



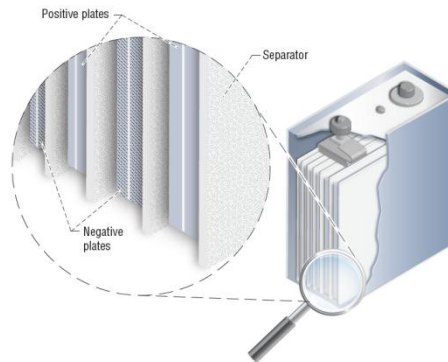
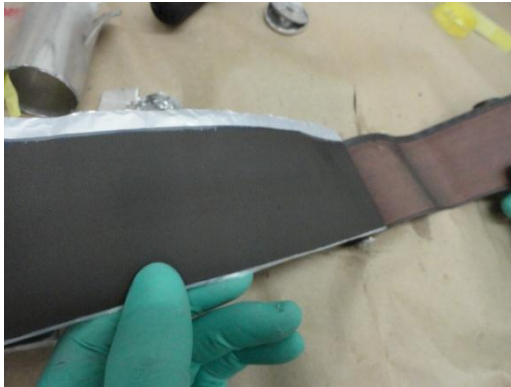
Advanced Materials and Component Development for Lithium-ion Cells for NASA Missions

Abstract

Human missions to Near Earth Objects, such as asteroids, planets, moons, libration points, and orbiting structures, will require safe, high specific energy, high energy density batteries to provide new or extended capabilities than are possible with today's state-of-the-art aerospace batteries. The National Aeronautics and Space Administration is developing advanced High Energy and Ultra High Energy lithium-ion cells to address these needs. In order to meet the performance goals, advanced, high-performing materials are required to provide improved performance at the component-level that contributes to performance at the integrated cell level. This paper will provide an update on the performance of experimental materials through the completion of two years of development. The progress of materials development, remaining challenges, and an outlook for the future of these materials in near term cell products will be discussed.



Advanced Materials and Components for Lithium-ion Cells for NASA Missions



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Objectives

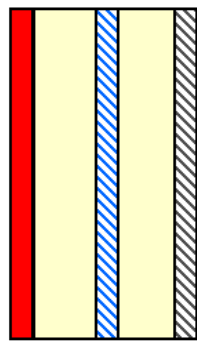
- **NASA is developing advanced Li-ion cells to enable or enhance future human missions to Near Earth Objects, such as asteroids, planets, moons, libration points, and orbiting structures.**
- **Advanced, high-performing materials are required to provide component-level performance that offer the required gains at the integrated cell level.**
- **This paper discusses results after two years of electrode materials development performed under NASA Research Announcement contracts and efforts that are continuing into a third year that offer the promise of delivering high performing, mature materials.**

*Specific details on many of the technical efforts discussed in the paper can be found in the papers from the focused session :“Advanced Materials and Cell Components for NASA’s Exploration Missions”, NASA Aerospace Battery Workshop, Huntsville, AL, Nov. 2009.



Advanced Li-ion Cell Development

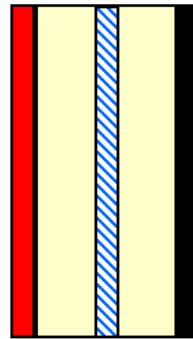
High Energy Cell



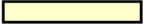
Conventional
Carbonaceous Anode

$\text{Li}(\text{LiNMC})\text{O}_2$
NASA Cathode

Ultra High Energy Cell



Si-composite
NASA Anode

-  Anode (commercial)
-  Anode (NASA)
-  Cathode (NASA)
-  Electrolyte (NASA)
-  Separator (commercial)

Safety devices (NASA)
incorporated into cell

High Energy Cell

- Lithiated mixed metal-oxide cathode $\text{Li}(\text{LiNMC})\text{O}_2$ / Graphite anode
- **180 Wh/kg** (100% DOD) @ cell-level, 0°C and C/10
- 80% capacity retention at **~2000** cycles
- Tolerant to electrical and thermal abuse with no fire (overcharge, over-temperature, reversal, short circuits)

Ultra High Energy Cell

- Lithiated mixed metal-oxide cathode $\text{Li}(\text{LiNMC})\text{O}_2$ / Silicon composite anode
- **260 Wh/kg** (100% DOD) @ cell-level, 0°C and C/10
- 80% capacity retention at **~200** cycles
- Tolerant to electrical and thermal abuse with no fire (overcharge, over-temperature, reversal, short circuits)

Preliminary system requirements given in: Reid, Concha, M., Miller, Thomas B., Manzo, Michelle A., and Mercer, Carolyn M., "Advanced Li-ion Cell Development for NASA's Constellation Missions", NASA Aerospace Battery Workshop, Huntsville, AL, Nov. 2008.



