The Use of Methyl Propionate-Based Electrolytes with Additives to Improve the Low Temperature Performance of $LiNiCoAlO_2$-Based Li-Ion Cells

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Outline

- Introduction
- Approach/Background
- Overview of Electrolyte Development
- Performance of MP-Based Electrolytes in 0.25Ah Cells
  - Discharge rate characterization at low temperature
  - Variable temperature cycling (-40 to +70°C)
  - 100 % DOD cycling (+50°C)
- Performance of MP-Based Electrolytes in 12Ah Cells
- Investigation of MP-Based Electrolytes with Additives
  - Three-Electrode Cell Data
  - Electrochemical Characterization of MCMB and LiNiCoAlO2 Electrode
- 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 !!*

- ***Low EC Electrolytes with Medium Ester Content***
  - ***20 % EC Content, 60% Ester Content***

  - ***Excellent conductivity at low temperature***
  - ***Reasonable resilience to high temperature exposure compared to solutions with higher ester content and lower EC content***
  - ***Wide operating temperature range***
  - ***Excellent rate capability at low temperatures***
  - ***Solutions optimized to give high rate capability at low temperature without impacting life dramatically.***

1.2 M $LiPF_6$ in EC+EMC+MP (20:20:60 v/v) MP = methyl propionate
1.2 M $LiPF_6$ in EC+EMC+EP (20:20:60 v/v) EP = ethyl propionate
1.2 M $LiPF_6$ in EC+EMC+MB (20:20:60 v/v) MB = methyl butyrate

The use of additives can improve the high temperature resilience, and in some cases improve the low temperature rate capability due to improved interfacial kinetics.

Quallion Prototype Li-Ion Cells (1st Batch)

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 " A2"
D) Quallion Low Temperature Electrolyte " A3"
E) JPL Low Temperature Electrolyte (EC+EMC+MP)
F) JPL Low Temperature Electrolyte (EC+EMC+EB)

- MCMB Carbon-$LiNiCoAlO_2$ Cells
  $Li_4Ti_5O_{12}$-$LiNiCoAlO_2$ Cells
- 300 mAh Size Cells
- Prismatic design
- Hermetically sealed
- Excellent heritage

General Test Plan

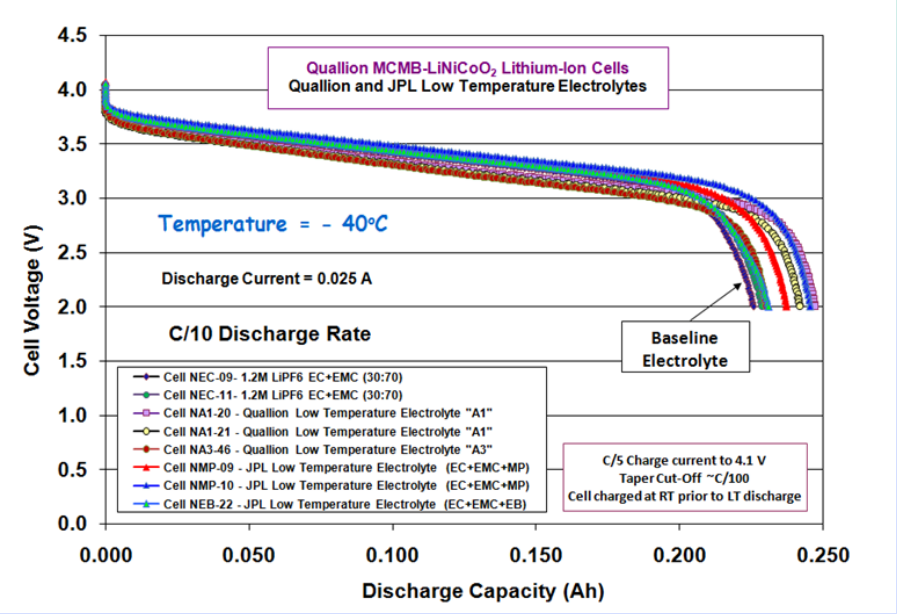
- Initial characterization at various temps (20, 0, -20°C)
- Discharge rate characterization at various temps (-60 to + 20°C)
- Wide range of discharge rates investigated (up to 15C)
- Variable temperature cycling (-40 to +70°C)
- High temperature cycling (-40 to +70°C)

The electrolytes were selected for the study based upon previous findings, primarily the observed low temperature performance capabilities.

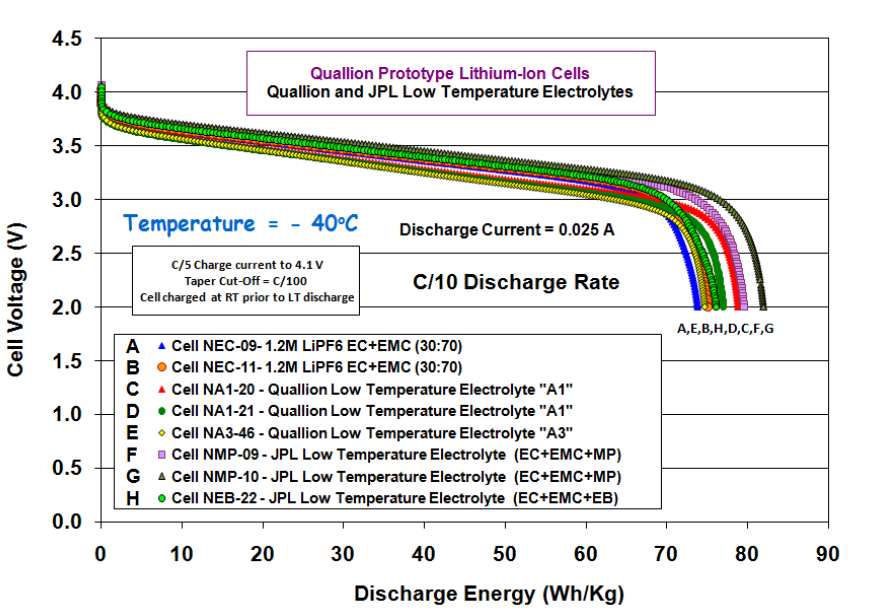
Preliminary results presented in: M. C. Smart, M. R. Tomcsi, C. Hwang, L. D. Whitcanack, B. V. Ratnakumar, M. Nagata, V. Visco, and H. Tsukamoto, "Improved Wide Operating Temperature Range of LiNiCoAlO2-Based Li-ion Cells with Methyl Propionate-Based Electrolytes", 221st Meeting of the Electrochemical Society, Seattle, WA, May 6-10, 2012.

Quallion Prototype Li-Ion Cells
Wide Operating Temperature Electrolytes
Discharge Characterization at Various Temperatures

C/10 Discharge at -40°C (Ah)



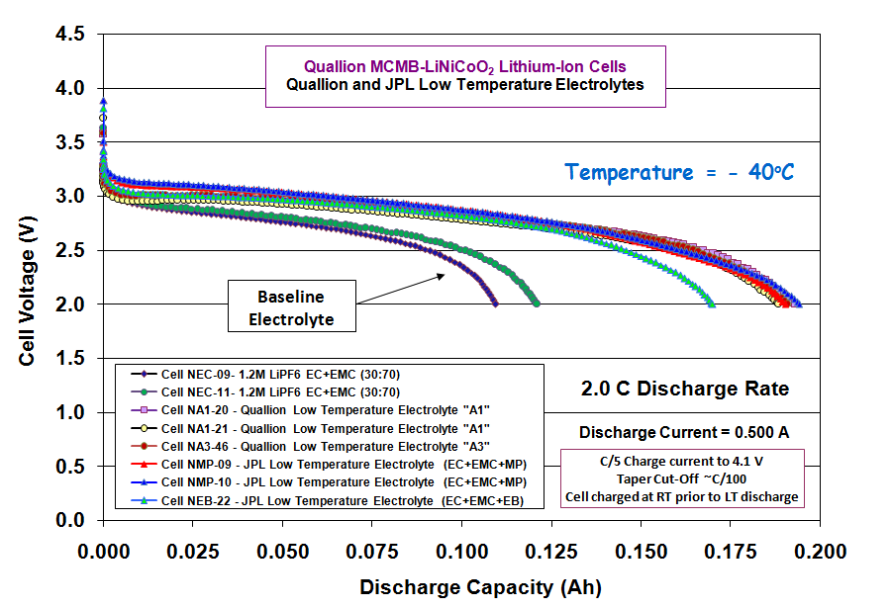
C/10 Discharge at -40°C (Wh/Kg)



