

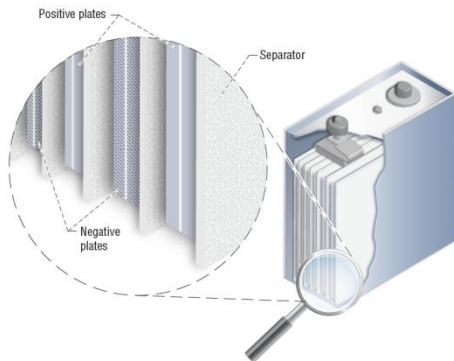
# **A Summary on Progress in Materials Development for Advanced Lithium-ion Cells for NASA's Exploration Missions**

Concha M. Reid

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. 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 can offer the required gains at the integrated cell level. Although there is still a significant amount of work yet to be done, the present state of development activities has resulted in the synthesis of promising materials that approach the ultimate performance goals. This paper on interim progress of the development efforts will present performance of materials and cell components and will elaborate on the challenges of the development activities and proposed strategies to overcome technical issues.



# A Summary on Progress in Materials Development for Advanced Lithium-ion Cells for NASA's Exploration Missions



Concha M. Reid, NASA Glenn Research Center

2011 Space Power Workshop

Los Angeles, CA

April 18-21, 2011



# Objectives

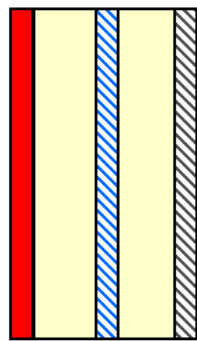
---

- **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 can offer the required gains at the integrated cell level.**
- **This paper on interim progress of the development efforts will present performance of materials and cell components, will elaborate on the challenges of the development activities, and proposed strategies to overcome technical issues.**



# Advanced Li-ion Cell Development

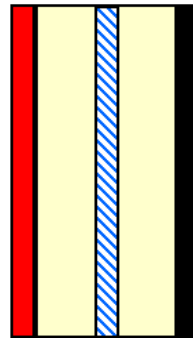
## High Energy Cell






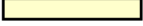

Conventional Carbonaceous Anode

Li(LiNMC)O<sub>2</sub>  
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

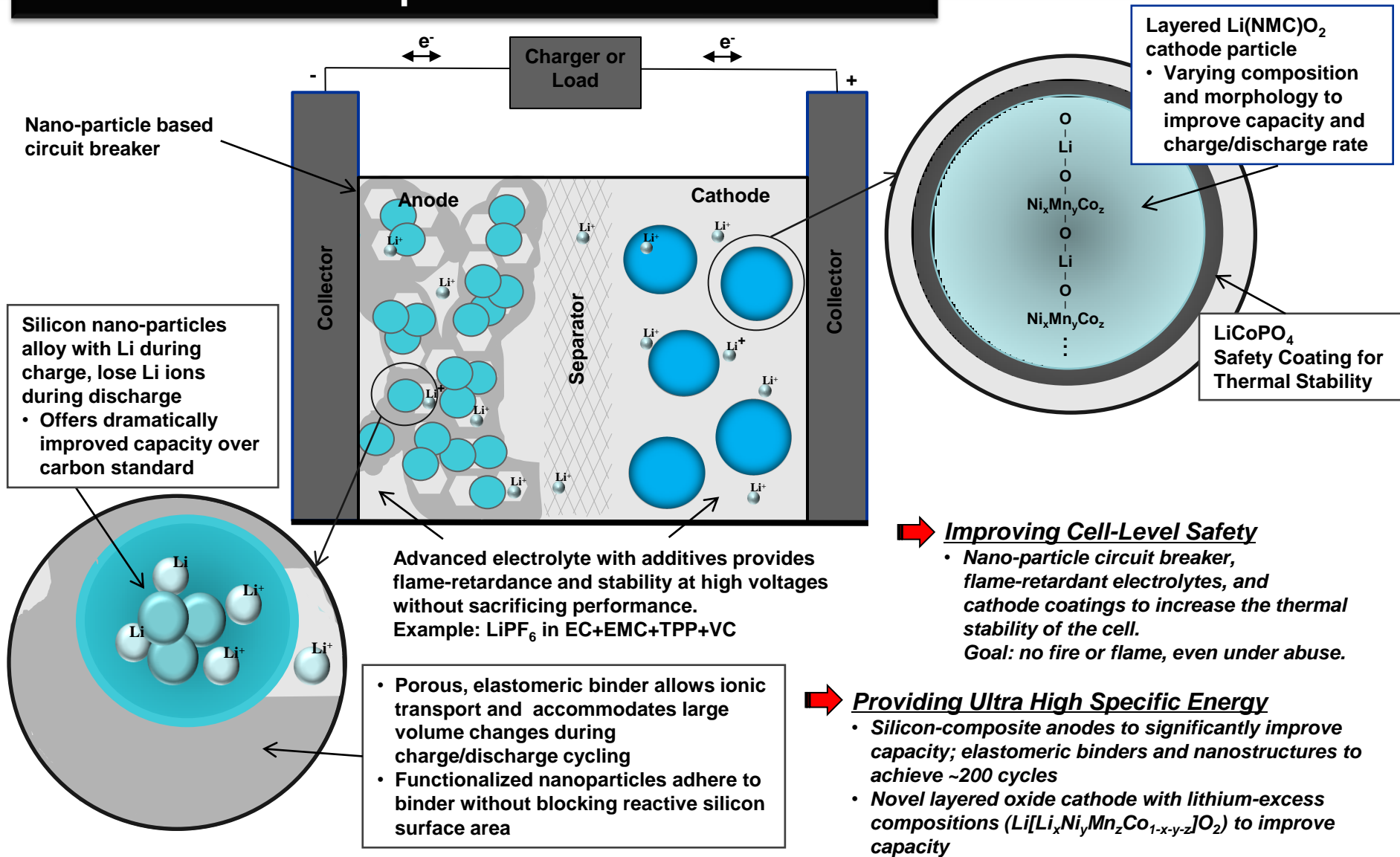
- Lithiated mixed metal-oxide cathode Li(LiNMC)O<sub>2</sub>/ Graphite anode
- **180 Wh/kg** (100% DOD) @ cell-level, 0°C and C/10
- 80% capacity retention at **~2000** cycles
- Tolerant to electrical and thermal abuse with no fire (overcharge, over-temperature, reversal, short circuits)