Summary of Two Years of Cathode Development

On Target:

- In Year One, very low first cycle reversible capacity was measured on all cathode deliverables (50-70% of charge capacity was delivered on the first discharge).
 - ✓ First cycle reversible capacity has improved and on some materials is now better than that of typical Li-ion cathodes.
- First year manufacturability studies revealed that Tap Density, a critical metric for raw powders, was too low to fabricate practical cathodes. Development efforts were directed to improve tap density in their second year.
 - ✓ Tap Density has improved to better than the minimum value necessary by using alternate synthesis methods (1.5 g/cc minimum).
- Specific capacity declined as a result of change in cathode synthesis methods to improve tap density.
 - ✓ Optimizations were performed to maximize specific energy while maintaining tap density at or above minimum levels necessary for manufacturability.

Still need improvement (current values not yet at or approaching goals):

- Specific Capacity, both at room temperature and at lower temperatures
- Temperature performance (percentage of room temperature capacity retained at 0° C)
- Discharge rate capability
- Cycle life
- **Combination of attributes that meet or exceed goals in one material**



Summary of Cathode Results

Metric	Goal	Best Values*		Values for Latest Materials	
		Value	Material	UTA 23 mo. coated	NEI 23 mo. uncoated (interim)
First Cycle Reversible Capacity (%)	81	87	UTA 18 & 23 mo. coated	87	65
Specific Capacity ,RT, C/10 to 3V (mAh/g)	311**	238	UTA 11 mo. uncoated	164	191
Specific Capacity, 0° C, C/10 to 3V (mAh/g)	280	135	UTA 11 mo. coated	126	130
RT Capacity Retention at 0° C (%)	90	72	NEI 23 mo. uncoated (interim)	85	72
Tap Density (g/cc)	≥ 1.5	> 2.3	NEI and UTA, both 18 mo. uncoated	2.02	1.34
Rate Capability at C/5 as compared to C/10 (%)	95	83	NEI 6 mo. uncoated***	***	***
HE Cycle Life (cycles)	2000	81	UTA****	****	****
UHE Cycle Life (cycles)	250	81	UTA****	****	****

Notes:

* Best Values are the highest value of that particular metric achieved from the development. Values are not necessarily for the same material.

** Expected minimum value based on desire to attain at least 10% of RT capacity when performing at 0° C.

*** Rate capability studies not performed routinely on all samples.

**** Cycle life studies not routinely performed. Number of cycles to 80% of initial capacity was projected from 60 cycles of data collected at the vendor on experimental materials (not necessarily provided as a deliverable).



Performance of NEI Corporation NMC Cathodes

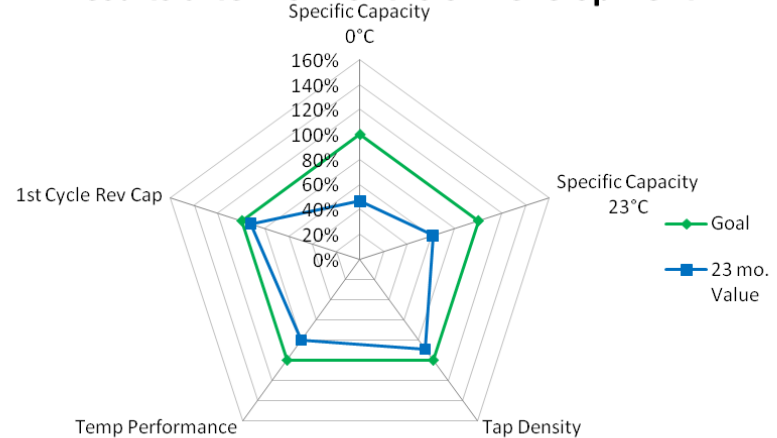
Accomplishments:

- Improvements in specific capacity, 1st cycle reversible capacity, temperature performance, and tap density
- Use of alternative annealing environments to improve tap density
- Performed studies of relationship between tap density, tape density, and surface area to improve loading and optimize materials for manufacturability
- Several conference papers and publications

Remaining Challenges to meet goals:

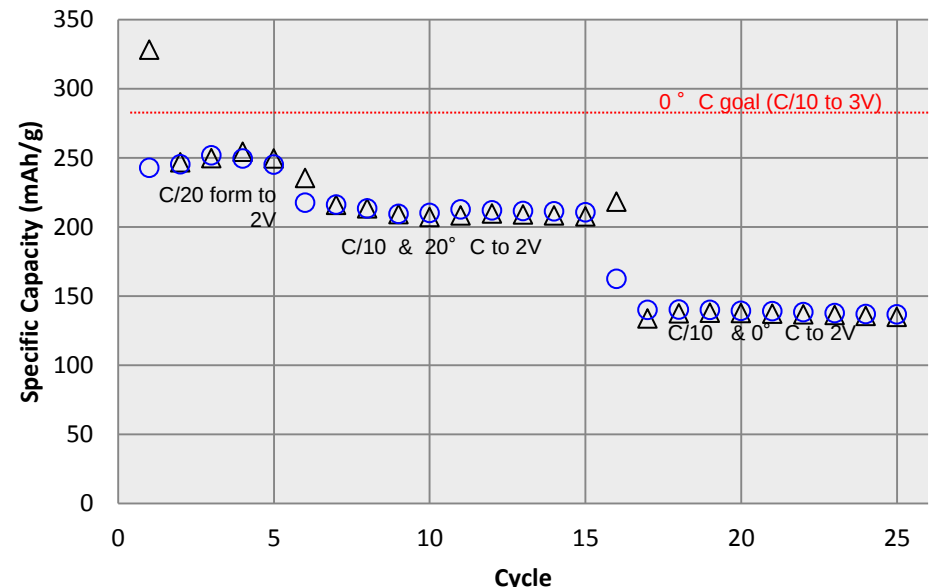
- Higher specific capacity at RT and low temperatures
- Higher tap density on higher capacity materials
- Higher 1st cycle reversible capacity
- Better temperature performance (higher percentage of RT capacity retained at low temperatures)
- Improved rate capability
- Demonstrated cycle life
- Combination of attributes that meet or exceed goals in one material

Results after 23 months of Development



NEI 23 mo. Deliverable

Δ Chg ○ Dischg





Performance of University of Texas at Austin (UTA) NMC Cathodes

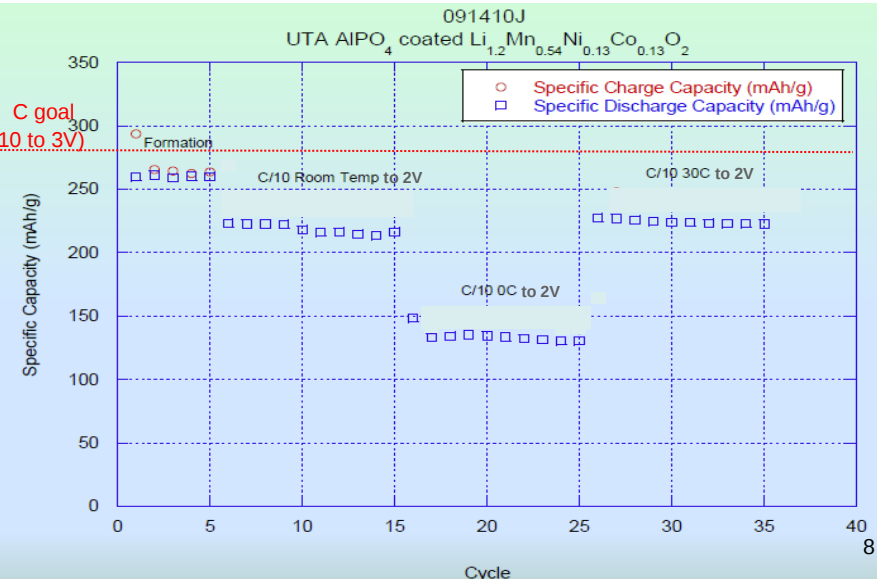
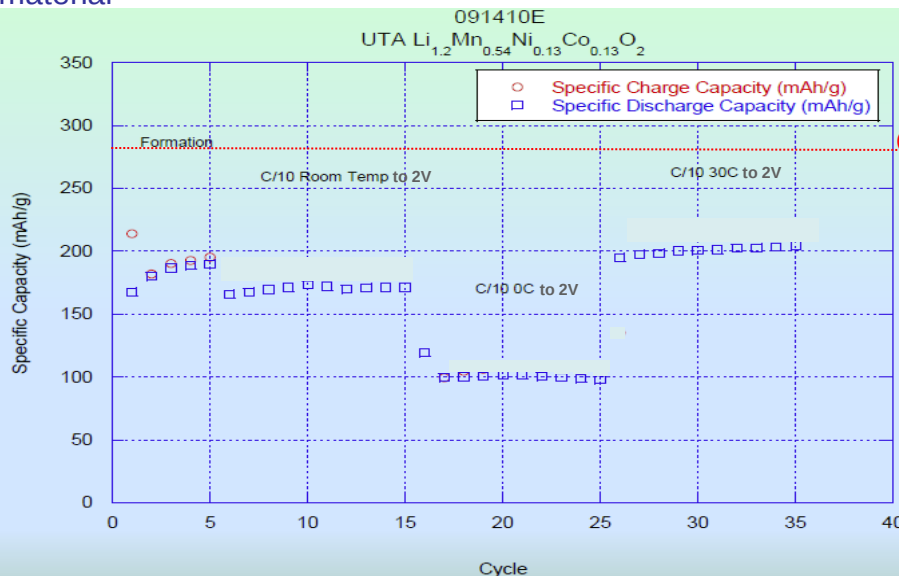
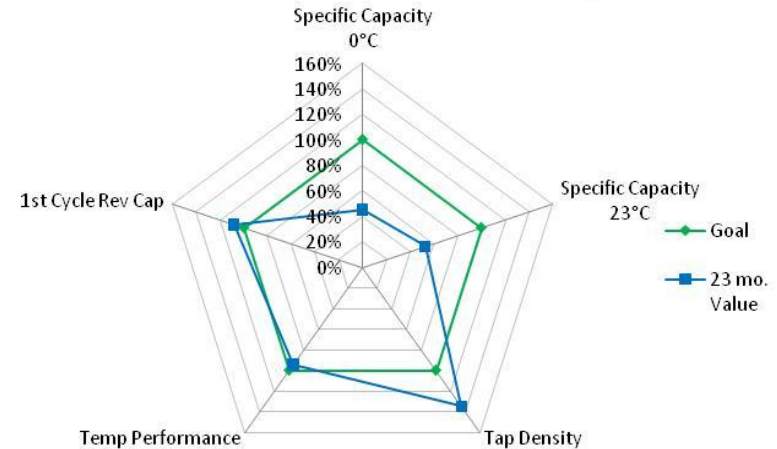
Accomplishments:

- Improvements in specific capacity, 1st cycle reversible capacity and temperature performance
- Tap density exceeds goals required for manufacturability
- Successful use of alternative cathode synthesis procedures and application of coatings to improve tap density and material performance
- Coated materials exhibit improved performance over uncoated
- Several conference papers and publications

Remaining Challenges to meet goals:

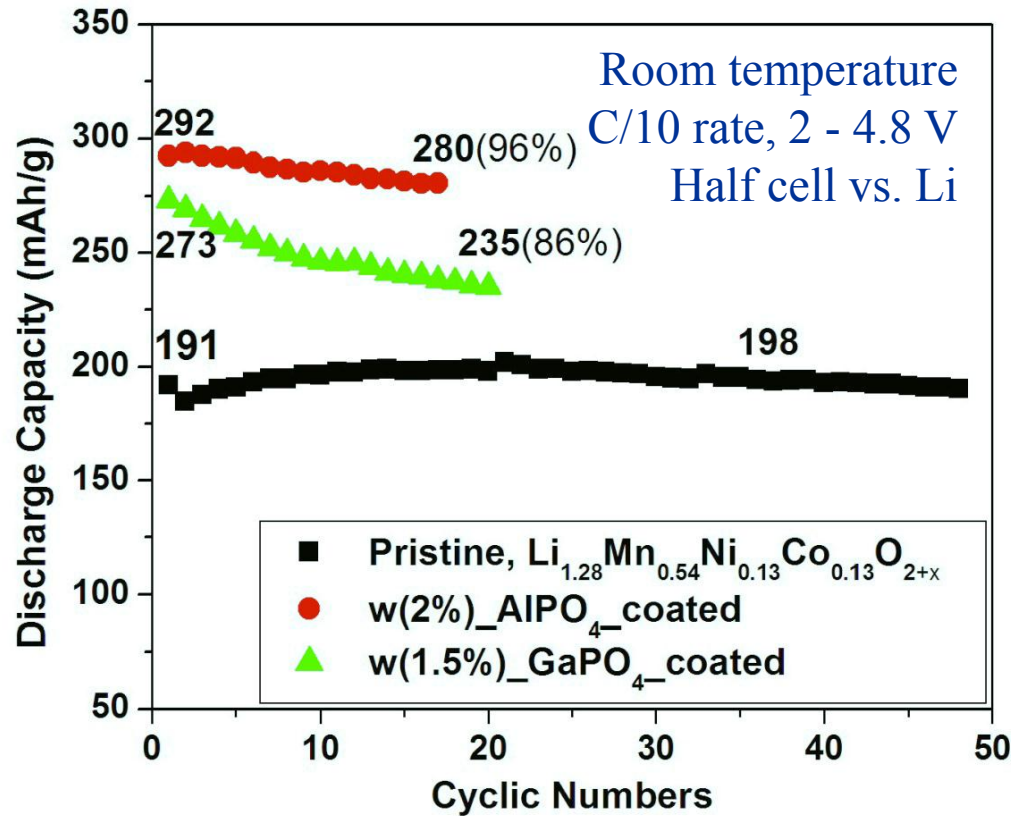
- Higher specific capacity at RT and low temperatures
- Better temperature performance (higher percentage of RT capacity retained at low temperatures)
- Improved rate capability
- Demonstrated cycle life
- Combination of attributes that meet or exceed goals in one material

