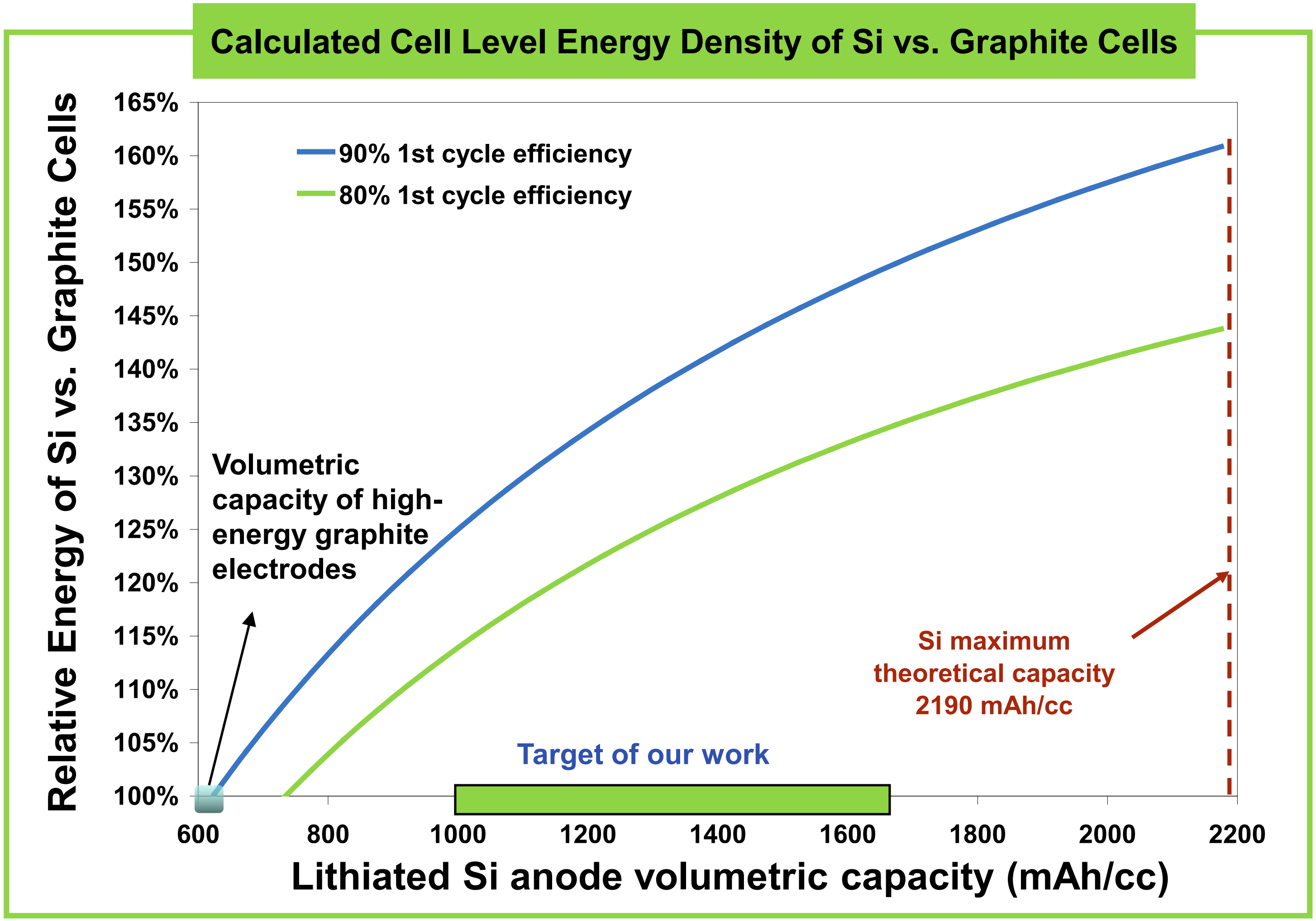


FIB/TEM



Technical Approach: Blended Si/Carbon Anode

Using a blended Si/carbon anode with >1000mAh/cc will allow us to meet pulse power targets, while exceeding the energy density of graphite cells.

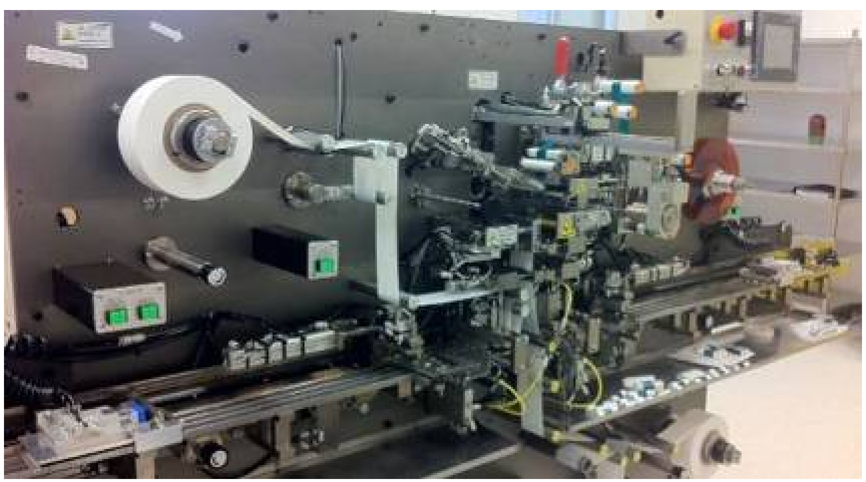


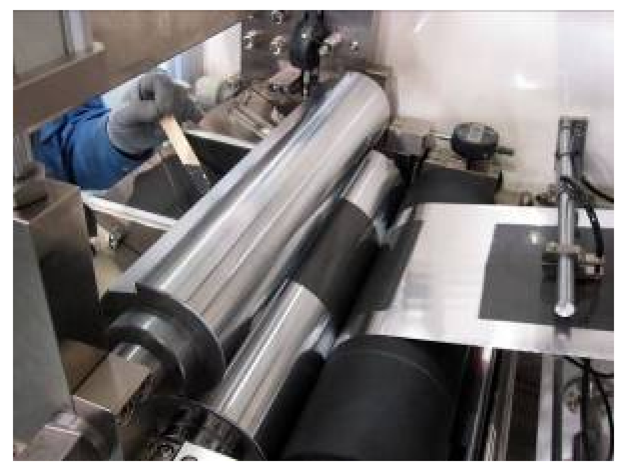
Fixed active material volume/electrode area design; CAM-7 cathode.

Technical Approach

TIAX's cell prototyping facility is facilitating material evaluation and implementation.

- Flexibility in cell formats:
  - Cylindrical
  - Wound prismatic
  - Stacked prismatic
- Cell capacities:
  - 1 – 4 Ah cylindrical
  - 2 - 10 Ah prismatic cells





Summary

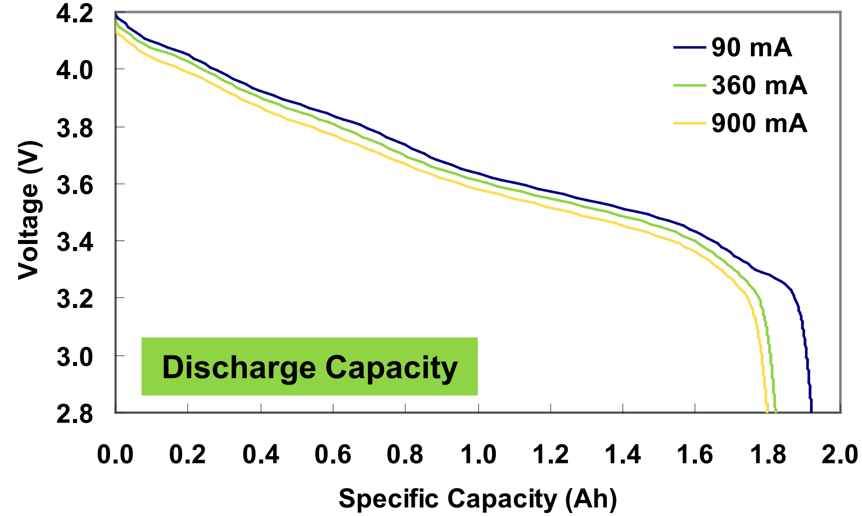
Work in this project to date has focused on:

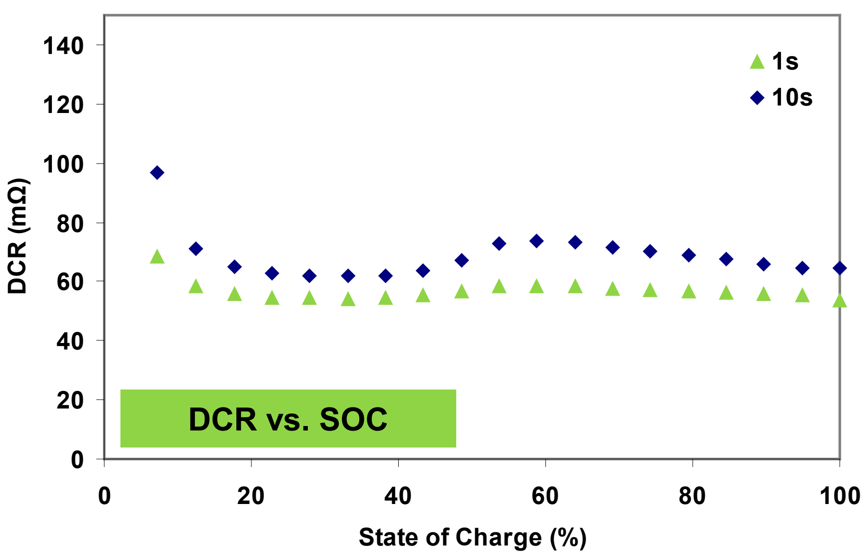
- Cathode materials development to increase capacity and improve cycle life. (ES-260)
- Silicon-based anode materials selection and electrode development. (ES-260)
- Assessment of strategies to improve cycle life of silicon-based anode cells. (ES-260)
- Design, assembly, performance and life testing of baseline 18650 CAM-7/Graphite Li-ion cells. (ES-209)
- Implementation of Si-based anode in an 18650 cells. (ES-209)
- Design, assembly, and testing of Gen 1 CAM-7/Si 18650 cells. (ES-209)

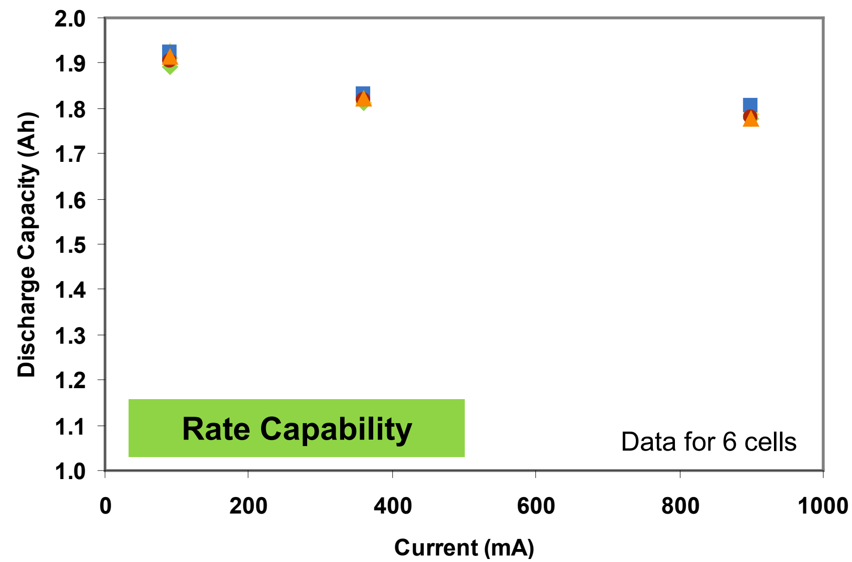
Technical Accomplishments and Progress

Baseline CAM-7/graphite cells for independent testing were fabricated in 2014.

- CAM-7 cathode / graphite anode
- Carbonate electrolyte
- 18650 design – 1.9Ah at C/20 (90mA)
- 10 mg/cm² or 2 mAh/cm² cathode active material loading

