Materials Development for High Energy High Power Battery Exceeding PHEV-40 Requirements.

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2015 DOE VTP Merit Review

Project ID# ES260

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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^{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

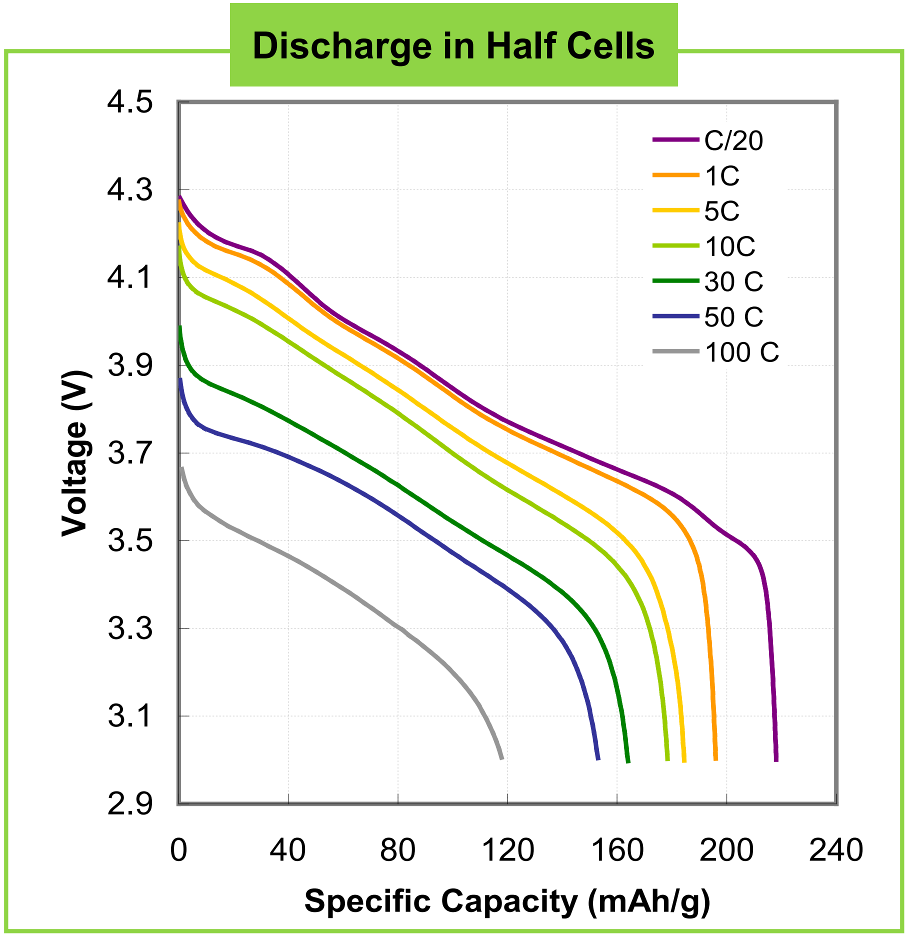
- Si-based materials – provide high energy, with state-of-the-art materials sourced from leading suppliers
- Hard carbon – excellent power-delivery but lower volumetric capacity
- Blend and electrode formulations optimized for energy, power, and life

Cell Design

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

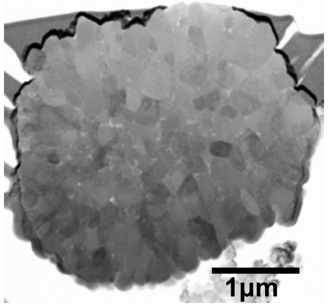
Technical Approach

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.

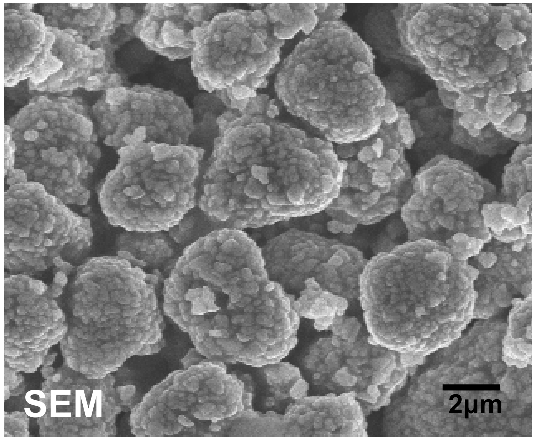


85:10:5, active:cc:PVdF, low-loading electrode,
Li metal anode, 1.0 M $LiPF_6$ in 1:1:1 EC:DMC:EMC + 1%VC electrolyte

- 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



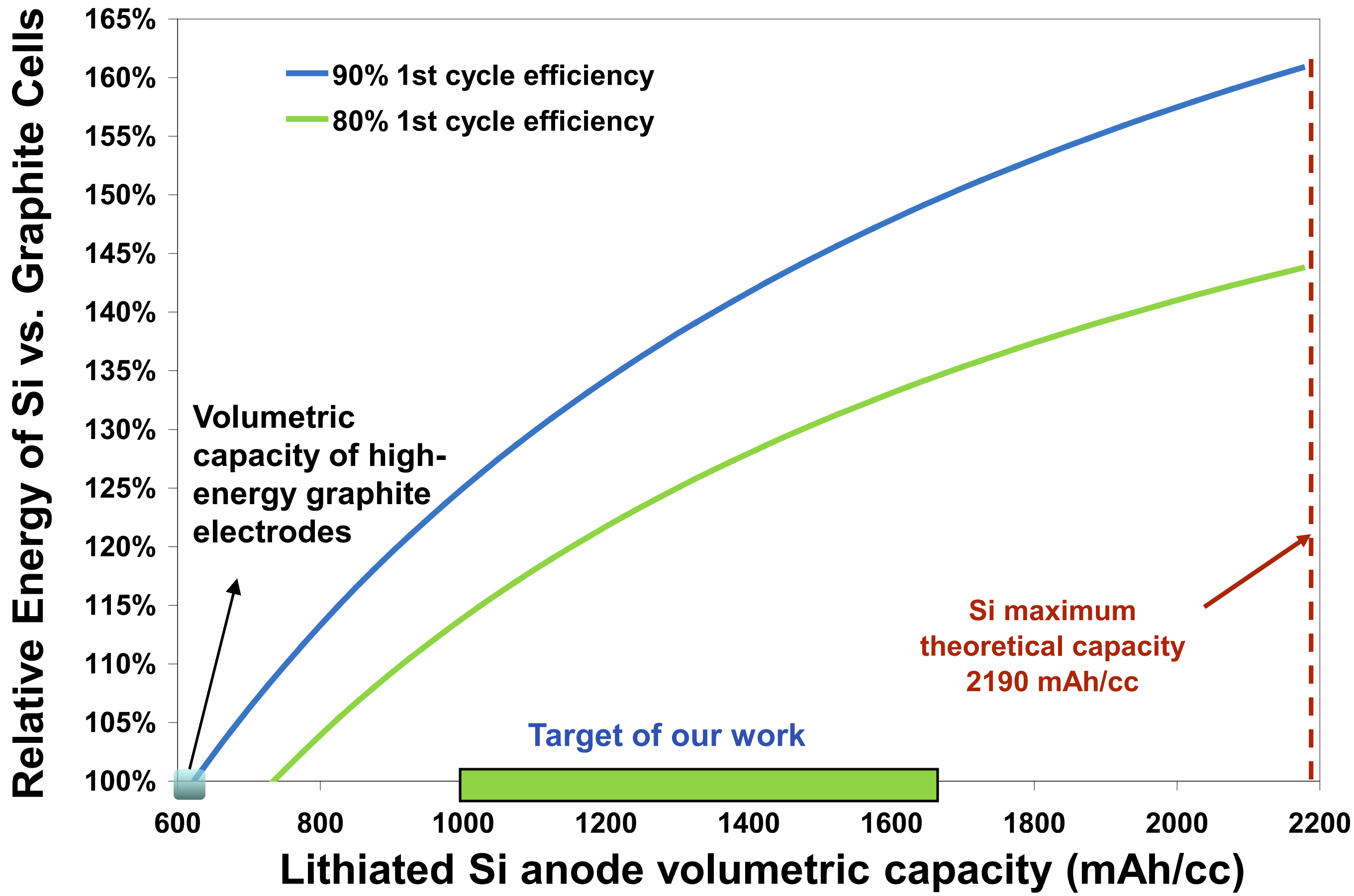
FIB/TEM



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.

