Li-Ion Batteries for Space Applications
High Specific Energy and Wide-operating temperature


* UT Austin, ** U. So. Cal

LITHIUM MOBILE POWER 2006
The 2nd Conference on Advances in Lithium Battery Technologies for Mobile Applications: Lithium Ion and Lithium Polymer

December 4 - 6, 2006
Miami Beach, FL
Functions of Rechargeable Batteries in Space missions

• Rechargeable batteries are utilized to provide power
  – during launch and post-launch (until the deployment of solar panels in Inner planetary missions)
  – For firing pyros and firing rockets for attitude control,
  – To correct cruise anomalies or support trajectory control maneuvers of the spacecraft,
  – To the spacecraft, its equipment and payload during Sun eclipse periods,
  – For nighttime or eclipse-time experimentation,
  – For communicating and data transmission,
  – To keep the electronics warm and for
  – Load leveling (to augment nuclear power source)
Desired Characteristics of Space Batteries

- Reliability and Robustness
- Light weight and compact for reducing the launch costs and maximizing payload and science instruments
- Ability to operate under extreme temperatures
  - As low as -120°C for Mars and as high as 475°C for Venus
- Good cycle life, e.g. orbiter missions and satellites
- Long calendar life
- Tolerance to high intensity radiations,
  - For example, of ~ 4 MRad in Jupiter environments.
- Safety, especially in human exploration missions
  - Astronaut’s suit
  - Crew Exploration Vehicle
  - Planetary stations (Habitat)
Lithium-Ion Batteries for Space Applications

Li-Ion Battery- A Preferred Solution over SOA

- Significant enhancement in the mission with 4X improvement in mass and ~8X enhancement in volume compared Ni-Cd and Ni-H₂.
- Enables missions (Mars and Lunar) due to wide range of operating temperatures, especially at low temperatures down to -40°C.
- Excellent coulombic and energy efficiency (reduced radiator).
- No compromise on cycle life comparable to nickel systems
  - About 30,000 cycles demonstrated at partial DOD.
- Calendar life as good as with nickel systems
  - Over six years demonstrated in real-time tests.
- Tolerance to high intensity radiations,
  - Demonstrated to over 16 MRad cumulative radiation.
- Reduced maintenance (reconditioning)
  - No memory effect (low voltage plateau).
- Safety, especially in human exploration missions
  - Safety demonstrated in robotic missions, with charge control electronics, when needed.
Lithium-Ion Batteries for Space Applications

NASA’s Upcoming EXPLORATION SYSTEMS MISSIONS (to Moon Mars and Beyond)

**CEV (CM/SM)**
5-10 kWh Li-Ion battery

**CLV (125 ton)**
Li-Ion Batteries

**LSAM**
13.5 kWh Li-Ion battery

**EVA Suit**
Li-ion/Fuel cell
200 W for 7 h

**Rovers/Landers**
Li-Ion Batteries – 1-10 kWh
Fuel cells 10 kWh

**Lunar Habitat**
Surface Power Systems
30 kW Li-Ion /Fuel cell

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**CEV (CM and SM), CLV, LSAM, Lunar Orbiters, Rovers and Landers**
(Pressurized and unpressurized). Probes. Impactors, Astronaut tools
Habitat and Extra vehicular Activities
Lithium-Ion Batteries for Space Applications

JPL’s On-going Studies on Space-Rated Li-ion Batteries

• Overall Objective
  – To develop, together with NASA/GRC, advanced, space-rated lithium-ion and the next generation Li polymer batteries and demonstrate their performance capabilities and usefulness for future human and robotic exploration applications,

• Specific Aims/objectives:
  – To develop advanced components and materials, i.e., electrolytes, electrodes and cell components, for improving the performance and safety
    • Develop cathode with high specific energy (1000 Wh/kg) and improved thermal stability
    • Development of electrolytes with wide operating temperature range and increased non-flammability
    • Identification of life-limiting processes through Destructive Physical Analyses (DPA) of cells cycled/stored/irradiated.
  – Assessment of performance and safety of prototype Li-ion cells and batteries.
## Materials for Advanced Li-Ion Batteries

