An Update on the Materials Development at JPL for Enhancing the Specific Energy and Safety of Li-Ion cells

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High Energy Li-Ion Cells for Future Space Missions

- Two parallel cell development approaches to meet future NASA mission requirements.
  - **High energy batteries for applications with long cycle/calendar life**
    - Safe, reliable Li-ion cell with > 200 Wh/kg and good cycle life (> 1000 Cycles)
    - Combination of high energy cathode, safe electrolyte with a carbonaceous anode with known heritage and performance
  - **Ultra-high energy batteries with Moderate Lifetime**
    - Safe and reliable Li-Ion cells with > 250 Wh/kg and cycle life > 200 cycles
    - Combination of high energy cathode, safe electrolyte, and a high energy lithium alloy anode (Li-Si)
    - Higher developmental risk than High Energy Cell
Material Developments at JPL

- High energy and Ultra-high energy Li-Ion cells with enhanced safety
  
  - Develop advanced components and materials, i.e., electrolytes, electrodes and cell components, for improving the performance and safety

  - Develop cathodes with high specific energy (1250 Wh/kg, i.e., high specific capacity and/or high voltage), with good cycle life and improved thermal stability.

  - Develop electrolytes with reduced flammability and compatibility high voltage cathodes reduced flammability
Cathode Performance Requirements

• High Specific Energy
  – High Specific capacity (> 180 mAh/g) and/or high voltage (> 4.2 V)

• High Discharge Rate Capability
  – High Reaction intercalation kinetics
  – High diffusivity for Li ion (SOA cathodes 10^{-10} cm^2/s)
  – Sub-micron primary particle size

• Good cycle life
  – No structural changes (layered to spinel for example)
  – No dissolution of metal ions (Ni or Mn) in the electrolytes that would deposit on anode or form cathode SEI (CEI)

• High Tap density (~ 2.1 g/cc)
  – Spherical morphology

• Good thermal stability
• No toxicity
# Cathodes for Lithium Ion Cells

<table>
<thead>
<tr>
<th>System</th>
<th>Sp. Capacity, mAh/g</th>
<th>Voltage vs Li</th>
<th>Sp. Energy,</th>
<th>TRL</th>
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<tr>
<td>LiCoO₂ (Lithiated Cobalt Oxide)</td>
<td>274 (Theoretical)</td>
<td>4.15</td>
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<td>Li(NCO) (LiNi₀.₈Co₀.₂O₂)</td>
<td>274 (Theoretical)</td>
<td>4.05</td>
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<td>LiMnPO₄ (Olivine)</td>
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<td>LiMn₁.₅Ni₀.₅O₄ (5 V Spinel)</td>
<td>148 (Theoretical)</td>
<td>4.8</td>
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</table>
High Specific Energy Cathode Materials

- **Li-excess Layered-Layered composites**
  - Layered oxide compositions belonging to the series layerd-layered composite
    \[ \text{Li}[\text{Li}_{1/3}\text{Mn}_{2/3}]\text{O}_2 \text{ (commonly designated as Li}_2\text{MnO}_3] \text{ and LiMO}_2 \text{ (M = Mn}_{0.5}\text{Ni}_{0.5}) \]
    \[ \times \text{Li}[\text{Li}_{1/3}\text{Mn}_{2/3}]\text{O}_2 + (1-x) \text{Li (Mn, Ni, Co)}\text{O}_2 \]
    e.g., \[ 0.5 \text{Li}[\text{Li}_{1/3}\text{Mn}_{2/3}]\text{O}_2 + 0.5 \text{Li (Mn}_{0.33}\text{, Ni}_{0.33}\text{, Co}_{0.34})\text{O}_2 \]
  - Loss of oxygen around 4.5 V during charge, which creates oxygen vacancies, reduction of nickel Ni\(^{+2}\) and an overall rearrangement of the lattice.
  - The plateau corresponding to oxygen loss is absent in subsequent charges.
  - Typical capacities are as high as 250 mAh/g on cycling them from 4.8 – 2.0 V.