Calculated Cell Level Energy Density of Si vs. Graphite Cells

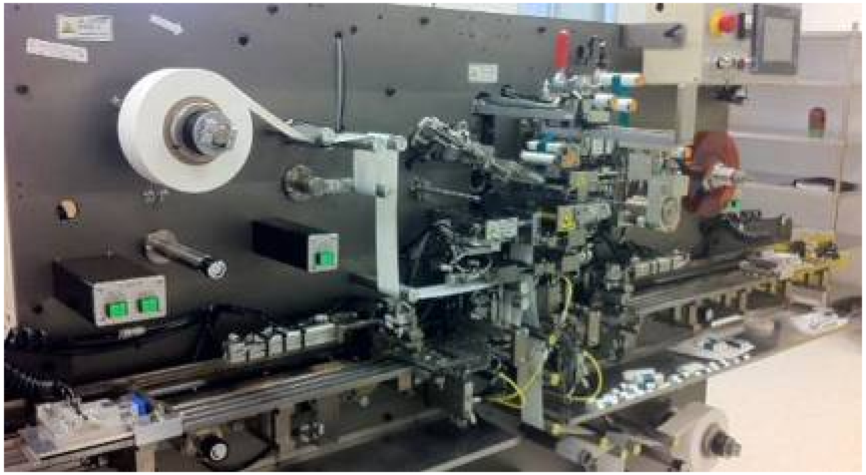


Fixed active material volume/electrode area design; CAM-7 cathode.

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

Cathode materials must satisfy a wide range of requirements to be successfully implemented in PHEV and EV Li-ion batteries.

Properties

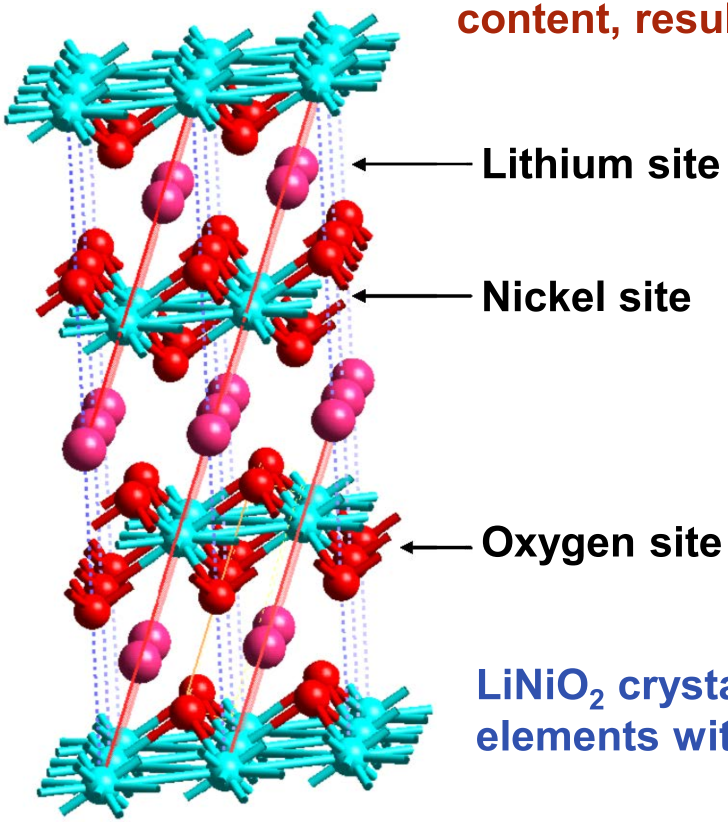
- Charge and discharge capacity
- Gravimetric and volumetric energy density
- Power capability
- Low temperature performance
- Cycle life (RT and HT)
- Calendar life

In this program, we are working on improving cathode material properties, with a focus on increasing cathode capacity, without significant loss in cycle life or impedance growth.

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 the minimum quantity of purpose-driven dopants exactly where they are needed, hence allowing the highest (stable) nickel content, resulting in highest capacity for an LNO class material.



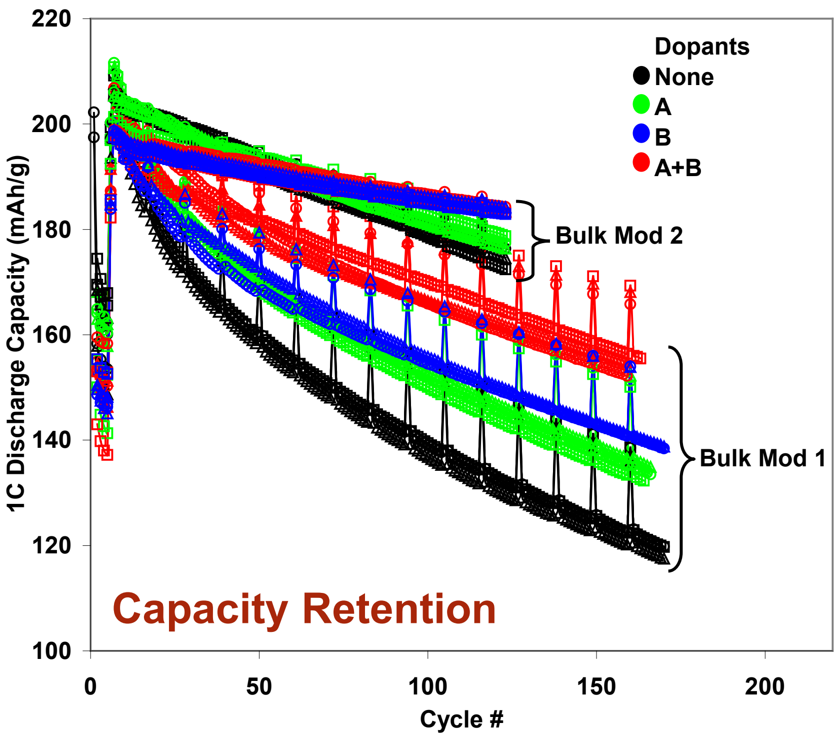
$LiNiO_2$ crystal structure doped with Mg, Co, and other elements with a gradient in Co from core to surface.

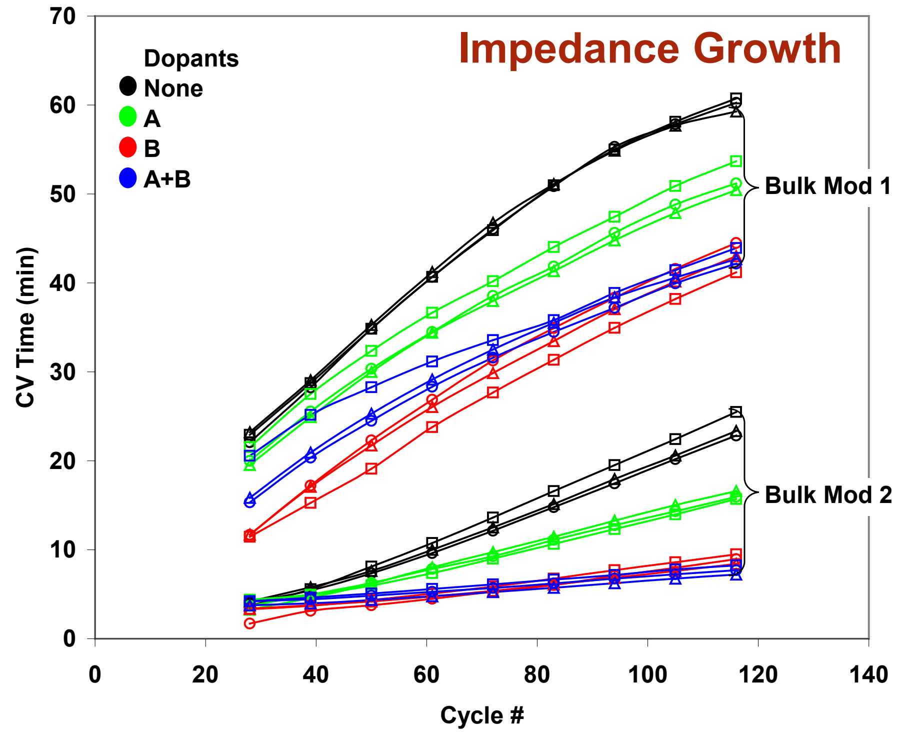
*Under development since 2002

Technical Accomplishments and Progress

We previously found that adjusting the cathode composition can result in better capacity retention and decreased impedance growth with cycling.