<table>
<thead>
<tr>
<th>Material</th>
<th>Cathodes Layered Mixed metal oxides</th>
<th>Composition</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>SOA</td>
<td></td>
<td>Li(Ni$<em>{0.8}$Co$</em>{0.2}$)O$_2$</td>
<td>Yardney electrodes</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Li(Ni$<em>{0.8}$Co$</em>{0.15}$Al$_{0.05}$)O$_2$</td>
<td>SAFT Electrodes, OMG powder</td>
</tr>
<tr>
<td>Gen 1</td>
<td></td>
<td>Li(Mn,Ni,Co,Li)O$_2$</td>
<td>Synthesized at JPL</td>
</tr>
<tr>
<td>Gen-2</td>
<td></td>
<td>Li(Ni$<em>{1/3}$Co$</em>{1/3}$Mn$_{1/3}$)O$_2$</td>
<td>UT Austin Powder, Electrodes from ANL and Enax, Max Power cells</td>
</tr>
<tr>
<td>Gen 3</td>
<td></td>
<td>Li(Mn,Ni,Co,Li)O$_2$</td>
<td>UT Austin Powder, Synthesized at JPL</td>
</tr>
</tbody>
</table>

Tested in coin cells or glass cylindrical (jelly roll) cells
SOA Li-Ion Cathodes Li/LiNi\textsubscript{x}Co\textsubscript{1-x}O\textsubscript{2} in Baseline Electrolyte Half Cell Results (400 mAh glass cylindrical cells)

Baseline Electrolyte = 1.00 M LiPF\textsubscript{6} EC+DEC+DMC (1:1:1 v/v %)

• ~70% Capacity at -20°C and 25% at -40°C with baseline electrolyte.
Lithium-Ion Batteries for Space Applications

**Generation-1 Cathode** \( \text{Li}(\text{Mn}_{0.61}\text{Li}_{0.21}\text{Ni}_{0.18})\text{O}_2 \)

Comparison of Standard OMG LiNiCoO\(_2\) with JPL-Fabricated Li[MnLiNi]O\(_2\) Cathode Material, Third Discharge

- Higher initial capacities (>200 mAh/g) at high charge voltages, but accompanied by faster capacity decay
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**Generation-2 Cathode** \( \text{Li}(\text{Mn}_{0.33}\text{Co}_{0.33}\text{Ni}_{0.33})\text{O}_2 \)

1/3, 1/3, 1/3 "Gen 2" layered cathode material from UT Austin, First Cycle Rate Capability Study

~0.021 g active material, 16 mm diameter active area
4.55 to 3 V Voltage Window

- Coin cells

- **180 mAh/g with Gen-2 Cathode at 25°C**
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High Specific Capacity Cathodes

Development Strategy (Manthiram, UT Austin)

- **Strategy**
  - Layered oxide compositions belonging to the series of solid solutions between layered Li[Li$_{1/3}$Mn$_{2/3}$]O$_2$ (commonly designated as Li$_2$MnO$_3$) and LiMnO$_2$ (M = Mn$_{0.5}$Ni$_{0.5}$) have been found to exhibit capacities as high as 250 mAh/g on cycling them to 4.8 V.

- **Problems**
  - Irreversible oxygen loss in the first charge, which decrease the oxidation state of Mn and Ni and thus enhances the discharge capacity subsequently.
  - Huge irreversible capacity loss (ICL) of 40 – 100 mAh/g in the first cycle, depending on the composition on charging to 4.8 V, attributed to a reaction of the cathode surface with the electrolyte, particularly with the high cutoff charge voltages of 4.8 V.

- **Solution**
  - Modify the cathode surface by coating with inert oxides and minimize the cathode-electrolyte interfacial reactions.
  - Examples: Al$_2$O$_3$, TiO$_2$, ZrO$_2$, MgO, and SnO$_2$
Comparison of the charge-discharge profiles (first 2 cycles) and cyclability of (a) unmodified and (b) modified layered Li(Li,Co,Ni,Mn)O₂ cathodes (sample 1).
### Lithium-Ion Batteries for Space Applications

