Lithium Batteries and Supercapacitors Capable of Operating at Low Temperatures for Planetary Exploration

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Outline

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• Challenges of Low Temperature Operation
• Low Temperature Rechargeable Li-ion Batteries
  • Summary of Electrolyte Development
  • LiFePO$_4$-Based Systems (A123 Systems)
  • LiNiCoAlO$_2$-Based Systems (Quallion, LCC)
• Low Temperature Lithium Primary Batteries
• Low Temperature Supercapacitors
• Conclusions
• Future Development
Low Temperature Li-Ion Batteries

- NASA desires Li-ion batteries that can operate over a wide temperature range for future planetary lander and rover applications (i.e., -60 to +30°C).
- 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.

Objectives and Approach

- Develop advanced Li-ion electrolytes that enable cell operation over a wide temperature range (i.e., -60 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.
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, due to the of non-aqueous electrolyte solutions.
  - Some of the recent electrolyte formulations extend this range to -60°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. Human-rated safety yet to be demonstrated.
Why Battery Performance Degrades at Low Temperatures?

- Increased cell 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 \((\text{Li}^+)\) 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 process.
Rechargeable Lithium-Ion Batteries
The Challenges of Operating at Very Low Temperatures

- **Low Operating Cell Potentials**
  - High cell impedance leading to severe polarization

- **Poor Discharge Rate Capability**
  - High cell impedance
  - Sluggish electrode kinetics
  - Low electrolyte conductivity

- **Poor Charge Capability**
  - Inability to fully charge the battery, even at low rates.
  - Possibility of lithium plating on anode, rather than intercalating
  - Sustained lithium plating leads to life limiting degradation

- **Potentially Poor Life Characteristics**
  - Aggressive low temperature electrolytes often degrade at high temperature
  - Reaction of plating lithium can lead to impedance growth
  - However, if the battery is managed properly, the low temperature operation can be beneficial to long life.
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

<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>
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<tr>
<td><img src="image" alt="Ethyl acetate" /></td>
<td>Ethyl acetate</td>
<td>-84°C</td>
<td>77°C</td>
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<td>0.902</td>
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<td><img src="image" alt="Methyl propionate" /></td>
<td>Methyl propionate</td>
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<td>79.8°C</td>
<td>0.431 cP</td>
<td>0.915</td>
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<td>99°C</td>
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<td>0.888</td>
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<td><img src="image" alt="Methyl butyrate" /></td>
<td>Methyl butyrate</td>
<td>-85.8°C</td>
<td>102.8°C</td>
<td>0.541 cP</td>
<td>0.898</td>
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<td><img src="image" alt="Ethyl butyrate" /></td>
<td>Ethyl butyrate</td>
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<td>120°C</td>
<td>0.639 cP</td>
<td>0.878</td>
<td>5.18</td>
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<td><img src="image" alt="Propyl butyrate" /></td>
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<td>164°C</td>
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<td>0.829</td>
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</table>
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 LiPF$_6$ in EC+EMC+MB (10:10:80)
- Cell both charged and discharge at -30°C
- The use the low viscosity, low melting ester co-solvent methyl butyrate results in high electrolyte conductivity at low temperatures.
A123 2.20 Ah High Power Lithium-Ion Cells
Discharge Rate Characterization Testing at -60°C

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Rate</th>
<th>AJ102</th>
<th>AJ103</th>
<th>AJ232</th>
<th>AJ233</th>
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<tr>
<td>20°C (Initial)</td>
<td>C/5</td>
<td>0.400</td>
<td>2.3217</td>
<td>7.5530</td>
<td>107.00</td>
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<td>-60°C</td>
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<td>0.0898</td>
<td>0.1910</td>
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<td>-60°C</td>
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<td>-60°C</td>
<td>C/10</td>
<td>0.220</td>
<td>1.4242</td>
<td>3.3823</td>
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<td>-60°C</td>
<td>C/20</td>
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<td>1.6361</td>
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<td>C/50</td>
<td>0.044</td>
<td>1.8093</td>
<td>4.6657</td>
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<td>-60°C</td>
<td>C/100</td>
<td>0.022</td>
<td>2.0490</td>
<td>5.5459</td>
<td>78.56</td>
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</table>

- Electrolyte = 1.4M LiPF₆ in EC+EMC+MB (10:10:80)
- Over 50Wh/kg can be delivered at -60°C using a C/20 discharge rate and over 47Wh/kg with at C/10 rate.