Effect of Composition – Baseline Synthesis





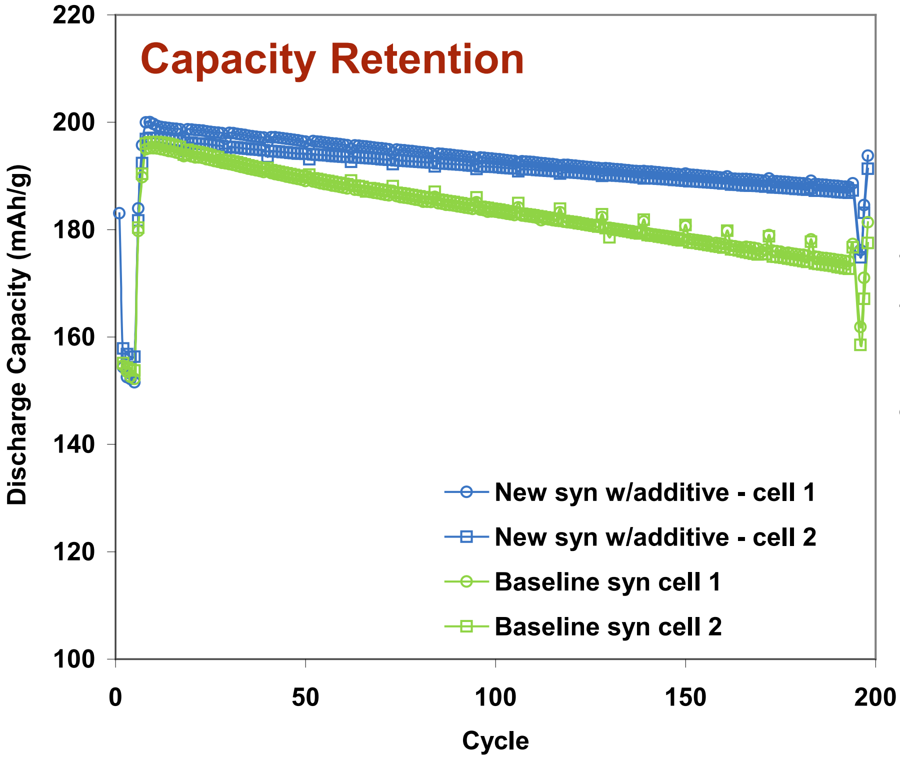
Accelerated cycle life testing – elevated temperature and high rate charge & discharge

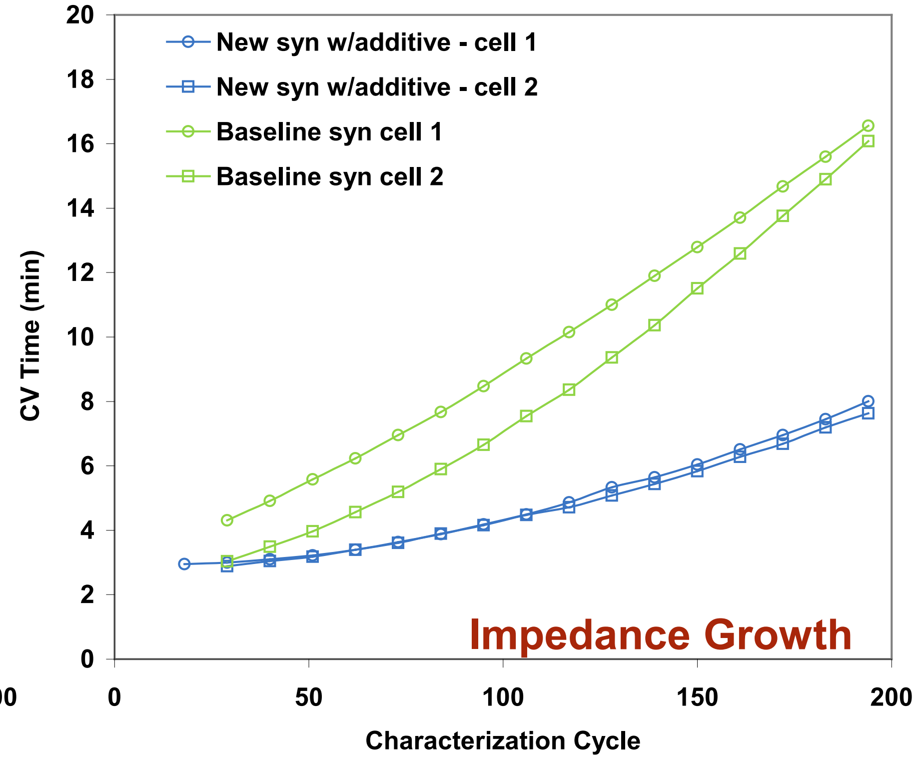
CAM-7/Graphite cells, ~2mAh/cm² loading. High rate cycling with 1C/1C characterization cycles at 45C between 4.2V and 2.7V.

Technical Accomplishments and Progress

We have found synthetic additives that improve capacity retention and reduce impedance growth, without significant change in cathode capacity.

Effect of Synthesis – Baseline Composition





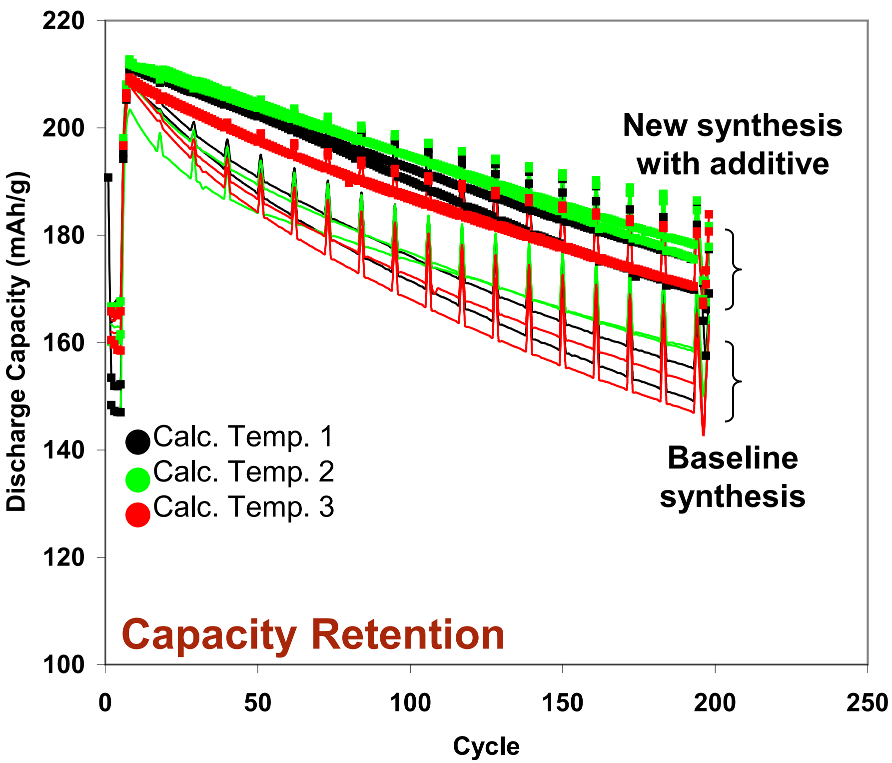
Accelerated cycle life testing – elevated temperature and high rate charge & discharge

