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

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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 development 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**
- Lithiated mixed metal-oxide cathode Li(LiNMC)O₂)/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)O₂)/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)

Development Goals Were Addressed Through a Combination of Contracted Efforts (NRA, SBIR) and NASA In-house Efforts

ANODES
- Georgia Tech Research Corporation (GTRC)
- Lockheed Martin Space Systems Company (LMSSC)
- NASA GRC

CATHODES
- University of Texas at Austin (UTA)
- NEI Corporation
- NASA JPL

SAFETY
- Physical Sciences, Inc.
- Giner Corporation

ELECTROLYTES
- Yardney Technical Products
- NASA JPL
Summary of Two Years of NRA Contract 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 NRA Cathode Results

<table>
<thead>
<tr>
<th>Metric</th>
<th>Goal</th>
<th>Best Values*</th>
<th>Values for Latest Materials</th>
</tr>
</thead>
<tbody>
<tr>
<td>First Cycle Reversible Capacity (%)</td>
<td>81</td>
<td>87</td>
<td>UTA 18 &amp; 23 mo. coated</td>
</tr>
<tr>
<td>Specific Capacity, RT, C/10 to 3V (mAh/g)</td>
<td>311**</td>
<td>238</td>
<td>UTA 11 mo. uncoated</td>
</tr>
<tr>
<td>Specific Capacity, 0° C, C/10 to 3V (mAh/g)</td>
<td>280</td>
<td>135</td>
<td>UTA 11 mo. coated</td>
</tr>
<tr>
<td>RT Capacity Retention at 0° C (%)</td>
<td>90</td>
<td>72</td>
<td>NEI 23 mo. uncoated</td>
</tr>
<tr>
<td>Tap Density (g/cc)</td>
<td>&gt; 1.5</td>
<td>&gt; 2.3</td>
<td>NEI and UTA, both 18 mo. uncoated</td>
</tr>
<tr>
<td>Rate Capability at C/5 as compared to C/10 (%)</td>
<td>95</td>
<td>83</td>
<td>NEI 6 mo. uncoated**</td>
</tr>
<tr>
<td>HE Cycle Life (cycles)</td>
<td>2000</td>
<td>81</td>
<td>UTA***</td>
</tr>
<tr>
<td>UHE Cycle Life (cycles)</td>
<td>250</td>
<td>81</td>
<td>UTA***</td>
</tr>
</tbody>
</table>

**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, 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

![Graph showing specific charge and discharge capacities for UTA Li$_{1.2}$Mn$_{0.84}$Ni$_{0.13}$Co$_{0.13}$O$_2$ and UTA AlPO$_4$ coated Li$_{1.2}$Mn$_{0.84}$Ni$_{0.13}$Co$_{0.13}$O$_2$ materials.](image)
Surface modification of the optimized sample demonstrates an initial specific capacity of 292 mAh/g and high tap density (>1.8 g/cm³).
Performance of NEI Corporation (NEI) 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
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

<table>
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<tr>
<th>Metric</th>
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<th>Best Values*</th>
<th>Values for Latest Materials</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Value</td>
<td>Material</td>
</tr>
<tr>
<td><strong>Total Reversible Capacity (after 2-3 cycles) (%)</strong></td>
<td>89</td>
<td>70</td>
<td>GTRC 23 mo.</td>
</tr>
<tr>
<td><strong>Specific Capacity ,RT, C/10 (mAh/g)</strong></td>
<td>1110</td>
<td>1660</td>
<td>LMSSC 6 mo.</td>
</tr>
<tr>
<td><strong>Specific Capacity, 0°C, C/10 (mAh/g)</strong></td>
<td>1000</td>
<td>1528</td>
<td>GTRC 23 mo.</td>
</tr>
<tr>
<td><strong>RT Capacity Retention at 0°C (%)</strong></td>
<td>90</td>
<td>107**</td>
<td>GTRC 18 mo.</td>
</tr>
<tr>
<td><strong>Loading (mAh/cm²)</strong></td>
<td>3.7</td>
<td>3.0</td>
<td>GTRC 11 mo.</td>
</tr>
<tr>
<td><strong>Rate Capability at C/2 as compared to C/10 (%)</strong></td>
<td>93</td>
<td>103**</td>
<td>GTRC 18 mo.</td>
</tr>
<tr>
<td><strong>Coulombic Efficiency (%)</strong></td>
<td>99.5</td>
<td>98.8</td>
<td>GTRC 23 mo.</td>
</tr>
<tr>
<td><strong>Projected Cycle Life (cycles to 80% of initial capacity)</strong></td>
<td>250</td>
<td>Virtually no fade after 45 cycles at C/2 at RT**</td>
<td>GTRC 23 mo.</td>
</tr>
</tbody>
</table>