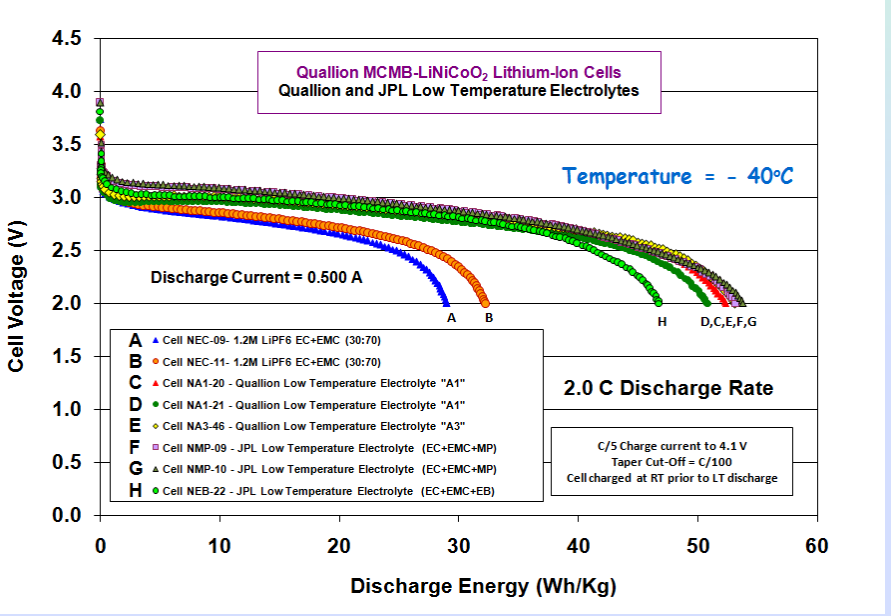
- In collaboration with Quallion, excellent low temperature rate capability has been demonstrated with advanced electrolytes.

Quallion Prototype Li-Ion Cells
Wide Operating Temperature Electrolytes
Discharge Characterization at Various Temperatures

2C Discharge at -40°C (Ah)



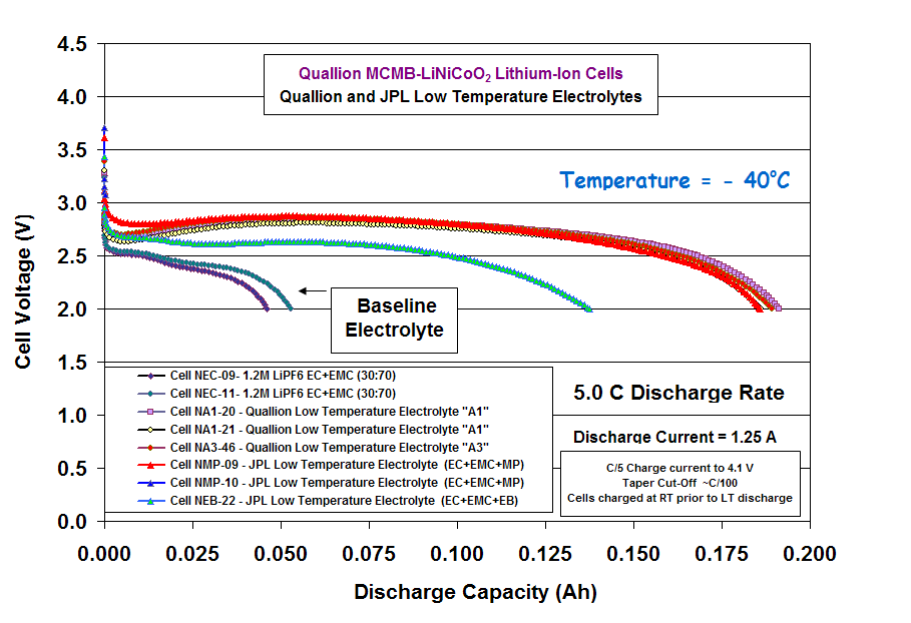
2C Discharge at -40°C (Wh/Kg)



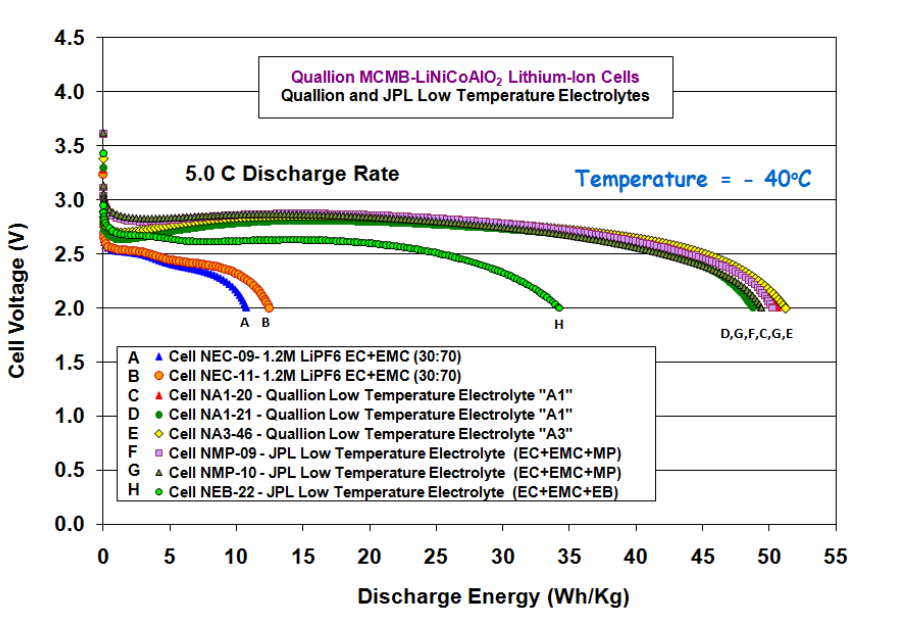
- In collaboration with Quallion, excellent low temperature rate capability has been demonstrated with advanced electrolytes.

Quallion Prototype Li-Ion Cells
Wide Operating Temperature Electrolytes
Discharge Characterization at Various Temperatures

5C Discharge at -40°C (Ah)



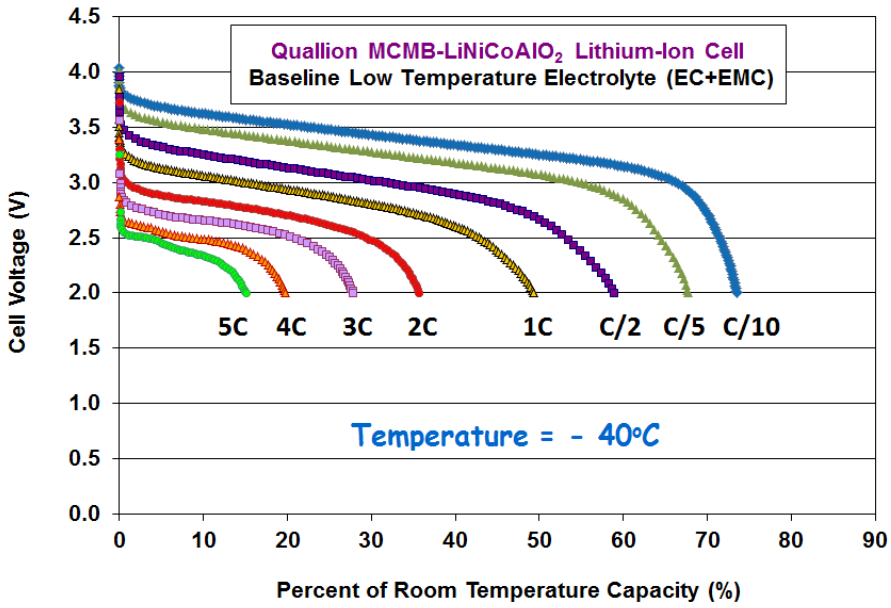
5C Discharge at -40°C (Wh/Kg)



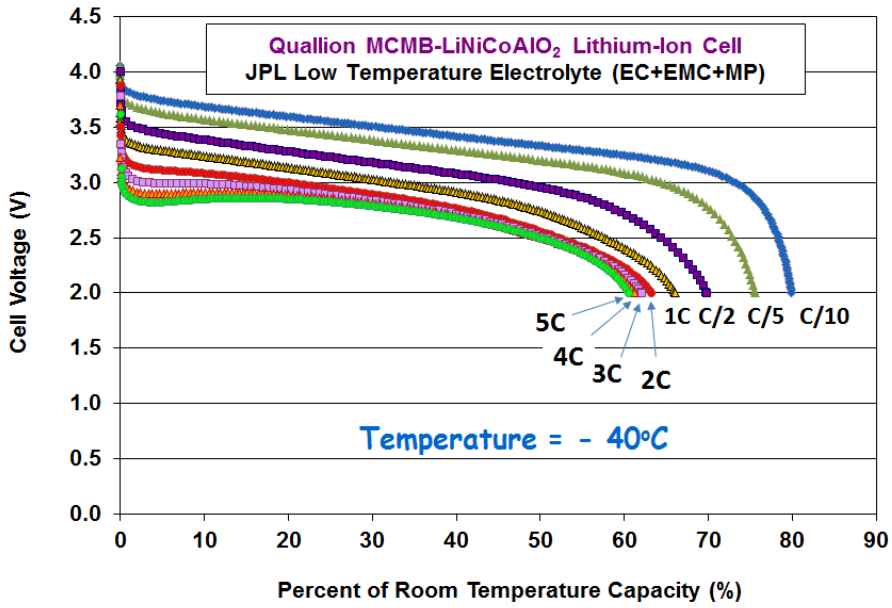
- In collaboration with Quallion, excellent low temperature rate capability has been demonstrated with advanced electrolytes.