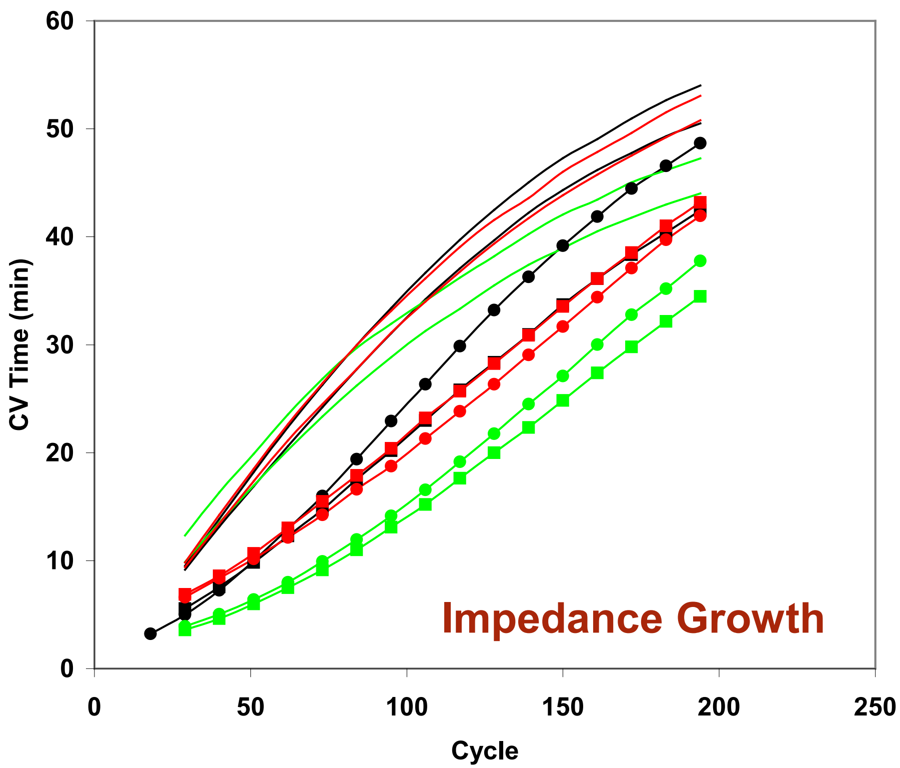
CAM-7/Graphite cells, ~2mAh/cm² loading. High rate cycling with 1C/1C characterization cycles at 45C between 4.2V and 2.7V.

Technical Accomplishments and Progress

We have optimized synthetic parameters to achieve the best cycle life for a given cathode dopant composition.

Effect of Synthesis – Modified Composition





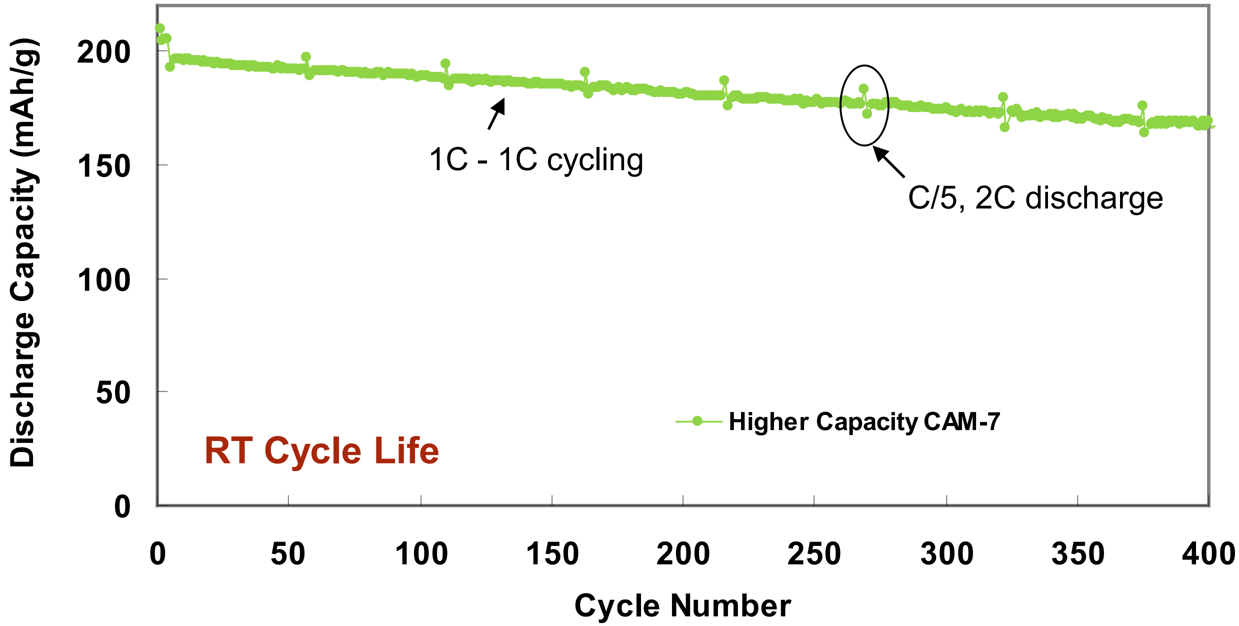
Accelerated cycle life testing – elevated temperature and high rate charge & discharge

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

Technical Accomplishments and Progress

Combining the doping strategy with synthetic modifications, we have developed a higher capacity CAM-7 cathode material that exhibits good cycle life even in un-optimized cells.

Half Cells vs. Li metal	Discharge Capacity (mAh/g)			
	C/20	C/10	C/5	1C
Baseline CAM-7	212	205	199	185
Higher Capacity CAM-7	224	218	212	201



85% retention after 400 cycles

Electrode: 94-3-3 formulation, ~10.7mg/cm^2 Active loading, ~2.9g/cm^3
CR2025 Full cells vs MCMB 25-28 anode, 1M $LiPF_6$ in EC:DMC:EMC (1:1:1) + 1%VC
1C-1C cycling 2.7-4.2V, CCCV charge with C/50 charge termination. Average of 2-3 cells per set.

Technical Approach: Blended Si/Carbon Anode

There are many approaches towards development of high capacity, long cycle life Si-based anodes.

- Nano-sizing to minimize localization of stresses associated with volume changes and suppress crystallization of $Li_{15}Si_4$.
- High porosity, high-conductive-carbon-content electrodes to absorb Si particle volume changes.
- Composites and multiphase compositions that dilute Si and can buffer volume changes.
- Composites with mixed conductive coating materials (e.g., carbons) that isolate Li-Si alloy particles from direct contact with organic electrolytes, to prevent excessive formation of SEI.
- Selection of inactive components: binders to accommodate the volume expansion of silicon and electrolyte additives for enhanced passivation of the silicon surface.

We have obtained several Si-based materials from commercial developers that utilize nano-sizing, composite formation, and/or carbon coating.

Technical Accomplishments and Progress

We have evaluated many Si-based anode materials that show promising performance.

- Sourced several state-of-the-art silicon 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.