## Ultra High Energy Cell

- Lithiated mixed metal-oxide cathode (Li(LiNMC)O<sub>2</sub>)/ 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)

# Lithium Ion Battery Technology Development

## Advanced Cell Components



Nano-particle based circuit breaker

Silicon nano-particles alloy with Li during charge, lose Li ions during discharge

- Offers dramatically improved capacity over carbon standard

Advanced electrolyte with additives provides flame-retardance and stability at high voltages without sacrificing performance.

Example:  $LiPF_6$  in EC+EMC+TPP+VC

- Porous, elastomeric binder allows ionic transport and accommodates large volume changes during charge/discharge cycling
- Functionalized nanoparticles adhere to binder without blocking reactive silicon surface area

Layered  $Li(NMC)O_2$  cathode particle

- Varying composition and morphology to improve capacity and charge/discharge rate

$LiCoPO_4$  Safety Coating for Thermal Stability

➔ **Improving Cell-Level Safety**

- Nano-particle circuit breaker, flame-retardant electrolytes, and cathode coatings to increase the thermal stability of the cell.

Goal: no fire or flame, even under abuse.

➔ **Providing Ultra High Specific Energy**

- Silicon-composite anodes to significantly improve capacity; elastomeric binders and nanostructures to achieve ~200 cycles
- Novel layered oxide cathode with lithium-excess compositions ( $Li[Li_xNi_yMn_zCo_{1-x-y-z}]O_2$ ) to improve capacity



# 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%)
  - ✓ 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 manufacturing cathodes from raw powders, was too low to manufacture 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
- 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 Best Cathode Results

Metric	Goal	Best Values*		Values for Latest Materials	
		Value	Material	UTA 18 mo. coated	NEI 23 mo. uncoated
First Cycle Reversible Capacity (%)	81	87	UTA 18 mo. coated	87	74
Specific Capacity ,RT, C/10 to 3V (mAh/g)	311**	238	UTA 11 mo. uncoated	172	191
Specific Capacity, 0°C, C/10 to 3V (mAh/g)	280	135	UTA 11 mo. coated	108	130
RT Capacity Retention at 0°C (%)	90	72	NEI 23 mo. uncoated	69	72
Tap Density (g/cc)	≥ 1.5	> 2.3	NEI and UTA, both 18 mo. uncoated	1.99	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).



