Improved Wide Operating Temperature Range of High Rate Nano-Lithium Iron Phosphate Li-Ion Cells with Methyl Butyrate-Based Electrolytes

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Outline

• Objectives and Approach
• Introduction
  • Performance of COTS A123 LiFePO$_4$-Based Li-Ion Cells
    • 100% DOD Cycle Life Performance
    • Partial DOD LEO Cycle Life Performance
    • Discharge Rate Capability at Different Temperatures
  • A123 LiFePO$_4$-Based Li-Ion Cells with JPL Electrolytes
    • Discharge Rate Capability at Low Temperatures
    • Cycle Life Performance at Room Temperature
    • Cycle Life Performance at High Temperatures (up to 60°C)
    • Variable Temperature Cycling
    • Charge Characteristics at Low Temperatures
• Conclusions
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Objectives and Approach

- Develop advanced Li-ion electrolytes that enable cell operation over a wide temperature range \((i.e., -30 \text{ to } +60^\circ C)\) and provide good life characteristics for HEV and PHEV applications.
- 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 \((i.e., -30 \text{ to } +60^\circ C)\) 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 Temperature Lithium Ion Electrolytes**

**Background: Use of Ester-Based Solvents**

- **Ohta, and coworkers (Matsushita):** have investigated the use of MA-, EP-, and MP-based systems (i.e., EC+DEC+MP)
  

- **At JPL, we have previously studied coworkers have studied MF-, EA-, MA-, EP-, and EB-based systems:**
  
  
  
  

- **Herreyre and coworkers have studied EA- and MB-based systems (SAFT):**
  

- **Shiao and coworkers have studied EA- and MA-based systems (Maxpower):**
  

- **Sazhin and coworkers have studied EP- and MA-based systems (Samsung):**
  

- **Jow and coworkers have studied EA- and GBL-based systems (Army Res. Lab.):**
  
## 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>D dissociation constant</th>
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<td>CH₃C(O)OCH₂CH₂CH₃</td>
<td>Methyl butyrate</td>
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</table>

## Ionic Conductivity of Ester Based Electrolytes

- **Gen I Baseline Solution (2003 MER Electrolyte)**: 0.02 mS/cm @ -60°C
- **2.66 mS/cm @ -60°C**
A123 2.20Ah High Power COTS Lithium-Ion Cells

100 % DOD Cycle Life Performance at 23°C

Discharge Capacity (Ah)

Discharge Energy (Wh/Kg)

- Excellent life characteristics have been displayed thus far, even when using aggressive rates (i.e., 3C charge and discharge).
- Over 90% of original capacity displayed after > 2,000 full discharge cycles.
A123 2.20 Ah High Power Lithium-Ion Cells
Low Earth Orbit (LEO) Cycle Life Performance

Watt-Hour Efficiency (%)

End of Discharge Voltage (EODV)

Capacity Loss During Cycling

- Excellent performance observed to-date, even when aggressive DOD’s are employed (i.e., up to 50 % DOD)
- Data represents over 4 years of cycling
A123 2.20 Ah High Power Lithium-Ion Cells
Discharge Rate Performance of COTS Cells

- Low voltage loss and capacity decrease even at high rates of > 6C indicative of high power capability
- Encouraging low temperature performance capability (cell charged at -20°C)

One intent is to improve the low temperature performance, while still preserving the excellent high temperature stability.
A123 2.20 Ah High Power Lithium-Ion Cells
Discharge Rate Characterization Testing at -30°C

Discharge Capacity (Ah)  
Discharge Energy (Wh/Kg)

- 1.4M LiPF₆ in EC+EMC+MB (10:10:80)
- Cell both charged and discharge at -30°C

Cells obtained from A123 Systems contains promising JPL developed electrolytes, namely

1.2M LiPF$_6$ in EC+EMC+MB (20:20:60 vol %) + 4% FEC and

1.2M LiPF$_6$ in EC+EMC+MB (20:20:60 vol %) + 2% VC

A123 Systems is actively developing Li-ion batteries for automotive applications

Currently testing technology over a wide range of conditions (i.e., -60 to +60°C).
# A123 LiFePO4-Based Lithium-Ion Cells

## Results of Initial Characterization

<table>
<thead>
<tr>
<th>Cell Series</th>
<th>Cell ID</th>
<th>Cell Weight (Grams)</th>
<th>Cell Weight (kg)</th>
<th>Initial Voltage</th>
<th>Initial Capacity (Ah)</th>
<th>Initial Watt-Hours</th>
<th>Initial Wh/kg</th>
<th>Calculated Impedance (mOhms) (10% SOC)</th>
<th>Calculated Impedance (mOhms) (50% SOC)</th>
<th>Calculated Impedance (mOhms) (80% SOC)</th>
<th>Calculated Impedance (mOhms) (90% SOC)</th>
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| Average     |        | 72.63               | 0.07              | 3.35            | 2.30                  | 7.46              | 102.86        | 17.16                                   | 17.75                                   | 17.90                                   | 18.27                                   | 18.74                                   |