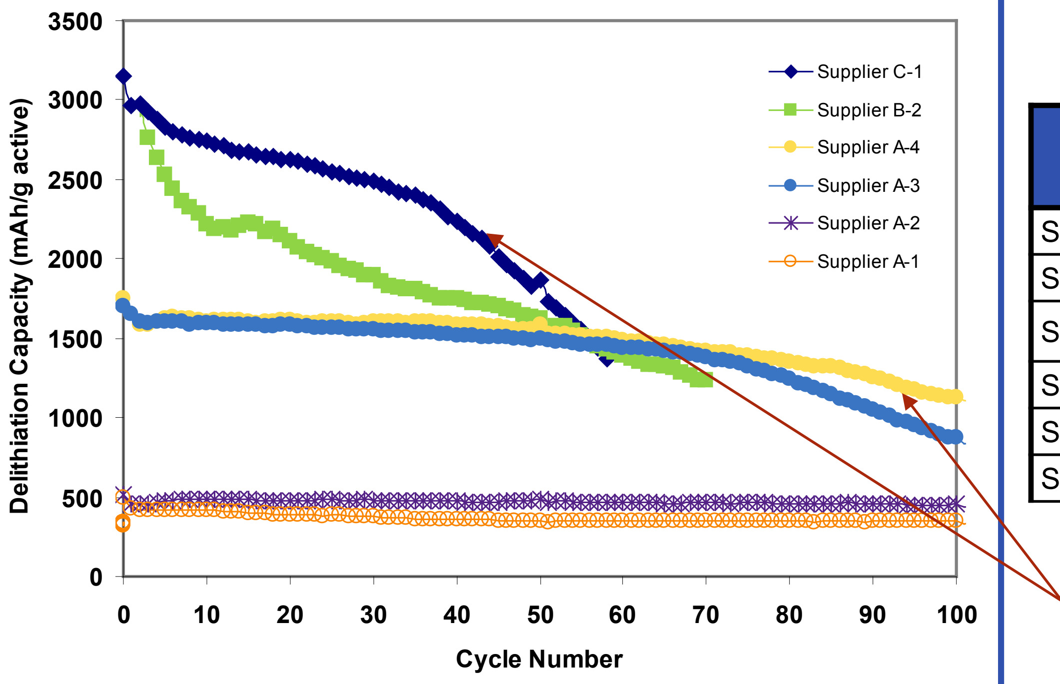
Representative Materials*	Description	Capacity (mAh/g)	1st Cycle Efficiency	Cycle Life	Columbic Efficiency
Supplier A-1	Si/Carbon composite	500	81%	Good	OK
Supplier A-2	Si/Carbon composite	515	81%	Good	OK
Supplier A-3	Si/Carbon composite	1700	86%	OK	OK
Supplier A-4	Si/Carbon composite	1750	85%	OK	OK
Supplier B-1	Micron-scale Si	3800	90%	Fast initial fade, then OK	Good
Supplier B-2	Micron-scale Si	3400	89%	Fast initial fade, then OK	Good
Supplier C-1	Nano-Si	3150	88%	Good	Poor

*all materials obtained under NDA

Capacities measured in coin cells vs. Li metal counter electrode. 1M $LiPF_6$ in EC:DMC:EMC 1:1:1 + 1%VC + 10%FEC electrolyte (EDEV1FEC10). C/10 CC to 5mV, CV at 5mV to C/50; C/10 delithiation to 1.2V;

Technical Accomplishments and Progress

We have evaluated many Si-based anode materials that show promising performance.



	Active	mg/cm²	g/cc	Description
Supplier A-1	75%	1.1	1.1	Si/Carbon composite
Supplier A-2	75%	1.1	1.0	Si/Carbon composite
Supplier A-3	75%	0.9	1.0	Si/Carbon composite
Supplier A-4	75%	1.0	1.0	Si/Carbon composite
Supplier B-1	75%	1.8	0.7	Micron-scale Si
Supplier C-1	60%	0.9	1.1	Nano-Si

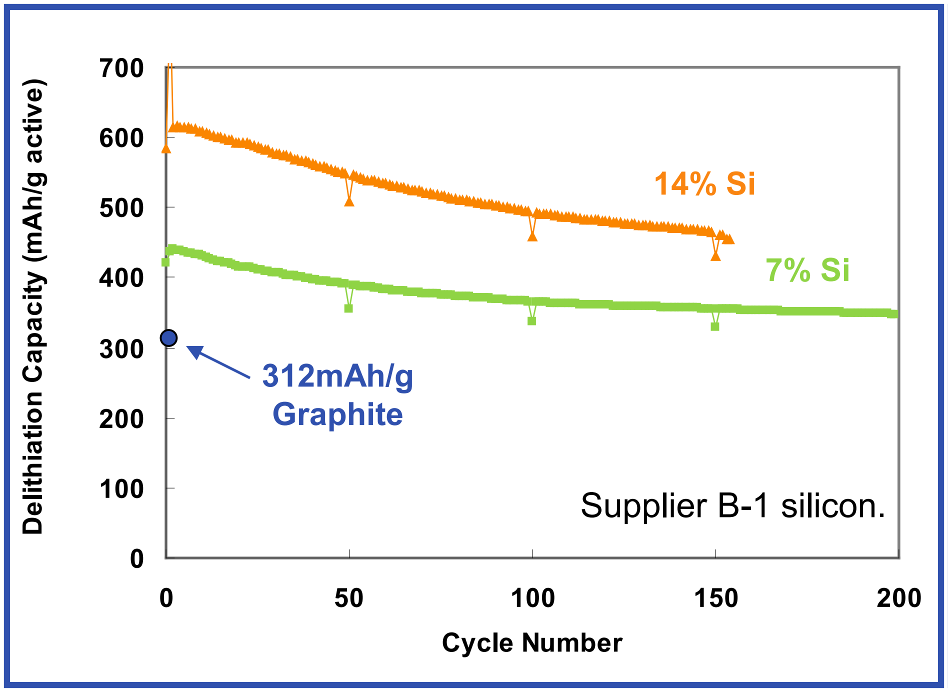
Lower capacity materials exhibit longer cycle life without loss of Si contact.

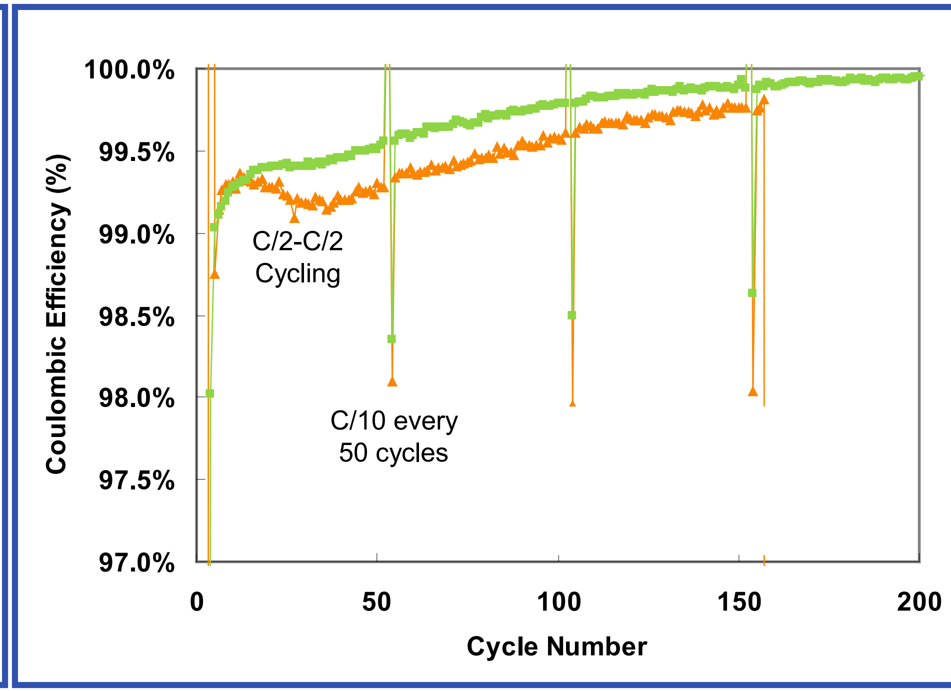
*all materials obtained under NDA
Capacities measured in coin cells vs. Li metal counter electrode. 1M $LiPF_6$ in EC:DMC:EMC 1:1:1 + 1%VC + 10%FEC electrolyte. All electrodes with 75% active, except C-1. PAA binder used for most electrodes, except B-1 material.

Technical Accomplishments and Progress

Combining micron-scale Si with graphite in small quantities, can boost electrode capacity.