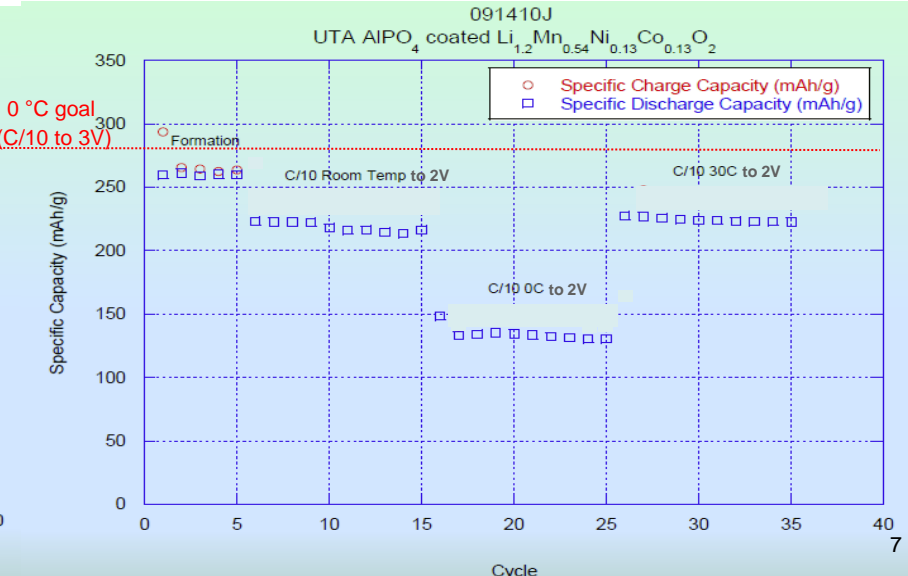
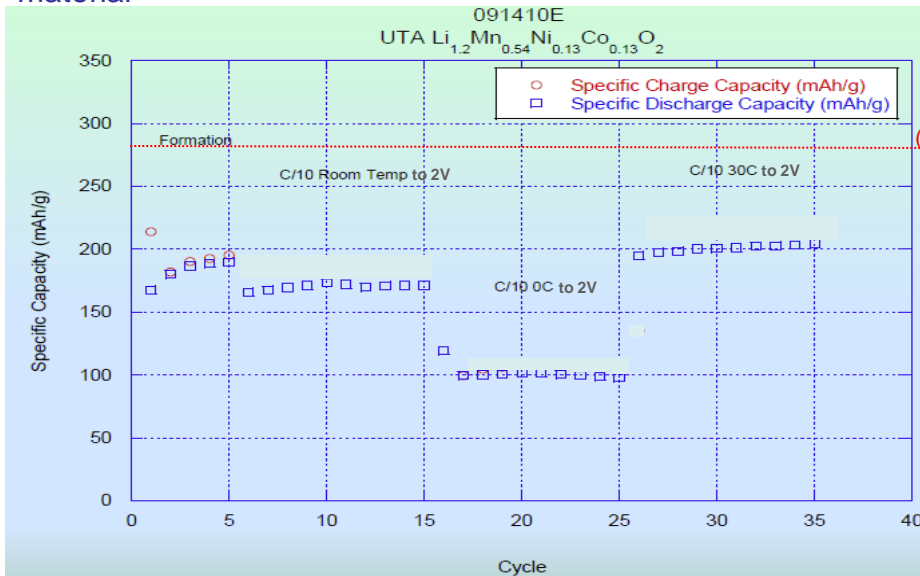
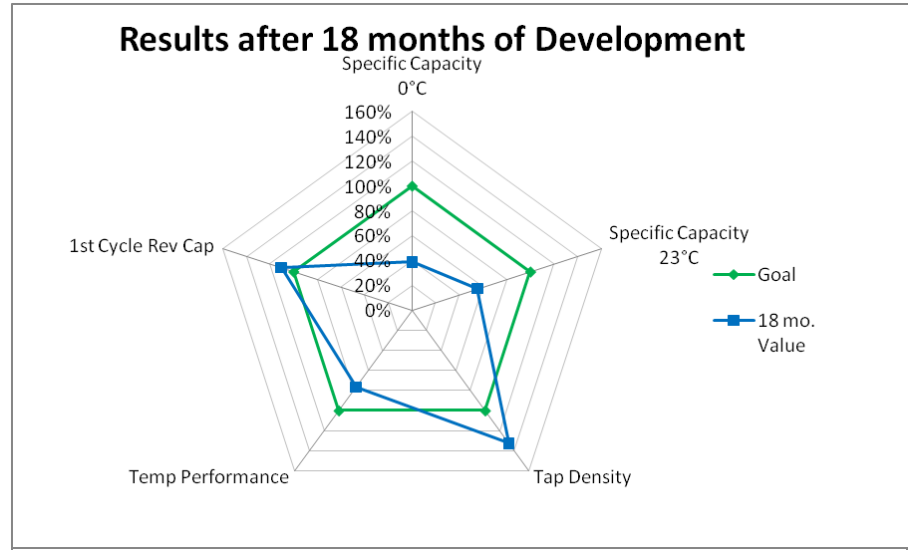
# Performance of University of Texas at Austin (UTA) NMC Cathodes

## Accomplishments:

- Improvements in specific capacity, 1<sup>st</sup> 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







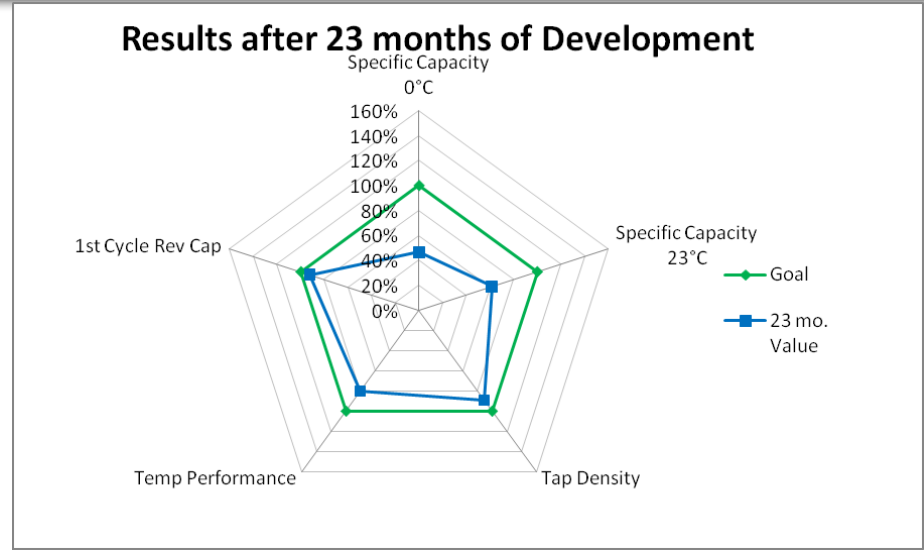
# Performance of NEI Corporation NMC Cathodes

