Wide Operating Temperature Range Electrolytes for High Voltage and High Specific Energy Li-ion Cells


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Outline

- Introduction
- Objective
- Background
- Approach and Methodology

- Ester-Based Electrolytes for LFP, NCO and NCA-Based Systems
- Graphite-Toda LiNiCoMnO₂ System
- Graphite-Toda HE-5050 LiNiCoMnO₂ (Argonne Developed) System
  - Low Temperature Discharge Characterization
  - Electrochemical Characterization (Tafel, EIS)
  - Cycle Life Performance

- Conclusions
Objectives and Approach

- Develop advanced Li-ion electrolytes that enable cell operation over a wide temperature range (i.e., -30 to +60°C).
- Improve the high temperature stability and lifetime characteristics of wide operating temperature electrolytes.
- Define the performance limitations at low and high temperature extremes, as well as, life limiting processes.
- Demonstrate the performance of advanced electrolytes in large capacity prototype cells.

Outline

- DOE desires Li-ion batteries that can operate over a wide temperature range (i.e., -30 to +60°C) and provide good life characteristics for HEV and PHEV applications.
- NASA also desires Li-ion batteries that can operate over a wide temperature range for future planetary lander and rover applications.
Why Battery Performance Degrades at Low Temperatures?

- Increased cell and electrode polarizations in general
  - Ohmic, kinetic as well as mass transfer
- Increased Ohmic polarization
  - Mainly contributed by the electrolyte
    - Reduced Ionic mobility in electrolyte.
      - Slow diffusion of ions mainly due to increased viscosity of solvent components
    - Reduced ionic strength due to lower solubility at low temperatures.
- Slower electrode kinetics
  - Slower charge transfer at the electrodes governed by Arrhenius dependence.
    - Charge-transfer over film-covered electrodes?
- Enhanced mass transfer polarization
  - Slow diffusion of (Li\(^+\)) ion in solution caused by increased electrolyte viscosity
  - Slower diffusion of reactant/product species in the electrode lattices (bulk diffusion).
    - Surface films complicating the charge transfer and diffusion process.
- Likelihood of lithium plating is possible at high charge rates at low temperatures
Low Temperature Lithium Ion Electrolytes
Electrolyte Development: Approach/Background
General Approaches to Improve Low Temperature Performance of SOA Electrolytes

- Optimization of linear carbonate type and concentration
- Optimization of cyclic carbonate concentration (i.e., EC content)
- Use of aggressive low viscosity co-solvents
- Optimization of electrolyte salt type and concentration
- Use of “SEI promoting” additives

- These approaches are often used in conjunction to achieve desired result.
- In addition, the specific application can influence low temperature electrolyte selection (i.e., low temperature requirement, life requirement, or the need for high temperature resilience, etc.).
Low Viscosity, Low Melting Electrolyte Co-Solvents
Candidate High Molecular Weight Ester-Based Co-Solvents

Properties of Ester Co-Solvents

<table>
<thead>
<tr>
<th>Chemical Structure</th>
<th>Name</th>
<th>m.p.</th>
<th>b.p.</th>
<th>Viscosity (25°C)</th>
<th>Density</th>
<th>Dielectric Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ethyl acetate</td>
<td>-84°C</td>
<td>77°C</td>
<td>0.331 cP</td>
<td>0.902</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Methyl propionate</td>
<td>-87.5°C</td>
<td>79.8°C</td>
<td>0.431 cP</td>
<td>0.915</td>
<td>6.200</td>
</tr>
<tr>
<td></td>
<td>Ethyl propionate</td>
<td>-73°C</td>
<td>99°C</td>
<td>0.541 cP</td>
<td>0.888</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Methyl butyrate</td>
<td>-85.8°C</td>
<td>102.8°C</td>
<td>0.639 cP</td>
<td>0.878</td>
<td>5.48</td>
</tr>
<tr>
<td></td>
<td>Ethyl butyrate</td>
<td>-93°C</td>
<td>120°C</td>
<td>0.639 cP</td>
<td>0.878</td>
<td>5.18</td>
</tr>
<tr>
<td></td>
<td>Propyl butyrate</td>
<td>-95.2°C</td>
<td>143°C</td>
<td>0.639 cP</td>
<td>0.878</td>
<td>4.3</td>
</tr>
<tr>
<td></td>
<td>Butyl butyrate</td>
<td>-91.5°C</td>
<td>164°C</td>
<td>0.639 cP</td>
<td>0.829</td>
<td></td>
</tr>
</tbody>
</table>

Ionic Conductivity of Ester Based Electrolytes

- 1.00M LiPF6 EC+EMC+MP (1:1:8)
- 1.00M LiPF6 EC+EMC+MB (1:1:8)
- 1.00M LiPF6 EC+EMC (1:9)
- 1.00M LiPF6 EC+EMC+EV (1:1:8)
- 1.00M LiPF6 EC+DEC+DMC+EMC (1:1:1:3)
- 1.00M LiPF6 EC+DEC+DMC (1:1:1)

- Gen I Baseline Solution
  (2003 MER Electrolyte)

- 2.66 mS/cm @ -60°C
- 0.02 mS/cm @ -60°C
A123 2.20 Ah High Power LFP-Based Lithium-Ion Cells
Discharge Rate Characterization Testing
Temperature = -30°C; Cells Discharged to 0.50V

The MB-based systems are capable of supporting greater than 11C discharge rates at -30°C, with over 90% of the room temperature capacity being delivered.