*cf: Dahn et al, Thacakery et al*
High Specific Energy Cathode Materials

- **Issues**
  - Oxygen released in the first charge needs to be vented.
  - Cation Disorder (transition metal ions, typically nickel, occupying the Li sites) and interfering with Li\(^+\) ion diffusion
  - Huge irreversible capacity loss
    - 50 – 100 mAh/g in the first cycle (~30% compared to 7-10% for SOA cathode)
    - **No lithium release to anode for the irreversible capacity**
  - Low Tap densities (0.6 to 2.0 g/cc)
    - Strongly dependent on the synthetic conditions and morphology
  - Low Power densities
    - High capacity is realizable only at low rates (C/20-C/10) and at ambient temperatures.
  - Broad voltage profile with more capacity available between 3.0 V and 2.5 V, even at moderate rates
Li\textsuperscript{+} Diffusion Coefficient From PITT
(Potentiostatic Intermittent Titration Technique)

- At room temperature, the diffusion coefficient for uncoated Li\textsubscript{1.17}Mn\textsubscript{0.56}Ni\textsubscript{0.135}Co\textsubscript{0.135}O\textsubscript{2} is slightly higher than that for the Al\textsubscript{2}O\textsubscript{3} coated material.
- The diffusion coefficient decreases much more steeply with decreasing temperature for the uncoated material relative to the Al\textsubscript{2}O\textsubscript{3} material.
- Note PITT cannot distinguish between bulk Li\textsuperscript{+} diffusion and Li\textsuperscript{+} diffusion in a passive film.
## UTA- Deliverables - Comparison

<table>
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<tr>
<th>Characteristics</th>
<th>11 month (Al₂O₃-coated)</th>
<th>18 month (AlPO₄-coated)</th>
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<td>First Cycle Discharge capacity (C/20) -2V</td>
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<td>First Cycle Discharge capacity (C/20) -3V</td>
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<td>First cycle Irreversible capacity (mAh/g)</td>
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<td>0C discharge at C/10- to 3V</td>
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Surface-modified Sample from Hydroxide -25 month UTA results

- Both the AlPO_4- and GaPO_4-coated samples show higher capacities
- AlPO_4-coated sample shows high capacity with good cycle life
### UTA-25m Supplemental

#### Coin cell studies validate UT Austin reported results of improved performance

- Room temperature formation cycle specific discharge capacity to 2V = 300 mAh/g
- RT C/10 2V discharge capacity = 281 mAh/g; 3V cutoff = 242 mAh/g
- KPP (0°C C/10 3V cutoff) = 141 mAh/g; compare to UT Austin 23 month deliverable of 126 mAh/g

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</table>
• Tap density = 1.48 g/cm³ (Toda measurement)
  1.45 g/cm³ (JPL measurement)
• Ave. 1st cycle capacity to 2V = 236 mAh/g
• Ave 1st cycle capacity to 3V = 227 mAh/g
• Ave. 1st cycle irreversible capacity = 88 mAh/g
• C/10 capacity to 3V = 208 mAh/g
XRD of the JPL method vs Chemically-synthesized

- a) $\text{Li}_{1.17}\text{Mn}_{0.56}\text{Ni}_{0.135}\text{Co}_{0.135}\text{O}_2$ prepared by conventional carbonate synthesis route, and b) JPL method. Asterisks indicate reflections associated with Si standard.
Mechanical Method: $\text{Li}_{1.2}\text{Mn}_{0.4}\text{Co}_{0.08}\text{Ni}_{0.32}\text{O}_2$

- $\text{Li}_2\text{MnO}_3$ phase activated
- Voltage profile similar to the chemically-synthesized materials with plateau at 4.5 V plateau on first charge comparable discharge capacity
(Mechanical) $\text{Li}_{1.2}\text{Mn}_{0.4}\text{Co}_{0.08}\text{Ni}_{0.32}\text{O}_2$ coated with $\text{AlPO}_4$

<table>
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<th>Rate</th>
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<td>Uncoated: 242, 2 wt% $\text{AlPO}_4$ Coated: 261</td>
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<td>C/10</td>
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<td>C/10</td>
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<td>C/10</td>
<td>30</td>
<td>Uncoated: 231, 2 wt% $\text{AlPO}_4$ Coated: 236</td>
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</table>

- Performance improved upon coating with $\text{AlPO}_4$ and is comparable to UTA samples
Irreversible Capacity in the High-Voltage Cathodes

- Irreversible Capacity mechanism involving the simultaneous removal of Li and O from the solid.
- The voltage plateau at 4.5 V results from the electrochemical removal of Li$_2$O (lithium extraction and oxygen loss) from the Li$_2$MnO$_3$ component (Dahn et al)
- Evolution of oxygen was observed from mass spec, at potentials above 4.5 V (also 10% of gas being CO$_2$ from an oxidation of the electrolyte). (Bruce et al)
  - As oxygen is evolved from the surface, lithium ions migrate from the octahedral sites in the transition metal layers into the lithium layers leaving vacancies, which are subsequently occupied through a cooperative displacement of the transition metal ions diffusing from the surface into the bulk, until all the octahedral sites vacated by the lithium ions are occupied by transition metals, at which point oxygen evolution ceases.
- Question: Does the Li released correspond to the total capacity (reversible and irreversible)?
Irreversible Capacity in the High-Voltage Cathodes