Delithiation Capacity (mAh/g)	Coulombic Efficiency (%)



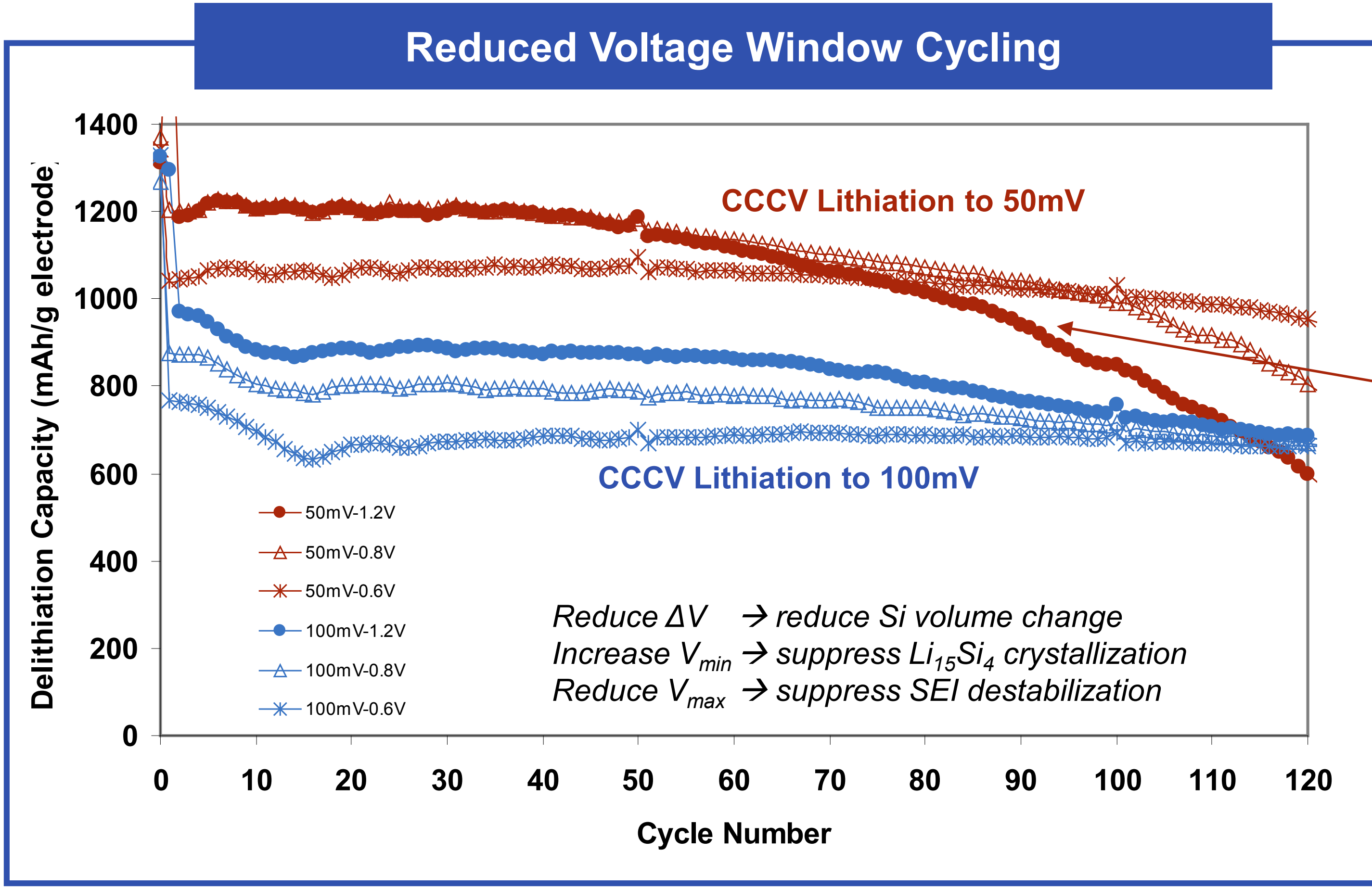


Capacity retention and Coulombic efficiency decrease at higher Si levels.

Cycle life in coin cells vs. Li metal counter electrode. 1M $LiPF_6$ in EC:DMC:EMC 1:1:1 + 1%VC + 10%FEC electrolyte.
Formation: C/10 CCCV 5mV to C/50, C/10 to 1.2V; Cycling C/2 CCCV, C/2; 1C = 600mAh/g nominal.

Technical Accomplishments and Progress

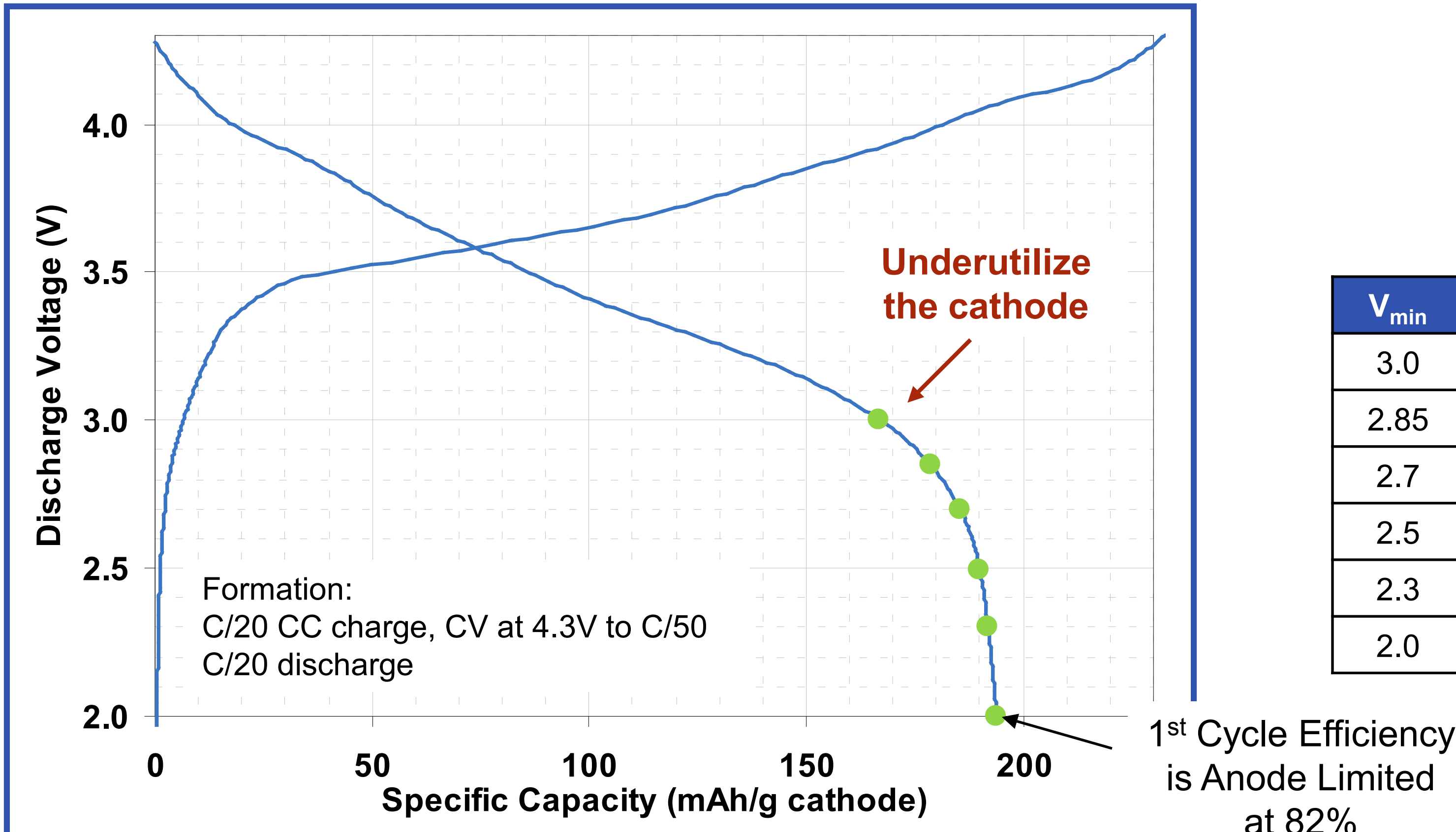
High Si content anodes can also achieve better capacity retention by reducing the cycling voltage window, but at the expense of capacity.