Whereas, negligible capacity delivered with the baseline system under similar conditions.

M. C. Smart, A. S. Gozdz, L. D. Whitcanack, and B. V. Ratnakumar,
220th ECS Meeting, Boston, MA, October 11, 2011.
Cells were demonstrated of supporting >11C discharge rates at -30°C, with over 90% of the room temperature capacity being delivered.

Impressive life characteristics were observed at 23°C, with ~5,000 cycles being demonstrated at 23°C (100% DOD cycling). The methyl butyrate-based electrolytes delivers comparable performance to the baseline electrolyte.

A123 2.20 Ah High Power LFP-Based Lithium-Ion Cells
High Temperature Cycling Performance

100 % DOD Cycle Life at 40-50°C

100 % DOD Cycle Life at 60°C

- Good life characteristics were observed at up to 50°C with the EC+EMC+MB+VC system, outperforming the baseline electrolyte with >2,500 cycles being demonstrated.
- Reasonable performance was obtained at 60°C, with cells possessing the EC+EMC+MB+VC formulation displaying increased degradation compared to the cells containing the baseline electrolyte (over 2,000 cycles being demonstrated).
In collaboration with Quallion, excellent low temperature rate capability has been demonstrated with advanced electrolytes.

Experimental lithium-ion cells (MCMB-LiNiCoO$_2$) fabricated with methyl butyrate–based electrolytes containing various additives.

- LiBOB and VC were observed to improve the low temperature performance.
- The benefit was determined to be due to improved kinetics at the cathode.

Experimental lithium-ion cells (MCMB-LiNiCoO$_2$) fabricated with methyl butyrate–based electrolytes containing various additives.

> Promising electrolyte additives were explored in a wide operating temperature range solvent systems (EC+EMC+MB) with the intent of improving high temperature resilience.
> Some additives have the beneficial effect of improving the lithium kinetics through the formation of desirable SEI layers on both electrodes.
> LiBOB and VC were observed to improve the kinetics at the cathode, whereas FEC appears to improve the kinetics at the anode.

Experimental Graphite-LiNi\textsubscript{1/3}Co\textsubscript{1/3}Mn\textsubscript{1/3}O\textsubscript{2} Cells
Argonne National Lab. Electrodes (K. Amine)
Discharge Characteristics

M. C. Smart, B. V. Ratnakumar, and K. Amine, 218\textsuperscript{th} ECS Meeting, Las Vegas, NV, Oct. 2010.
A number of electrolytes with flame retardant additives have been developed for high voltage NMC based cathodes under a NASA-funded program.

A number of triphenyl phosphate (TPP)-based electrolytes have been shown to work effectively with NCO and NCA systems, however, poor performance was observed when coupled with high voltage NMC based cathode.

The use of LiBOB as an electrode additive dramatically improved the compatibility of these systems, allowing the use of 15% TPP, and outperforming the baseline solutions.

For wide operating temperature range electrolytes, the use of LiBOB was anticipated to provide effective stabilization of the cathode interface, allowing the use of low viscosity, low melting co-solvents, such as methyl butyrate.
Electrolytes with Improved Safety for the MPG-111-Toda System
Comparison of Electrolyte Types (After Formation)

The use of LiBOB dramatically improved the compatibility of TPP-containing electrolytes when coupled with high voltage NMC cathodes.

Formation Characteristics of MPG-111-Toda Experimental Cells

Discharge Capacity

- Nearly identical reversible capacity was obtained with both electrolyte types.
- The discharge voltage profiles are very similar also.