Quallion Prototype Li-Ion Cells
Wide Operating Temperature Electrolytes
Discharge Characterization at -40°C

Baseline Electrolyte



MP-Based Electrolyte

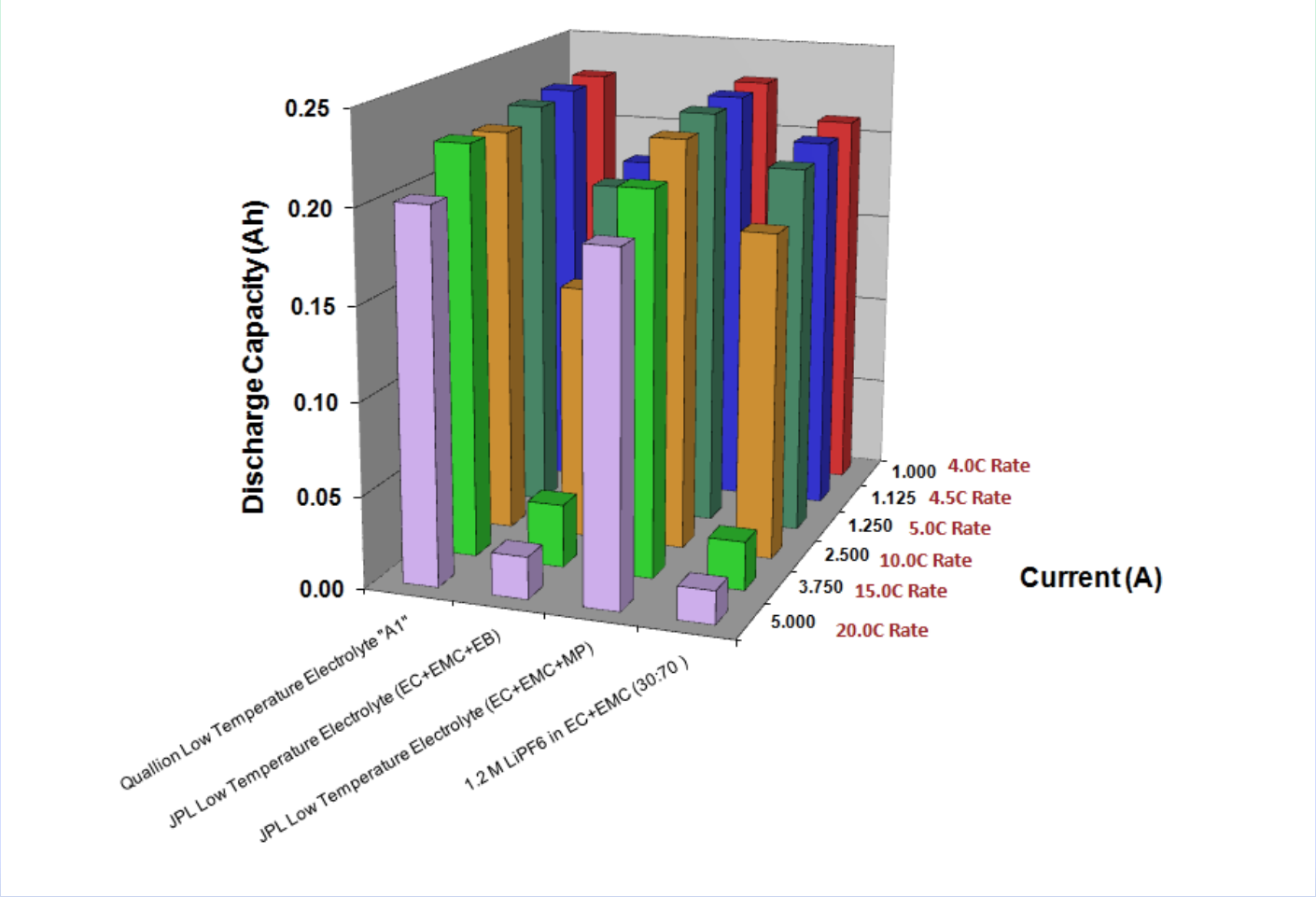


Methyl propionate containing electrolytes have displayed dramatically improved rate capability at -40°C compared to the baseline DOE formulation (i.e., 1.2M $LiPF_6$ in EC+EMC (30:70).

- **This electrolyte, as well as a variant containing FEC, was successfully demonstrated in larger**
  - **Capacity 12 Ah cells (in collaboration with Quallion, LCC).**

Significantly higher capacity and operating voltage delivered at high rate .

Quallion Prototype Li-Ion Cells
Wide Operating Temperature Electrolytes
Discharge Rate Characterization at -20°C

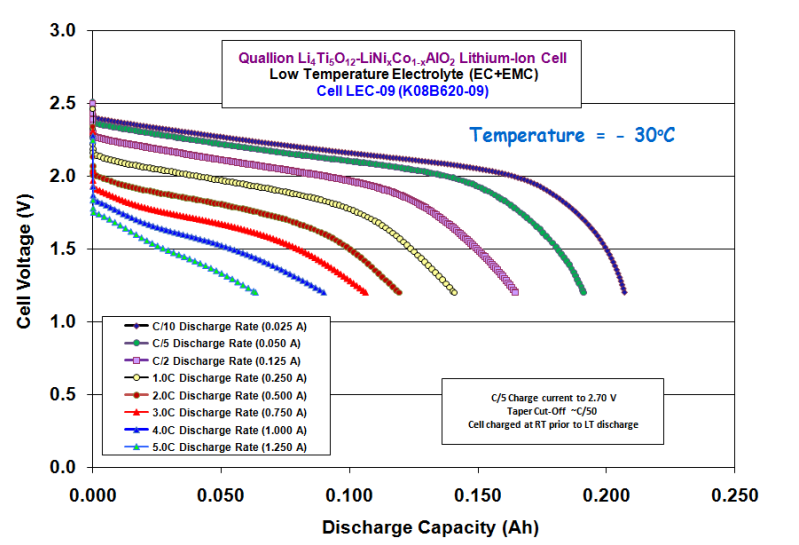


- ***Up to 20C discharge rates are supported by the MP-based blend and the Quallion formulation, outperforming the baseline all-carbonate based electrolyte.***