**Gen-III Cathode Material (from UTA)**

<table>
<thead>
<tr>
<th>Composition</th>
<th>Surface modification</th>
<th>First charge capacity (mAh/g)</th>
<th>First discharge capacity (mAh/g)</th>
<th>Irreversible capacity loss, ICL (mAh/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li[Li$<em>{0.25}$Mn$</em>{0.57}$Ni$<em>{0.1}$Co$</em>{0.1}$]O$_2$</td>
<td>Unmodified</td>
<td>299</td>
<td>218</td>
<td>81</td>
</tr>
<tr>
<td></td>
<td>Al$_2$O$_3$ coated</td>
<td>295</td>
<td>246</td>
<td>49</td>
</tr>
<tr>
<td>Li[Li$<em>{0.2}$Mn$</em>{0.54}$Ni$<em>{0.13}$Co$</em>{0.13}$]O$_2$</td>
<td>Unmodified</td>
<td>328</td>
<td>253</td>
<td>75</td>
</tr>
<tr>
<td></td>
<td>Al$_2$O$_3$ coated</td>
<td>326</td>
<td>285</td>
<td>41</td>
</tr>
<tr>
<td>Li[Li$<em>{0.17}$Mn$</em>{0.5}$Ni$<em>{0.17}$Co$</em>{0.17}$]O$_2$</td>
<td>Unmodified</td>
<td>304</td>
<td>231</td>
<td>73</td>
</tr>
<tr>
<td></td>
<td>Al$_2$O$_3$ coated</td>
<td>301</td>
<td>258</td>
<td>43</td>
</tr>
<tr>
<td>Li[Li$<em>{0.12}$Mn$</em>{0.47}$Ni$<em>{0.2}$Co$</em>{0.2}$]O$_2$</td>
<td>Unmodified</td>
<td>290</td>
<td>227</td>
<td>63</td>
</tr>
<tr>
<td></td>
<td>Al$_2$O$_3$ coated</td>
<td>283</td>
<td>248</td>
<td>35</td>
</tr>
<tr>
<td>Li[Li$<em>{0.1}$Mn$</em>{0.43}$Ni$<em>{0.22}$Co$</em>{0.23}$]O$_2$</td>
<td>Unmodified</td>
<td>290</td>
<td>227</td>
<td>63</td>
</tr>
<tr>
<td></td>
<td>Al$_2$O$_3$ coated</td>
<td>288</td>
<td>250</td>
<td>38</td>
</tr>
<tr>
<td>Li[Li$<em>{0.17}$Mn$</em>{0.58}$Ni$_{0.25}$]O$_2$</td>
<td>Unmodified</td>
<td>309</td>
<td>249</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>Al$_2$O$_3$ coated</td>
<td>284</td>
<td>254</td>
<td>30</td>
</tr>
</tbody>
</table>

- Reduced irreversible capacity loss with surface coating of alumina
- High Reversible capacities.
Lithium-ion Batteries for Space Applications

Gen-III Cathode Material (from UTA)
Reversible capacity and reversibility (UT Austin)

Comparison of the cyclability data of (a) Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2, (b) Li[Li_{0.1}Mn_{0.43}Ni_{0.23}Co_{0.23}]O_2, and (c) Li[Li_{0.17}Mn_{0.58}Ni_{0.25}]O_2 at C/20 rate and 2.0 – 4.8 V before and after surface modification with Al_2O_3. The closed and open symbols refer to, respectively, discharge and charge capacities. Triangles and squares refer, respectively, to the unmodified and surface modified samples.
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Gen-III Cathode Material (JPL)

- \( \text{Li}(\text{Li}_{0.17}\text{Ni}_{0.25}\text{Mn}_{0.58})\text{O}_2 \) synthesized following the recipe reported in Y. J. Park et al., *J. Power Sources*, 129, 288 (2004).
- High Irreversible capacity of ~ 60 mAh/g, but reversible capacity is around 250 mAh/g.
  - About 210 mAh/g at C/5
- Detailed electrochemical measurements underway.
- Requires surface coating to mitigate high irrev. capacity and also improve intercalation kinetics
- Currently examining coatings of either ionic or electronic semiconductors for improved interfacial properties (rate, low temp. performance and cycle life)
Low Temperature Electrolytes