**Cell TM01**
Baseline Electrolyte

<table>
<thead>
<tr>
<th>Cycle #</th>
<th>Charge (Ah)</th>
<th>Discharge Capacity (Ah)</th>
<th>Irreversible Capacity (Ah)</th>
<th>Efficiency (%)</th>
<th>Reversible Capacity (mAh/g)</th>
<th>Irreversible Capacity (mAh/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.28674</td>
<td>0.20135</td>
<td>0.085</td>
<td>70.22</td>
<td>162.38</td>
<td>68.86</td>
</tr>
<tr>
<td>2</td>
<td>0.25745</td>
<td>0.23368</td>
<td>0.024</td>
<td>90.77</td>
<td>188.45</td>
<td>19.17</td>
</tr>
<tr>
<td>3</td>
<td>0.25257</td>
<td>0.24971</td>
<td>0.003</td>
<td>98.86</td>
<td>201.38</td>
<td>2.31</td>
</tr>
</tbody>
</table>

Cumulative Irreversible Capacity Loss = 0.1120 Ah
Cumulative Irreversible Capacity Loss = 90.34 mAh/g

**Cell TM02**
JPL Generation II Electrolyte

<table>
<thead>
<tr>
<th>Cycle #</th>
<th>Charge (Ah)</th>
<th>Discharge Capacity (Ah)</th>
<th>Irreversible Capacity (Ah)</th>
<th>Efficiency (%)</th>
<th>Reversible Capacity (mAh/g)</th>
<th>Irreversible Capacity (mAh/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.24729</td>
<td>0.17637</td>
<td>0.071</td>
<td>71.32</td>
<td>142.35</td>
<td>57.19</td>
</tr>
<tr>
<td>2</td>
<td>0.26617</td>
<td>0.22849</td>
<td>0.038</td>
<td>85.84</td>
<td>184.41</td>
<td>30.39</td>
</tr>
<tr>
<td>3</td>
<td>0.25655</td>
<td>0.24780</td>
<td>0.009</td>
<td>96.59</td>
<td>200.00</td>
<td>7.06</td>
</tr>
</tbody>
</table>

Cumulative Irreversible Capacity Loss = 0.11735 Ah
Cumulative Irreversible Capacity Loss = 94.64 mAh/g
The MB-based electrolyte displays improved rate capability at low temperature compared to an all carbonate-based formulation.

Electrochemical measurements suggest that the cathode kinetics is dominating the poor rate capability at low temperature rather than electrolyte type.

Improved low temperature rate capability will most likely be achieved with lower loading cathode (resulting in diminished specific energy of the cell).
TPP-Based Electrolytes Evaluated in the MPG-111-Toda System
Cycle Life Characteristics at Room Temperature

- The use of esters and TPP does not significantly affect the cycle life performance compared with a baseline formulation with LiBOB. Capacity fade is less dramatic if discharging down to 2.0V.
A number of methyl butyrate-based electrolytes have been evaluated in the high voltage system involving the LLC-NMC (received from Argonne) and compared with a baseline NCA system. The MB-based formulations containing LiBOB delivered the best rate capability at low temperature, which is attributed to improved cathode kinetics. Whereas, the use of lithium oxalate as an additive lead to the highest reversible capacity and lower irreversible losses. At lower temperature and higher rates, the advantages of utilizing the high voltage system diminishes, again attributed to the relative cathode kinetics.
## Characterization of Three Electrode Conoco Graphite/Toda HE5050 LiNiCoMnO₂ Cells

<table>
<thead>
<tr>
<th>Electrolyte Type</th>
<th>1.0M LiPF₆ + 0.10M LiBOB EC+EMC+MB (20:20:60 vol%)</th>
<th>1.0M LiPF₆ EC+EMC+MB (20:20:60 vol%) + 1.5% VC</th>
<th>1.0M LiPF₆ EC+EMC+MB (20:20:60) + lithium oxalate</th>
<th>1.2M LiPF₆ EC+EMC (30:70 vol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Temperature</strong></td>
<td><strong>Current (mA)</strong></td>
<td><strong>Capacity (Ahr)</strong></td>
<td><strong>Capacity (mAh/g)</strong></td>
<td><strong>Percent (%)</strong></td>
</tr>
<tr>
<td>23°C</td>
<td>C/20</td>
<td>0.1100 243.87 100.00</td>
<td>0.1018 224.33 100.00</td>
<td>0.1168 257.10 100.00</td>
</tr>
<tr>
<td></td>
<td>C/10</td>
<td>0.1059 234.95 96.34</td>
<td>0.1001 220.53 98.31</td>
<td>0.1130 248.60 96.69</td>
</tr>
<tr>
<td></td>
<td>C/5</td>
<td>0.0973 215.91 88.54</td>
<td>0.0947 208.66 93.01</td>
<td>0.1039 228.57 88.90</td>
</tr>
<tr>
<td></td>
<td>C/2</td>
<td>0.0843 186.92 76.65</td>
<td>0.0840 185.03 82.48</td>
<td>0.0900 197.97 77.00</td>
</tr>
<tr>
<td>10°C</td>
<td>C/20</td>
<td>0.0972 215.59 88.40</td>
<td>0.0829 182.73 81.45</td>
<td>0.0974 214.33 83.37</td>
</tr>
<tr>
<td></td>
<td>C/10</td>
<td>0.0911 201.99 82.82</td>
<td>0.0798 175.82 78.37</td>
<td>0.0894 196.81 76.55</td>
</tr>
<tr>
<td></td>
<td>C/5</td>
<td>0.0798 177.06 72.60</td>
<td>0.0717 158.05 70.46</td>
<td>0.0798 175.55 68.28</td>
</tr>
<tr>
<td></td>
<td>C/2</td>
<td>0.0636 141.14 57.88</td>
<td>0.0526 116.01 51.71</td>
<td>0.0585 128.72 50.07</td>
</tr>
<tr>
<td></td>
<td>C/2</td>
<td>0.0642 142.39 58.39</td>
<td>0.0500 110.25 49.15</td>
<td>0.0567 124.85 48.56</td>
</tr>
<tr>
<td>0°C</td>
<td>C/20</td>
<td>0.0848 187.98 77.08</td>
<td>0.0668 147.14 65.59</td>
<td>0.0808 177.86 69.18</td>
</tr>
<tr>
<td></td>
<td>C/10</td>
<td>0.0745 165.15 67.72</td>
<td>0.0559 123.14 54.89</td>
<td>0.0670 147.33 57.30</td>
</tr>
<tr>
<td></td>
<td>C/5</td>
<td>0.0646 143.21 58.72</td>
<td>0.0467 102.91 45.88</td>
<td>0.0559 123.02 47.85</td>
</tr>
<tr>
<td></td>
<td>C/2</td>
<td>0.0491 108.92 44.66</td>
<td>0.0235 51.71 23.05</td>
<td>0.0334 73.53 26.80</td>
</tr>
</tbody>
</table>