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

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

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

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]
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)
Physical Sciences, Inc. NASA SBIR Overview

Key SBIR Program Accomplishments:
- Material synthesis scale-up to 50 gram batches achieved in Phase II with path identified for ~500 gm batch synthesis
- Demonstrated equivalent coin and pouch cell performance
- Developed a technique to reduce the composite agglomeration
- Demonstrated 1000 mAh/g performance at up to C/2 rate in full cells
- Demonstrated improved cycling performance with VC addition in full cells
- Casting procedure scaled-up to produce higher electrode loadings ( > 3 mAh/cm²)
- Developed a setup and plan to produce ~20 feet electrode casts

Material Advantages:
- High in free volume;
- Free of polycrystalline domains (not achievable for silicon anode by CVD);
- Tailorable silicon loadings;
- Supporting matrix forms an electronically conductive framework;
- Processable using established procedure and equipment.

C. Lang, et. al., Electrochemical Performance of Silicon Whisker and Carbon Nanofiber Composite Anode, 220th ECS Meeting, Boston, MA, October 2011
Electrolytes

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

<table>
<thead>
<tr>
<th>Technology Challenges</th>
<th>Current approaches to address</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrolyte that is stable up to 5V.</td>
<td>Experiment with different electrolyte formulations and additives with potential to improve high voltage stability. Study interactions at both electrodes.</td>
</tr>
<tr>
<td>Non-flammable or flame retardant electrolyte.</td>
<td>Develop electrolytes containing additives with known flame retardant properties. Perform flame retardance assessments on developments that exhibit suitable electrochemical performance.</td>
</tr>
<tr>
<td>High voltage stable, non-flammable or flame retardant electrolyte (combination of both properties in one electrolyte system).</td>
<td>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.</td>
</tr>
<tr>
<td>Electrolytes possessing the requisite physical properties to ensure good rate capacity (adequate conductivity) and compatibility (wettability).</td>
<td>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.</td>
</tr>
</tbody>
</table>
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.

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

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

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<table>
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<tr>
<th>Description</th>
<th>Electrolyte</th>
<th>Percentage Flame Retardant Additive</th>
<th>SET/s</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>“Baseline” Electrolyte</td>
<td>1.0M LiPF₆ in EC/EMC (3:7) None</td>
<td>33.4</td>
<td>3.4</td>
<td></td>
</tr>
<tr>
<td>JPL GEN #1 Electrolyte</td>
<td>1.0M LiPF₆ in EC/EMC/TPP (2:7.5:0.5) + 2% VC</td>
<td>5% TPP</td>
<td>22.45</td>
<td>2.3</td>
</tr>
<tr>
<td>JPL Electrolyte</td>
<td>1.0M LiPF₆ in EC/EMC/TPP (2:7:1) + 2% VC</td>
<td>10% TPP</td>
<td>9.57</td>
<td>0.9</td>
</tr>
<tr>
<td>JPL Electrolyte Salt and carbonate blend</td>
<td>15% DMMP</td>
<td>15% TPP</td>
<td>3.78</td>
<td>1.2</td>
</tr>
<tr>
<td>Yardney/URI GEN #2 Electrolyte</td>
<td>1.0M (95% LiPF₆ + 5% LiBOB) in EC/EMC/DMMP (3/5.5/1.5)</td>
<td>15% DMMP</td>
<td>1.8</td>
<td>1.5</td>
</tr>
<tr>
<td>Yardney/URI GEN #1 Electrolyte</td>
<td>1.0M (95% LiPF₆ + 5% LiBOB) in EC/EMC/DMMP (3/5/2)</td>
<td>20% DMMP</td>
<td>0.4</td>
<td>0.4</td>
</tr>
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Discharge capacity of MCMB-LiNiCoO₂ cells with YTP/URI DMMP-containing electrolytes as compared to an all carbonate-based formulation.
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.