## Accomplishments:

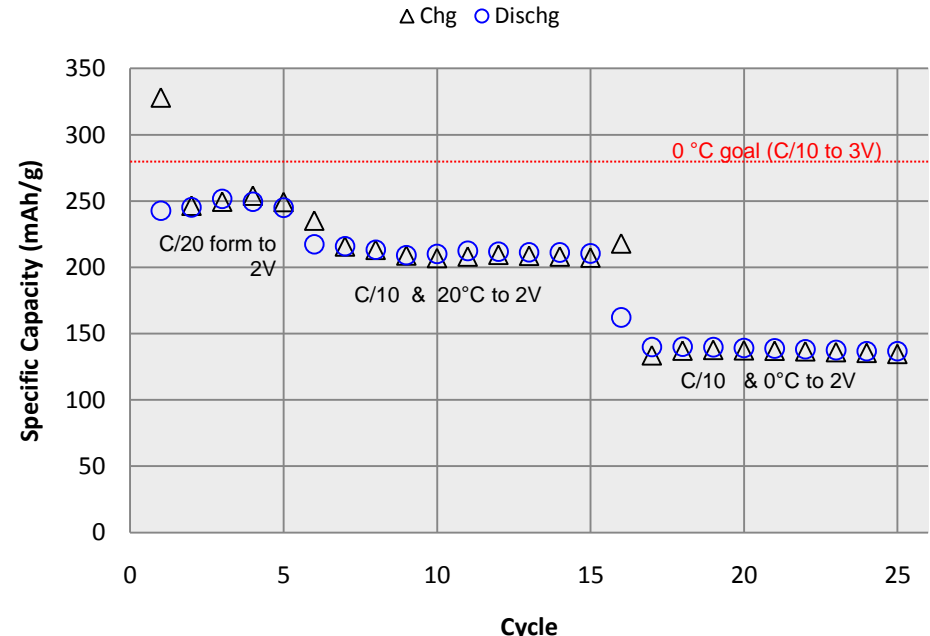
- Improvements in specific capacity, 1<sup>st</sup> cycle reversible capacity, temperature performance, and tap density
- Use of alternative annealing environments to improve tap density
- Performed studies of relationship between tap density, tape density, and surface area to improve loading and optimize 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 1<sup>st</sup> 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



## NEI 23 mo. Deliverable





# Summary of Two Years of Anode Development

## On Target:

- Specific capacity at C/10 and 0°C has exceeded goal value, outperforming SOA carbonaceous anodes by >3X
- 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 full cells



# Summary of Best 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 <sup>2</sup> )	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.

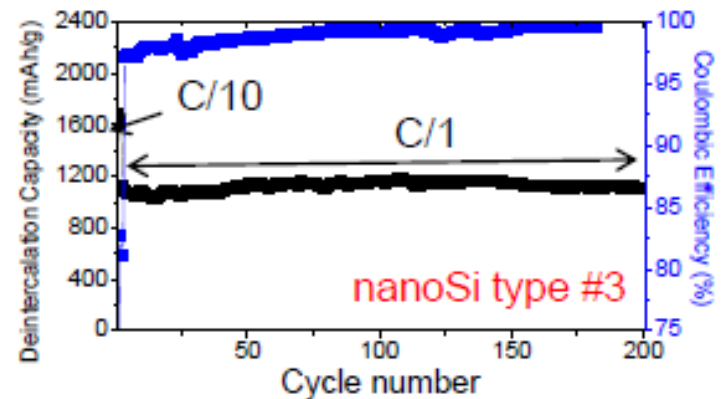
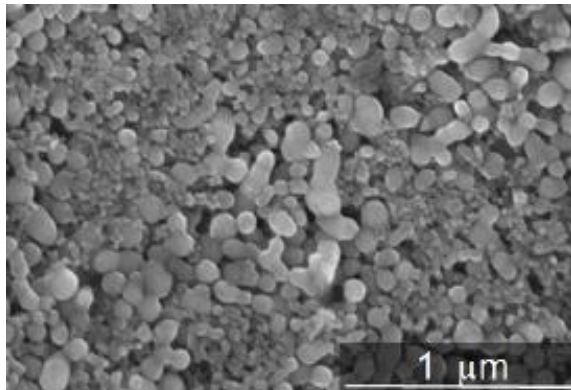


# Ultra High Energy Lithium-ion Battery Anode Development

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.

