



High Energy High Power Battery Exceeding PHEV-40 Requirements

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June 18th, 2014

2014 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: 25% (time)
- ◆ Percent complete: 18% (budget)

Budget

- ◆ Total project funding: \$2,184,733
 - ◆ DOE share: \$1,747,787
 - ◆ Contractor share: \$436,946
- ◆ Funding received in FY13: \$118,534
- ◆ Funding for FY14: \$1,107,410

Barriers

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

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™/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.
 - Optimize electrode designs in coin cells to demonstrate that electrodes composed of blended Si/carbon anode opposite CAM-7™ cathode can achieve all PHEV-40 scaled-power targets.
 - Select anode binder and formulate electrolyte additives that facilitate achievement of PHEV-40 cycle life target in cells implementing Si-based anode and CAM-7™ cathode.
- ◆ 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 will employ 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

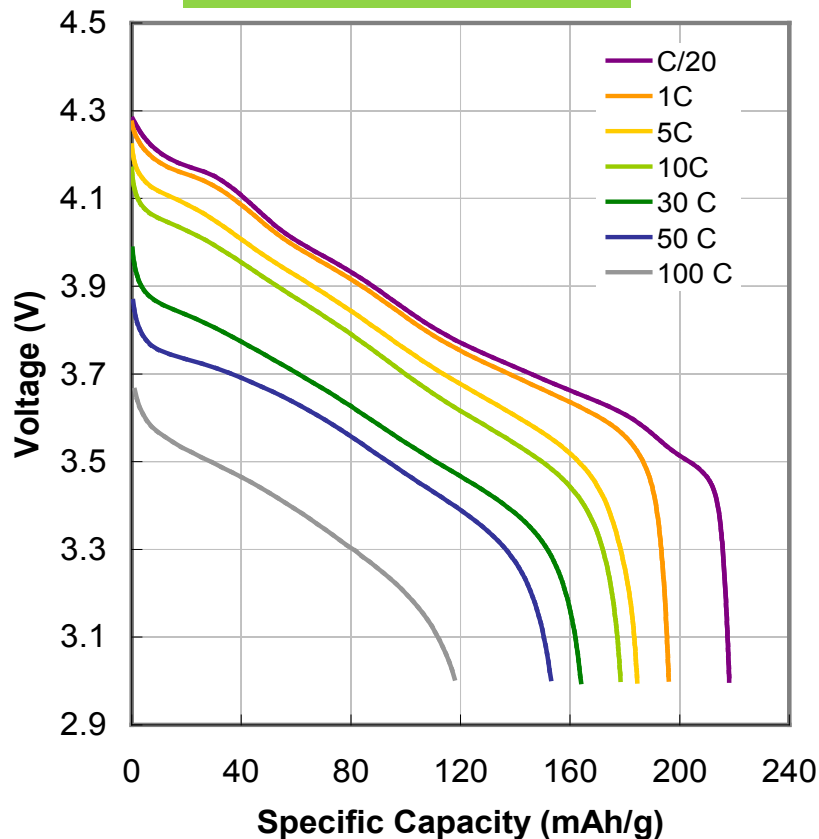
Cell Design

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

Technical Approach: CAM-7™ Cathode

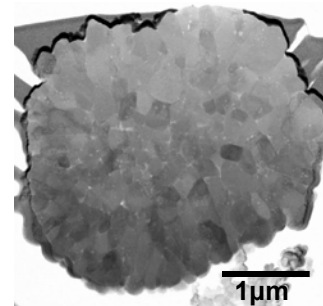
CAM-7 can deliver >200 mAh/g at rates below C/5 and 120 mAh/g at 100C discharge making it attractive for vehicle applications.

Discharge in Half Cells

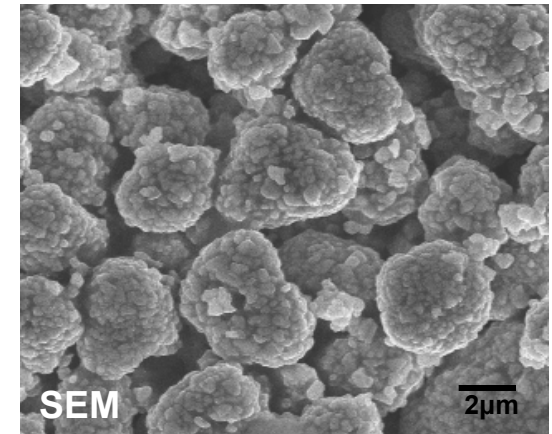


85:10:5, active:cc:PVdF, low-loading electrode,
Li metal anode, 1.0 M LiPF₆ in 1:1:1 EC:DMC:EMC + 1%VC electrolyte