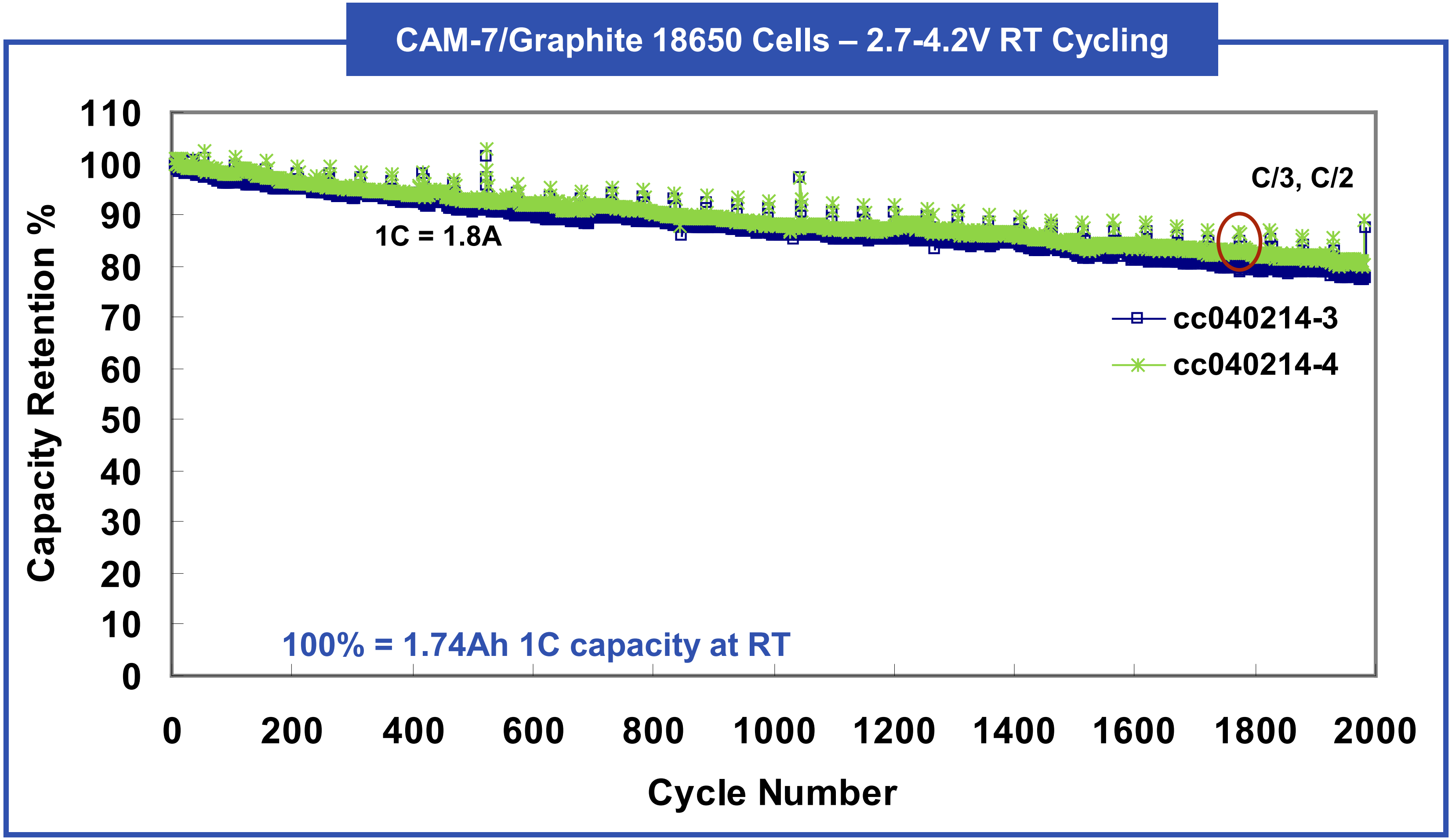






Technical Accomplishments and Progress

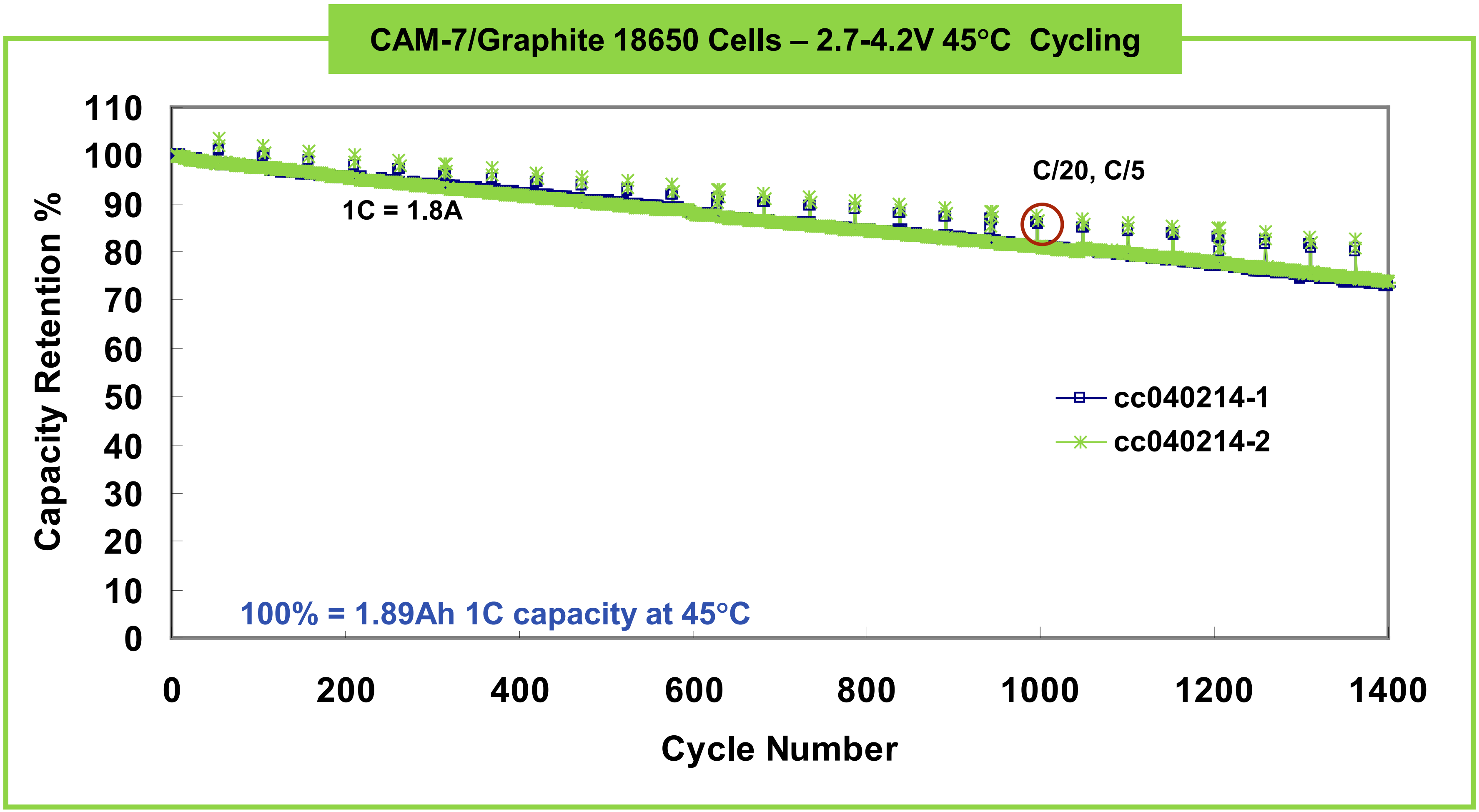
Baseline CAM-7/Graphite 18650 cells show stable capacity cycling at room temperature over the full DOD range.



18650 cells with CAM-7/Graphite. C/2 charge - 1C discharge, 4.2 to 2.7V; C/3 & C/2 discharge every 50 cycles.

Technical Accomplishments and Progress

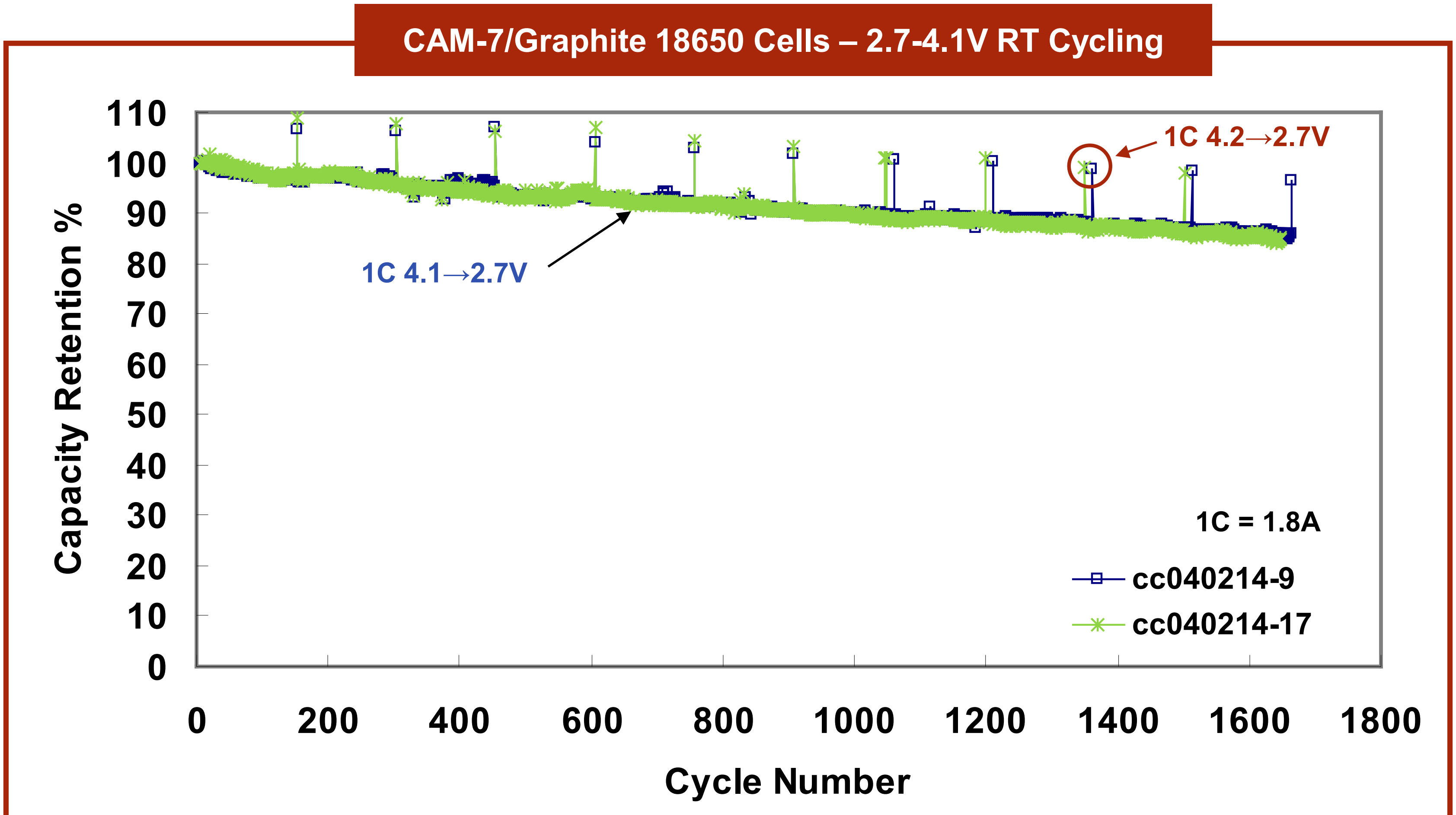
Baseline CAM-7/Graphite 18650 cells show stable capacity cycling at 45°C over the full DOD range.



18650 cells with CAM-7/Graphite. C/2 charge - 1C discharge, 4.2 to 2.7V; C/20 & C/5 discharge every 50 cycles.