Supplier A-4 silicon-containing anode. 1g/cc density, 1.3-1.5mg/cm² total loading or ~2mAh/cm² capacity loading.
Cycle life in coin cells vs. Li metal counter electrode. 1M $LiPF_6$ in EC:DMC:EMC 1:1:1 + 1%VC + 10%FEC electrolyte.
Formation: C/10 CCCV 5mV to C/50, C/10 to 1.2V; Cycling C/2 CCCV, C/2; 1C = 1500mAh/g nominal.

Technical Accomplishments and Progress

The lower voltage cutoff can also be increased in full cells to improve cycle life, however it leads to reduction in cathode utilization.



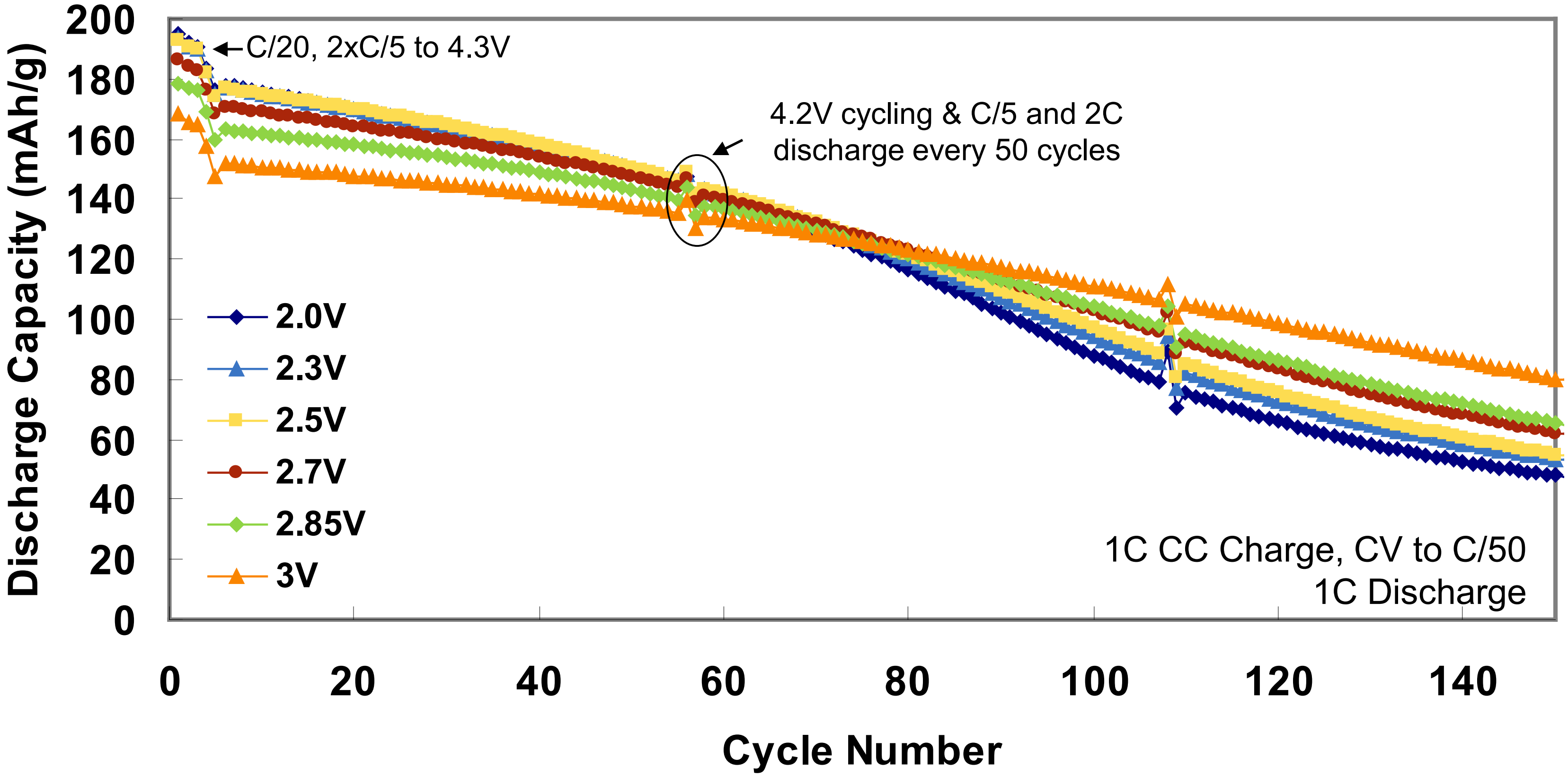
V_{min}	% Cathode Cap
3.0	86%
2.85	92%
2.7	96%
2.5	98%
2.3	99%
2.0	100%

CAM-7/Supplier A-4 Si anode, cathode at ~11mg/cm² loading, anode pressed to 1g/cc.
Full coin cells with 1M $LiPF_6$ in 1:1:1 EC:DMC:EMC + 1%VC + 10%FEC electrolyte.

Technical Accomplishments and Progress

Increasing the lower voltage cutoff improves full-cell cycle life, but reduces cathode utilization.

Reduced Voltage Window Cycling – Full Cell Discharge Capacity (mAh/g cathode)

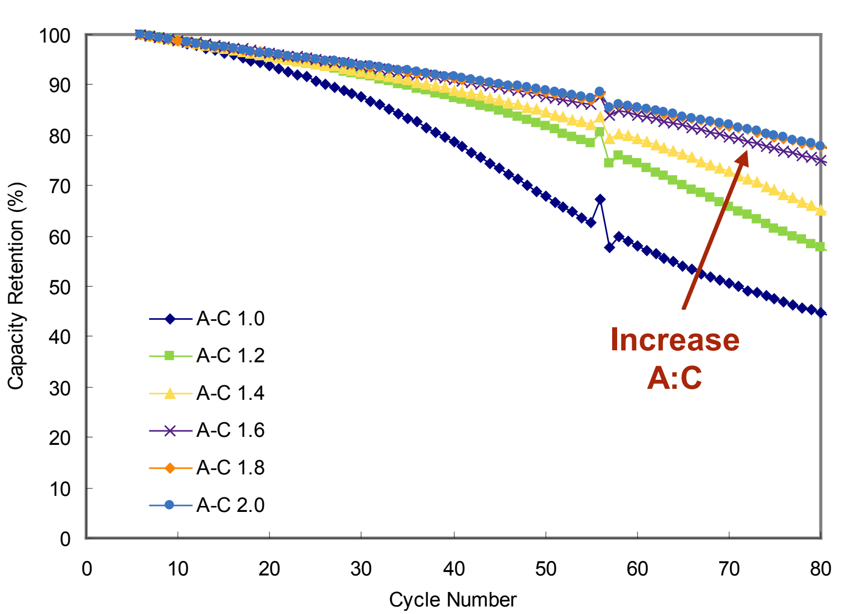


CAM-7/Supplier A-4 Si anode, cathode at ~11mg/cm² loading, anode pressed to 1g/cc. Anode:Cathode ~ 1.2.
Full coin cells with 1M $LiPF_6$ in 1:1:1 EC:DMC:EMC + 1%VC + 10%FEC electrolyte. Nominal 1C = 200mAh/g cathode.