- ◆ 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



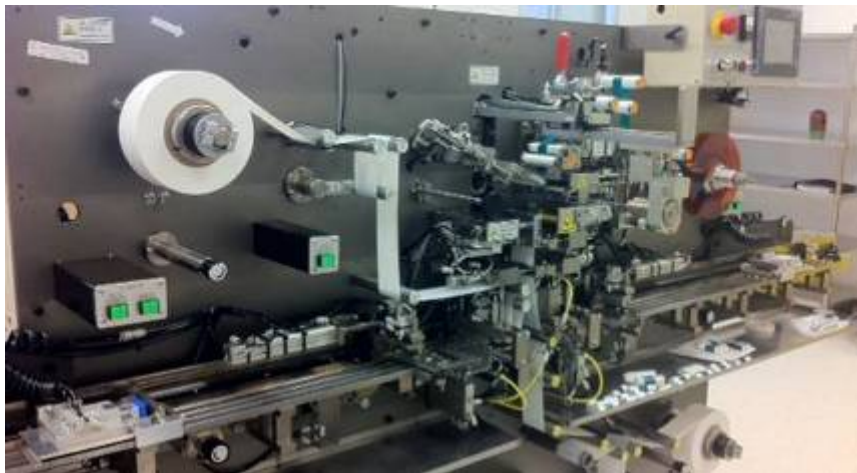
SEM

Technical Approach: CAM-7™ Cathode

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

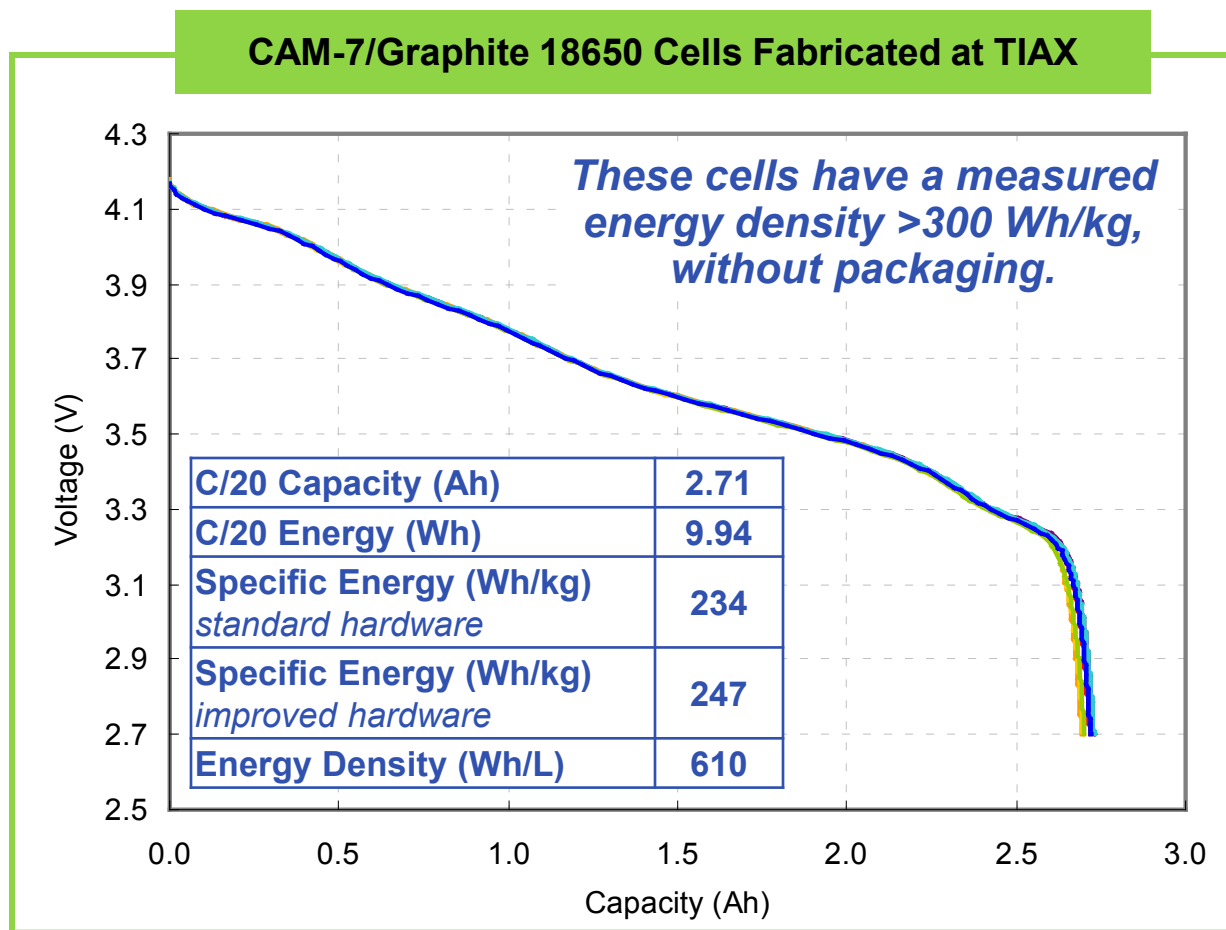


- ◆ Flexibility in cell formats:
 - Cylindrical
 - Wound prismatic
 - Stacked prismatic
- ◆ Cell capacities:
 - 1 – 4 Ah cylindrical
 - 2 - 10 Ah prismatic cells



Technical Approach: CAM-7™ Cathode

We have implemented CAM-7 in high energy 18650 cells with graphite anodes that can deliver 2.7Ah and 247Wh/kg.

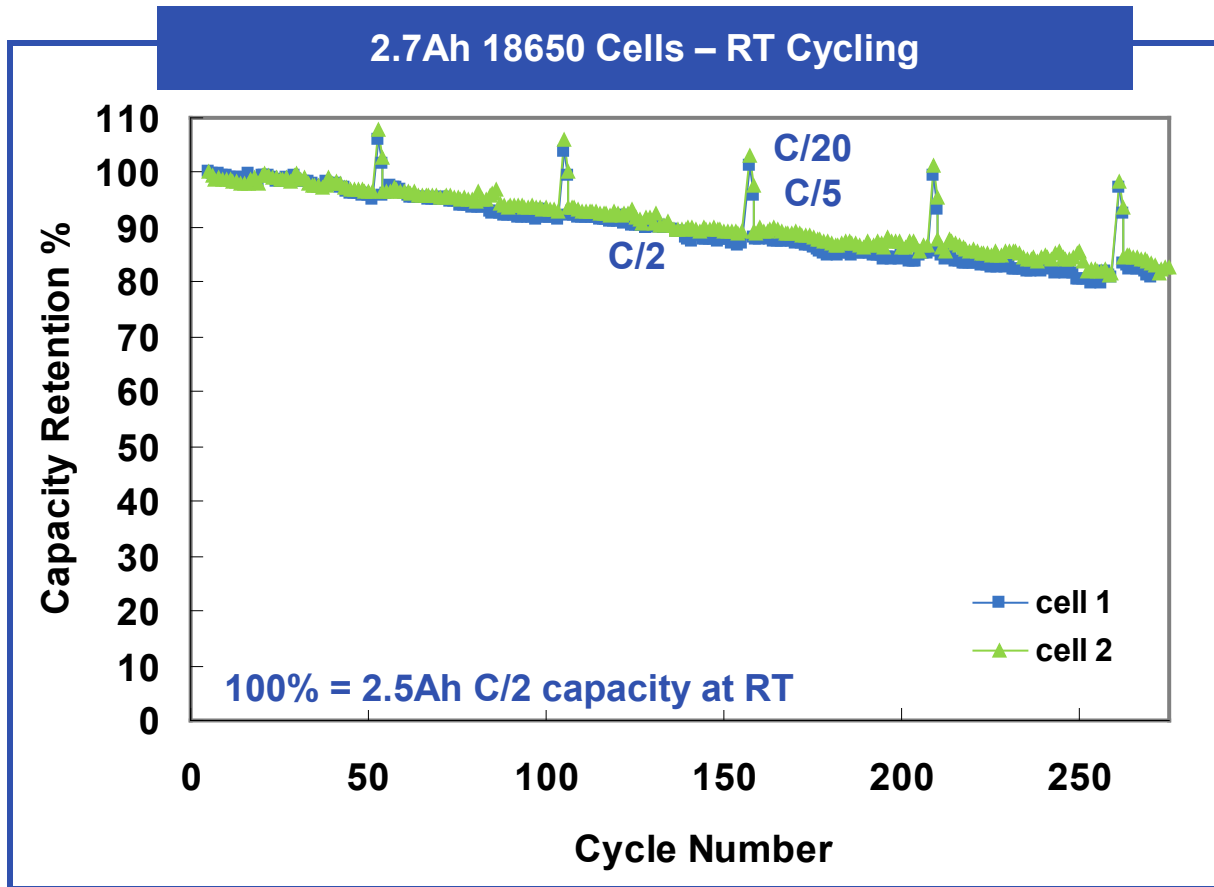


**Cell performance
was verified in
independent
testing at ARL**

Cathode – CAM-7:AB:PVDF (97:1:2), 25.6mg/cm², 3.64g/cc
Anode – Graphite:SBR+CMC (96:0:4), 16.3mg/cm², 1.74g/cc