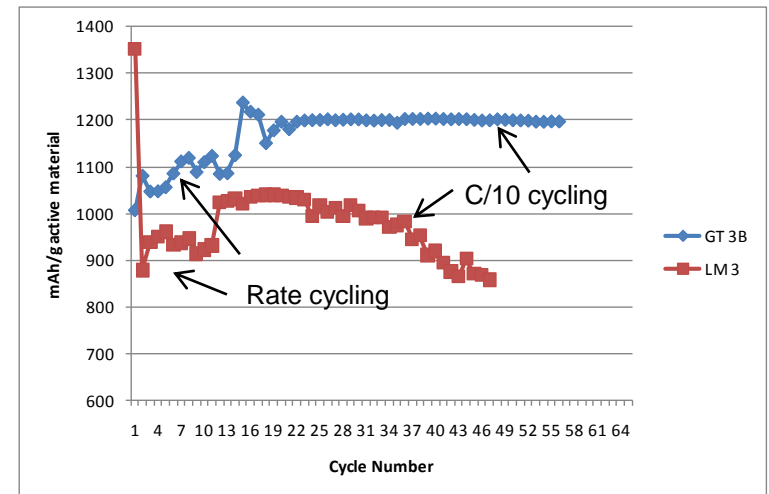
## Fundamental Studies Addressed:

- 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

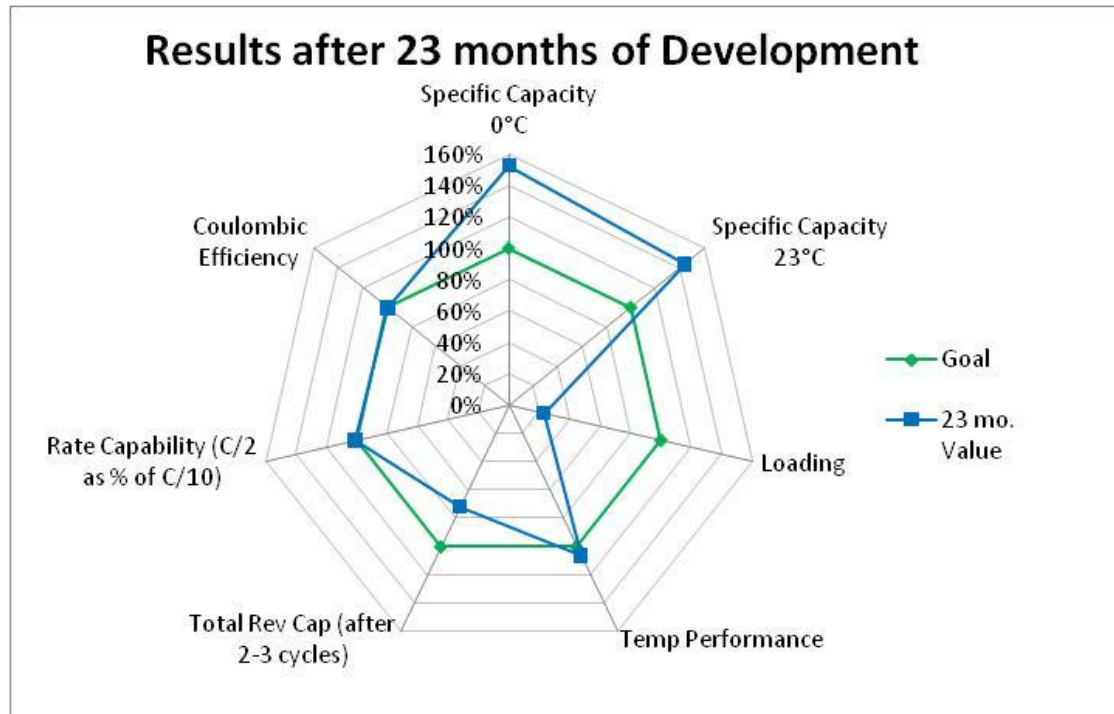
Technical approaches to address these issues have been proposed



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





# Electrolytes

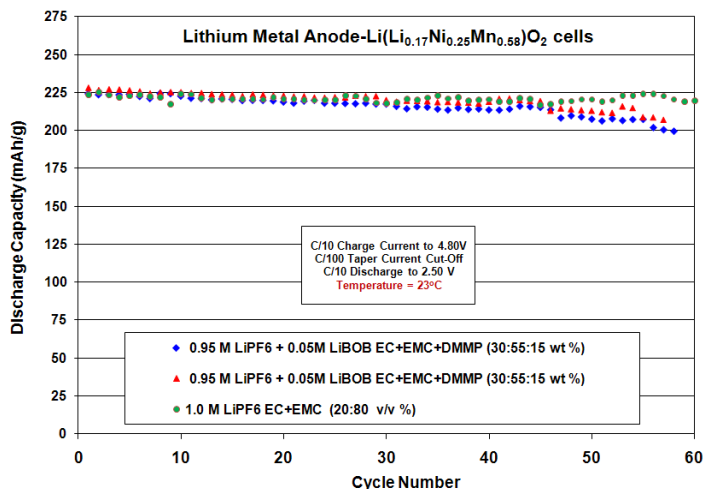
- Goal: Develop flame-retardant and/or non-flammable electrolytes that are stable up to 5V

Technology Challenges	Current approaches to address
Electrolyte that is stable up to 5V	Experiment with different electrolyte formulations and additives with potential to improve high voltage stability. Study interactions at both electrodes
Non-flammable or flame retardant electrolyte	Develop electrolytes containing additives with known flame retardant properties. Perform flame retardance assessments on developments that exhibit suitable electrochemical performance
High voltage stable, non-flammable or flame retardant electrolyte (combination of both properties in one electrolyte system)	Combine flame retardant additives with electrolyte formulations with high voltage stability. Operate systems to high voltages and investigate impacts on rate capability, specific energy, energy density and life.
Electrolytes possessing the requisite physical properties to ensure good rate capacity (adequate conductivity) and compatibility (wettability).	Develop electrolytes that are not excessively viscous to ensure that the ionic conductivity is sufficiently high over the desired temperature range and the separator wettability is adequate.