Cf: Publications of M. Smart et al

- **Mixed Solvents (multi-component) approach**
  - Ensure anode filming with sufficient EC and PC
  - Identify newer co-solvents,
    - Are liquid over a wide temperature range,
    - Have low viscosity (at low temperatures),
    - Good electrochemical stability,
    - Adequate interfacial stability,
  - Examples of co-solvents
    - carbonates (EMC, DEC),
    - High molecular weight esters, e.g., methyl propionate and ethyl butyrate
    - Low proportions of ethylene carbonate (EC).
- Electrolyte additives and new salts for high temperature resilience.
- Fluorination of solvents/co-solvents for reduced flammability
Lithium-ion Batteries for Space Applications

Materials for Advanced Li-Ion Batteries

<table>
<thead>
<tr>
<th>Material</th>
<th>Electrolytes</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>SOA</td>
<td>1.0 MLiPF$_6$ in 1:1:1 EC+DMC+DEC</td>
<td>JPL</td>
</tr>
<tr>
<td>Gen 1</td>
<td>1.0 MLiPF$_6$ in 1:1:1:3 EC+DMC+DEC+EMC</td>
<td>JPL</td>
</tr>
<tr>
<td>Gen-2</td>
<td>1.0 M LiPF$_6$ in EC+EMC with low-viscosity co-solvents and 2) 1:4 EC+EMC</td>
<td>JPL</td>
</tr>
</tbody>
</table>

Tested in coin cells or glass cylindrical (jelly roll) cells
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Generation -1 Electrolyte at -20°C
with Li/LiNi$_{x}$Co$_{1-x}$O$_{2}$ cathode Half Cell Results

- Similar performance at -20°C of Baseline Electrolyte: 1 M LiPF$_{6}$ EC+DEC+DMC (1:1:1 v/v %) and Gen I Electrolyte = 1 M LiPF$_{6}$ EC+DEC+DMC+EMC (1:1:1:3 v/v %)
Lithium-Ion Batteries for Space Applications
Generation -1 Electrolyte at -40°C
with Li/LiNi_{x}Co_{1-x}O_{2} cathode Half Cell Results

- Improved performance at -40°C compared to the baseline electrolyte
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Gen 2 Electrolytes at Low Temperatures

Evaluation of Electrolytes with Fluorinated co-solvents

- MCMB Carbon-LiNiCoO$_2$ Cells
  - 25 mA Discharge current to 2.00 V
  - Temp = -40°C

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Voltage (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0 M LiPF$_6$ EC+EMC (10:90 v/v %)</td>
<td>3.00</td>
</tr>
<tr>
<td>1.0 M LiPF$_6$ EC+EMC (20:80 v/v %)</td>
<td>2.90</td>
</tr>
<tr>
<td>1.0 M LiPF$_6$ EC+EMC+ FCS (20:60:20 v/v %)</td>
<td>2.80</td>
</tr>
<tr>
<td>1.0 M LiPF$_6$ EC+EMC+ FCS (20:40:40 v/v %)</td>
<td>2.70</td>
</tr>
<tr>
<td>1.0 M LiPF$_6$ EC+DEC+DMC+EMC (1:1:1:3)</td>
<td>2.60</td>
</tr>
</tbody>
</table>

- 25 mA Discharge to 2.00 V (~ C/14 Discharge Rate)
- Performance similar to Gen-1, but with the advantage of non-flammability
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**Generation 2 Cathodes in Low Temperature Electrolytes**

- **Electrodes:** Graphite-LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$
  
  Supplied by Argonne National Lab. (Courtesy of K.Amine)

- **Electrolytes:**
  - 1.0 M LiPF$_6$ EC+EMC (20:80 v/v %) – AN01
  - 1.2 M LiPF$_6$ EC+EMC (20:80 v/v %) – AN02
  - 1.2 M LiPF$_6$ EC+EMC (30:70 v/v %) (DOE Electrolyte) – AN03

- **Test Cells:** Glass cylindrical cells with o-ring seals and flooded electrolyte design
  Single-sided coated electrodes; 120-140 mAh Size
  Li metal reference electrodes

- **Performance:** Detailed electrochemical performance; Charge/discharge behavior at various rates and temperatures, especially at low temperatures; High temperature resilience (storage)

- **Electrochemistry:** Different types of techniques for understanding electrochemical behavior and determining electrochemical kinetics;
  - Electrochemical Impedance Spectroscopy (EIS)
  - DC Polarization Techniques: Micropolarization and Tafel Polarization
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Performance of Graphite-LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ Cells at 20°C
In Carbonate-Based Low Temperature Electrolytes