Technical Approach: CAM-7™ Cathode

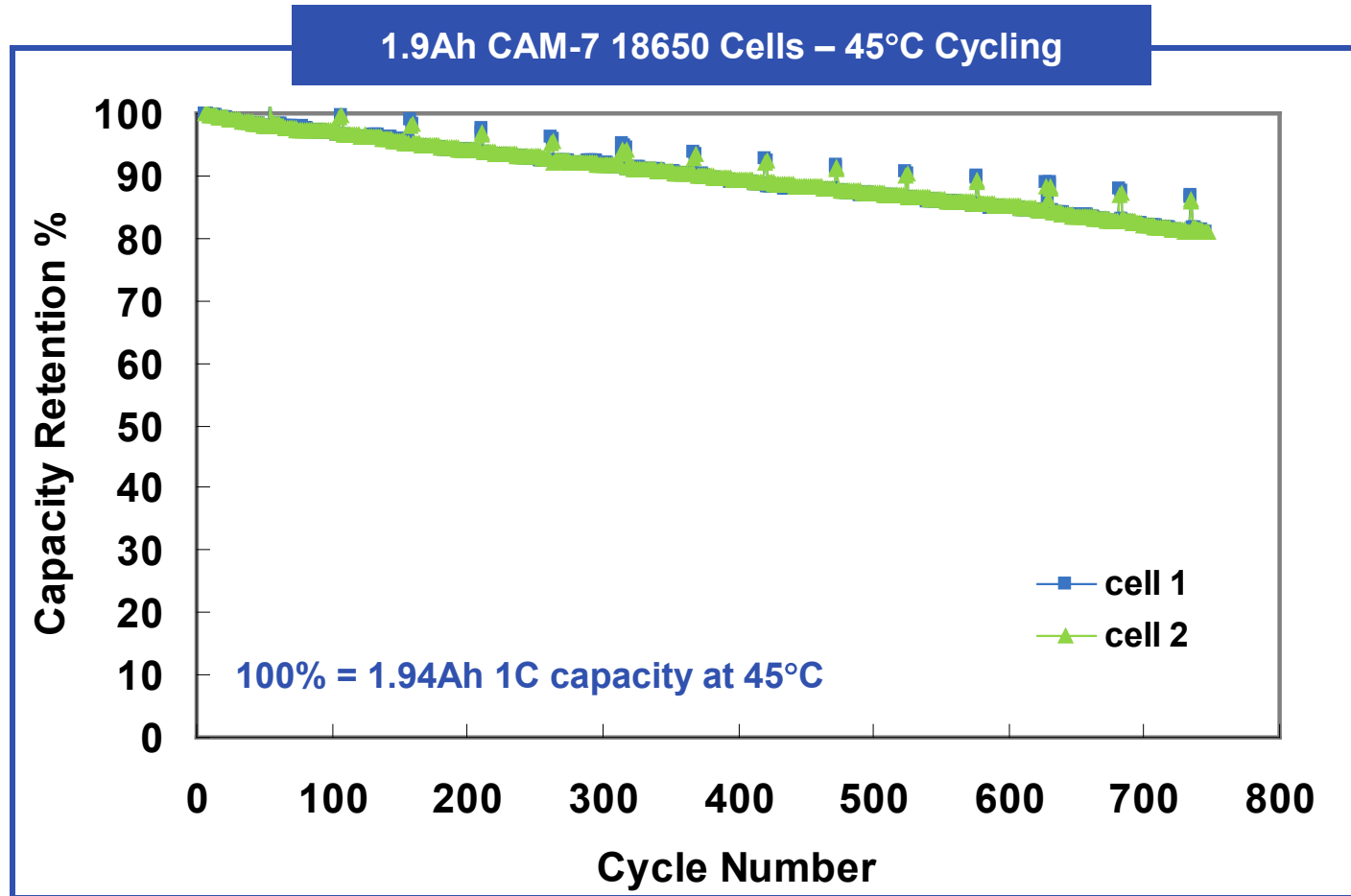
CAM-7/Graphite high energy 18650 cells show stable capacity cycling at room temperature.



C/5 charge – C/2 discharge, 4.2 to 2.7V; C/20 & C/5 discharge every 50 cycles.

Technical Approach: CAM-7™ Cathode

CAM-7 has been tested in higher power 18650 cells, demonstrating stable capacity cycling at room temperature and at 45°C over the full DOD range.