However, there is a further desire to improve the high temperature life characteristics.
A123 LiFePO₄-Based Lithium-Ion Cells

Results of Initial Characterization

- Cells obtained from A123 Systems contain promising JPL developed electrolytes, namely:
  - 1.2M LiPF₆ in EC+EMC+MB (20:20:60 vol %) + 4% FEC
  - 1.2M LiPF₆ 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).
- The use of electrolyte additive intended to improve the high temperature life characteristics.
A123 2.20 Ah High Power Lithium-Ion Cells
Discharge Rate Characterization Testing
Temperature = -30°C; Cells Discharged to 0.50V

Baseline Electrolyte

- 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 = -60°C; Rate = C/5; Cells Discharged to 0.50V
In collaboration with Quallion (NASA SBIR Program), excellent low temperature rate capability has been demonstrated with advanced electrolytes.

In collaboration with Quallion (NASA SBIR Program), excellent low temperature rate capability has been demonstrated with advanced electrolytes.

Methyl propionate-based electrolyte was previously demonstrated to have dramatically improved rate capability compared to the baseline DOE formulation (i.e., 1.2M LiPF$_6$ in EC+EMC (30:70) in 0.25 Ah cells.

Performance successfully demonstrated in larger capacity prismatic 12 Ah cells.

Quallion collaboration supported by NASA SBIR Program.
(H. Tsakamoto, M. Tomcsi, M. Nagata, and V. Visco)
Methyl propionate-based electrolyte demonstrated to have good performance down to -60°C, whereas the baseline electrolyte displays negligible capacity under these conditions.

Currently performing life tests (~50% DOD) in which the capacity, impedance, and rate capability at low temperature will be periodically measured.

It is anticipated that the addition of FEC will improve the life characteristics.

Quallion collaboration supported by NASA SBIR Program.
(H. Tsakamoto, M. Tomcsi, M. Nagata, and V. Visco)
Electrolytes selected for evaluation include methyl propionate-based electrolytes with increasing FEC content and the use of LiBOB as an additive.

All electrolytes are observed to provide improved performance at high rates at very low temperatures compared with the baseline electrolytes, with the LiBOB outperforming all formulations.

The incorporation of LiBOB has been attributed to increase cathode kinetics at low temperatures, as determined by Tafel Polarization measurements performed on 3-electrode cells.

C Rate Discharge at -50°C
Lithium Batteries Capable of Operating at Very Low Temperatures

Performance Testing of High Rate, Gel Polymer Electrolyte Li-Ion Cells

Performance of Ester-Based Electrolytes at Low Temperatures

PAUSE Aerobot Load Simulation at –60ºC

Investigated possibility of using low temperature Li-ion cells for the Picosat and UAV Systems Engineering (PAUSE) Project (collaboration with Dr. Alberto Behar, JPL).

The PAUSE project utilizes a zero-pressure balloon and a prototype Mars aerobot science gondola to study the atmosphere, and is potentially subjected to very low temperatures depending upon location and altitude.

Objective is to replace the currently used Li-SO2 primary batteries, which are unable to operate effectively below – 40ºC under current load profile.

At –60ºC, the high power cell containing the methyl-butyrate (MB)-containing electrolyte delivered over 12 hours of operation under PAUSE load profile.