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Current (mA)</th>
<th>Rate</th>
<th>Capacity (Ah)</th>
<th>Percent (%)</th>
<th>Capacity (Ah)</th>
<th>Percent (%)</th>
<th>Capacity (Ah)</th>
<th>Percent (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20°C</td>
<td>25.00</td>
<td>0.20 C</td>
<td>0.13064</td>
<td>100.00</td>
<td>0.13220</td>
<td>100.00</td>
<td>0.12349</td>
<td>100.00</td>
</tr>
<tr>
<td></td>
<td>50.00</td>
<td>0.40 C</td>
<td>0.12529</td>
<td>95.90</td>
<td>0.12729</td>
<td>96.28</td>
<td>0.12086</td>
<td>97.87</td>
</tr>
<tr>
<td></td>
<td>100.00</td>
<td>0.80 C</td>
<td>0.11650</td>
<td>89.18</td>
<td>0.11963</td>
<td>90.49</td>
<td>0.11520</td>
<td>93.29</td>
</tr>
</tbody>
</table>

Better rate capability at 20°C with 1) Higher salt concentration and 2) Higher EC content.
Low temperature Performance of Graphite-LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ Cells 
In Carbonate-Based Low Temperature Electrolytes

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Current (mA)</th>
<th>Rate</th>
<th>Capacity (Ah)</th>
<th>Percent (%)</th>
<th>Capacity (Ah)</th>
<th>Percent (%)</th>
<th>Capacity (Ah)</th>
<th>Percent (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>23°C</td>
<td>25.00</td>
<td>C/5</td>
<td>0.13582</td>
<td>100.00</td>
<td>0.13911</td>
<td>100.00</td>
<td>0.12652</td>
<td>100.00</td>
</tr>
<tr>
<td>-40°C</td>
<td>6.25</td>
<td>C/20</td>
<td>0.08337</td>
<td>61.38</td>
<td>0.08163</td>
<td>58.68</td>
<td>0.08181</td>
<td>64.66</td>
</tr>
<tr>
<td></td>
<td>8.33</td>
<td>C/15</td>
<td>0.08172</td>
<td>60.17</td>
<td>0.08193</td>
<td>58.89</td>
<td>0.07946</td>
<td>62.80</td>
</tr>
<tr>
<td></td>
<td>12.50</td>
<td>C/10</td>
<td>0.07891</td>
<td>58.10</td>
<td>0.08029</td>
<td>57.72</td>
<td>0.07365</td>
<td>58.21</td>
</tr>
<tr>
<td></td>
<td>25.00</td>
<td>C/5</td>
<td>0.07089</td>
<td>52.19</td>
<td>0.07503</td>
<td>53.94</td>
<td>0.04636</td>
<td>36.64</td>
</tr>
<tr>
<td></td>
<td>41.67</td>
<td>C/3</td>
<td>0.03462</td>
<td>25.49</td>
<td>0.03609</td>
<td>25.94</td>
<td>0.01732</td>
<td>13.69</td>
</tr>
<tr>
<td></td>
<td>62.50</td>
<td>C</td>
<td>0.01394</td>
<td>10.26</td>
<td>0.01618</td>
<td>11.63</td>
<td>0.01110</td>
<td>8.77</td>
</tr>
<tr>
<td>-50°C</td>
<td>6.25</td>
<td>C/20</td>
<td>0.05091</td>
<td>37.48</td>
<td>0.05421</td>
<td>38.97</td>
<td>0.04468</td>
<td>35.31</td>
</tr>
<tr>
<td></td>
<td>8.33</td>
<td>C/15</td>
<td>0.03605</td>
<td>26.54</td>
<td>0.04065</td>
<td>29.22</td>
<td>0.03216</td>
<td>25.42</td>
</tr>
<tr>
<td></td>
<td>12.50</td>
<td>C/10</td>
<td>0.02613</td>
<td>19.24</td>
<td>0.03546</td>
<td>25.49</td>
<td>0.01651</td>
<td>13.05</td>
</tr>
<tr>
<td></td>
<td>25.00</td>
<td>C/5</td>
<td>0.01188</td>
<td>8.74</td>
<td>0.01325</td>
<td>9.53</td>
<td>0.00528</td>
<td>4.17</td>
</tr>
</tbody>
</table>