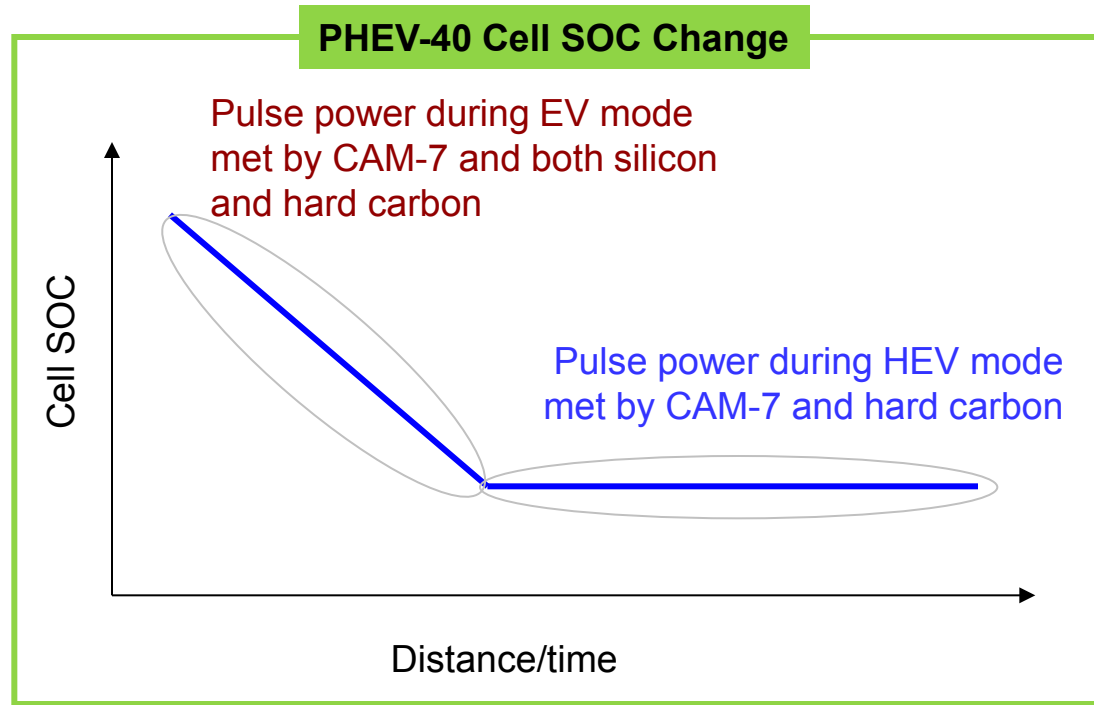


18650 cell with CAM-7/Graphite fabricated at TIAX.
C/2 charge – 1C discharge, 4.2 to 2.7V; C/20 & C/5 discharge every 50 cycles.

Technical Approach: Blended Si/Carbon Anode

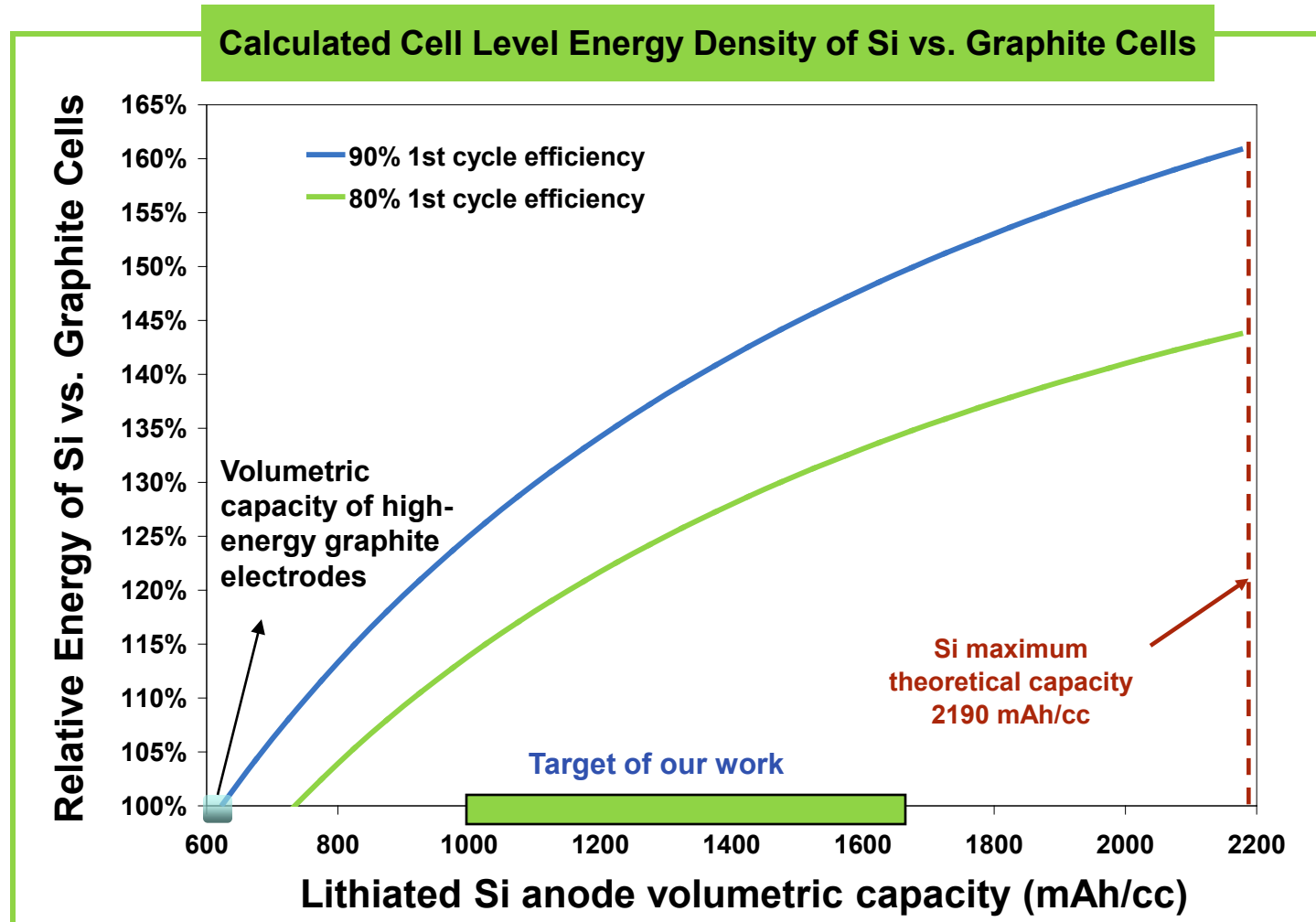
Using a blended Si/hard carbon anode will allow us to design cells capable of delivering high energy during EV operation and high power during HEV mode of the battery.

Silicon to provide high capacity while hard carbon will meet discharge and regen power targets