Technical Accomplishments and Progress

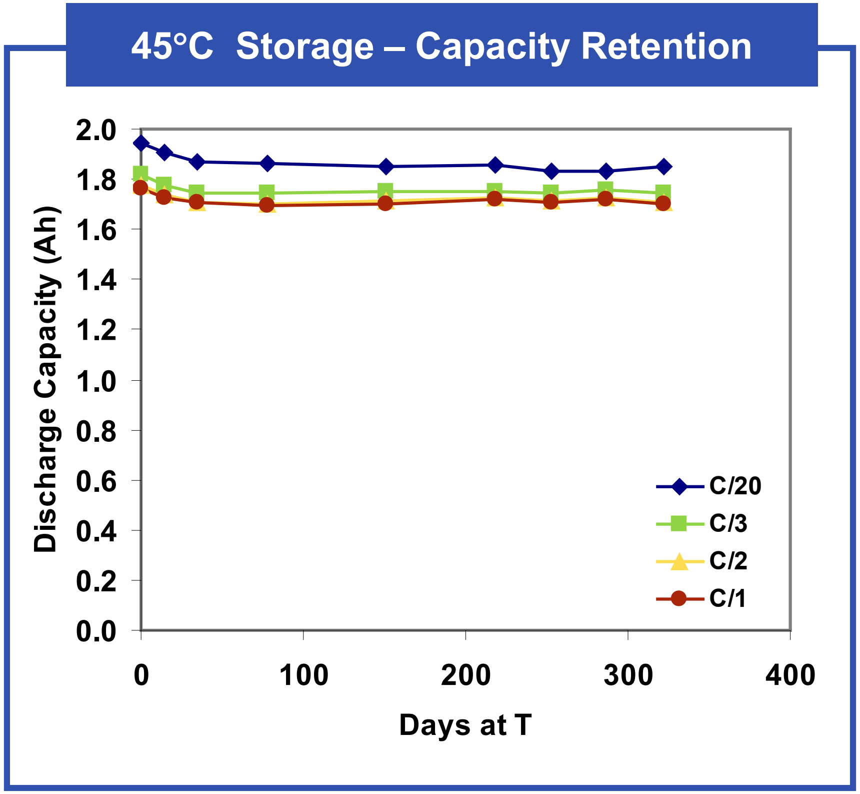
Baseline CAM-7/Graphite 18650 cells show >85% capacity retention after 1600 cycles at room temperature between 2.7 and 4.1V.

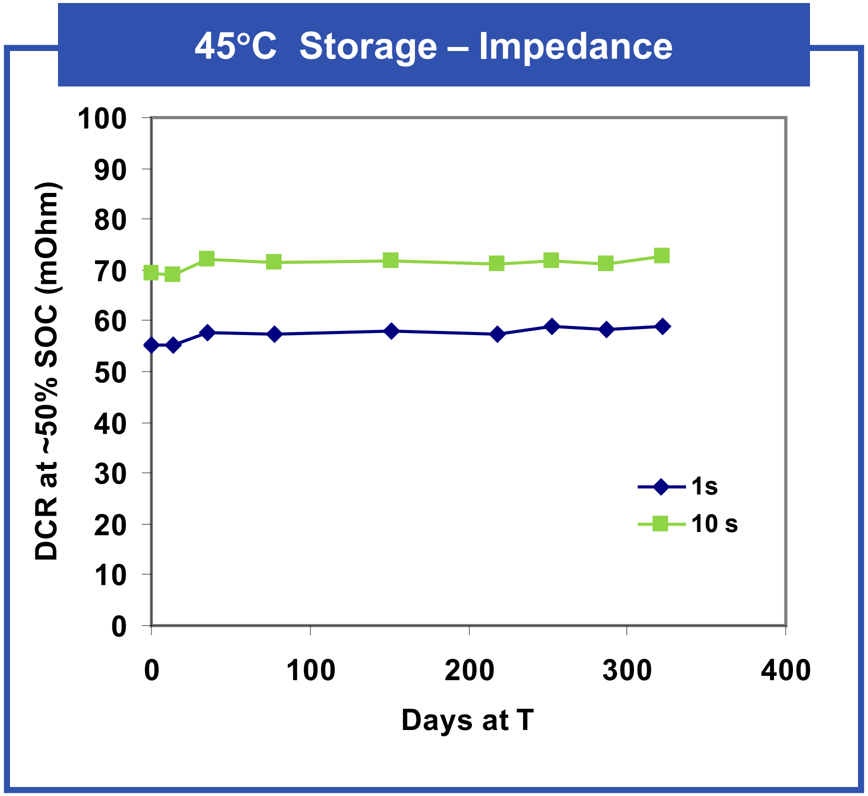


18650 cells with CAM-7/Graphite. C/2 charge - 1C discharge, 4.1 to 2.7V; 1C 4.2 to 2.7V discharge every 150 cycles.

Technical Accomplishments and Progress

Baseline CAM-7/Graphite 18650 cells show little capacity loss or impedance rise during 4.1V open circuit storage at 45ºC.



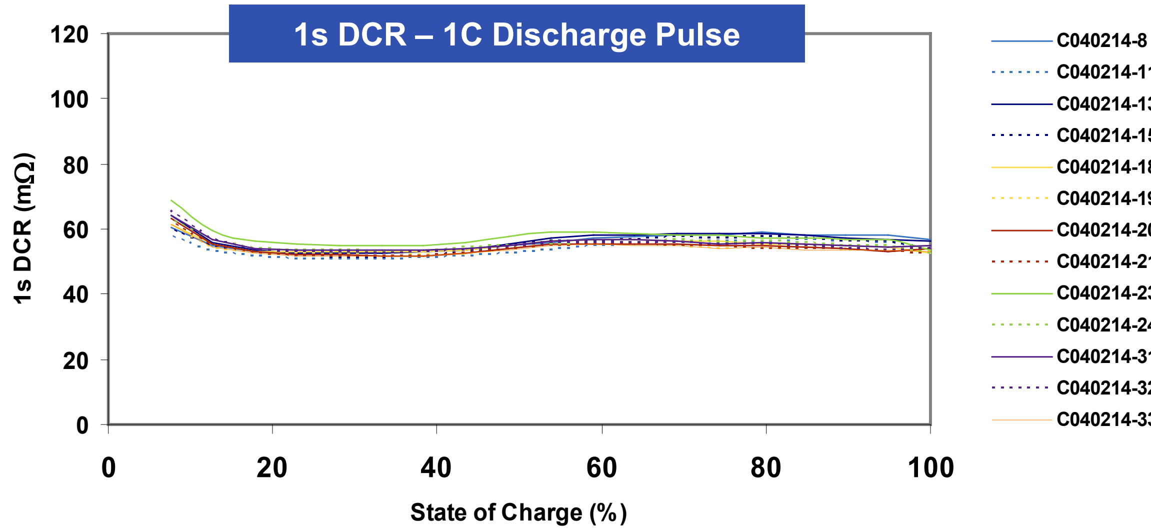


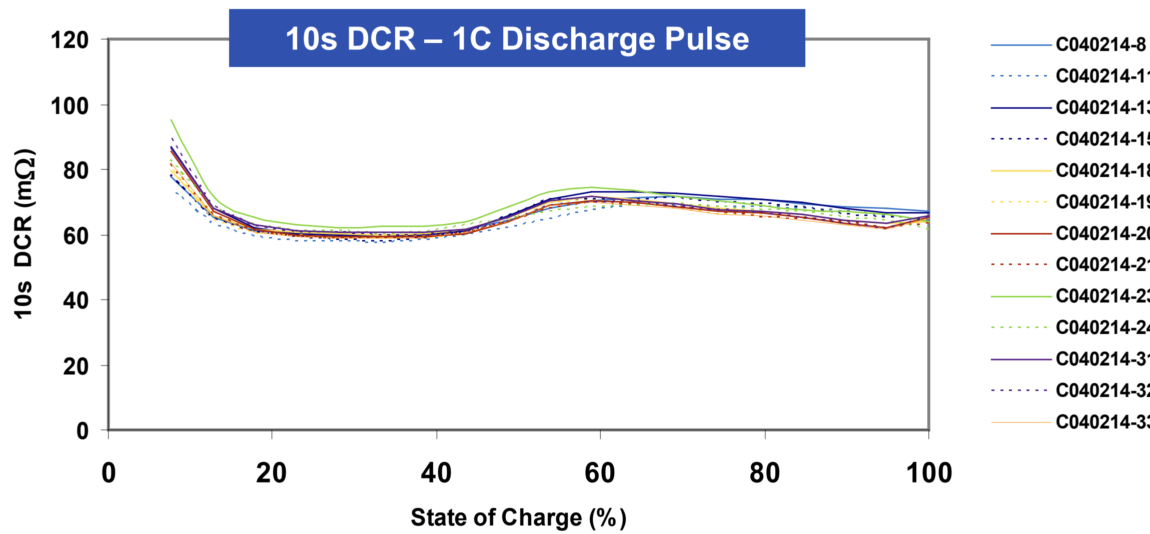
18650 cells with CAM-7/Graphite. Cells stored at 4.1V open circuit at 45ºC. Rate capability characterized intermittently at room temperature using continuous discharge between 4.2 and 2.7V and using 1C/1C HPPC pulse power.