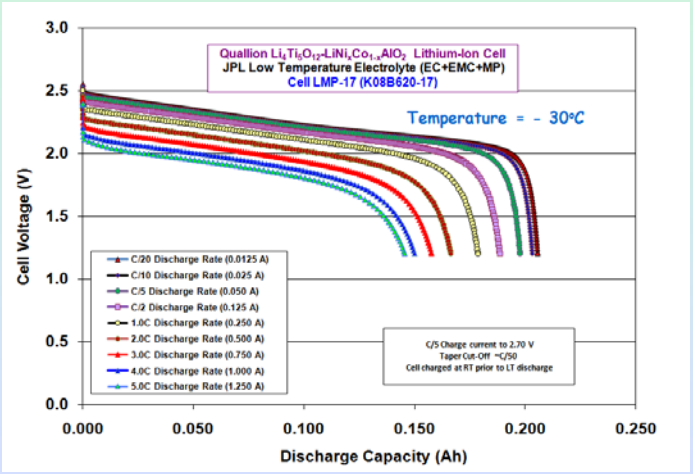
Quallion Prototype Li-Ion Cells

Discharge Rate Characterization at -30°C

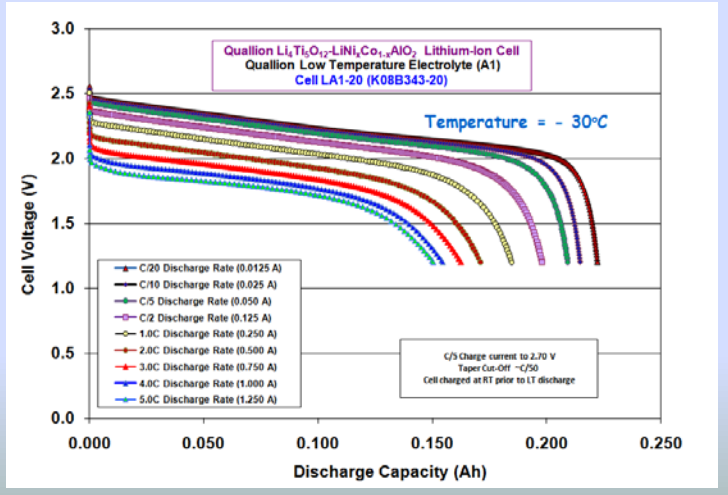
Baseline Electrolyte



MP-Based Electrolyte



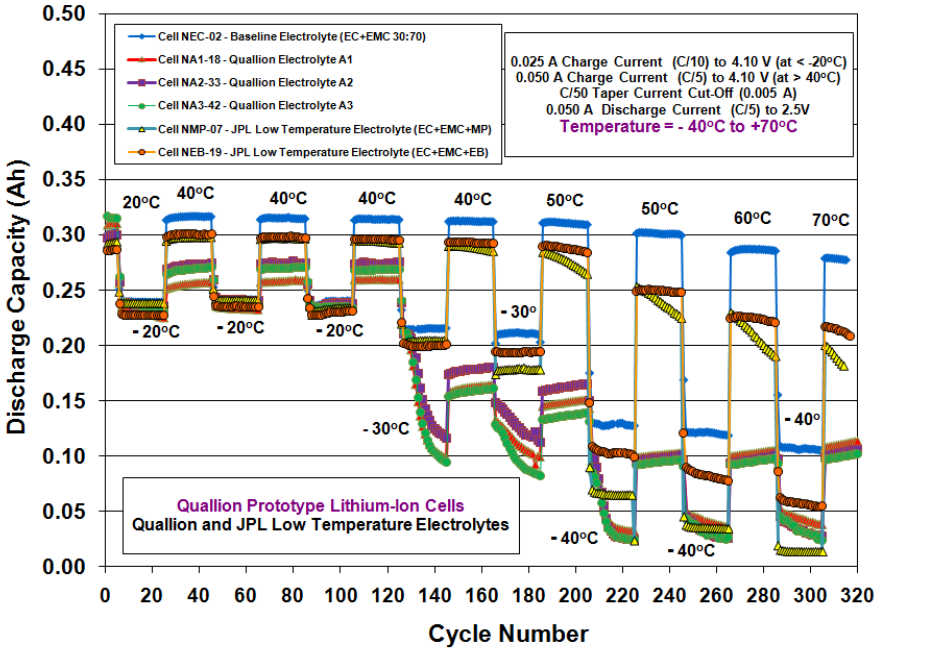
Quallion "A1" Electrolyte

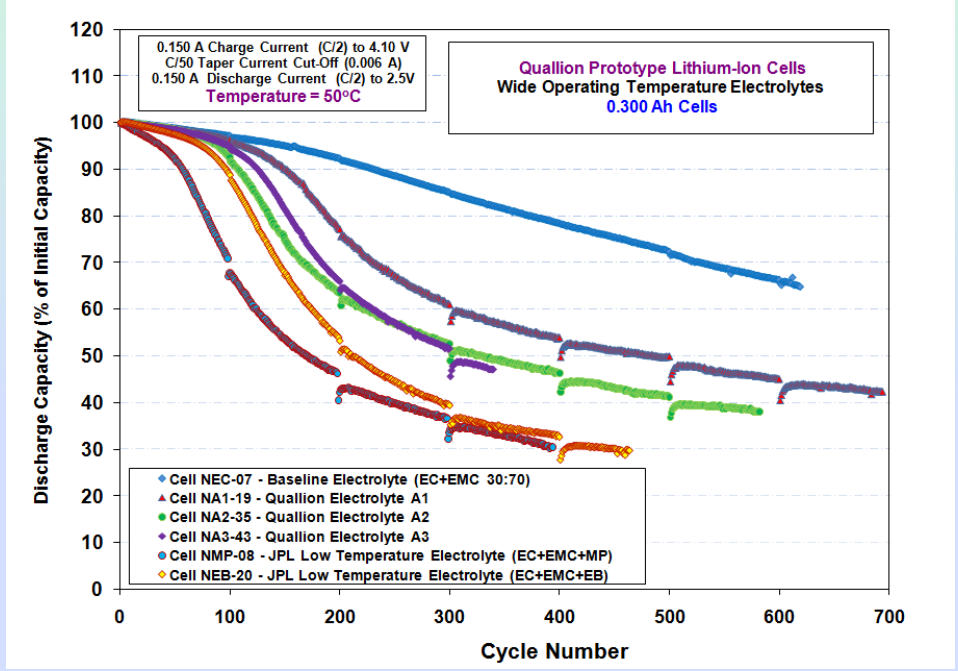


Both Quallion and JPL electrolytes have displayed improved rate capability at -30°C compared to the baseline DOE formulation (i.e., 1.2M $LiPF_6$ in EC+EMC (30:70) in $Li_4Ti_5O_{12}$-$LiNi_xCo_{1-x}AlO_2$ Lithium-Ion Cells

Significantly higher capacity and operating voltage delivered at high rate .

Quallion Prototype Li-Ion Cells
Wide Operating Temperature Electrolytes
Cycle Life at 50°C and Variable Temperature Cycling over a Wide Temperature Range

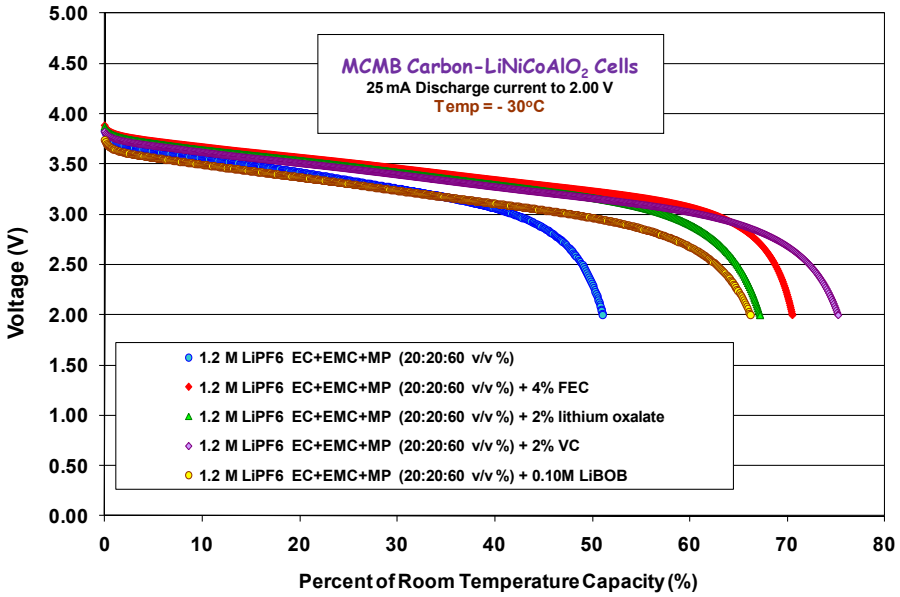


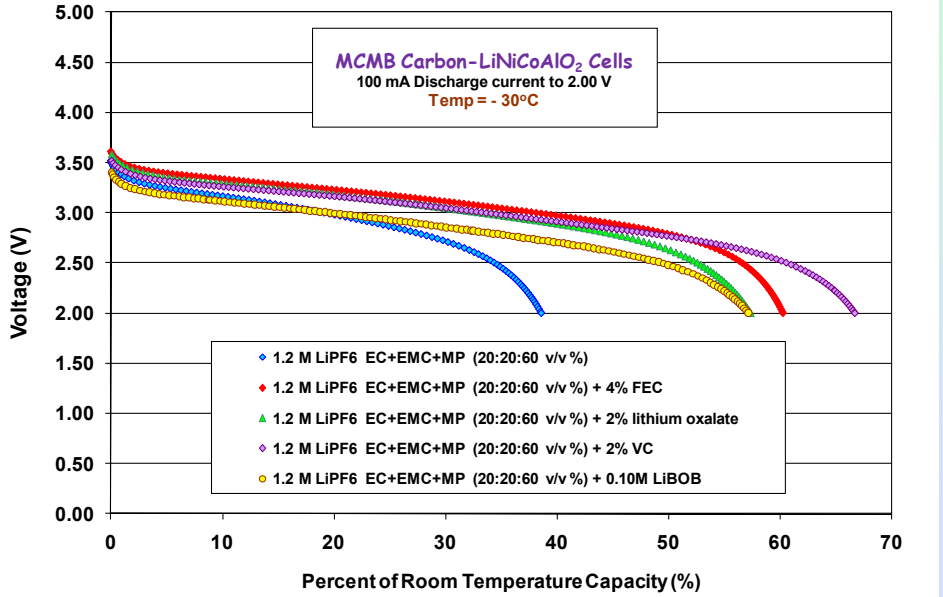


- **Although reasonable cycle life is observed at 50°C, the advanced wide operating temperature electrolytes display higher capacity fade compared to DOE baseline chemistry.**
- **Both JPL and Quallion developed electrolyte display wide operating temperature range (-40 to +70°C).**

There is room for improvement with regard to the high temperature resilience.