Technical Approach: Blended Si/Carbon Anode

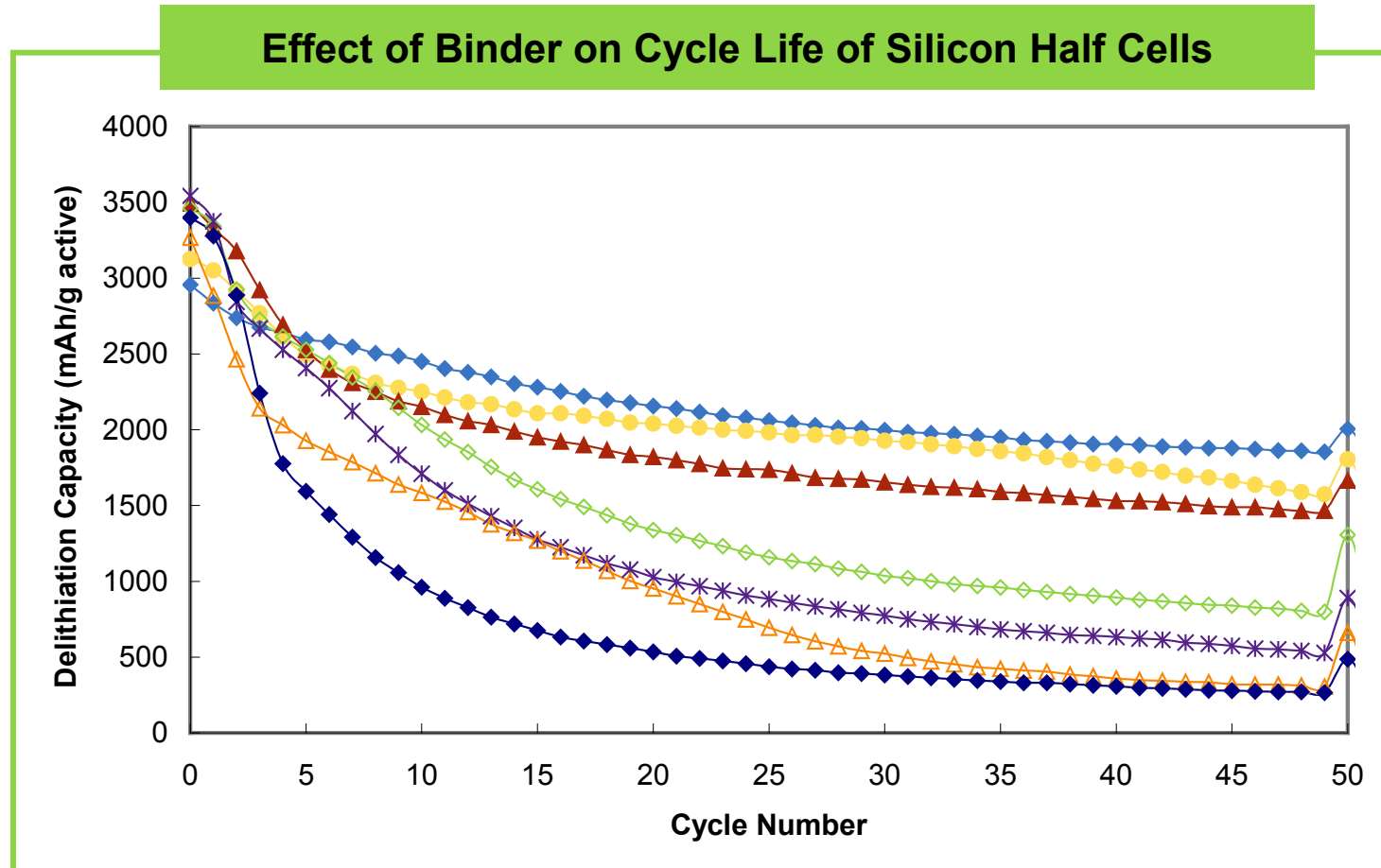
Using a blended Si/hard carbon anode with $>1000\text{mAh/cc}$ will allow us to meet pulse power targets, while exceeding energy density of graphite cells.



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

Technical Approach: Cell Design

Binder selection and electrolyte formulation can significantly impact silicon based anodes and we will optimize these components to achieve life targets.

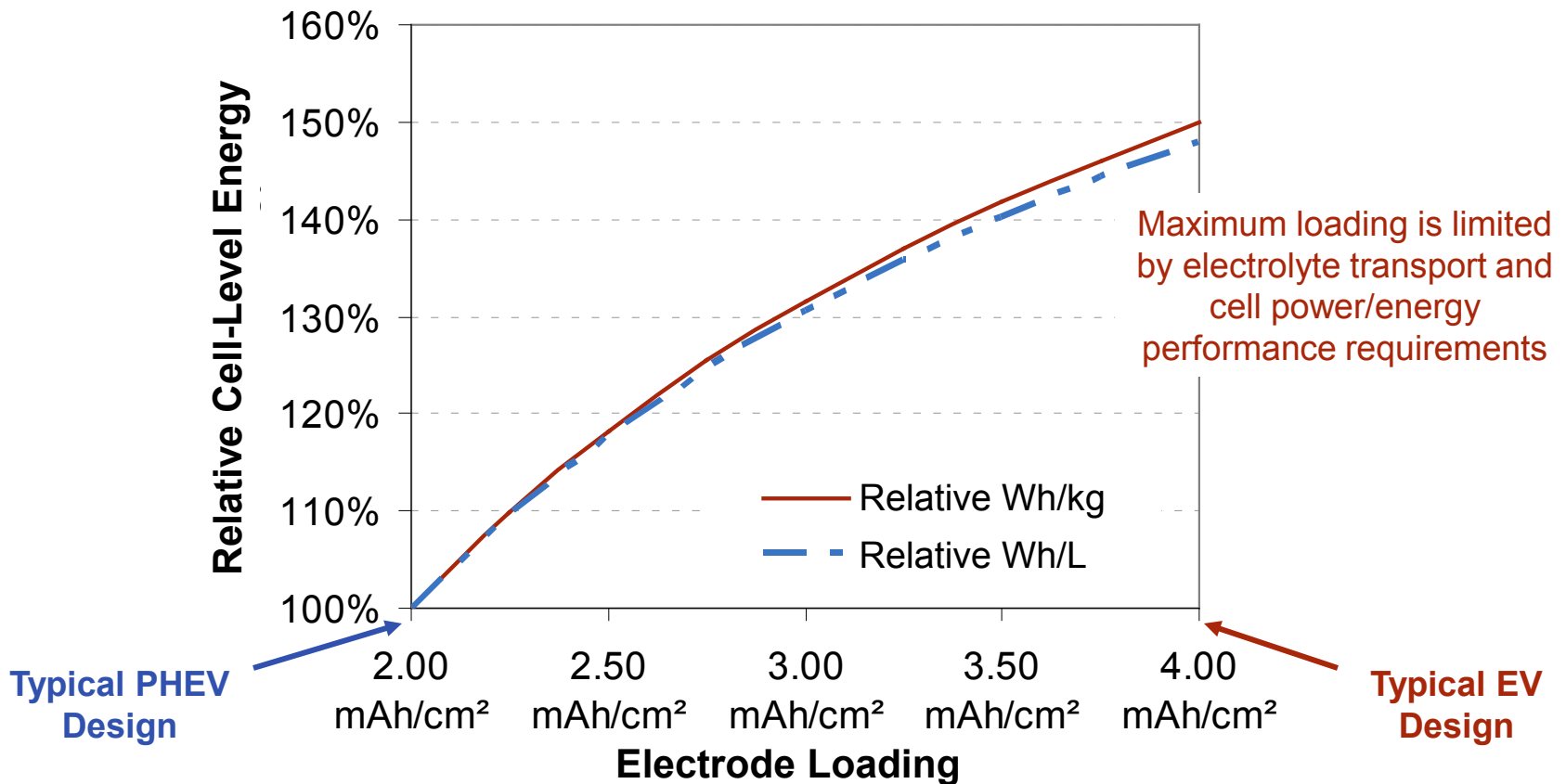


Nano-Silicon:Conductive Carbon:Binder. Lithiation to 5mV; delithiation to 1.5V;
Electrodes pressed to ~0.75g/cc; 1M LiPF₆ electrolyte in 1:1:1 EC:DMC:EMC + 1%VC + 5%FEC

Technical Approach: Cell Design

Optimizing cell designs with components that facilitate increased loading will allow us to further boost the cell level energy density.