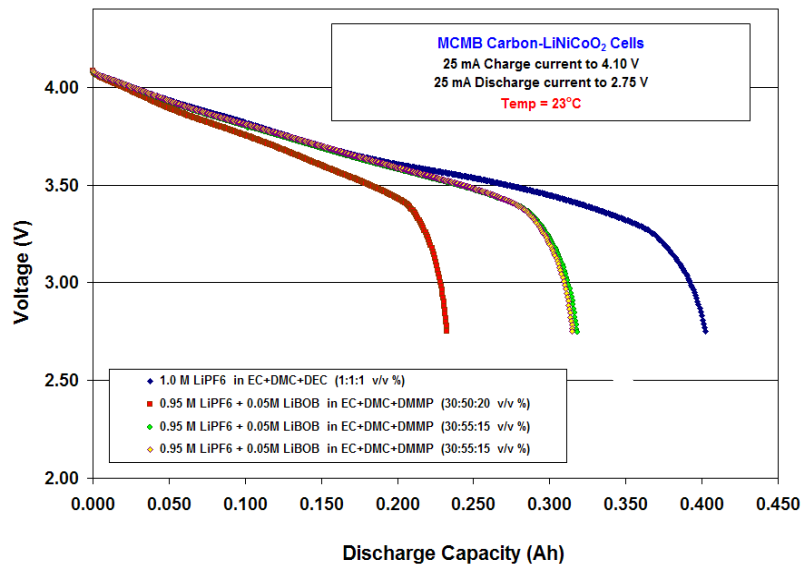


# Electrolytes

Yardney Technical Products (YTP) in partnership with the University of Rhode Island (URI)



High voltage cycling performance of cells with YTP/URI DMMP-containing electrolytes as compared to an all carbonate-based formulation.



Discharge capacity of MCMC-LiNiCoO<sub>2</sub> cells with YTP/URI DMMP-containing electrolytes as compared to an all carbonate-based formulation

Description	Electrolyte	Percentage Flame Retardant Additive	SET/s	Standard Deviation
"Baseline" Electrolyte	1.0M LiPF <sub>6</sub> in EC/EMC (3:7)	None	33.4	3.4
JPL GEN #1 Electrolyte	1.0M LiPF <sub>6</sub> in EC/EMC/TPP (2:7.5:0.5) + 2% VC	5% TPP	22.45	2.3
JPL Electrolyte	1.0M LiPF <sub>6</sub> in EC/EMC/TPP (2:7:1) + 2% VC	10% TPP	9.57	0.9
JPL Electrolyte	Salt and carbonate blend	15%TPP	3.78	1.2
Yardney/URI GEN #2 Electrolyte	1.0M (95% LiPF <sub>6</sub> + 5% LiBOB) in EC/EMC/DMMP (3/5.5/1.5)	15% DMMP	1.8	1.5
Yardney/URI GEN #1 Electrolyte	1.0M (95% LiPF <sub>6</sub> + 5% LiBOB) in EC/EMC/DMMP (3/5/2)	20% DMMP	0.4	0.4

Self-Extinguishing Times of Developmental Electrolytes. Data was generated by the University of Rhode Island.

➤ Flame-retardant electrolytes containing dimethyl methyl phosphonate (DMMP) display excellent self extinguishing properties and good stability at high voltages (4.8V), but exhibit poor capacity in cells containing graphite.



# Electrolytes

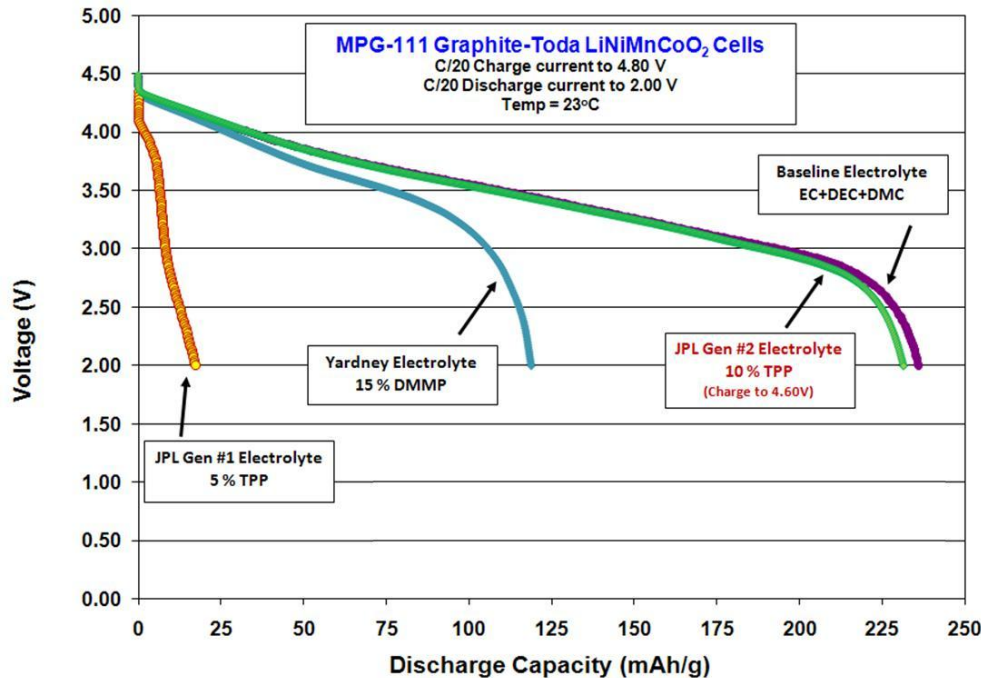
➤ Flame-retardant electrolytes containing triphenyl phosphate (TPP) display good self extinguishing properties and stability at high voltages (4.8V), and exhibit excellent capacity retention and cycling stability in cells containing graphite

