Improved Wide Operating Temperature Range of LiNiCoAlO$_2$-Based Li-Ion Cells with Methyl Propionate-Based Electrolytes

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Outline

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- Performance of MP Electrolytes with Additives in 0.25Ah Cells
  - Discharge rate characterization at low temperature
  - 100 % DOD cycling (+40°C)
- Conclusions
Outline

- DOE desires Li-ion batteries than 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 than can operate over a wide temperature range for future planetary lander and rover applications.

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.
Wide Operating Temperature Range Lithium Ion Electrolytes
Electrolyte Development: Approach/Background

- **Electrolyte Selection Criteria**
  - High conductivity over a wide range of temperatures
    - 1 mS cm\(^{-1}\) from –60 to 40°C
  - Wide liquid range (low melting point)
    - -60 to 75°C
  - Good electrochemical stability
    - Stability over wide voltage window (0 to 4.5V)
    - Minimal oxidative degradation of solvents/salts
  - Good chemical stability
  - Good compatibility with chosen electrode couple
    - Good SEI characteristics on electrode
    - Facile lithium intercalation/de-intercalation kinetics
  - Good thermal stability
  - Good low temperature performance throughout life of cell
    - Good resilience to high temperature exposure
    - Minimal impedance build-up with cycling and/or storage

- In addition to meeting these criteria, the electrolyte solutions should be ideally have low flammability and be non-toxic!!
Quallion Prototype Li-Ion Cells

Wide Operating Temperature Range Electrolytes Selected for Evaluation in Prototype Li-Ion Cells

A) 1.2 M LiPF$_6$ EC+EMC (30:70 vol %) (Baseline)
B) Quallion Low Temperature Electrolyte “A1”
C) Quallion Low Temperature Electrolyte “A1”
D) Quallion Low Temperature Electrolyte “A1”
E) JPL Low Temperature Electrolyte (EC+EMC+MP)
F) JPL Low Temperature Electrolyte (EC+EMC+MP)

• MCMB Carbon-LiNiCoAlO$_2$ Cells
  Li$_4$Ti$_5$O$_{12}$-LiNiCoAlO$_2$ Cells
  • 300 mAh Size Cells
  • Prismatic design
  • Hermetically sealed
  • Excellent heritage

General Test Plan

• Initial characterization at various temps (20, 0, -20°C)
• Discharge rate characterization at various temps (-60 to +20°C)
• Wide range of discharge rates investigated (up to 15C)
• Variable temperature cycling (-40 to +70°C)
• High temperature cycling (-40 to +70°C)

The electrolytes were selected for the study based upon previous findings, primarily the observed low temperature performance capabilities.
**Discharge Rate Characterization (18 Cells in 3 Batches)**

- **Cells charged at room temperature prior to discharge at low temperatures**
- A number of discharged rates evaluated (C/50 to 15C rates)
- All C rates based on nameplate capacity of 0.250Ah
- Range of temperatures evaluated (-60°C to +20°C)
- Cells charged at C/3 rate to 4.10 V (with C/50 taper current cut-off)
- Cells discharged to 2.00 V at lower temperatures
- Cells allowed to soak in chamber at least 6 hours prior to testing
- Thermocouples present on some cells (attached to side of cell can)
In collaboration with Quallion, excellent low temperature rate capability has been demonstrated with advanced electrolytes.
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Methyl propionate containing electrolytes have displayed dramatically improved rate capability at -40°C compared to the baseline DOE formulation (i.e., 1.2M LiPF$_6$ in EC+EMC (30:70). S**ignificantly higher capacity and operating voltage delivered at high rate**.
Quallion Prototype Li-Ion Cells
Wide Operating Temperature Electrolytes
Discharge Rate Characterization at -20°C
Both Quallion and JPL electrolytes have displayed improved rate capability at -30°C compared to the baseline DOE formulation (i.e., 1.2 M LiPF$_6$ in EC+EMC (30:70) in Li$_4$Ti$_5$O$_{12}$-LiNi$_x$Co$_{1-x}$AlO$_2$ Lithium-Ion Cells). Significantly higher capacity and operating voltage delivered at high rate.
Quallion Prototype Lithium-Ion Cells
Summary of Variable Temperature Cycling (3rd Group of Cells)

Variable Temperature Cycling (6 Cells)