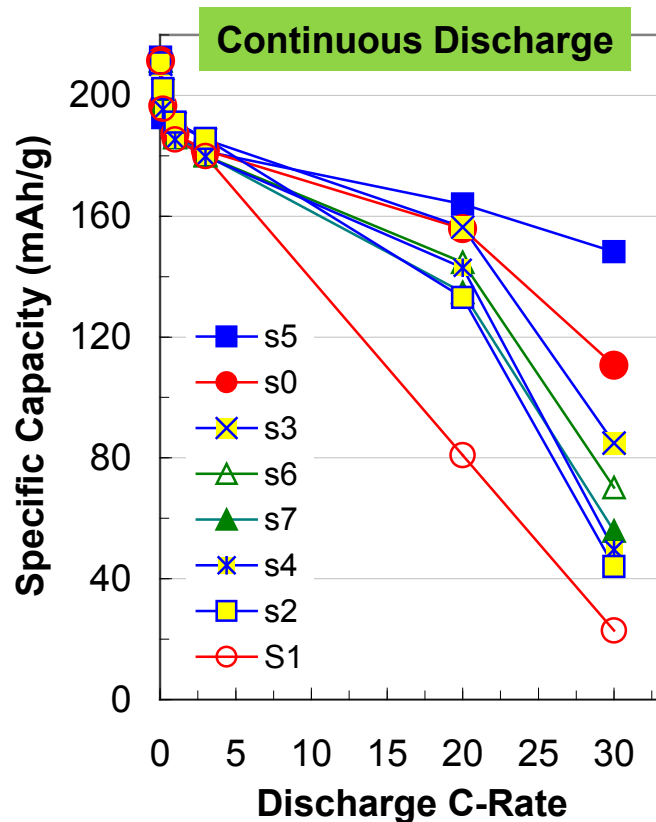
Estimated relative specific energy and energy density for CAM-7/Blended Si as a function of electrode loading level.



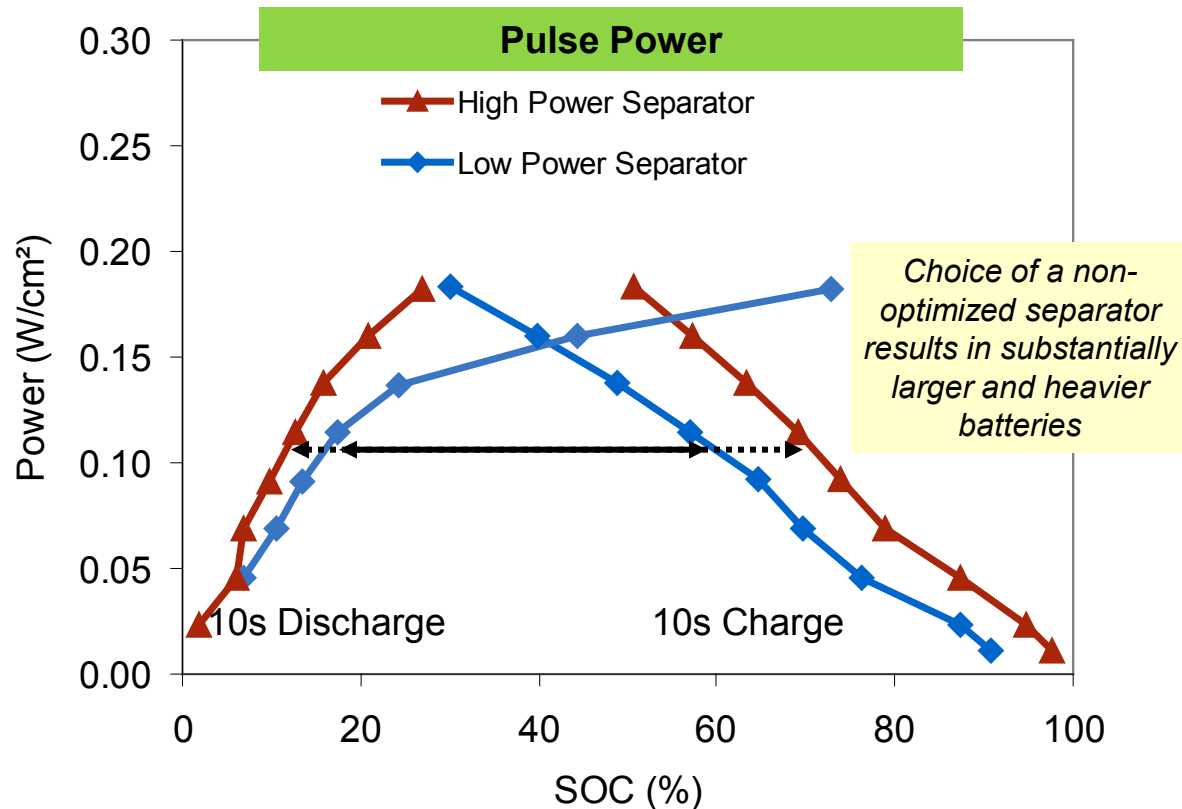
Technical Approach: Cell Design

Inactive component selection plays a crucial role in achieving power, usable energy, and life targets.

We have identified high power separators that support high power pulse capability over a broad SOC window.