Description	Electrolyte	Percentage Flame Retardant Additive	SET/s	Standard Deviation
"Baseline" Electrolyte	1.0M LiPF <sub>6</sub> in EC/EMC (3:7)	None	33.4	3.4
JPL GEN #1 Electrolyte	1.0M LiPF <sub>6</sub> in EC/EMC/TPP (2:7.5:0.5) + 2% VC	5% TPP	22.45	2.3
JPL Electrolyte	1.0M LiPF <sub>6</sub> in EC/EMC/TPP (2:7:1) + 2% VC	10% TPP	9.57	0.9
JPL Electrolyte	Salt and carbonate blend	15%TPP	3.78	1.2
Yardney/URI GEN #2 Electrolyte	1.0M (95% LiPF <sub>6</sub> + 5% LiBOB) in EC/EMC/DMMP (3/5.5/1.5)	15% DMMP	1.8	1.5
Yardney/URI GEN #1 Electrolyte	1.0M (95% LiPF <sub>6</sub> + 5% LiBOB) in EC/EMC/DMMP (3/5/2)	20% DMMP	0.4	0.4

Self-Extinguishing Times of Developmental Electrolytes.  
Data was generated by the University of Rhode Island.

Next steps:

- Optimization of flame-retardant electrolytes that are compatible with Si
- Incorporation of electrolyte advancements into production cells



Discharge capacity of graphite-Li(LiNMC)O<sub>2</sub> cells at high voltage with NASA JPL TPP-containing electrolytes as compared to an all carbonate-based formulation





# Summary of Safety Component Development with Physical Sciences, Inc. (PSI)

## Objective:

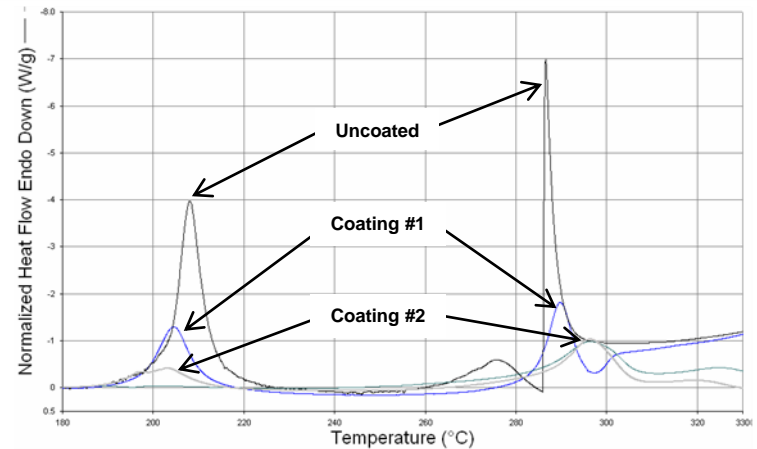
- Coat metal oxide cathodes with lithium cobalt phosphate coatings to improve thermal stability.

## Accomplishments:

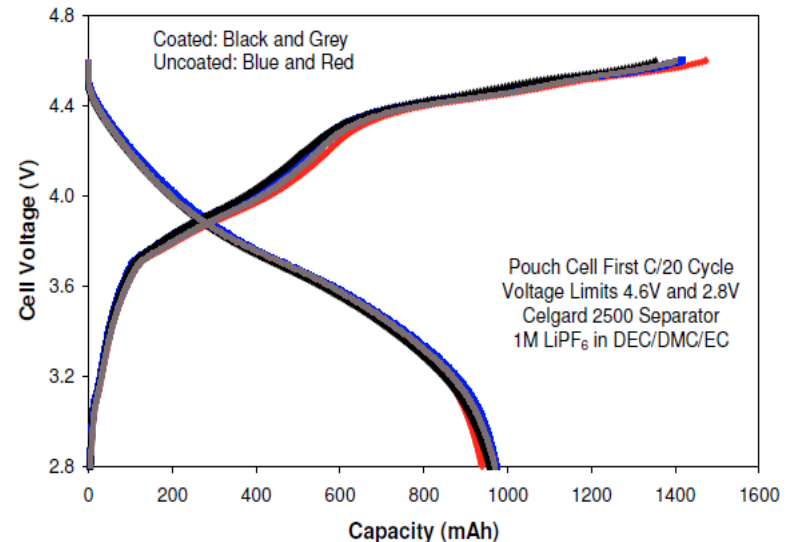
- Demonstrated robust adhesion of coating on  $\text{LiCoO}_2$  cathodes in half cells for 200 cycles, cycling at C-rate with capacity retention of ~90% of 1st cycle capacity
- Developed coating and processes to coat NMC cathode materials
- Coated TODA 9100 NMC cathodes demonstrated <1% loss in discharge capacity over 50 cycles at a C/5 rate.
- Demonstrated to reduce exotherms without reducing performance on high voltage cathodes (Toda 9100 NMC).
- Higher capacity, higher tap density lower irreversible capacity, and better cycling stability demonstrated on coated Toda 9100 NMC cathodes as compared to uncoated cathodes.