• Alternating 20 cycles performed at -20°C and +40°C
  Cells charged at a C/10 or C/5 rate to 4.10 V
  (with C/50 taper current cut-off)
• Cells discharged at a C/5 rate (0.050 A) to 2.50 V
• Current-interrupt impedance measurements performed routinely
  (every 20 cycles at respective temperature)
• Thermocouples present on some cells (attached to side of cell can)
• Cells selected for evaluation:
  • NEC-02: Baseline Low Temperature Electrolyte (EC+EMC)
  • NA1-18: Quallion Low Temperature Electrolyte “A1”
  • NA2-33: Quallion Low Temperature Electrolyte “A2”
  • NA3-42: Quallion Low Temperature Electrolyte “A3”
  • NEB-19: JPL Low Temperature Electrolyte (EC+EMC+EB)
  • NMP-07: JPL Low Temperature Electrolyte (EC+EMC+EB)
Both JPL and Quallion developed electrolyte display wide operating temperature range (-40 to +70°C).

There is room for improvement with regard to the high temperature resilience.
Although reasonable cycle life is observed at 50°C, the advanced wide operating temperature electrolytes display higher capacity fade compared to DOE baseline chemistry.
Experimental lithium-ion cells (MCMB-LiNiCoAlO2) fabricated with methyl propionate–based electrolytes containing various additives.

- The use of electrolytes additives, such as FEC, VC, LiBOB, and lithium oxalate, were employed with the intent of improve the high temperature resilience.
- The additives were observed to have a beneficial impact upon the low temperature lithium intercalation/de-intercalation kinetics.
- At low temperatures, the best performance was obtained with the addition of VC and FEC to the MP-based electrolyte formulations.
- The polarization of the cell containing LiBOB was more pronounced that the other cells with additives, presumably due to the filming process at the anode.
Experimental lithium-ion cells (MCMB-LiNiCoAlO$_2$) fabricated with methyl propionate–based electrolytes containing various additives.

**Tafel Polarization Measurements**

**Anode Measurements**

- **Temperature = -20°C**

**Cathode Measurements**

- **Temperature = -20°C**

➢ Promising electrolyte additives were explored in a wide operating temperature range solvent systems (EC+EMC+MP) with the intent of improving high temperature resilience.

- **FEC was observed to enhance the lithium kinetics of the MCMB anode, whereas the other additives appeared to impede the kinetics (especially LiBOB).**
- **VC and LiBOB were observed to most dramatically enhance the kinetics of the cathode at low temperatures. All additives appeared to improve the kinetics somewhat.**
Experimental lithium-ion cells (MCMB-LiNiCoAlO₂) fabricated with methyl propionate–based electrolytes containing various additives.

- FEC and lithium oxalate were observed to result in low film impedance on the MCMB anode, whereas LiBOB resulted in high film and charge transfer resistance.
- Although LiBOB resulted in low film and charge transfer resistance at the cathode, usually high series resistance was observed which is attributed to the filming behavior (i.e., a composite film composed of a compact portion and a diffuse, porous layer with low conductivity).

Promising electrolyte additives were explored in a wide operating temperature range solvent systems (EC+EMC+MP) with the intent of improving high temperature resilience.
Methyl propionate-based electrolyte was previously demonstrated to have dramatically improved rate capability compared to the baseline DOE formulation (i.e., 1.2M LiPF₆ 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)
Quallion Prototype 0.25 Ah Li-Ion Cells
Discharge Characterization at Low Temperatures

- 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.
• 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.
Thus far, the cells containing the MP-based wide operating temperature range electrolytes provide good life at 40°C, with the LiBOB outperforming all formulations. Increased degradation was observed when FEC was used as the only cyclic carbonate present. Additional life tests will be performed at higher temperatures, as well as with baseline electrolytes.
SUMMARY and CONCLUSIONS

• **Demonstration of wide operating temperature range Li-ion electrolytes**
  – Methyl propionate-based wide operating temperature range electrolytes were demonstrated to provide dramatic improvement of the low temperature capability of Quallion prototype Li-ion cells (MCMB-LiNiCoAlO$_2$).
  – Some formulations were observed to deliver over 60% of the room temperature capacity using a 5C rate at -40°C!! Represents over a 4-fold improvement over the baseline electrolyte system.
  – Demonstrated operational capability of a number of systems over a wide temperature range (-40 to +70°C)
  – *Demonstrated reasonably good long term cycle life performance at high temperature* (i.e., at +40º and +50ºC)
  – A number of formulations containing electrolytes additives (i.e., FEC, VC, LiBOB, and lithium oxalate) have been shown to have enhanced lithium kinetics at low temperature and promising high temperature resilience.
  – Demonstrated good performance in larger capacity (12 Ah) Quallion Li-ion cells with methyl propionate-based electrolytes. Current efforts focused upon performing life studies and the impact upon low temperature capability.
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