**Baseline Electrolyte**

- 1.2M LiPF₆ in EC+EMC+MB (20:20:60 vol %) + 2% VC
- 1.2M LiPF₆ in EC+EMC+MB (20:20:60 vol %) + 4% FEC
A123 2.20 Ah High Power Lithium-Ion Cells
Discharge Rate Characterization Testing
Temperature Range - 20 to - 50°C; Cells Discharged to 0.50V

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Rate</th>
<th>Current (A)</th>
<th>ACC-05</th>
<th>AVC-05</th>
<th>AFC-05</th>
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<td>C/5</td>
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</table>

**BASELINE Electrolyte**
1.2M LIPF6 in EC+EMC+MB
(20:20:60 v/v %) + 2% VC

**1.2M LIPF6 in EC+EMC+MB**
(20:20:60 v/v %) + 4% FEC

Energy (Wh/kg)
Energy (Wh/kg)
The MB-based systems are capable of supporting greater than 11C discharge rates at -20°C, with over 90% of the room temperature capacity being delivered. Whereas, only moderate rates can be support with baseline system under similar conditions.
A123 2.20 Ah High Power 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.
A123 2.20 Ah High Power Lithium-Ion Cells
Discharge Rate Characterization Testing
Temperature = -40°C; Cells Discharged to 0.50V
Discharge Rate Characterization Testing: Cell Discharged to 0.50V

**Discharge Capacity vs. Temperature (C/5 Discharge Rate)**

The MB-based containing FEC was observed to deliver good performance down to -60°C, being able to support high discharge rates.
A123 2.20 Ah High Power Lithium-Ion Cells
Discharge Rate Characterization Testing
Temperature = -60°C; Rate = C/5; Cells Discharged to 0.50V
A123 2.20 Ah High Power Lithium-Ion Cells
100% DOD Cycle Life Characterization Testing at 23°C
Test Articles (Three Different Electrolyte Variations)

Discharge Capacity (Ah)

Watt-Hour Efficiency (%)

- Although modestly higher capacity fade rates were observed with the MB-based electrolytes compared with the baseline, generally good cycle life characteristics were observed (i.e., over 90% of the initial capacity after 2,000 cycles).
- Observed trend (in increasing capacity fade rate): Baseline < MB+VC < MB+FEC
A123 2.20 Ah High Power Lithium-Ion Cells

100% DOD Cycle Life Characterization Testing at 40 and 50°C

Test Articles (Three Different Electrolyte Variations)

Cycling at High Temperature

Variable Temperature Cycling

- Generally good resilience to high temperature cycling observed with the MB+VC and MB+FEC systems.
- Good resilience to low temperature charging also observed (no apparent lithium plating).

Testing involves alternating between performing 20 cycles at -20°C (using C/10 charge and C/5 discharge) and performing 20 cycles at 40°C (using C/5 charge and C/5 discharge).
A123 2.20 Ah High Power Lithium-Ion Cells

100% DOD Cycle Life Characterization Testing at 40 and 50°C

Test Articles (Three Different Electrolyte Variations)

Discharge Capacity at 60°C

- Good performance has been demonstrated thus far when cycling continuously at +60°C
- SOA aerospace cells do not operate well at such temperatures without rapid capacity fade with the possibility of venting.

Percent of Initial Capacity at 60°C
SUMMARY and CONCLUSIONS

• **Performance of COTS A123 Li-ion Cells**
  - Excellent cycle life performance has been obtained to-date under a number of conditions (i.e., 100% DOD life at various temperatures and LEO cycling using different DODs)
    - Over 7,000 cycles demonstrated with a 100% DOD cycle life test using 2C rates
    - Excellent, stable LEO cycle life performance exhibited thus far.
  - Excellent rate capability demonstrated at the cell and battery level

• **Performance of A123 Cells Containing Low Temperature Electrolytes**
  - Demonstrated good cycle life and improved low temperature of A123 Systems LiFePO₄-based cells using methyl butyrate-based electrolytes:
    - 1.2M LiPF₆ EC+EMC+MB (20:20:60) + 4% FEC
    - 1.2M LiPF₆ EC+EMC+MB (20:20:60) + 2% VC
  - Demonstrated operational capability over a wide temperature range (-60° to +60°C)
  - Systems are capable of supporting >11C discharge rates at -30°C, with over 90% of the room temperature capacity being delivered.
  - The cells were observed to perform well down to -60°C, with 80% of the room temperature capacity being delivered using a C/10 rate.
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