• For designing the cells, it is required to have an understanding of the irreversible capacity in terms of Li content.
  • Cathode is the lithium source in a Li-ion cell and its reversible and irreversible capacities determine the amount of the anode
  • Anode consumes some lithium to form the SEI
  • After the formation cycling and completion of SEI formation, anode is generally in excess both geometrically and in reversible capacity, compared to cathode
• Preliminary studies by SAFT reveal that the irreversible capacity exceeds that estimated from Li analysis.
  • Is it due to part of the Li being utilized in the SEI formation?
• Studies against SEI-free anodes will be helpful
Note that the lithiation of MoS$_2$ from Li metal results in two plateaus. The transition between these plateaus (taken as 0.9V vs. Li/Li$^+$) occurs at an average of 250 mAh/g.
Note that the lithiation of MoS$_2$ from the Toda cathode results in two plateaus, but the transition between these plateaus (taken as 0.9V vs. Li/Li$^+$) occurs at 339 mAh/g anode basis.
Toda Cathode-Irreversible Capacity

Irreversible Capacity as a function of Charge Voltage

- Higher irreversible capacity from cathode - not in the form Li
Thermal Stability of layer-layer composite

\[ x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2 \]

• From the DSC measurements of charged composite shows the intermediate thermal stability in between LNCA and LNCM(111).

*Cf: SAFT presentation at the Space Power Workshop 2010*
DSC UTA - uncoated

Unrinsed

Rinsed

Measurements made at Contour Energy by Dr Arunkumar
• In general, the DMC rinsed cathodes exhibit a higher thermal breakdown temperature than the corresponding unrinsed cathodes.

*Measurements made at Contour Energy by Dr Arunkumar*
The thermal stability of the Al$_2$O$_3$ coated UTA cathodes is not improved compared to the corresponding uncoated cathodes.

*Measurements made at Contour Energy by Dr Arunkumar*
DSC of UTA - AIPO$_4$ coated

Measurements made at Contour Energy by Dr Arunkumar
DSC Observations

• In general un rinsed cathodes show thermal response at low temperatures (pre-peak or shoulder).

• Surface coating, especially, AlPO$_4$, seem to suppress the pre-peak from electrolyte, even without rinsing. Surface coating keeps the electrode free from electrolyte-oxidation species.

• In rinsed cathodes, the surface coating, either Al$_2$O$_3$ or AlPO$_4$ coating, appears to have only a minimal effect on the thermal stability.
Safe Electrolytes in Li-ion Batteries

• Retain the carbonate solvent mixture, add small but adequate amounts of FRAs (Flame Retardant Additives) to the electrolyte and assess their electrochemical compatibility.
  – Triethyl phosphate, triphenyl phosphate, tributyl phosphate, triphenyl phosphite, Tris(2,2,2-trifluoroethyl) phosphate, Bis-(2,2,2-trifluoroethyl) methyl phosphonate and Diethyl phenyl phosphonate.

• Add fluorinated co-solvents for the carbonates for reduced flammability
  – FEC and trifluoro ethylene carbonate

• Evaluate for different anode and cathode chemistries and modify their stability with additives, if required.
Development of Electrolytes Containing Flame Retardant Additives

Electrolytes and approaches investigated in NCA and NCO systems:

- 1.0M LiPF$_6$ EC+EMC+TPP (20:75:5 vol %)
- 1.0M LiPF$_6$ EC+EMC+TPP (20:70:10 vol %)
- 1.0M LiPF$_6$ EC+EMC+TPP (20:65:15 vol %)
- 1.0M LiPF$_6$ EC+EMC+DTFEC+TPP (20:50:20:10 vol %)
- 1.0M LiPF$_6$ EC+EMC+DTFEC+TPP (20:30:40:10 vol %)
- 1.0M LiPF$_6$ EC+EMC+TFEMC+TPP (20:50:20:10 vol %)
- 1.0M LiPF$_6$ FEC+EMC+TPP (20:70:10 vol %)
- 1.0M LiPF$_6$ FEC+EMC+TPP (20:65:15 vol %)
- 1.0M LiPF$_6$ FEC+EMC+TFEMC+TPP (20:50:20:10 vol %)
- 1.0M LiPF$_6$ FEC+EMC+TPP (20:75:5 vol %) + 1.5% VC
- 1.0M LiPF$_6$ EC+EMC+TPP (20:75:5 vol %) + 1.5% VC
- 1.0M LiPF$_6$ EC+EMC+TPP (20:65:15 vol %) + 1.5% VC
- 1.0M LiPF$_6$ FEC+EMC+TPP (20:65:15 vol %) + 1.5% VC