Results after 23 months of Development





University of Texas at Austin Cathode Development Follow-on Effort Preliminary Results



Surface modification of the optimized sample demonstrates an initial specific capacity of 292 mAh/g and high tap density ($>1.8 \text{ g/cm}^3$).



Summary of Two Years of NRA Contract Si-composite Anode Development

On Target:

- Specific capacity at C/10 and 0° C has exceeded goal value, outperforming SOA carbonaceous anodes by >3X (>1200 mAh/g vs. ~372 mAh/g).
- Excellent capacity retention has been achieved at 0° C, and has a tendency to improve with cycling in some materials.
- Rate capability at C/2 has exceeded that of SOA carbonaceous anodes (as % of C/10 capacity retained at C/2 rate and RT).
 - 93% for MPG-111 and >94-100% in Si:C anodes.

Still need improvement (current values not yet at or approaching goals/metrics of SOA materials):

- Reversible capacity
- Loading
- Coulombic efficiency
- Demonstration of cycle life in cells



Summary of NRA Anode Results

Metric	Goal	Best Values*		Values for Latest Materials	
		Value	Material	GTRC 23 mo.	LMSSC 23 mo.
Total Reversible Capacity (after 2-3 cycles) (%)	89	70	GTRC 23 mo.	70	4
Specific Capacity ,RT, C/10 (mAh/g)	1110	1660	LMSSC 6 mo.	1598	1209
Specific Capacity, 0°C, C/10 (mAh/g)	1000	1528	GTRC 23 mo.	1528	1186
RT Capacity Retention at 0°C (%)	90	107**	GTRC 18 mo.	96	98
Loading (mAh/cm ²)	3.7	3.0	GTRC 11 mo.	0.9	2.7
Rate Capability at C/2 as compared to C/10 (%)	93	103**	GTRC 18 mo.	94	81
Coulombic Efficiency (%)	99.5	98.8	GTRC 23 mo.	98.8	97.9
Projected Cycle Life (cycles to 80% of initial capacity)	250	Virtually no fade after 45 cycles at C/2 at RT**	GTRC 23 mo.	Virtually no fade after 45 cycles at C/2 at RT**	~23***

Notes:

*Best Values are the highest value of that particular metric achieved from the development. Values are not necessarily for the same material.

**Capacity improved with cycling.

***Issue of significant capacity fade observed in half-cell testing. Issue of high irreversible capacity and low operational/useable capacity implies difficulty in meeting cell-level specific energy goals.

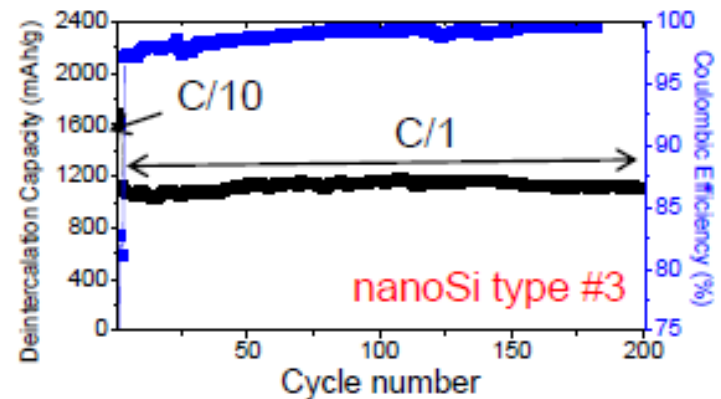
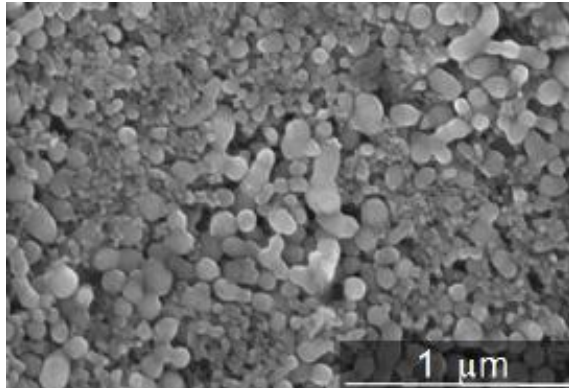