- Cells charged at room temperature (23°C, C/5 rate to 4.30V) prior to discharge.
- Higher capacities at -50°C with electrolyte with low EC proportion and low salt concentration.
EIS of Graphite-LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ Cells
In Carbonate-Based Low Temperature Electrolytes

- Impedance from EIS measurements of LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ cathode in 1) 1.0 M LiPF$_6$/EC:EMC (20:80), 2) 1.2 M LiPF$_6$/EC:EMC (20:80) and 3) 1.2 M LiPF$_6$/EC:EMC (30:70) electrolyte solutions as a function of temperature at A) 200 Hz, B) 1Hz and C) 50 mHz, respectively.
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Cathode Kinetics in the Three Different Electrolytes

Cathode Exchange Currents from Tafel

- Similar trend in the kinetics as the discharge performance
The anode kinetics also decrease with temperatures, but at the same rate in the three electrolytes.

Similar behavior observed in the kinetics from EIS and DC Micropolarization.
### Lithium-ion Batteries for Space Applications

**Comparison of SOA, Gen-1, Gen-2 and Gen-3 Materials**

#### Cathode Materials

<table>
<thead>
<tr>
<th>Cathode</th>
<th>Composition</th>
<th>Performance Summary</th>
</tr>
</thead>
</table>
| SOA           | Layered \( \text{Li(Ni}_{0.8}\text{Co}_{0.2})_2 \text{O}_2 \) | • ~165 mAh/g when charged to 4.1 V.  
• Low irreversible capacity (< 30 mAh/g) & Good Cycle life |
| Generation 1  | Layered \( \text{Li(Mn, Ni, Co, Li)}_2 \text{O}_2 \) | • > 200 mAh/g when charged to 4.6 V.  
• High irr. Cap. (> 30% mAh/g)? Rapid fade at high Voltage |
| Generation-2  | Layered \( \text{Li(Ni}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33})_2 \text{O}_2 \) | • > 180 mAh/g reversible capacity  
• 30 mAh/g of irrrev. capacity and good cyclability |
| Generation 3  | Layered \( \text{Li(Mn, Ni, Co, Li)}_2 \text{O}_2 \) | • > 240 mAh/g reversible capacity  
• 30 mAh/g of irrrev. capacity and good cyclability |

#### Electrolytes

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Composition</th>
<th>Performance Summary</th>
</tr>
</thead>
</table>
| SOA           | 1.0 MLiPF$_6$ in 1:1:1 EC+DMC+DEC  | • Good for -20°C. (70% capacity)  
• Good Cycle life and calendar life |
| Generation 1  | 1.0 MLiPF$_6$ in 1:1:1:3 EC+DMC+DEC+EMC | • Good for -40°C. (70% capacity)  
• Good Cycle life and calendar life |
| Generation-2 and Generation-3 | 1.0 MLiPF$_6$ in EC+EMC mixtures with fluorinated co-solvents | • Good for -40°C. (70% capacity)  
• Non flammability |
Prototype Cells with Advanced Cell Components
(Low Temperature Electrolytes)

• Prototype Li-ion cells from with advanced low temperature electrolytes.
  – Three different electrolytes:
    • 1.0 M LiPF$_6$ EC+DEC+DMC (1:1:1 v/v %)
    • 1.0 M LiPF$_6$ EC+DEC+DMC+ EMC (1:1:1:3 v/v %) and
    • 1.0 M LiPF$_6$ EC+ EMC (1:4 v/v %).
  – Fifteen cells were fabricated by Yardney (7Ah cell hardware)
  – Eight cells being tested at JPL and seven shipped to GRC.
  – Fifteen DD cells are being made at SAFT with similar electrolytes.
  – Discharge characterization of the Lithion cells over a wide temperature range.
    • Temperature Range = -70 to 20°C.
    • Range of Rate = C/100 to C Rate (Nameplate Capacity = 7Ah)
Discharge rate characterization tests at various discharge rates and temperatures:

- $20^\circ C = C, C/2, C/5, C/10, C/20, C/50, C/100$
- $0^\circ C = C, C/2, C/5, C/10, C/20, C/50, C/100$
- $-10^\circ C = C, C/2, C/5, C/10, C/20, C/50, C/100$
- $-20^\circ C = C, C/2, C/5, C/10, C/20, C/50, C/100$
- $-30^\circ C = C, C/2, C/5, C/10, C/20, C/50, C/100$
- $-40^\circ C = C, C/2, C/5, C/10, C/20, C/50, C/100$
- $-50^\circ C = C, C/2, C/5, C/10, C/20, C/50, C/100$
- $-60^\circ C = C/5, C/10, C/20, C/50, C/100$
- $-70^\circ C = C/50, C/100, C/150$
- $-80^\circ C = C/300$

- All cells charged at $20^\circ C$ prior to low temperature discharge
  - $C/5$ Charge current (1.40 A) to 4.1V,
  - 0.070 A Taper current cut-off (C/100)
- All cells allowed to soak at desired temperature for at least 8 hours
- Cells discharged to 2.0 V
Lithion/Yardney 7 Ah Lithium-Ion Cells for ESMD Applications

Summary of Discharge Rate Performance at Low Temperature

Baseline Electrolyte - MER Chemistry (1.0 M LiPF$_6$ in EC+DEC+DMC)

- 1.400 Amp Charge current (C/5) to 4.1 V
  Taper Cut-Off at 0.025 A (~ C/280)
  Cell charged at RT prior to LT discharge

- Lithion/Yardney 7 Ahr Li-Ion Cell
  MCMB Carbon-LiNiCo$_2$
  1.0 M LiPF$_6$ EC+DEC+DMC (1:1:1 v/v %)

- Capacity at -40 (C/2 Discharge Rate)
- Capacity at -40 (C/5 Discharge Rate)
- Capacity at -40 (C/10 Discharge Rate)
- Capacity at -40 (C/20 Discharge Rate)
- Capacity at -40 (C/50 Discharge Rate)

Cell LW242
Lithion/Yardney 7 Ah Li-Ion Cells With Advanced Electrolytes
Summary of Discharge Rate Performance at Low Temperature

Temperature = -40°C

![Discharge Capacity vs. Current Graph](image-url)
Lithion/Yardney 7 Ah Li-Ion Cells With Advanced Electrolytes

Summary of Discharge Rate Performance at Low Temperature

Temperature = -50°C

- Current (A)
- Discharge Capacity (Ah)
Lithion/Yardney 7 Ah Li-Ion Cells With Advanced Electrolytes

Summary of Discharge Rate Performance at Low Temperature

<table>
<thead>
<tr>
<th>Temperature</th>
<th>0.047</th>
<th>0.070</th>
<th>0.140</th>
<th>0.350</th>
<th>0.700</th>
<th>1.400</th>
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<tr>
<td>6.0000</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>5.0000</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>≈-60°C</td>
<td>-</td>
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Current (A)
Lithium-Ion Batteries for Space Applications

Life-Limiting Processes in Li-Ion Cells
Destructive Physical Analyses of Cells

• Goals:
  – Gain insight into battery cycle life degradation mechanisms
  – Examine the nature of the SEI formation in various electrolyte solvent/salt combinations

• Test vehicles
  – JPL Laboratory cells (3-electrode cells)
  – Prototype (Industrial) cells: 18650’s, larger cylindrical and prismatic

• Analytical methods to be used (as needed):
  – SEM for morphology
  – XEDS (with ion-beam sample sectioning to obtain SEI cross section detail)
  – TEM for microstructure
  – X-ray diffraction for composition, crystallinity and disorder
  – X-ray absorption spectroscopy (XANES, EXAFS) for
  – Raman backscattering
  – XPS
Lithium-Ion Batteries for Space Applications

Cells Subjected to Radiation Tests

- 18650 Li-Ion Cells from Sony with the following history.
  - SX091 – Cell exposed to a cumulative radiation level of 9 Mrad at low dose, followed by ~ 3,500 cycles (100% DOD).
  - SX042 – Blank cell for Low Rate Radiation Cell (Blank) subjected to ~ 3,500 cycles (100% DOD).
  - SX027 - High Rate Radiation Cell (16.5 MRad Total).
  - SX004 - High Rate Radiation Cell (Blank)
SONY 18650-Size (1.2 Ahr) Lithium-Ion Cells (ABSL)
Capacity Retention upon Irradiation (\(^{60}\)Co \(\gamma\)-rays)