CAM-7/Li half cells, continuous discharge from 4.3V. 1.5mAh/cm²



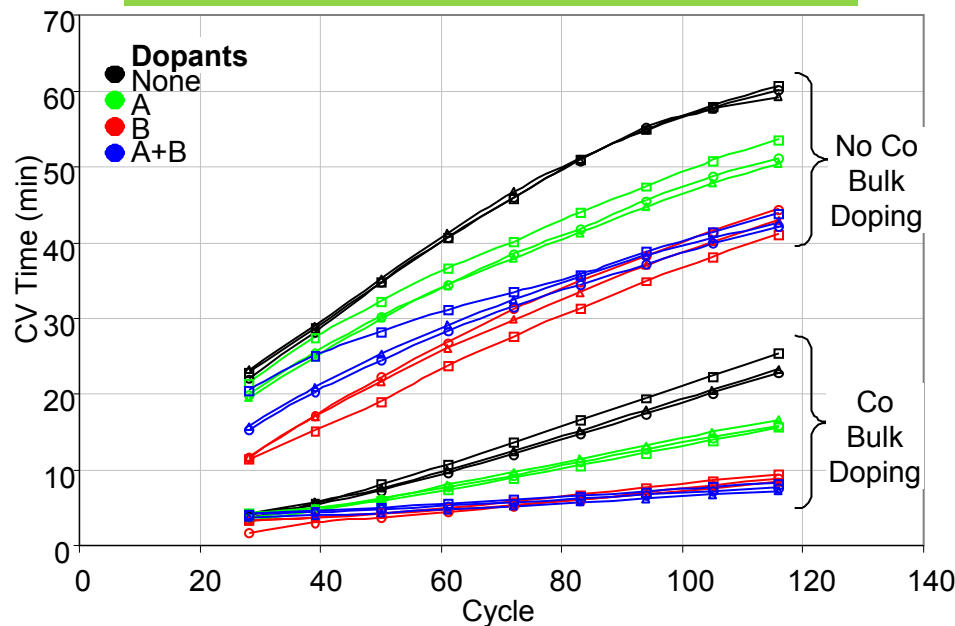
10s charge and discharge constant power pulse.
CAM-7/Graphite, 3.5mAh/cm².

Accomplishments and Progress: Cathode

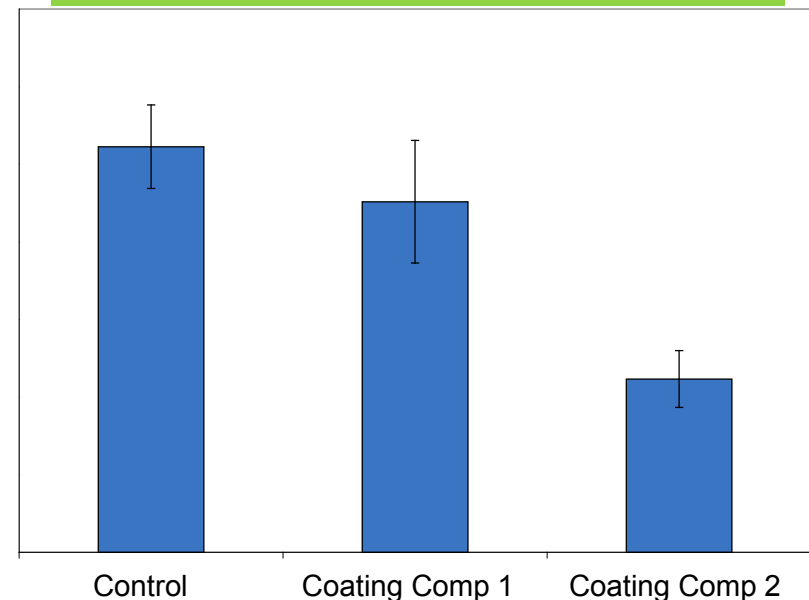
Cathode development work is focused on further improving high temperature cycle life of CAM-7.

- ◆ Improve high temperature capacity retention and reduce impedance growth.
- ◆ Explore cathode surface coating and test compositional changes to the bulk.
- ◆ Develop accelerated testing protocols to rapidly screen material modifications.

CV Charge Time at 45°C



Rate of Impedance Growth at 45°C



CAM-7/Graphite cells, ~2mAh/cm² loading. 1C/1C characterization cycles at 45C between 4.2V and 2.7V.

Accomplishments and Progress: Anode

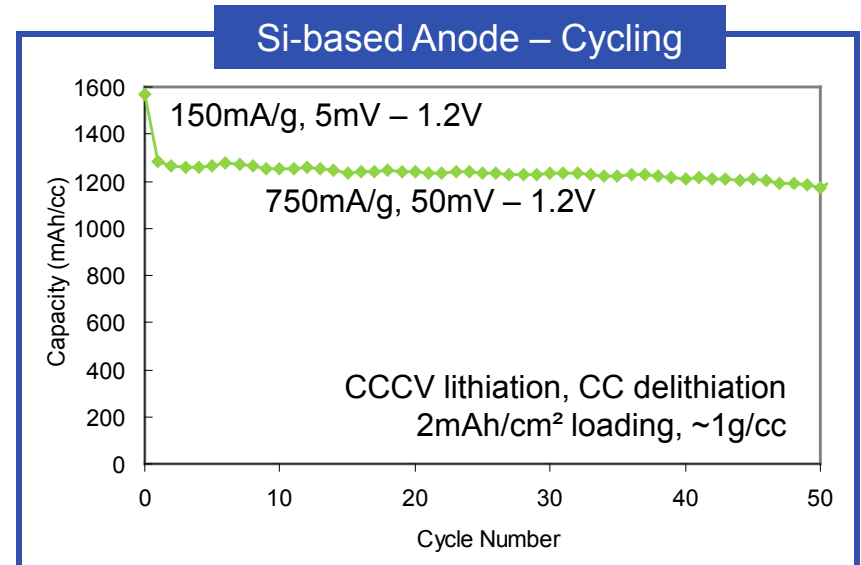
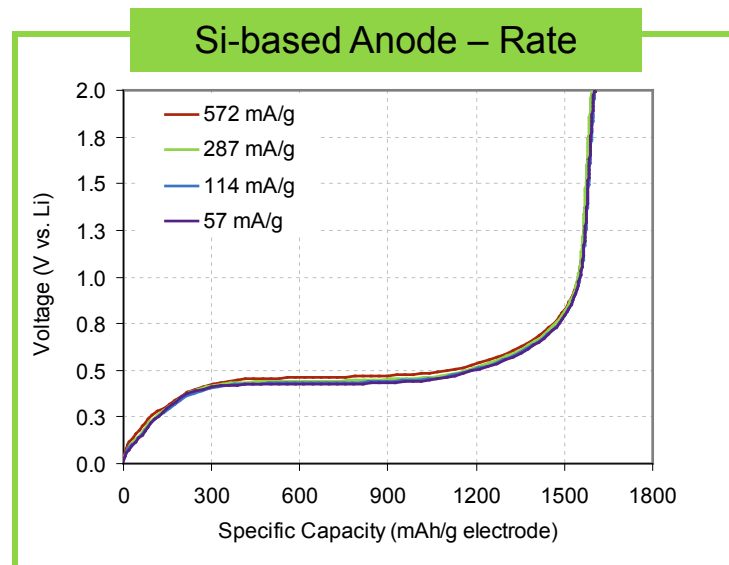
We have started testing commercial Si-based materials that show promising volumetric capacity and capacity retention.