Ultra High Energy Lithium-ion Battery Anode Development

Georgia Institute of Technology (GT) and Georgia Tech Research Corporation (GTRC)
in partnership with Clemson University

Anode Material:

Nano-silicon-carbon composite with binder



Achieved >1100 mAh/g capacity at a C/1 rate for 200 cycles with GT materials. Data was collected at GT.

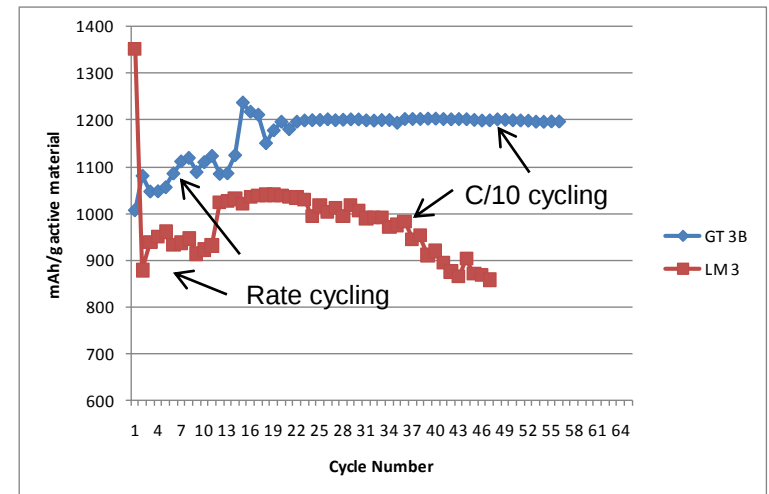
Fundamental Studies Addressed:

- Binder properties & modifications
- Electrolyte additives
- Silicon-binder interfacial properties
- Silicon SEI properties
- Cell “conditioning” effects
- Theoretical modeling

Technical Issues:

- SEI stabilization to reduce capacity fade
 - Optimal cell “conditioning” parameters
- Low electrode loading
- Stabilization of silicon volume changes
- Optimal electrolyte composition, salts & additives to achieve long-term cycling ability

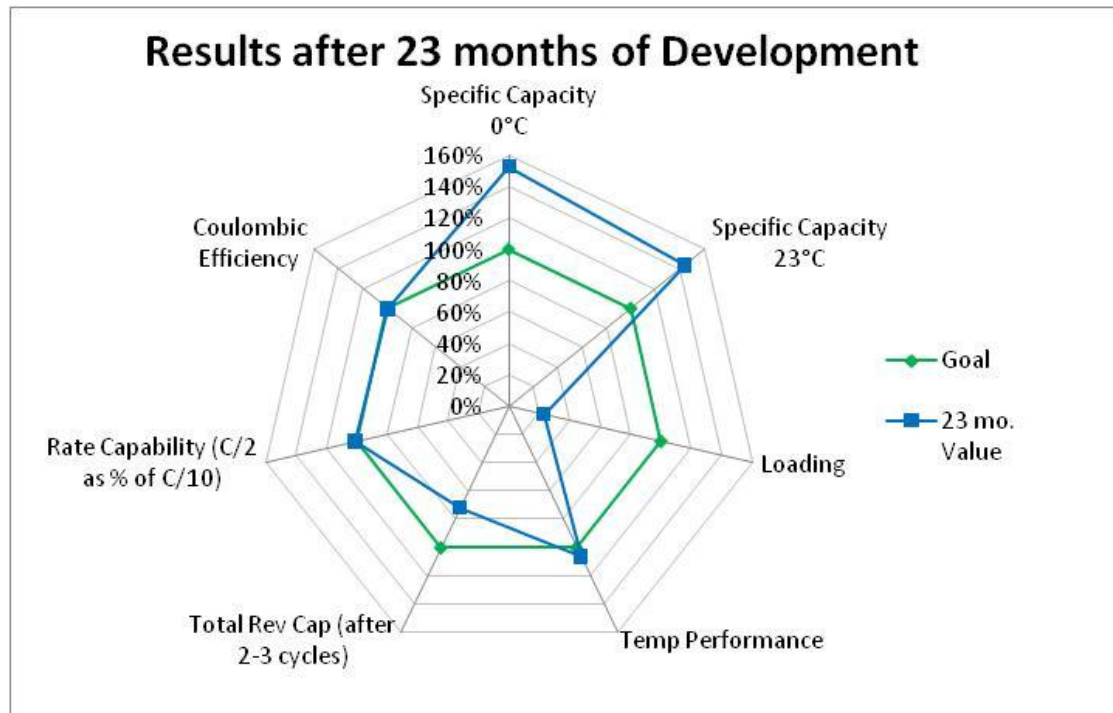
Technical approaches to address these issues have been proposed