Low Temperature Lithium Primary Batteries

Background: Mars DS2 Microprobe Spacecraft

- Launched on January 1999
- Two microprobes (2.4kg) piggybacked on Mars Polar Lander mission
- Intended as a low cost, high risk/high payoff mission
- Design:
  - No parachute: dropoff penetrator
  - Aftbody with batteries & telecom stays on surface
  - Forebody penetrates, ~ 1 meter
  - Drill scoops soil sample into chamber
  - Heat, vaporize, and analyze for H₂O
  - Transmit water and other science data
Low Temperature Lithium Primary Batteries

Background: Mars DS2 Battery

- Lithium-Thionyl Chloride Chemistry
  - Li anode|0.5M LiGaCl₄ in SOCl₂
catholyte|porous carbon cathode current collector
- Predicted operational temperature at nominally -80°C
- “Pancake” electrode design (vertical stacking)
- Two 4 cell batteries per spacecraft
- Battery voltage: 6-14V
- Battery Capacity:
  - 550 mAhr capacity @ -80°C
  - 2 Ah at 25°C
- Shelf Life: 2.5 Years
- Shock Tolerance: >80,000 g shock
- Developers/Suppliers:
  - JPL/Yardney Technical Products
Low Temperature Lithium Primary Batteries
Motivation for New Battery Research

• How does an analogous penetrator mission to outer planetary moons (e.g. Europa, Titan) at ca. -160°C draw power?
  – Maximum solar flux at Europa is only 34 W/m² vs. 1371 W/m² at low earth orbit
  – Lowest possible operating temperature for any battery is -80°C
  – Heaters add undesirable power drains, mass, complexity
  – Radioisotope heaters or radioisotope thermoelectric generators are generally more costly than other heating technologies and have low power density

• Proposed solution: Develop advanced catholytes with lower liquid range to infuse into existing cell design to allow for low-cost, ultra-low temperature batteries.
“Optimized” Catholyte System

- Base catholyte: Sulfuryl chloride fluoride (SO$_2$ClF); m.p. -125°C, b.p. 7°C
  - SOClF disproportionates with storage, SO$_2$F$_2$ low b.p., and not likely to reduce readily by Li
- Co-solvent: chlorodifluoromethane; m.p. (CHClF$_2$); m.p. -175°C, b.p. -41°C
  - Wide range of alkanes, halocarbons, chloroethane-butynitrile binaries examined
- Salt: LiGaCl$_4$
  - Better low temperature conductivity than LiAlCl$_4$
- Surfactant: 3 vol % of perfluoroether: Galden HT55
  - Below -120°C, 1:1 SO$_2$ClF:CHClF$_2$ phase separates
  - Addition of a perfluoroether suppresses the temperature of phase separation
- Halogen Passivation: Bromine (Br$_2$)
  - Li-SOCl$_2$ cells with BrCl, Cl$_2$ additives show reduced voltage delay

• Polarization of electrodes dominated by cathode for baseline thionyl chloride and optimized low temperature formulation (non-vacuum filling issue).

• At lower temperature, the anode polarization becomes a more significant contributor to cell polarization

• Low temperature formulation at -130°C outperforms baseline formulation at -80°C

TC denotes the cell with 0.5 M LiGaCl₄ in SOCl₂ formulation and SCF denotes the cell with Br₂ passivated 0.25 M LiGaCl₄ in 1:1 SO₂ClF:CHClF₂–HT55 formulation.

Low Temperature Lithium Primary Batteries

Cell Discharge Studies

- Discharging at -80°C, low temperature formulation has flat discharge profile, unlike sloped discharge for baseline formulation.
- When temperature is reduced to -130°C, baseline formation fails as expected.
- Low temperature formulation discharges continuously with no slope in discharge profile- **lowest operating temperature battery ever reported**.
- Lower temperatures briefly examined, may be capable as low as -145°C.

Discharge of 0.5M LiGaCl₄ in SOCl₂ cell and Br₂-passivated 0.25M LiGaCl₄ in 1:1 SO₂ClF:CHClF₂-HT55 cell. The cells were filled at -80°C, equilibrated for 1 h, discharged first at -80°C, and then cooled while discharging to -130°C.