## Next steps:

- Physical Sciences, Inc.
  - Coat NEI 23 mo. deliverable with coating and process developed for Toda NMC materials
- Under separate effort (most likely with Saft)
  - Produce electrodes from PSI-coated NEI cathodes
  - Build cells containing PSI-coated NEI cathodes
- NASA independent assessments:
  - Determine impact on safety in full cells
  - Demonstrate cycling, rate, and low temperature performance



Preliminary results show reduced heat flow in exotherms of coated Toda 9100 NMC cathode. Data was collected at PSI.

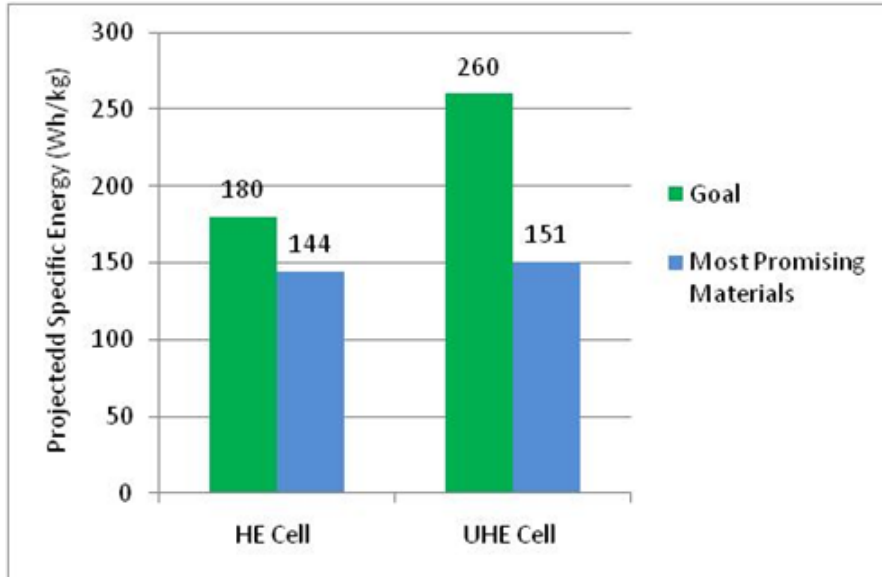


Cells containing uncoated and coated TODA 9100 NMC (2 cells of each) display similar first cycle capacity. Data was collected at PSI.

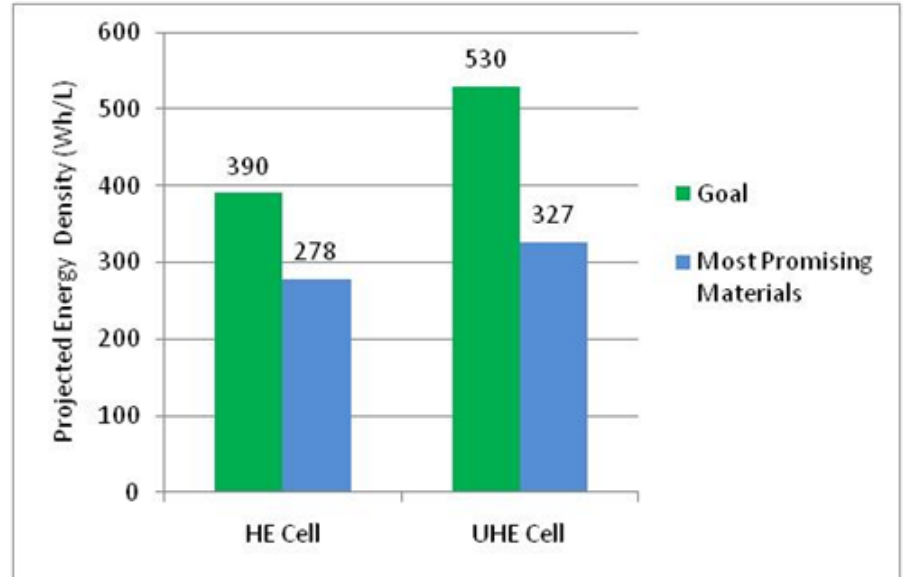


# Cell Specific Energy and Energy Density Projections using Most Promising Materials Developed to Date

## 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.**