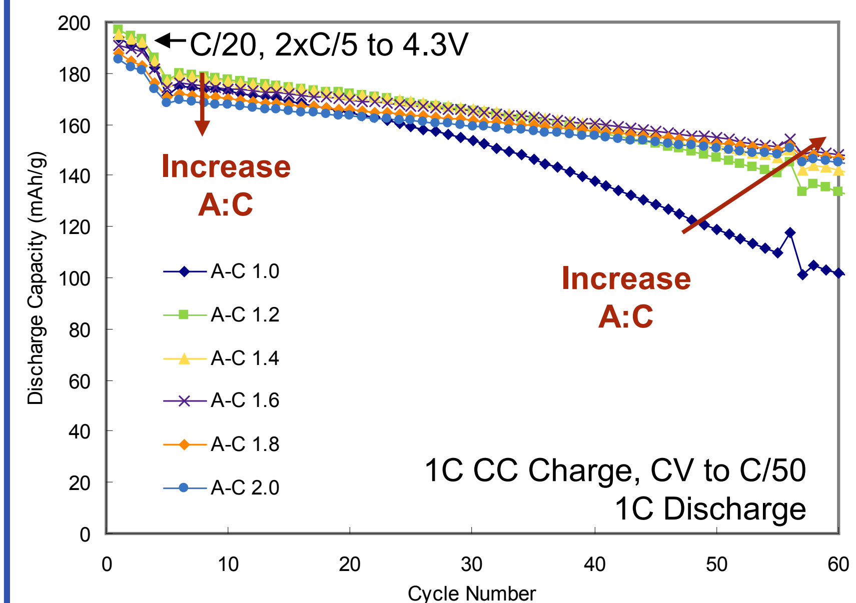
Technical Accomplishments and Progress

Full cell cycle life can also be improved by increasing the A:C ratio (i.e. , by reducing Si anode volume changes), but again at the expense of gravimetric capacity.

Capacity Retention (%)



Discharge Capacity (mAh/g cathode)



CAM-7/Supplier A-4 Si anode, cathode at ~11mg/cm² loading, anode pressed to 1g/cc. Anode:Cathode ~ 1.2.
Full coin cells with 1M $LiPF_6$ in 1:1:1 EC:DMC:EMC + 1%VC + 10%FEC electrolyte. Nominal 1C = 200mAh/g cathode.

Technical Accomplishments and Progress

We are evaluating anode pre-lithiation methods that would allow us to use Si-based anodes in full cells with high A:C ratios.

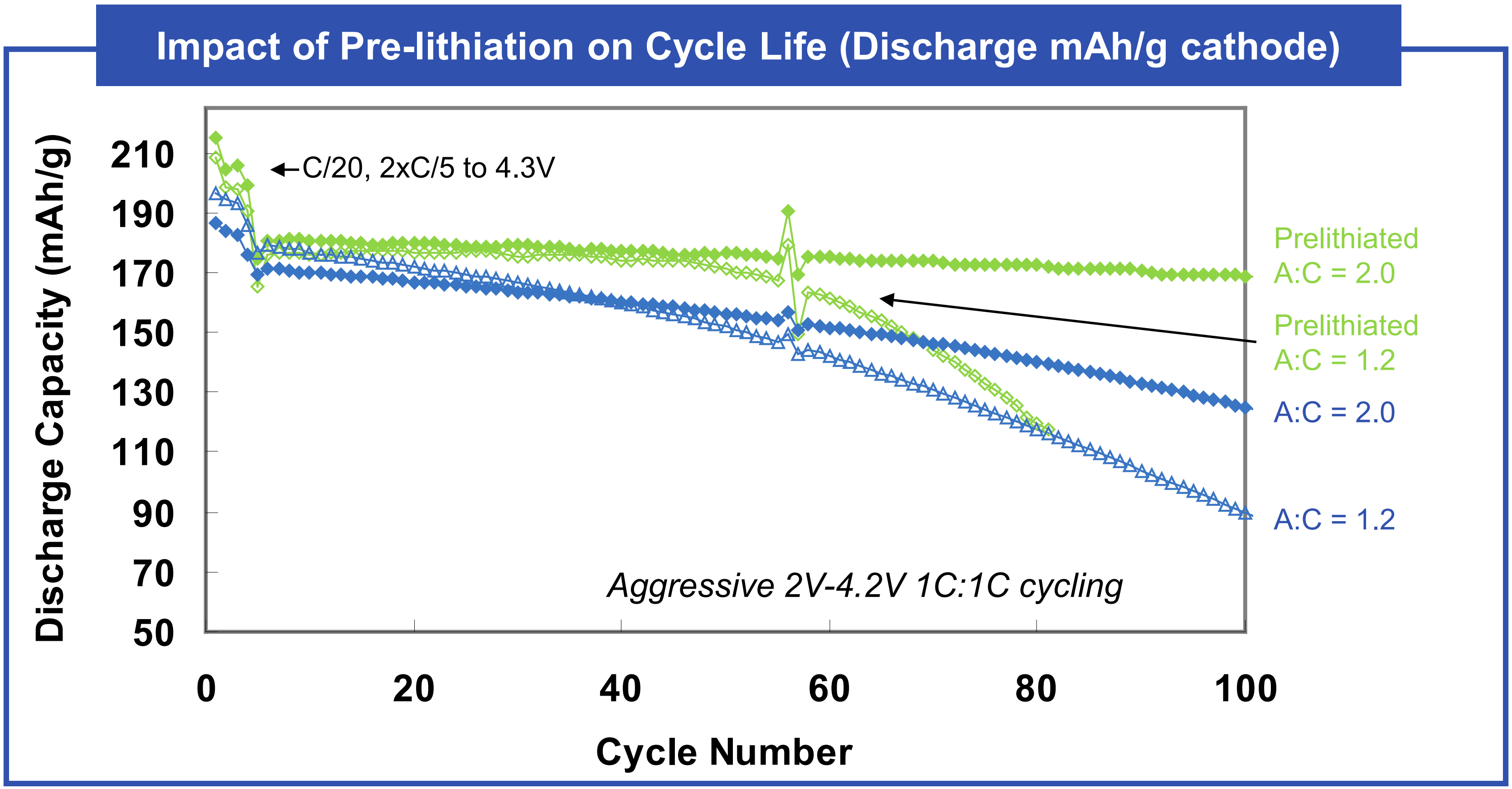
mAh/g cathode active	1st C/20 Charge to 4.3V	1st C/20 Discharge from 4.3V	C/5 Discharge from 4.3V	1C Discharge from 4.2V	Retention at 50 cycles
Prelithiated, A:C = 2.0	233	215	206	181	97%
Prelithiated, A:C = 1.2	227	209	198	176	95%
No prelithiation, A:C = 2.0	234	187	183	171	90%
No prelithiation, A:C = 1.2	231	197	193	179	82%

Pre-lithiation enhances cathode utilization in full cells utilizing Si-based anodes at high A:C ratios.

CAM-7/Supplier A-4 Si anode, cathode at ~13.3mg/cm² loading, anode pressed to 1g/cc.
Full coin cells with 1M $LiPF_6$ in 1:1:1 EC:DMC:EMC + 1%VC + 10%FEC electrolyte. Nominal 1C = 200mAh/g cathode.

Technical Accomplishments and Progress

Using pre-lithiation and overbalancing (i.e., high A:C ratio) we can reduce volume expansion of the anode and improve full cell capacity retention.



CAM-7/Supplier A-4 Si anode, cathode at ~13.3mg/cm² loading, anode pressed to 1g/cc.
Full coin cells with 1M $LiPF_6$ in 1:1:1 EC:DMC:EMC + 1%VC + 10%FEC electrolyte. Nominal 1C = 200mAh/g cathode.

Summary

- Identified CAM-7 dopant composition and a synthetic additive that can result in better capacity retention and decreased impedance growth with cycling.
- Developed a higher capacity CAM-7 cathode with good cycle life, by combining the doping strategy with synthetic modifications.
- Evaluated many Si-based anode materials that show promising performance.
- Assessed strategies to improve cycle life of silicon-based anodes:
  - Demonstrated improved cycle life with reduced voltage window cycling and in cell designs with increased anode:cathode ratio, but at the expense of gravimetric capacity.
  - Showed that by implementing pre-lithiation and using cells with high anode:cathode ratio, we can improve full cell capacity retention while fully utilizing the cathode.
- Work conducted on implementing these materials in baseline CAM-7/Graphite and Gen1 CAM-7/Si 18650 cells is highlighted in ES209 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 can improve capacity retention in full cells.
  - Our initial work on pre-lithiation 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.