Technical Accomplishments and Progress

Thirteen baseline CAM-7/Graphite cells were shipped to Argonne National Laboratory for testing.

	C/5 Ah	C/5 Wh	Weight (g)
C040214-8	1.85	6.81	40.0
C040214-11	1.86	6.83	40.0
C040214-13	1.82	6.68	39.4
C040214-15	1.84	6.78	39.7
C040214-18	1.87	6.89	39.9
C040214-19	1.87	6.85	39.8
C040214-20	1.85	6.79	39.7
C040214-21	1.86	6.84	39.7
C040214-23	1.83	6.73	39.4
C040214-24	1.87	6.86	40.2
C040214-31	1.85	6.79	39.8
C040214-32	1.84	6.75	39.8
C040214-33	1.86	6.84	39.8



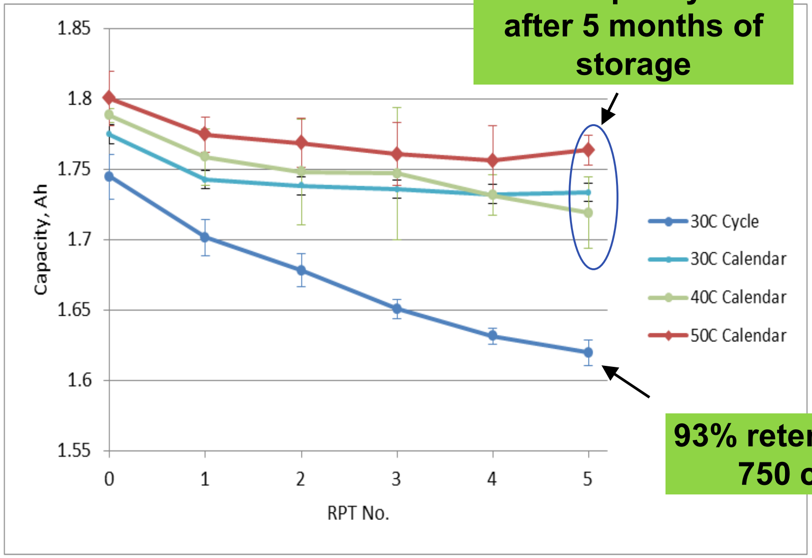


Technical Accomplishments and Progress

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

Capacity Aging Data - Tiax Baseline ABR-IC3P EV

Little capacity fade after 5 months of storage



93% retention after 750 cycles

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

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

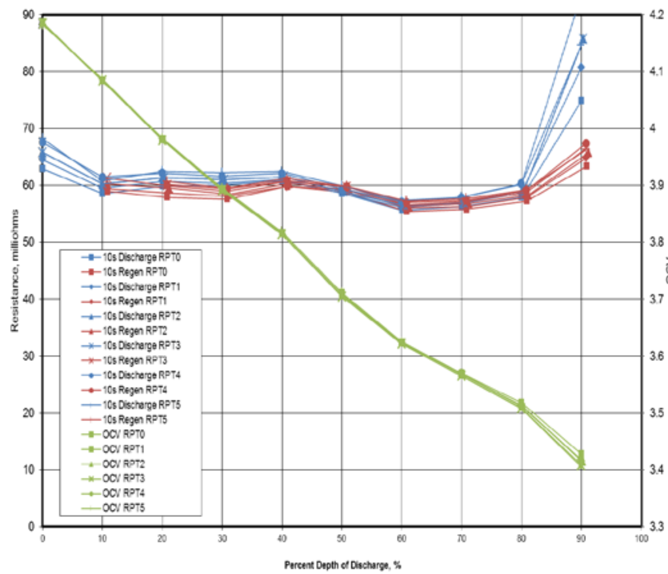
ANL PROTECTED BATTERY INFORMATION

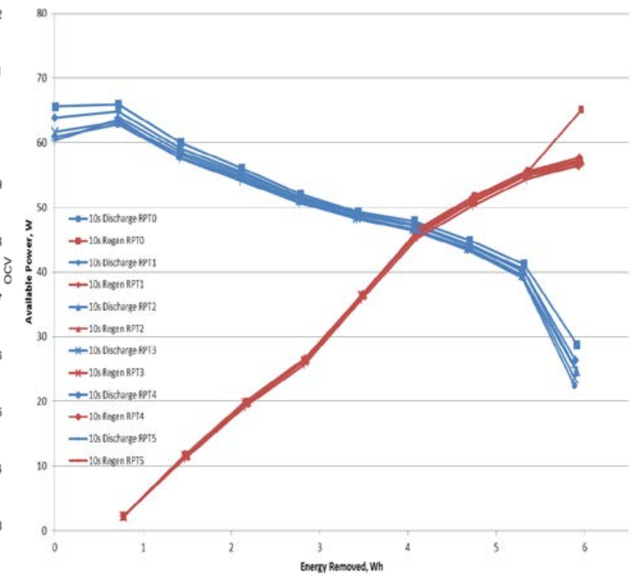
Technical Accomplishments and Progress

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

Calendar Life Testing at 30°C – Tiax Baseline ABR-IC3P EV

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

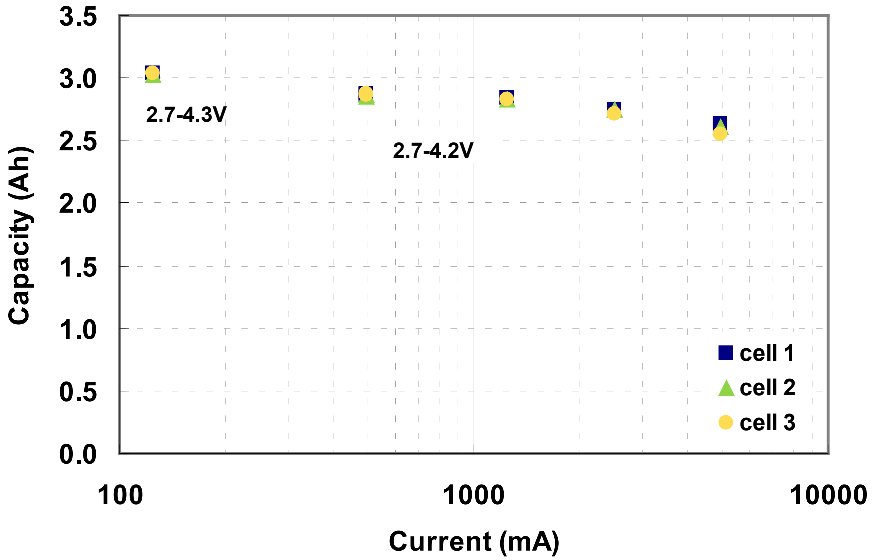


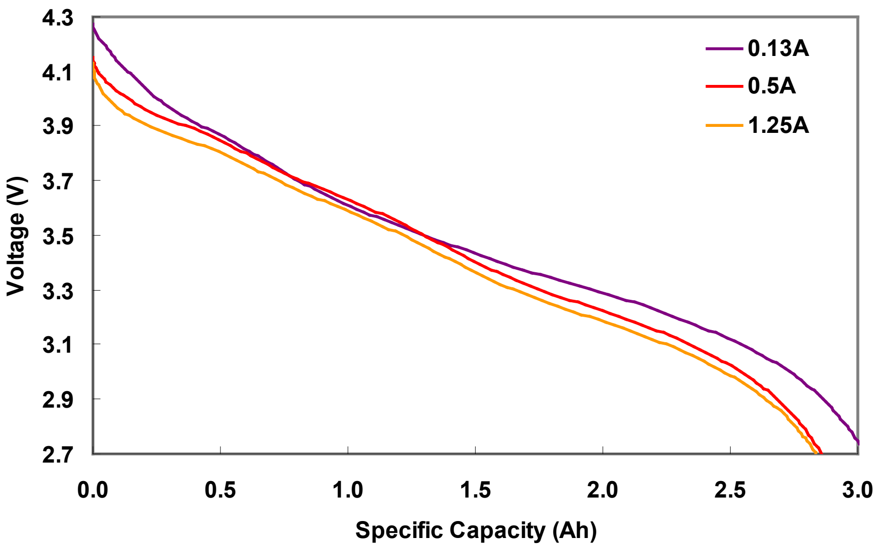


5RPT ~5 months of storage

Technical Accomplishments and Progress

First generation CAM-7/Si 18650 cells were fabricated and tested, demonstrating higher capacity and energy density than the baseline cells.