Experimental lithium-ion cells (MCMB-$LiNiCoAlO_2$) fabricated with methyl propionate–based electrolytes containing various additives.



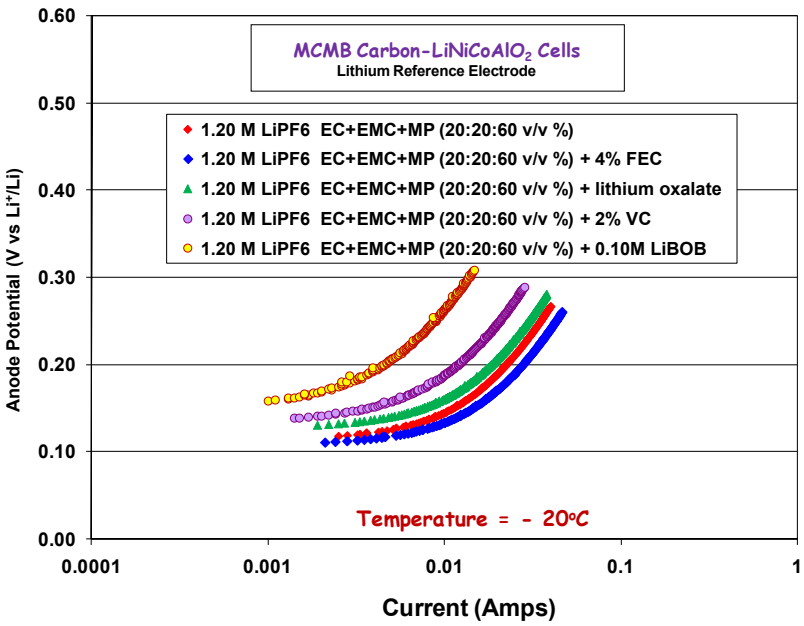


- ***The use of electrolytes additives, such as FEC, VC, LiBOB, and lithium oxalate, were employed with the intent of improve the high temperature resilience.***
- ***The additives were observed to have a beneficial impact upon the low temperature lithium intercalation/de-intercalation kinetics.***
- ***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.***

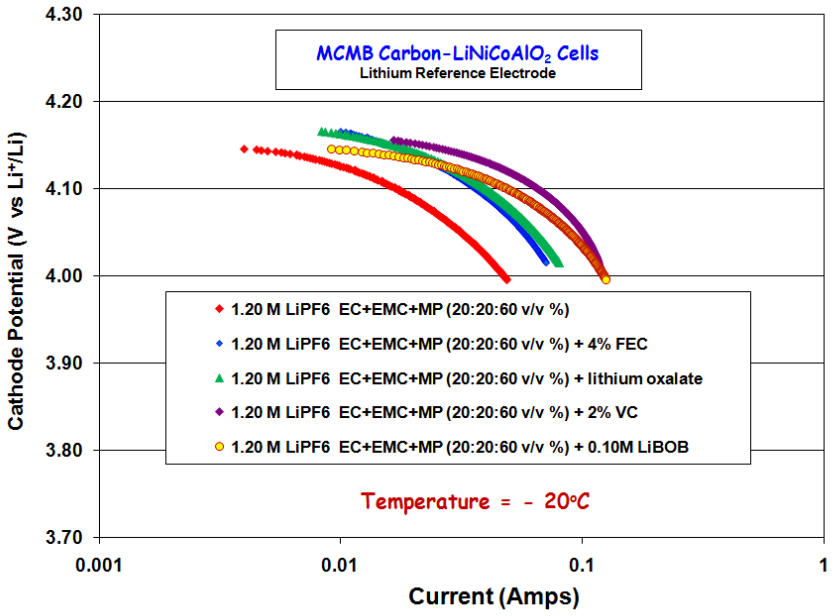
Experimental lithium-ion cells (MCMB-$LiNiCoAlO_2$) fabricated with methyl propionate–based electrolytes containing various additives.

Tafel Polarization Measurements

Anode Measurements



Cathode Measurements



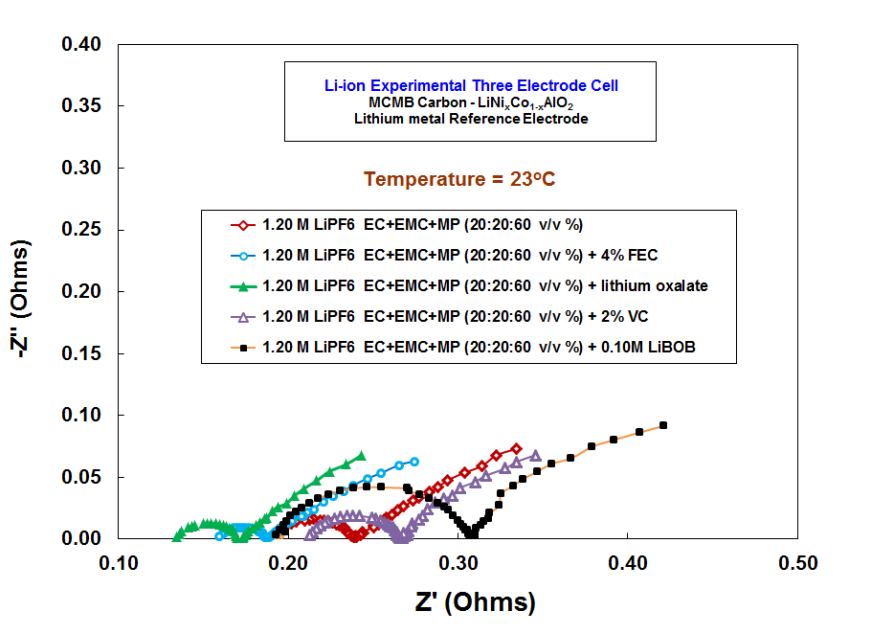
- **Promising electrolyte additives were explored in a wide operating temperature range solvent systems (EC+EMC+MP) with the intent of improving high temperature resilience**

- ***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.***

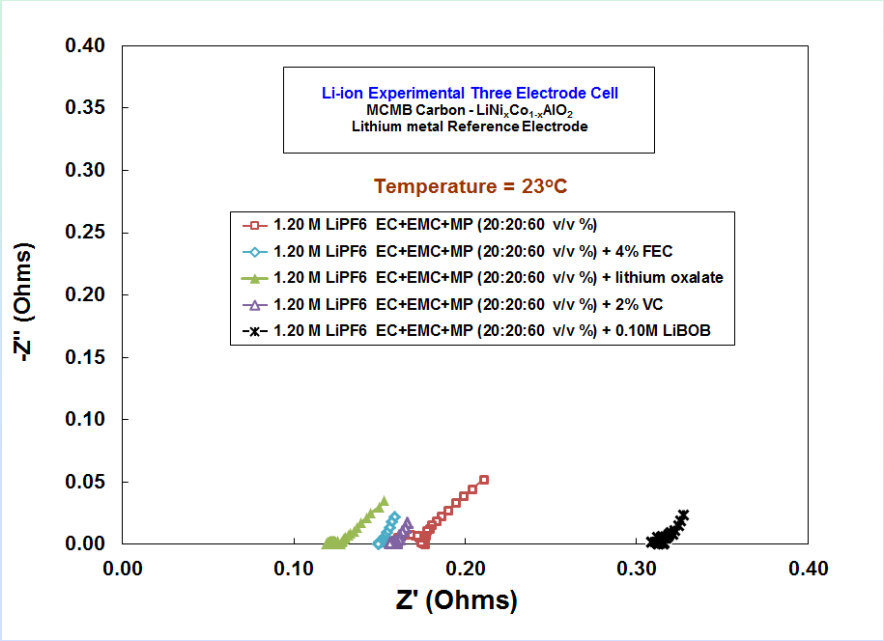
Experimental lithium-ion cells (MCMB-$LiNiCoAlO_2$) fabricated with methyl propionate–based electrolytes containing various additives.