Radiation Dosage (M Rads) vs. Discharge Capacity (AHR)

- SONY 18650-Size Lithium Ion Cells
  - 0.250 Amp Charge Current (C/5) to 4.1 V
  - 0.025 Amp taper current cut-off (C/50)
  - 0.250 Amp Discharge Current to 3.0 V
  - Temperature = 23°C

Discharge Curves:
- 25°C Discharge
- 0°C Discharge

Legend:
- SX 027 - Cell subjected to radiation
- SX 004 - Blank sample
- SX 027 - Cell subjected to radiation (at 0°C)
- SX 004 - Blank sample (at 0°C)

B. V. Ratnakumar et al. JECS 2006
Lithium-Ion Batteries for Space Applications

SONY 18650-Size (1.2 Ahr) Lithium-Ion Cells (AEA)
Post-radiation Cycling at 23°C

SONY 18650-Size Lithium Ion Cells

Unexposed Cell (Control)

Subjected to 10.5 MRad Low Rate Radiation

100% DOD Cycling

0.250 Amp Charge Current (C/5) to 4.1 V
0.025 Amp taper current cut-off (C/50)
0.250 Amp Discharge Current (C/5) to 3.0 V

Temperature = 23°C
- Coin cell made with extracted cathode was fully functional over multiple cycles
Sony 18650 – Radiation cells

Irradiated cycled cell: “MO91”

- Irradiated cell exhibited substantial discoloration on the anode and separator layers.

Non-irradiated, cycled cell: “H004”
Evidence of some SEI formation on cathode active particle surface
Cathode from Non-Irradiated (Control) cycled cell (H004)

Some SEI formation also on these cathode active material particles
Anode from Irradiated (Low Rate) cycled cell (MO91)

Significant, localized build-up of precipitate on anode particles
Precipitate accumulation is not as pronounced as for irradiated sample. Active graphite particles have clean surface or a very thin SEI.
Compositional Analyses of the Electrodes (From Irradiated and Control cells)

**Cathodes:**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mole Fraction (%)</th>
<th>F fraction</th>
<th>P fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>h004</td>
<td>2.014</td>
<td>70.594</td>
<td>20.376</td>
</tr>
<tr>
<td>MO91</td>
<td>3.083</td>
<td>64.1</td>
<td>25.49</td>
</tr>
</tbody>
</table>

**Anodes:**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mole Fraction (%)</th>
<th>F/P ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>h004</td>
<td>7.91</td>
<td>61.3178295</td>
</tr>
<tr>
<td>MO91</td>
<td>8.11</td>
<td>26.503268</td>
</tr>
</tbody>
</table>

- Irradiated sample had larger fractions of atomic species found in electrolyte.
- SEI growth more pronounced upon irradiation, especially on the anode surface.
Lithium-Ion Batteries for Space Applications

Summary

• Compared to the conventional Ni-Co oxides (with or without Al additions), the NMC (1/3:1/3:1/3) cathode provides marginal improvement in specific capacity. However, some of the formulations based on the solid solutions of layered Li$_2$MnO$_3$ and LiMO$_2$ (M = Mn$_{0.5}$Ni$_{0.5}$) have shown capacities as high as 250 mAh/g, combined with high cell voltages (4.5 V) and with the likelihood of enhanced thermal stability.

• Multi-component electrolytes with low EC-proportions and selected co-solvents provide significant improvement in the low temperature performance, down to -60°C, combined with the non-flammable attribute from the co-solvents.

• The NMC cathode shows good compatibility with the carbonate-based low temperature electrolytes. Impressive performances have been realized at low temperatures of ≤ -30°C.
  - Electrolytes with high salt concentration and high EC content fare well at room temperatures, while the formulations with low EC content and low salt concentration are preferred at low temperatures.

• DPA studies reveal increased SEI growth on the electrodes, especially anode, upon irradiation.

• Performance of low temperature electrolytes in prototype cells corroborate the findings from laboratory cells.
Acknowledgements

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