Half-cell cycling performance of a GT anode (blue) compared to Lockheed Martin Space Systems Company (LMSSC) anode material (red) [stable capacity retention on GT materials achieved with the addition of VC (vinylene carbonate) to the electrolyte, no impact on LMSSC materials]



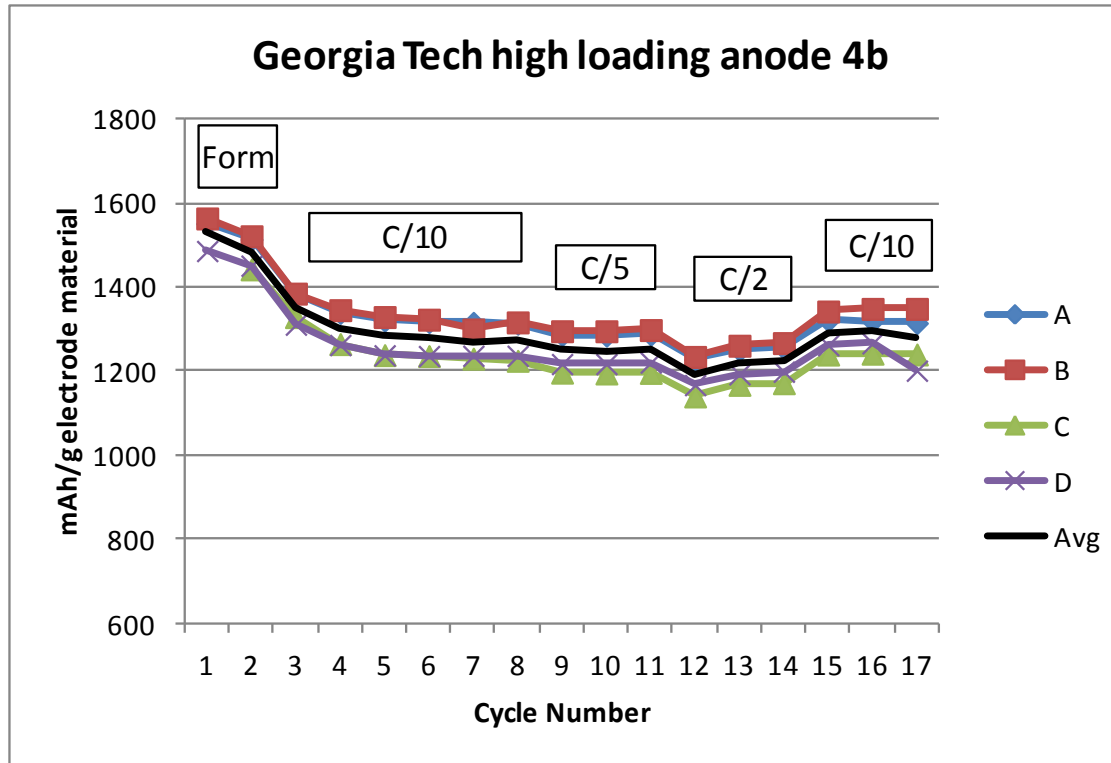
Performance of Georgia Tech Anodes as Compared to Goal or SOA Values as a function of Development Time