Electrochemical Impedance Spectroscopy (EIS) Measurements

Anode Measurements



Cathode Measurements



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

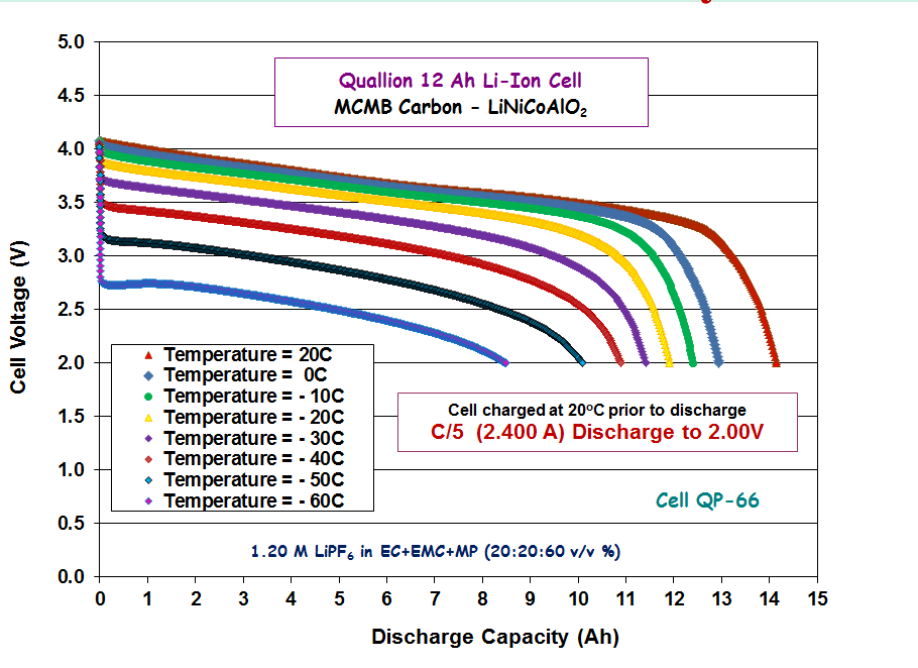
- ***FEC and lithium oxalate were observed to result in low film impedance on the MCMB anode, whereas LiBOB resulted in high film and charge transfer resistance.***
- ***Although LiBOB resulted in low film and charge transfer resistance at the cathode, usually high series resistance was observed which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

Quallion Prototype 12 Ah Li-Ion Cells with JPL Electrolytes

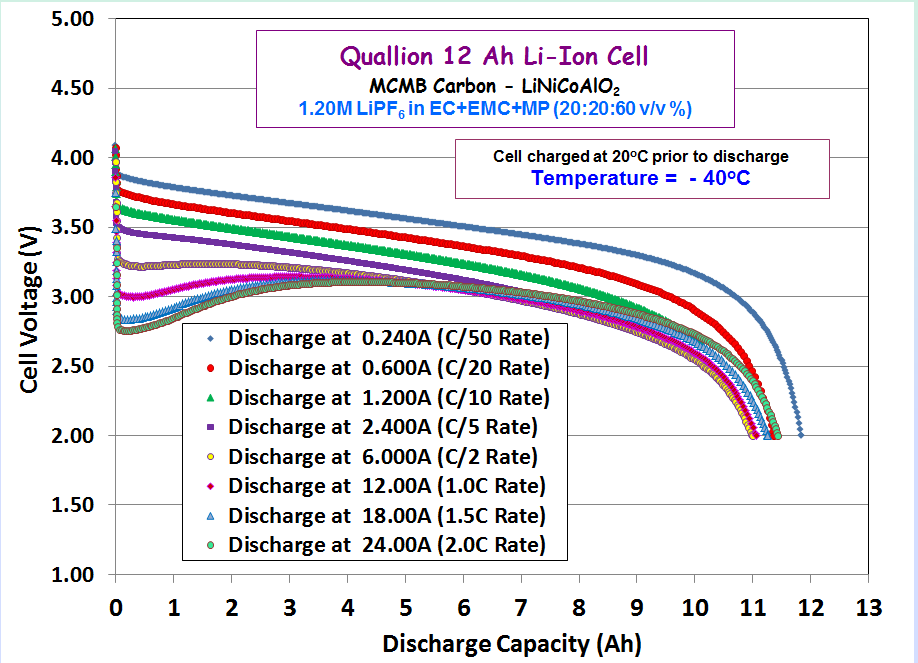
Low Temperature Performance Characterization

- *Methyl propionate-based electrolytes were successfully demonstrated in large capacity cells*

DOE Baseline Electrolyte

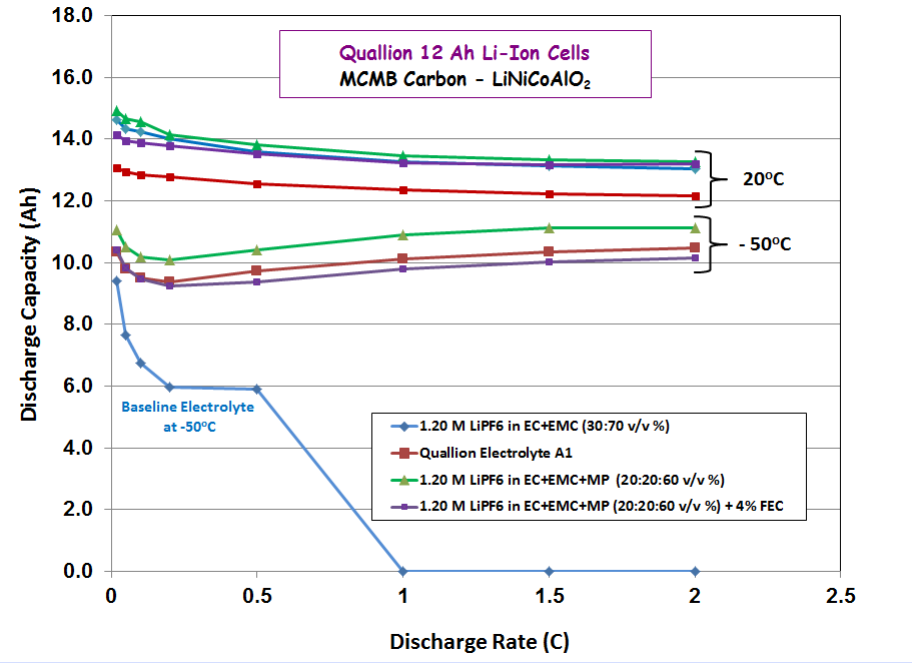


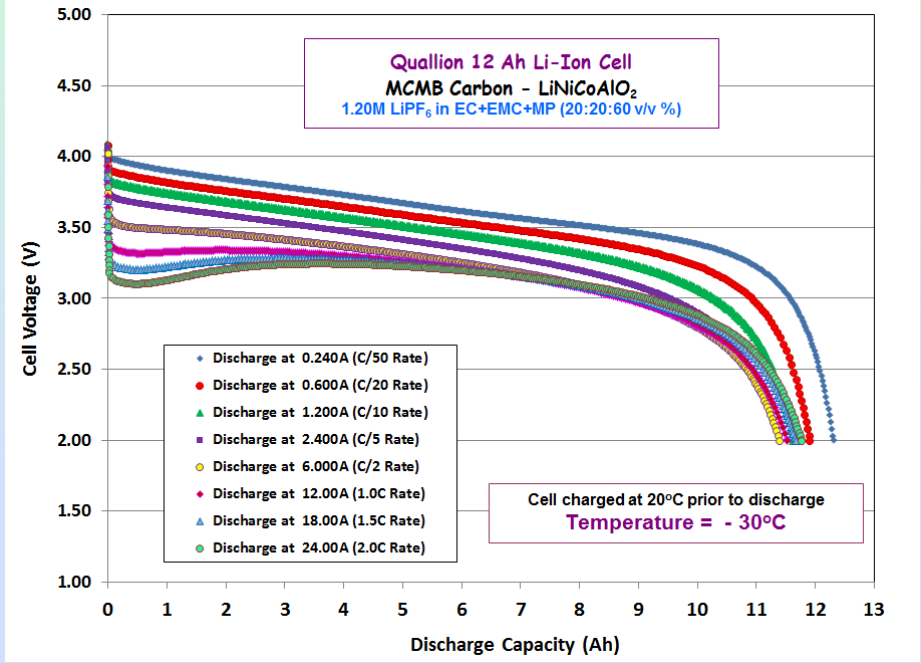
MP-Based Electrolyte



- In collaboration with Quallion, large capacity (12 Ah) MCMB/NCA cells were tested with (i) 1.20M $LiPF_6$ in EC+EMC+MP (20:20:60 vol %) and (ii) 1.20M $LiPF_6$ in EC+EMC+MP (20:20:60 vol %) + 4% FEC.
- Excellent performance was demonstrated down to temperatures as low as -50°C, with over 75% of the room temperature capacity being delivered up to 2C rates with both formulations.