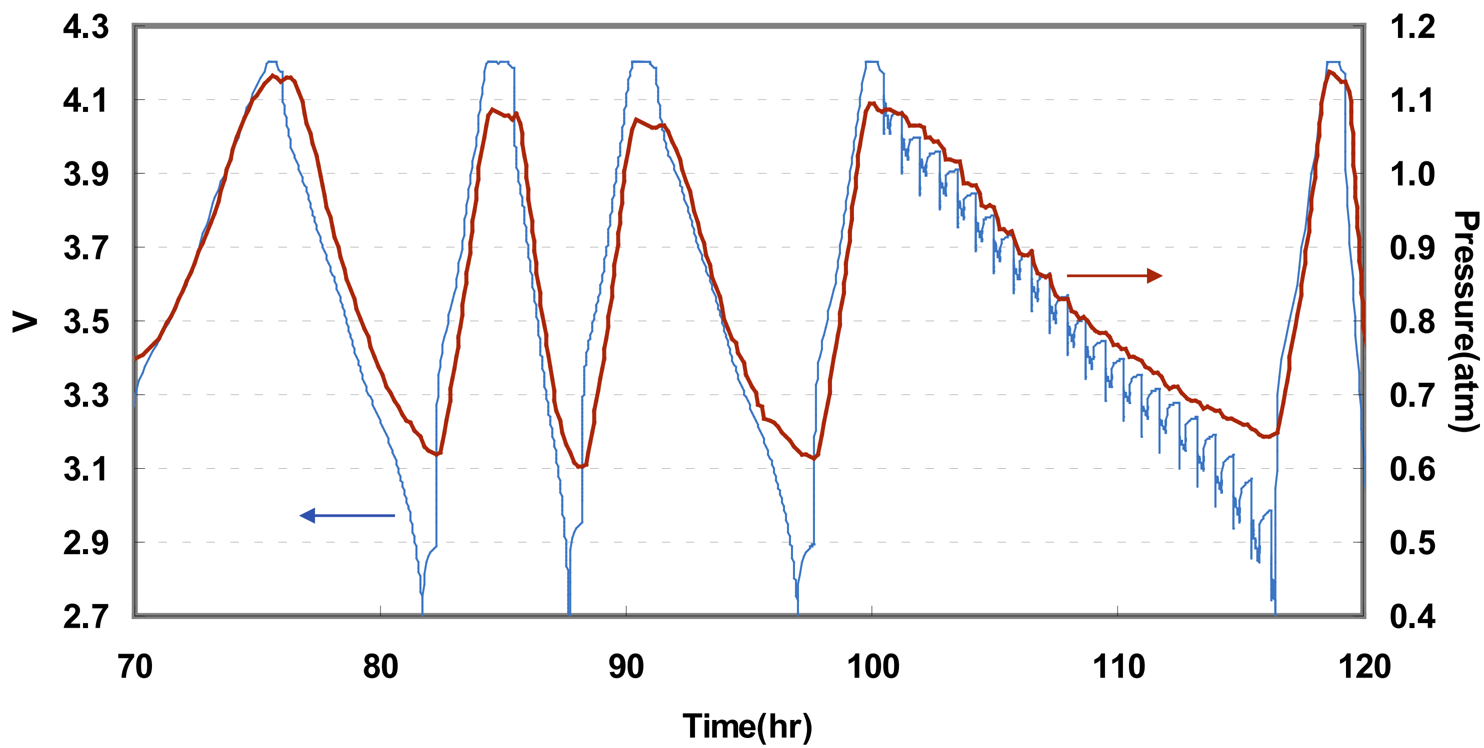


	CAM-7/Graphite Baseline	CAM-7/Si Composite Gen 1
C/5 Capacity (Ah)	1.83	2.85
C/5 Energy (Wh)	6.70	9.85

18650 cells with CAM-7/Si. 20 mg/cm² or 4 mAh/cm² cathode active material loading. Carbonate electrolyte with FEC. 4.3V C/20 charge formation. C/2 charge to 4.2V for rate characterization.

Technical Accomplishments and Progress

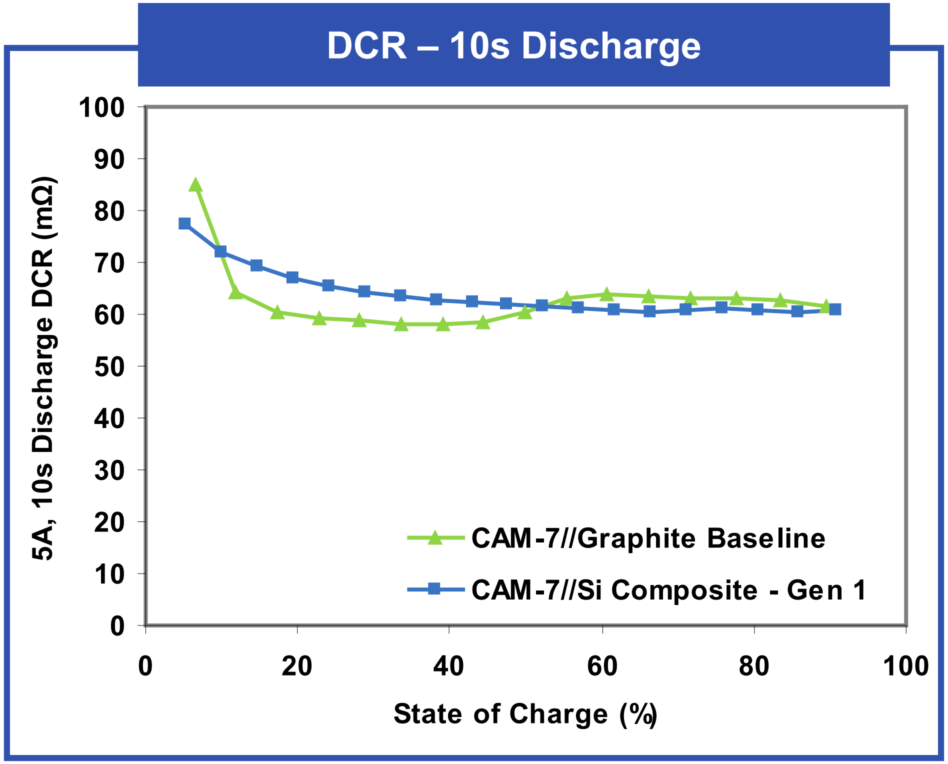
Using a specially designed set-up we are able to monitor the rise in internal cell pressure due to silicon anode volume expansion during cycling.

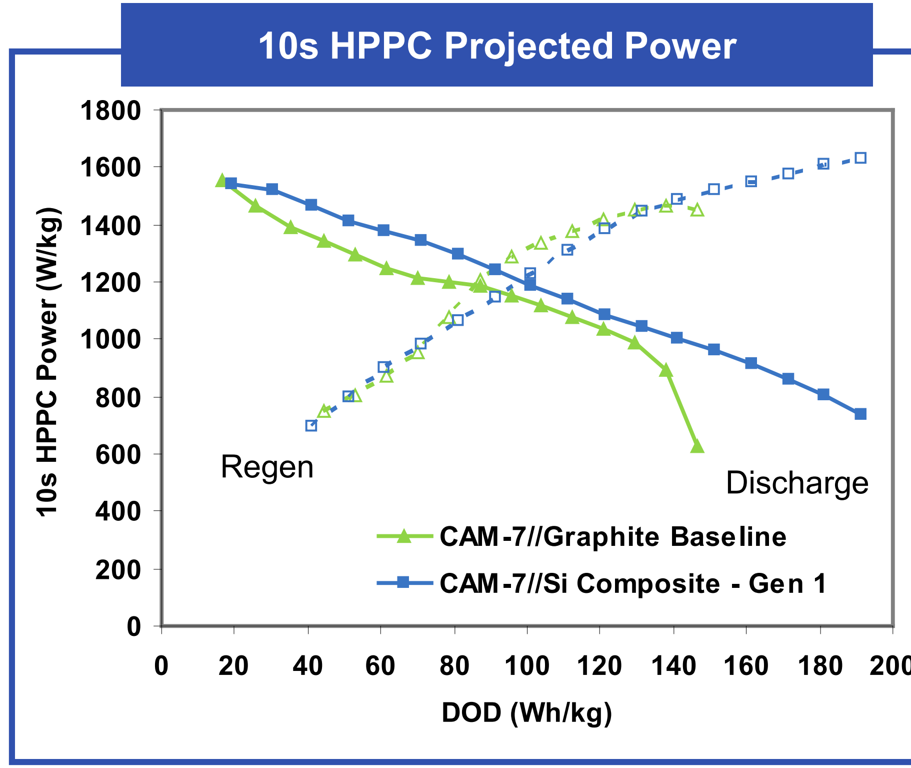


18650 cells with CAM-7/Si. Shown: C/5 - C/5, C/2 - C/2, C/2 - C/5, C/2 Charge with 1C 10s pulse discharge. Charge steps with CV steps to C/20 or C/50. 1C = 2.5A nominal.