Si anode materials

- ◆ Source several state-of-the-art silicon anode materials.
- ◆ Evaluate materials for capacity, cycle life, and coulombic efficiency in Li-metal coin cells.

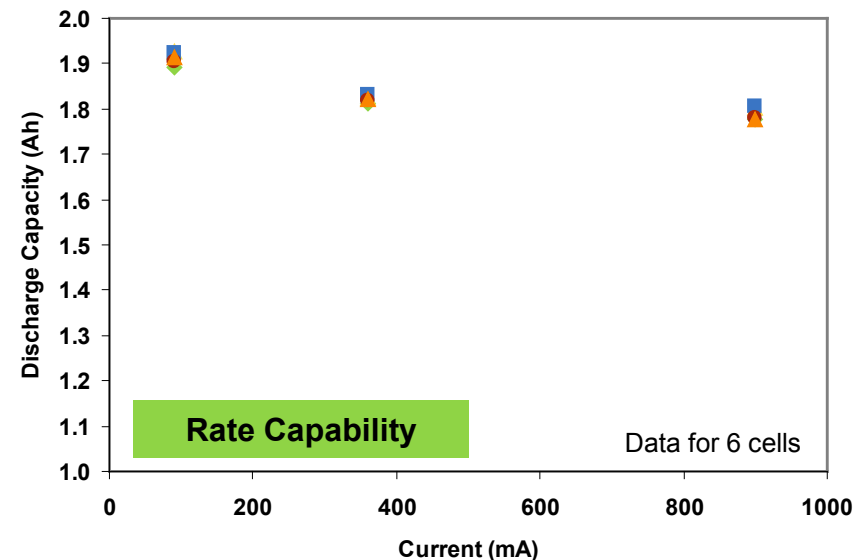
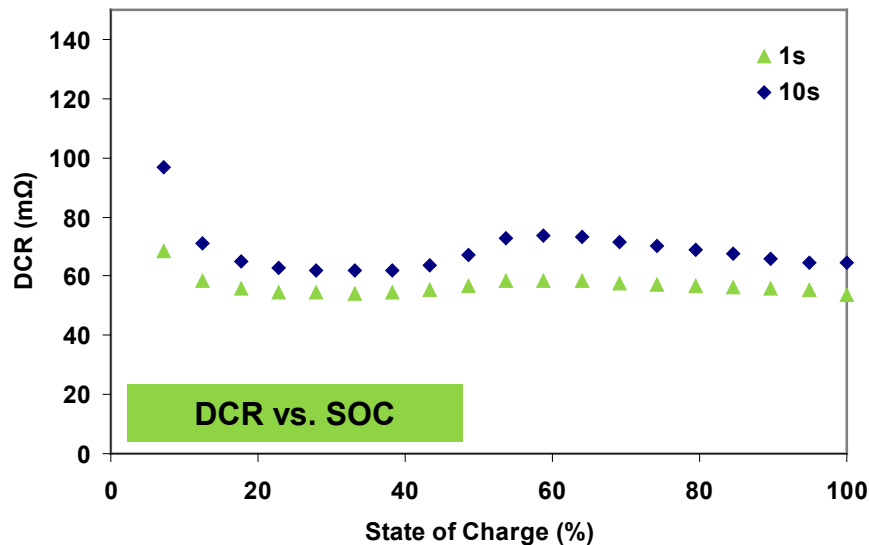
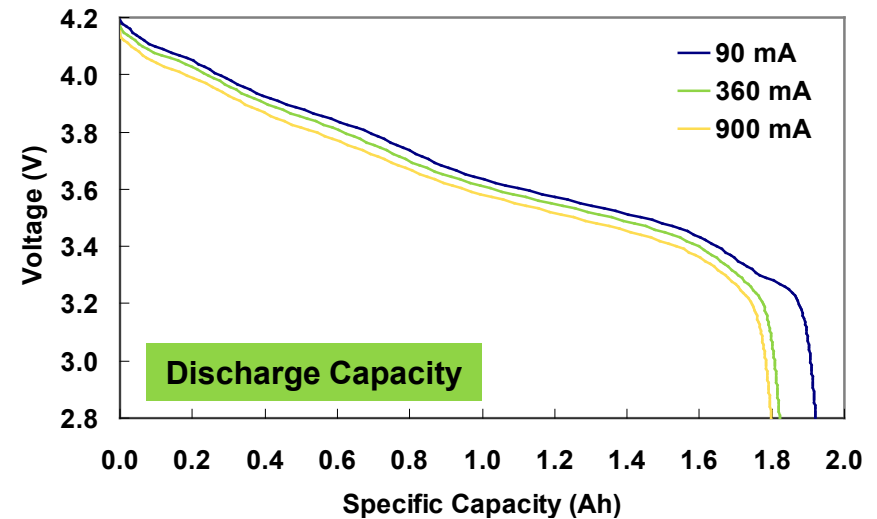
Inactive materials

- ◆ Identify binders and electrolyte additives that improve cycle life and coulombic efficiency of the Si anodes.



Baseline CAM-7/graphite cells for independent testing have been fabricated.

- ◆ CAM-7 cathode / graphite anode
- ◆ Carbonate electrolyte
- ◆ 18650 design – 1.9Ah
- ◆ Cell testing is ongoing



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.

Summary

Work in this project to date has focused on:

- ◆ Evaluation of approaches to further improve high temperature cycle life of CAM-7 cathode.
- ◆ Screening of Si-based active materials from several domestic and international suppliers.
- ◆ Identification of inactive components to improve cycle life of Si-based materials.
- ◆ Design, assembly, and testing of baseline 18650 CAM-7/Graphite Li-ion cells.

Future Work

- ◆ Continue cathode materials development to improve high temperature cycle life.
- ◆ Down-select cathode formulation for full cell optimization.
- ◆ Continue screening Si-based anode materials and evaluate blended anodes.
- ◆ Optimize cathode and anode electrode designs to meet power and energy targets.
- ◆ Screen and optimize electrolyte additives to increase cycle life.
- ◆ Fabricate and optimize demonstration cells.