Quallion Prototype 12 Ah Li-Ion Cells
Wide Operating Temperature Electrolytes
Discharge Characterization at Various Temperatures





- **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.**

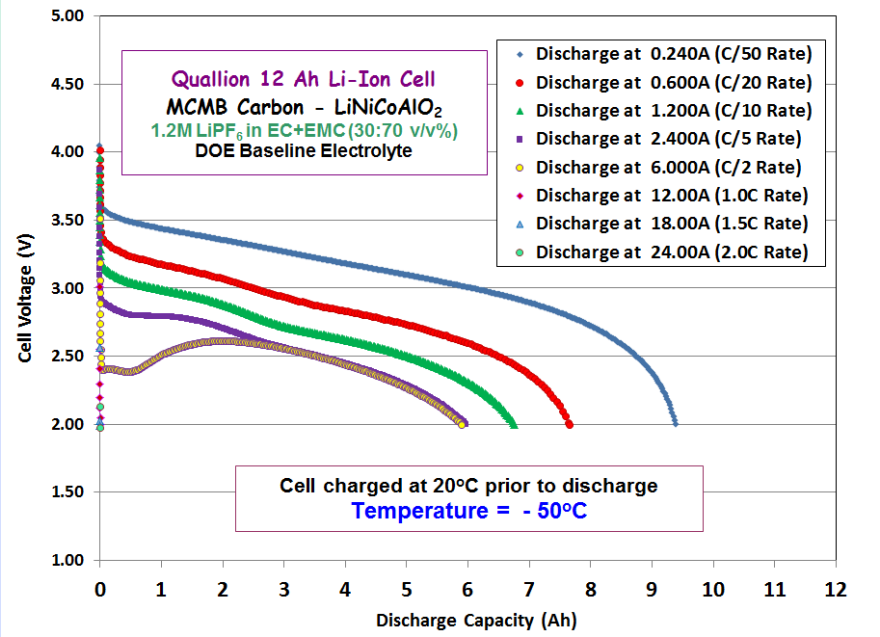
➢ *Quallion collaboration supported by NASA SBIR Program.*
(H. Tsakamoto, M. Tomcsi, M. Nagata, and V. Visco)

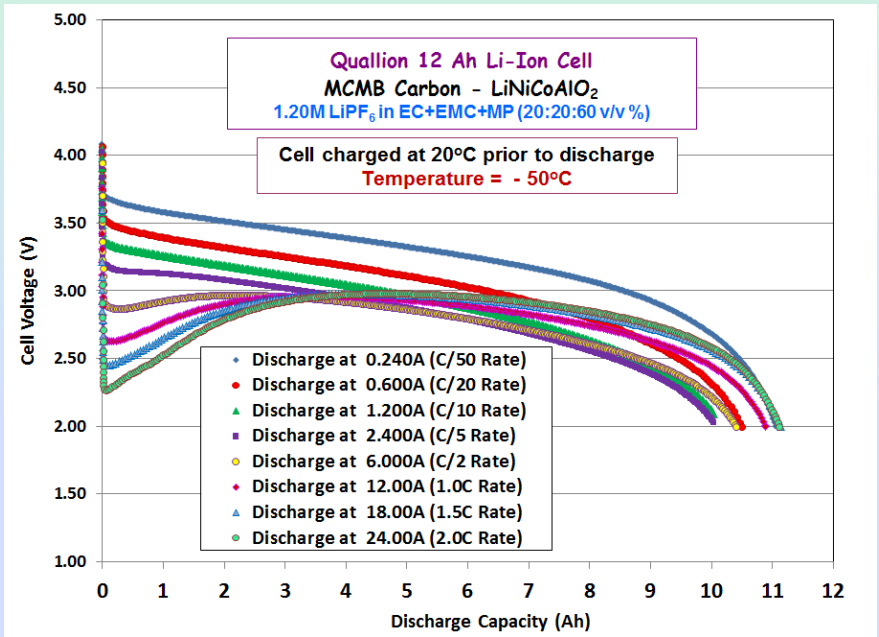
Technical Accomplishments

Quallion Prototype 12 Ah Li-Ion Cells

Wide Operating Temperature Electrolytes

Discharge Characterization at Various Temperatures

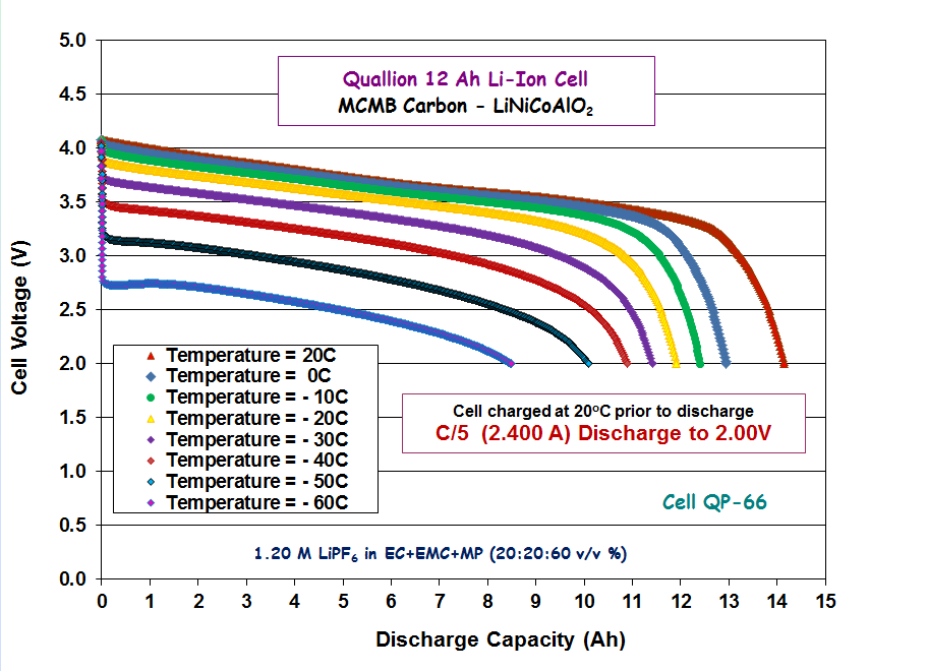


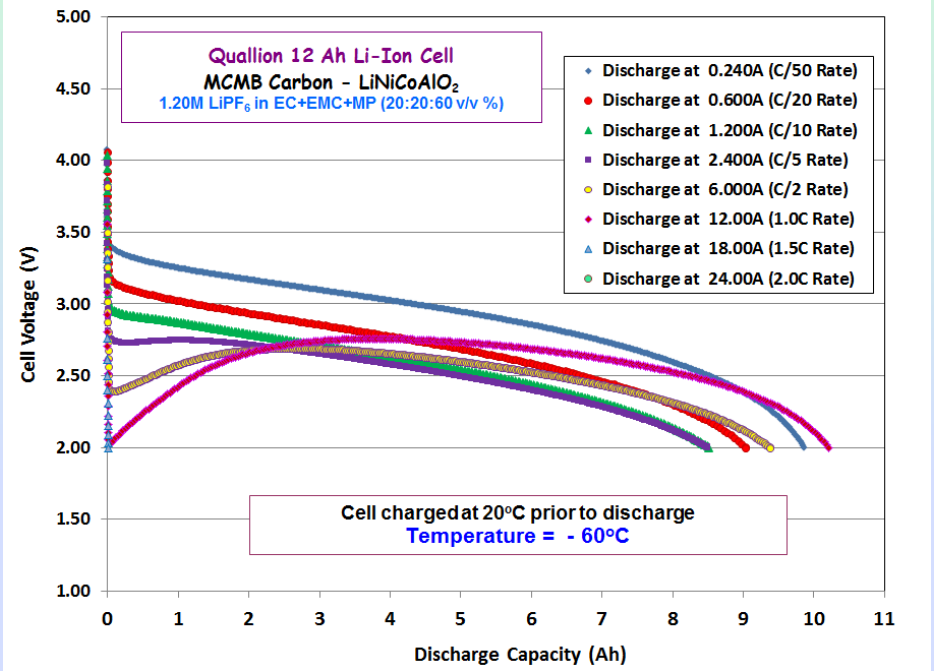


- **Performance of methyl propionate based electrolytes demonstrated in large capacity 12 Ah cells.**
- **Improved power capability demonstrated with methyl propionate-based electrolytes over a wide temperature range (able to support 2C rates down to -60°C), outperforming the baseline electrolyte under these conditions.**
- **Currently performing life tests (~ 50% DOD) in which the capacity, impedance, and rate capability at low temperature is measured periodically (every 100 days).**

➢ *Quallion collaboration supported by NASA SBIR Program.*
(H. Tsakamoto, M. Tomcsi, M. Nagata, and V. Visco)

Quallion Prototype 12 Ah Li-Ion Cells
Methyl Propionate-Based Wide Operating Temperature Electrolytes
Discharge Characterization at Various Temperatures