Technical Accomplishments and Progress

HPPC testing shows that the Gen 1 CAM-7/Si cells can provide comparable power while providing higher energy density than the baseline 18650 cells.





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

Si: 5A 10s Discharge, 3.75A 10s Charge. V_{min} = 2.0V, V_{max} = 4.3V for HPPC power calculation.

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

Technical Accomplishments and Progress

The Gen 1 CAM-7/Si cells can provide comparable power while providing higher energy density than the baseline 18650 cells.

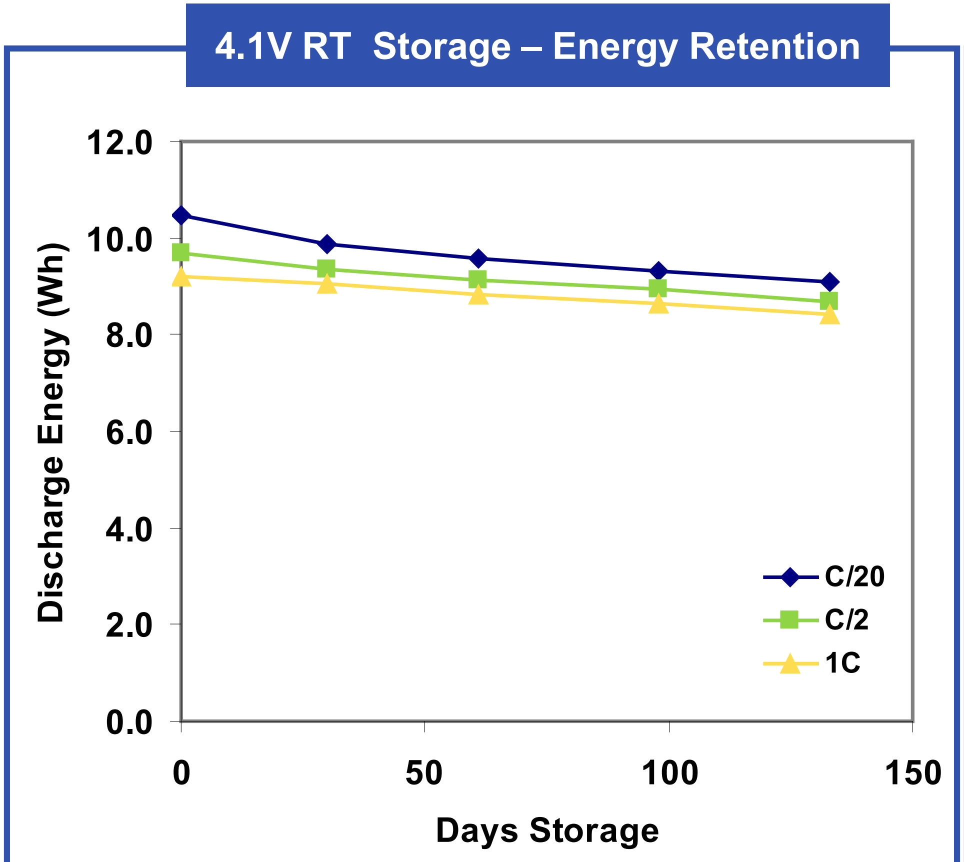
	CAM-7/Graphite Baseline	Gen 1 CAM-7/Si Composite
C/5 Discharge Capacity (Ah)	1.83	2.85
C/5 Discharge Energy (Wh)	6.70	9.85
Total / Available Energy with 90% SOC Range (Wh/kg* and Wh/kg electrode stack only)	167 / 152 *(235 / 210)***	230 / 207 *(310 / 280)***
Discharge Power at 10% SOC (W/kg* and W/kg electrode stack only)	800 *(1110)***	735 *(985)***

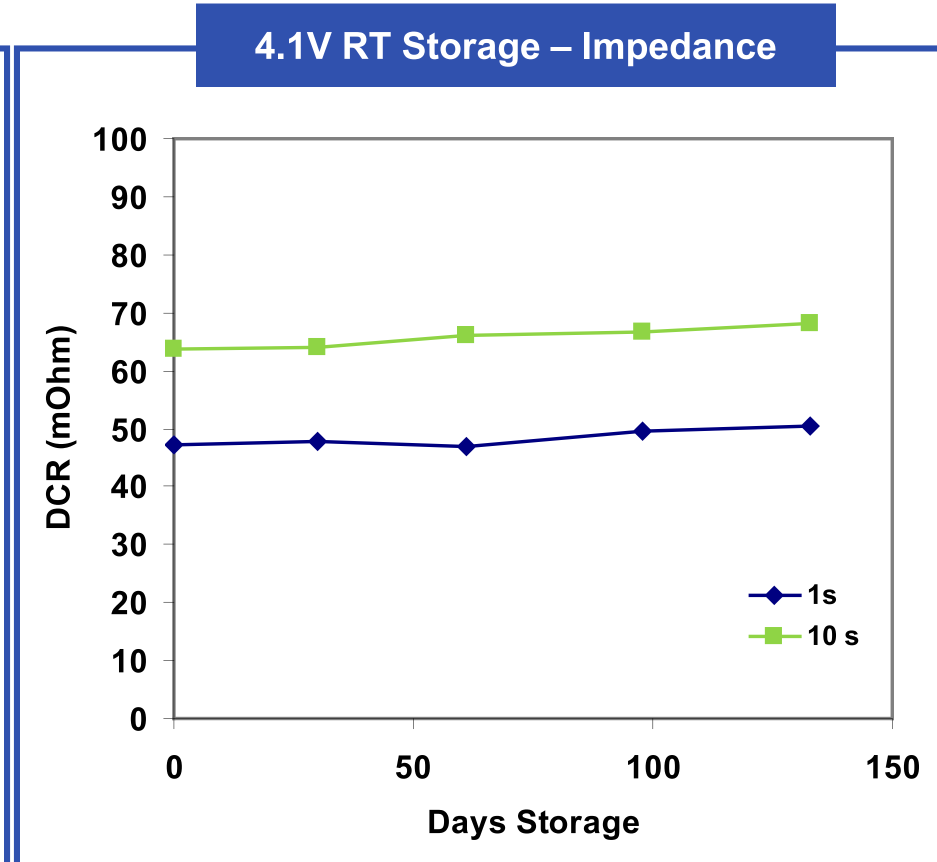
18650 hardware circa 2004, ~5-10% higher specific energy and power can be achieved with current 18650 hardware

*** 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

In storage experiments, Gen 1 CAM-7/Si cells show some capacity fade after four months at 4.1V.