Need for low temperature power

- **Current practice**: avionics in warm electronics box (WEB) with radioisotope heat source to maintain -40°C to +40°C
- Extensive cabling presents design, integration and test challenge
- Battery power de-rated at lower temperatures
- **Possible solution**: Hybrid low temperature battery-capacitor power systems
Double-layer capacitors for low temperature energy storage and power delivery

Technology need
- Storing electrical energy and delivering power at low temperatures (<-30°C) remains a significant challenge
- Difficult to deliver high power effectively at low temperatures (batteries derated due to slow kinetics)

Objectives
- Utilize the advantage of double-layer capacitors, which store energy at the electrochemical double-layer (rather than intercalation and redox processes, which are highly temperature sensitive)
- Develop low temperature electrolytes to extend beyond -40°C limit with commercial cells
- Target low equivalent series resistance (ESR) to effectively deliver power at low temperature

Potential applications
- Hybrid battery/capacitor low temperature power systems (with the capacitor providing pulse power at low temperatures)
- Capacitor-only power systems, for low duty cycle distributed sensor platforms on planetary surfaces (with limited thermal management)
- Fully testable thermal battery replacements
Low Temperature Supercapacitors
Survey of Commercially Available Technology

Technical Approach: Design non-aqueous electrolyte formulations that have high conductivity at low temperature, and much lower freezing points.

Ionic Conductivity vs. Temperature

- Mixed electrolyte co-solvent blends (i.e., AN-based) were observed to provide the desired properties.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Freezing point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂C=C=NNH₂ (acetonitrile (AN))</td>
<td>-43.84</td>
</tr>
<tr>
<td>H₂C=OC(==O)CH₃ (methyl formate)</td>
<td>-100</td>
</tr>
<tr>
<td>H₂C=OC(==O)CH₂CH₃ (methyl acetate)</td>
<td>-98</td>
</tr>
<tr>
<td>H₂C=OC(==O)CH₂CH₂CH₃ (ethyl acetate)</td>
<td>-83.6</td>
</tr>
</tbody>
</table>

Acetonitrile : methyl formate (3:1 vol/vol%) -70
Acetonitrile : methyl acetate (3:1 vol/vol%) -71
Acetonitrile : ethyl acetate (3:1 vol/vol%) -72
Low Temperature Supercapacitors
Survey of Commercially Available Technology

10 F cell
Discharge current = 1 A

Poor performance is observed at temperatures below -50°C
Low Temperature Supercapacitors
Advanced Low Temperature Chemistries Evaluated in Experimental Coin Cells

- 2032 coin cells
- Separator: 25 micron polyethylene (Tonen)
- Electrodes: PACMM 203 activated carbon
- Salt: Tetraethylammonium tetrafluoroborate

Electrolyte = 0.250 M TEATFB in 1:1 acetonitrile / methyl formate

Extended operation to < -80°C as revealed by DC data
At -70°C, cell displays ~520 F capacity at 1 A and $V_{\text{max}} = 1.5$ V with very linear discharge characteristics.
SUMMARY and CONCLUSIONS

- **Demonstration of low temperature Li-ion batteries**
  - Demonstrated improved performance with wide operating temperature electrolytes containing ester co-solvents (i.e., methyl propionate and ethyl butyrate) in a number of prototype cells.
  - Successfully scaled up low temperature technology to 12 Ah size prismatic Li-ion cells (Quallion, LCC), and demonstrated good performance down to -60°C.
  - Demonstrated wide operating temperature range performance (-60°C to +60°C) in A123 Systems LiFePO₄-based lithium-ion cells containing methyl butyrate-based low temperature electrolytes. These systems were also demonstrated to have excellent cycle life performance at ambient temperatures, as well as the ability to be cycled up to high temperatures.

- **Development of ultra-low temperature primary batteries**
  - New ultra-low temperature battery systems have been identified based on sulfuryl chloride fluoride catholytes, Li₆GaCl₄ salt, chlorofluorocarbon co-solvents, perfluoroether surfactants, and halogen passivation.
  - We report a first known demonstration of cell operation at temperatures as low as -130°C, about 60°C lower than any other battery system reported.
  - Further studies need to be performed to incorporate the technology into commercially produced prototype cells.

- **Development of ultra-low temperature supercapacitors**
  - Demonstrated capacitor operation to -80°C, enabled by AN-based/TEATFB formulation with the addition of low melting formates and esters.
  - Key electrolyte design factors include volume of co-solvent and electrolyte salt concentration.
  - Continuing efforts include demonstrating in larger scale cells and investigating formulation targeted at lower temperatures.
The work described here was carried out at the Jet Propulsion Laboratory, California Institute of Technology, under contract with the National Aeronautics and Space Administration (NASA).