Where DTFEC = di-2,2,2-trifluoroethyl carbonate
TFEMC = 2,2,2-trifluoroethyl methyl carbonate
FEC = mono-fluoroethylene carbonate
TPP = triphenyl phosphate

Varying Concentration of TPP
Use of Fluorinated Linear Carbonates
Use of Fluorinated Ethylene Carbonate
Use of Additives (Vinylene Carbonate)

Flammability tests have been performed on select samples by Prof. Lucht at Univ. Rhode Island
FRAs in Prototype (Yardney 7 Ah) cells
100 % DOD Cycle Life Testing at Room Temperature

- Cells containing an electrolyte with a flame retardant additive (i.e., 1.0 M LiPF$_6$ in EC+EMC+TPP+VC) are observed to display good cycle life compared to the baseline formulation.
Cells which possess electrolytes with (a) higher TPP content (up to 15%), (b) the use of FEC in lieu of EC, and (c) the addition of 2,2,2-trifluoroethyl methyl carbonate (TFEMC). Initial results are very promising, suggesting good compatibility with the system.
Comparable performance was obtained with the JPL Gen #2 electrolytes (containing LiBOB) compared with the baseline solution.

There is no observed capacity (or voltage) benefit observed with charging to 4.80V.
Stability of Electrolytes at 5 V

- Carbonate blends show some stability towards high voltage cathodes. Are they good for > 1000 cycles?
- Low columbic efficiencies in general aren’t encouraging.
- Performance in half cells is often more encouraging than in full cells (due to abundant counter electrode)!
- Electrolyte systems needs to be tuned to the chemistry
The use of ester co-solvents to improve the conductivity of TPP electrolytes

The incorporation of TPP in conjunction with methyl butyrate or methyl propionate do not appear to dramatically impact the life characteristics of the cells. The use of ester co-solvents was employed to off-set the increase of viscosity associated with the addition of TPP.
In both cells, in terms of the lithium kinetics the cathode appears to be the limiting electrode as determined by Tafel polarization measurements.

However, due to decreased kinetics at the anode of the cell containing the JPL Gen II electrolyte, the difference between the anode and cathode lithium kinetics is less dramatic.
Electrolytes with Reduced Flammability


<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>SET, S</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0M (95% LiPF6+ 5% LiBOB) in EC/EMC/DMMP (3/5.5/1.5)</td>
<td>1.8</td>
<td>1.5</td>
</tr>
<tr>
<td>1.0M LiPF6 in EC/EMC/TPP (2/6.5/1.5)</td>
<td>3.78</td>
<td>1.2</td>
</tr>
<tr>
<td>1.0M LiPF6 in EC/EMC/TPP (2/7/1)</td>
<td>9.57</td>
<td>0.9</td>
</tr>
<tr>
<td>1.0M LiPF6 in EC/EMC/TPP (2/7.5/0.5)</td>
<td>22.45</td>
<td>2.3</td>
</tr>
<tr>
<td>1.0M LiPF6 in EC/EMC (3:7)</td>
<td>33.4</td>
<td>3.4</td>
</tr>
<tr>
<td>1.0M (95% LiPF6+ 5% LiBOB) in EC/EMC/DMMP (3/5/2)</td>
<td>0.4</td>
<td>0.4</td>
</tr>
</tbody>
</table>

- Electrolytes with other with higher amounts of TPP, and other FRAs and with fluorinated so-solvents are being developed.
Electrolyte with TPP flame retardant shows better thermal stability than the regular electrolyte.

Measurements made at Contour Energy by Dr Arunkumar
Summary and Conclusions

• High Energy Materials (Cathodes, anodes and high voltage and safe electrolyte are required to meet the needs of the future space missions.

  – Cathodes
    • The layered layered composites of Li$_2$MnO$_3$ and LiMO$_2$ are promising
    • Power capability of the materials, however requires further improvement.
    • Suitable morphology is critical for good performance and high tap (packing) density
    • Surface coatings help in the interfacial kinetics and stability.

  – Electrolytes
    • Small additions of Flame Retardant Additives improves flammability without affecting performance (Rate and cycle life).
    • 1.0 M in EC+EMC+TPP was shown to have good performance against the high voltage cathode; Performance demonstrated in large capacity prototype MCMB-LiNiCoO$_2$ Cells. Formulations with higher proportions are looking promising.
    • Still requires further validation through abuse tests (on 18650 cells).
Acknowledgments

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