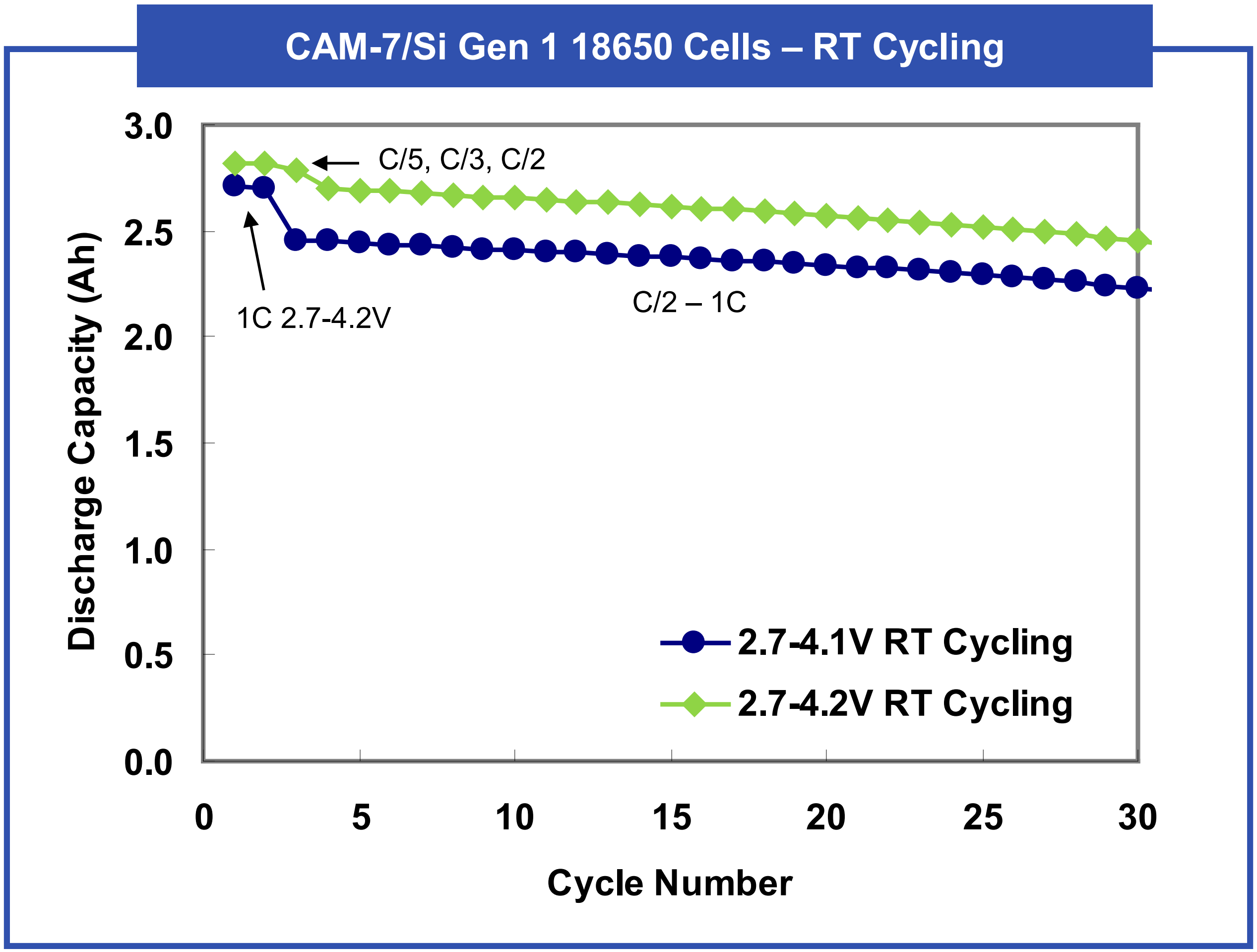




18650 cells with CAM-7/Si.

Technical Accomplishments and Progress

We observed capacity fade in Gen 1 CAM-7/Si cells during both full DOD (2.7-4.2V) and reduced DOD (2.7-4.1V) cycling.



18650 cells with CAM-7/Si composite. C/2 CCCV charge - 1C discharge.

Summary

- We have designed, assembled and tested baseline 18650 CAM-7/Graphite Li-ion cells demonstrating:
  - Excellent cycle life with ~80% capacity retention for full DOD operation between 2.7-4.2V, after 1000 cycles at 45ºC and 2000 cycles at RT.
  - Over 85% capacity retention after 1600 cycles between 2.7-4.1V at RT and little capacity loss or impedance rise during storage at 4.1V.
- Baseline cell performance and life were validated in independent testing by Argonne National Laboratory.
- We have designed, assembled, and tested Gen 1 CAM-7/Si 18650 cells, showing:
  - Gen 1 CAM-7/Si cells can provide comparable power while providing higher energy density than the baseline 18650 cells almost meeting the 200Wh/kg and 800W/kg energy and power targets.
- Work conducted on materials and electrode design on this program is highlighted in ES260 presentation.

Remaining Challenges and Barriers

- Capacity retention of Si-containing anodes remains a challenge.
- We are working on strategies to improve cycle life without sacrificing cell-level energy density.
  - Utilizing blended anodes with lower Si content (see ES-260) can improve capacity retention in full cells.
  - Our initial work on pre-lithiation (see ES-260) shows promise in improving cycle life.

Proposed Future Work

- Finalize cathode composition for program demonstration cells.
- Continue to optimize cathode and anode electrode designs to meet power and energy targets.
- Screen and optimize electrolyte additives to improve cycle life of Si-based cells.
- Fabricate and test next generation Si-based 18650 cells.
- Deliver optimized cells for independent testing at ANL.

Responses to Previous Year Reviewers' Comments

Comment	Response
"..it was important for the authors to show data in larger cells, and that was clearly stated in the program and the results that were shown with the 18650 Li-ion cells.	♦ During last AMR meeting we were in the early stages of the program. Since then, we have implemented baseline CAM-7/Graphite chemistry in the 18650 format and have tested these cells extensively. Best performing Si-anode chemistry has also been implemented in the Gen 1 18650 cells with performance of those cells presented here.
"CAM-7/Graphite high energy 18650 cells showed stable cycleabilty up to 275 cycles, for commercial purpose 1000 cycle was necessary.	♦ Baseline CAM-7/Graphite cells have been cycled for almost 2000 cycles with 80% capacity retention in our labs and to 750 cycles with 93% capacity retention during ongoing performance validation at ANL.
"The importance of irreversible capacity was not discussed nor was the anode efficiency."	♦ Irreversible capacity is one of the initial screening metrics we employed for anode materials selection. Specifically, only anodes with >80% efficiency were considered for further experimental evaluation. In additional, we are exploring the use of anode pre-lithiation to boost full-cell first cycle efficiency and improve cell cycle life.
"Even though the cathode material had been available since at least 2010, few properties were disclosed in the presentation."	♦ Since AMR presentations contain only non-proprietary information, we chose not to disclose specific composition of CAM-7, which is not yet a commercial product. Instead, we have focused on reporting material performance in a wide variety of electrochemical tests.
"cathode results still showed severe impedance growth in most coating formulations at 45 degrees. The reviewer then remarked that indeed, it was not clear what the goal for the project was with regard to 45 degree cycling, so any result would be within the goals.	♦ While only 45°C storage is the DOE life target, many electric vehicle developers are also interested in high temperature cycle life. Tests we routinely carry out are very aggressive with high rate cycling at elevated temperature, with the goal of providing accelerated aging conditions.

Responses to Previous Year Reviewers' Comments

Comment	Response
"the capacity 1.9-2.7 Ah at C/20 for the 18650 form factor appeared to be surprisingly low compared to those of commercial products."	♦ 18650 cells are produced in-house using prototyping equipment and circa 2004 18650 cell hardware (e.g. 17.3mm vs. 18mm inner diameter cans currently used in mass production). With better cell hardware and manufacturing tolerances, we would expect ~5-10% higher energy density for the same electrode design (e.g. 253Wh/kg vs. 230Wh/kg obtained).
"it should be beneficial to collaborate with DOE lab, especially on accelerated testing protocols."	♦ Our focus has been on establishing electrochemical protocols that allow us to identify subtle differences in materials cycle life in a short time frame (<2weeks). In future projects, we welcome collaboration with DOE labs on accelerated testing and diagnosis protocols.
"the interaction with partners for continuous improvement was not clear." "…the authors were relying on experimental materials produced by other." "it was not very clear the collaboration the authors may have had with other institutions."	♦ We are working closely with several companies that are providing us with their state-of-the-art materials. During the program, we supply them with regular feedback on materials performance in our testing. This continuous feedback, has led to improved materials development for our vendors and led to subsequent rounds of improved material sampling. This of course is a unique approach, where we provide valuable data to our suppliers, making this a synergistic collaboration.
"third party verification of the main results, obtained by the authors, was highly recommended."	♦ Baseline CAM-7/Graphite 18650 cells were submitted for performance validation at ANL. Demonstration cells will be submitted at the end of the program.

Collaboration and Coordination

TIAX has a strong working relationship with our materials suppliers.

Active Material Suppliers

- Si based materials – domestic and international suppliers are providing us state-of-the-art Si and Si-based composites.
- Carbon anodes – domestic and international suppliers of graphite and hard carbon.

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.