Georgia Tech Anode Development Follow-on Effort

Preliminary Results



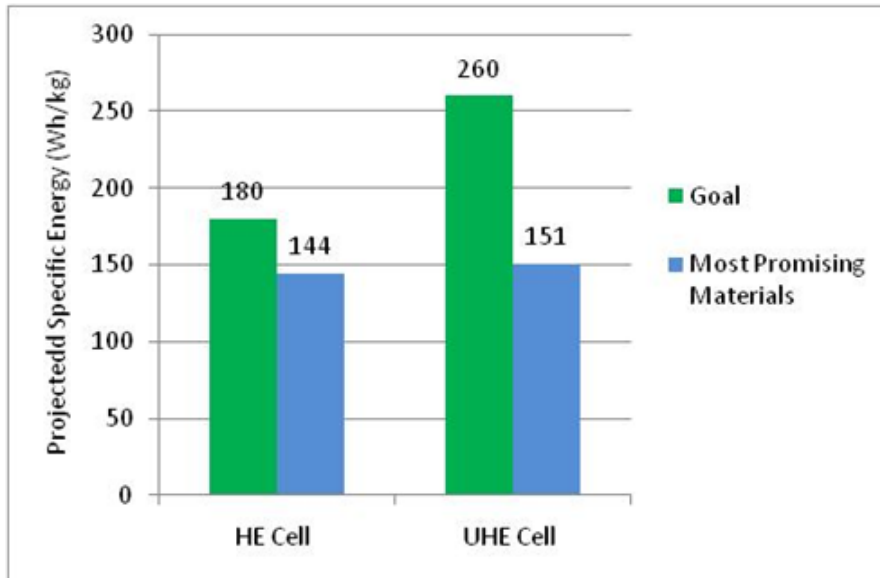
Total electrode material mass loading of 2.2 – 2.6 mg/cm² (based upon loading needed to match NMC cathode in a full cell)

- High-loading anodes demonstrated better specific capacity than the low-loading anodes during the initial cycles (>1300 mAh/g at C/10 at both 20° C & 0° C), but demonstrated significant capacity fade with continued cycling
- High-loading anodes cycled at C/2 & 20° C at GRC showed capacity fade to ~600 mAh/g after ~75 cycles, whereas the low-loading anodes demonstrated superior cycle-life performance with continued high capacity (> 80% retention at >250 cycles & 23° C)

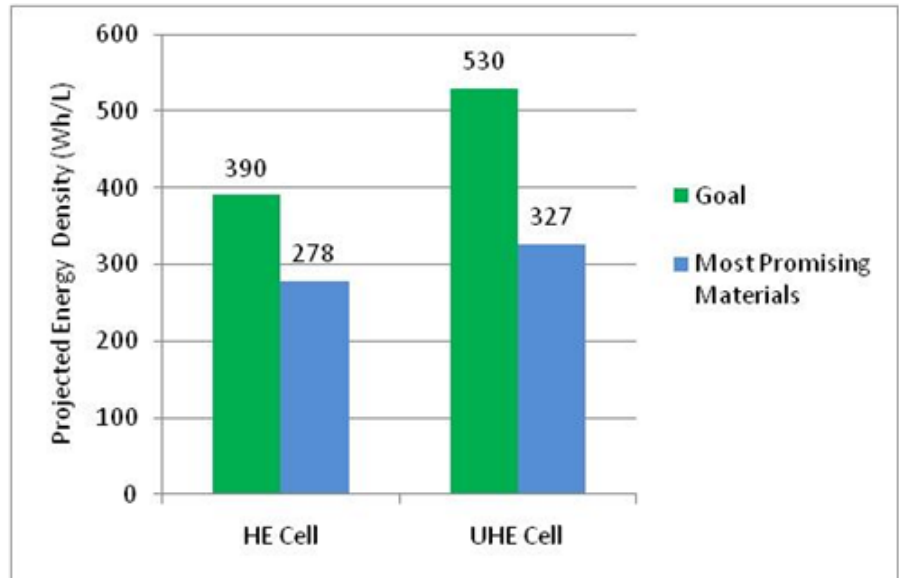


Cell Specific Energy and Energy Density Projections using Most Promising Materials Developed to Date

Projected Specific Energy vs. Goal



Projected Energy Density vs. Goal



Note:

- Cell specific energy and energy density are based on projections using data on materials' performance at C/10 and 0° C to 3V



Summary

- Vehicles and stand-alone power systems that enable the next generation of human missions to the moon will require energy storage systems that are safer, lighter, and more compact than current state-of-the-art (SOA) aerospace quality lithium-ion (Li-ion) batteries.
- The present state of development activities has resulted in the synthesis of promising materials that approach the ultimate performance goals.
- Although there is still a significant amount of work yet to be done, we have identified performance attributes for each component that need targeted solutions and have proposed some strategies to overcome the technical issues.