- **A The MB-based formulations containing LiBOB delivered the best rate capability at low temperature, which is attributed to improved cathode kinetics. Whereas, the use of lithium oxalate as an additive lead to the highest reversible capacity and lower irreversible losses.**
- **At lower temperature and higher rates, the advantages of utilizing the high voltage system diminishes, again attributed to the relative cathode kinetics.**
Of the electrolytes evaluated, the MB-based system with LiBOB consistently displayed the best low temperature performance, which is attributed to (i) improved kinetics at the cathode and to a lesser extent (ii) improved ionic conductivity of the electrolyte at low temperature.
When Tafel polarization measurements were performed each electrode (using 3-electrode cells), both the NCA and NMC electrodes displayed poorer lithium kinetics compared to the anode.

Of the different cathodes, the LLC-NMC electrodes (received from Argonne) displayed much lower lithium de-intercalation kinetics compared to the NCA electrodes (attributed to poor charge transfer resistance of the electrodes), which is exacerbated at lower temperatures.

Of the electrolytes evaluated, the MB-based system with LiBOB displayed the best cathode kinetics.
When EIS measurements were performed each electrode (using 3-electrode cells), both the NCA and NMC electrodes dominated the cell impedance. Of the different cathodes, the LLC-NMC electrodes (received from Argonne) displayed a more dramatic charge transfer resistance, which is exacerbated at lower temperatures.
The discharge rate capability and cycle life performance of a number of cells containing methyl butyrate-based electrolytes was also evaluated at 23°C in coin cells.

The presence of LiBOB in the methyl butyrate-based systems was observed to improve the cycle life characteristics.

An electrolyte with low flammability containing triphenyl phosphate, was observed to provide improved cycle life performance compared to the baseline.
SUMMARY and CONCLUSIONS

- **Wide Operating Temperature Electrolytes Demonstrated in Conoco Graphite/ Toda HE5050 LiNiCoMnO₂ Cells**
  - A number of methyl butyrate-based electrolytes have been evaluated in the high voltage LLC-NMC system and compared with a baseline NCA system.
  - All MB-based solution outperformed the baseline electrolyte.
  - The MB-based formulations containing LiBOB delivered the best rate capability at low temperature, which is attributed to improved cathode kinetics.
  - The use of lithium oxalate as an additive lead to the highest reversible capacity and lower irreversible losses.
  - At lower temperature and higher rates, the advantages of utilizing the high voltage system diminishes, again attributed to the relative cathode kinetics.

- **Electrochemical Characterization of Conoco Graphite/ Toda HE5050 LiNiCoMnO₂ Cells**
  - When Tafel polarization measurements were performed each electrode (using 3-electrode cells), both the NCA and NMC electrodes displayed poorer lithium kinetics compared to the anode.
  - Of the different cathodes, the LLC-NMC electrodes (received from Argonne) displayed much lower lithium de-intercalation kinetics compared to the NCA electrodes (attributed to poor charge transfer resistance of the electrodes), which is exacerbated at lower temperatures.
  - Of the electrolytes evaluated, the MB-based system with LiBOB displayed the best cathode kinetics.
Acknowledgments

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