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<td>0.4</td>
<td>0.4</td>
</tr>
</tbody>
</table>

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
- Incorporate electrolyte advancements into production cells

Discharge capacity of graphite-Li(LiNMC)O₂ cells at high voltage with NASA JPL TPP-containing electrolytes as compared to an all carbonate-based formulation.
Objective:
- Coat metal oxide cathode powders with lithium cobalt phosphate coatings to improve thermal stability.

Accomplishments:
- Demonstrated robust adhesion of coating on 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 and abuse in full cells.
  - Demonstrate cycling, rate, and low temperature performance.

![Differential Scanning Calorimetry](image)

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

![Graph](image)

Cells containing uncoated and coated TODA 9100 NMC (2 cells of each) display similar first cycle capacity. Data was collected at PSI.
In-house NASA efforts continue to address select components and technical issues necessary to continue to advance technology

- Anode fundamental studies
- Cathode development
- Electrolyte Development
- Cell Integration
NASA in-house anode fundamental studies (GRC)

- Optimization of anode formation and cycling procedures
- SEI layer formation
- Understanding of electrolyte impact, and additives
- EIS (impedance) and cyclic voltammetry studies
- Analytical studies - morphology, changes with cycling

### Graph A

![Graph A](image)

- Si anode
- Graphite anode

### Table

<table>
<thead>
<tr>
<th>Anode type</th>
<th>R_{\text{int}} (\Omega)</th>
<th>R_{\text{ct}} (\Omega)</th>
<th>C_{\text{dil}} (F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-anode</td>
<td>1.62</td>
<td>94.12</td>
<td>6.34x10^{-6}</td>
</tr>
<tr>
<td>C-anode</td>
<td>1.43</td>
<td>125.44</td>
<td>5.02x10^{-6}</td>
</tr>
</tbody>
</table>
Employing mechanical methods to improve performance

- Ball milling and annealing improved tap density (2.0 g/cm³)
- Surface modification improved specific capacity over uncoated samples
- Coated samples demonstrated less 1st cycle irreversible capacity loss than similar NMC materials (24 mAh/g)
• Developing high voltage flame retardant electrolytes that are compatible with graphite/NMC and Si-based/NMC systems.

• Preliminary results show improved performance with some flame-retardant blends over baseline, however capacity fade is much greater in Si-based/NMC cells (cathode-limited) than in Si-based/Li half cells.
Cell Integration (GRC)

- Understanding of electrolyte impact, additives, and quantities
- Optimization of cell cycling protocols
- Study of component compatibility
- EIS (impedance) and cyclic voltammetry studies
- Cell modeling and projections

Electrochemical impedance spectroscopy (EIS) of cell containing Si-based anode and NMC cathode (w/reference)
Next steps in Developing NASA’s Advanced UHE Li-ion Cells

- Component development efforts will culminate in the delivery of components for test, verification, and integration studies at NASA and Saft America
- VL3A-design cells (nominal 6.5 Ah with standard components) are scheduled to be built with components that have reached maturity
  - Cells containing JPL flame-retardant electrolyte, commercial NMC cathode and graphite anode currently in production at Saft America
- Next sets of cells scheduled to be built March 2012
  - Will contain Georgia Tech Si-based anode, UTA NMC cathode, and JPL flame-retardant electrolyte
- Cells will be tested at NASA for electrical performance, safety and abuse
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