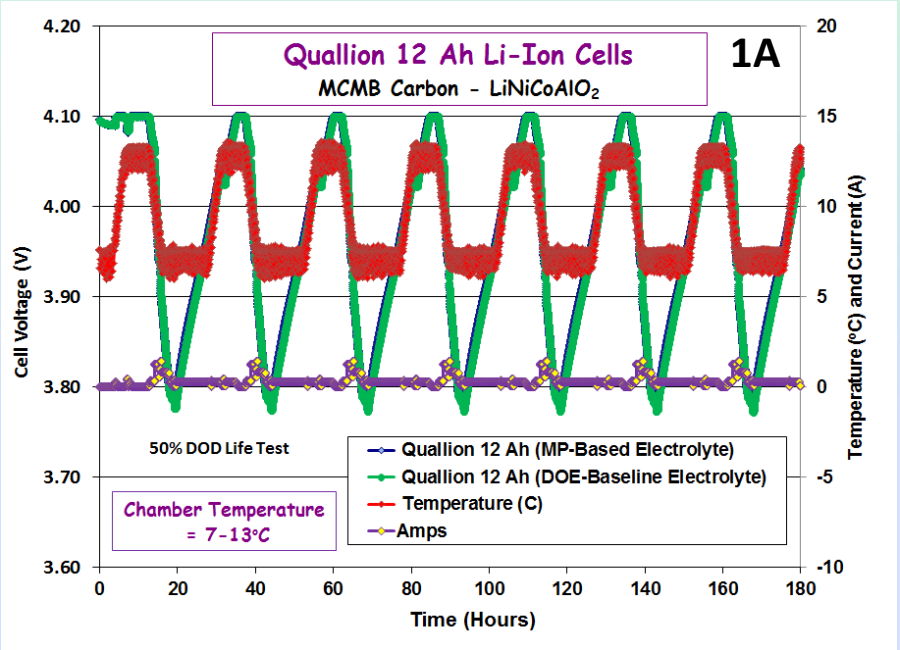
- **Methyl propionate-based electrolyte demonstrated to have good performance down to -60°C, whereas the baseline electrolyte displays negligible capacity under these conditions.**
- **Currently performing life tests (~ 50% DOD) in which the capacity, impedance, and rate capability at low temperature will be periodically measured.**
- **It is anticipated that the addition of FEC will improve the life characteristics.**

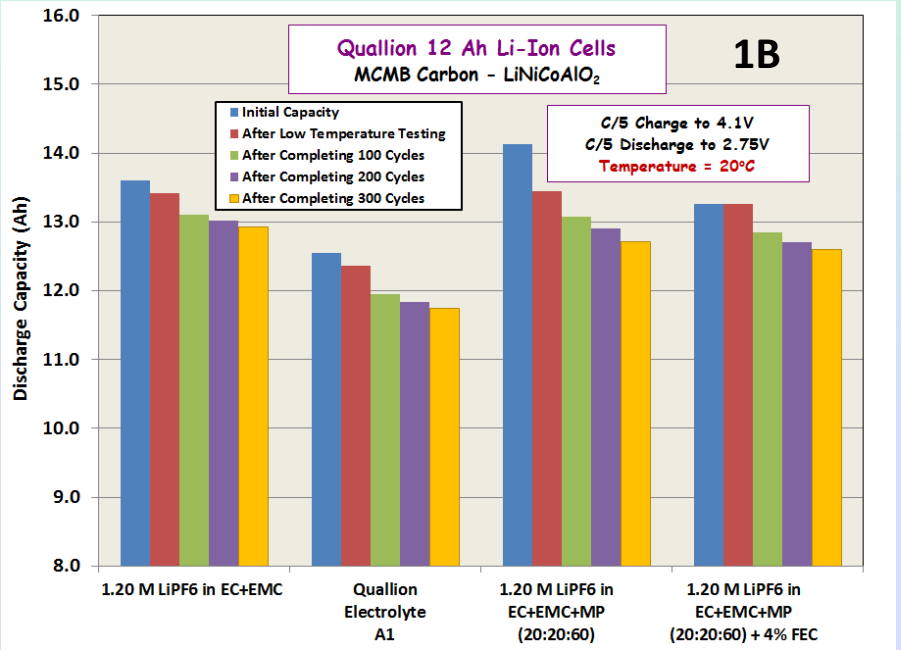
➢ *Quallion collaboration supported by NASA SBIR Program.*
(H. Tsakamoto, M. Tomcsi, M. Nagata, and V. Visco)

Quallion Prototype 12 Ah Li-Ion Cells with JPL Electrolytes

Low Temperature Performance Characterization

- Received four 12 Ah Quallion NCA cells containing JPL wide operating temperature range electrolytes and undergoing performance testing (rate characterization and life testing).



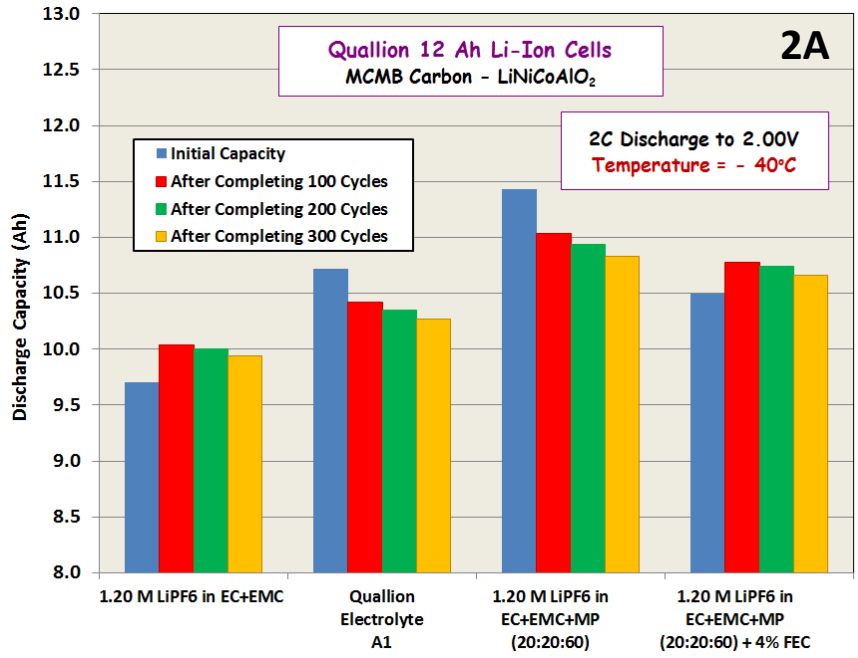


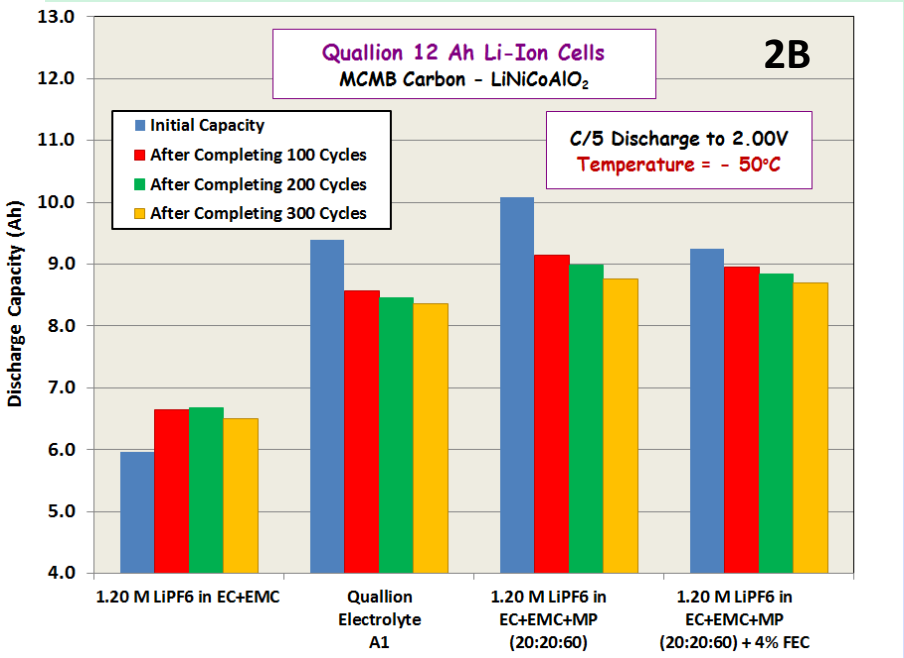
Quallion 12 Ah Cell

- **Partial DOD cycling (~ 50% DOD) is being performed on four 12 Ah Quallion Cells (Fig. 1A).**
- **Cells have completed 300 cycles (300 days of operation) and have been recently characterized down to -50°C**
- **Periodically measuring the capacity, impedance, and rate capability at low temperature (every 100 days) to demonstrate the performance throughout the life of the cell.**
- **The addition of FEC improves the capacity retention as a result of cycling.**

➢ *Quallion collaboration supported by NASA SBIR Program (M. Tomcsi, M. Nagata, and V. Visco)*

Quallion Prototype 12 Ah Li-Ion Cells
Wide Operating Temperature Electrolytes
Discharge Characterization at Various Temperatures





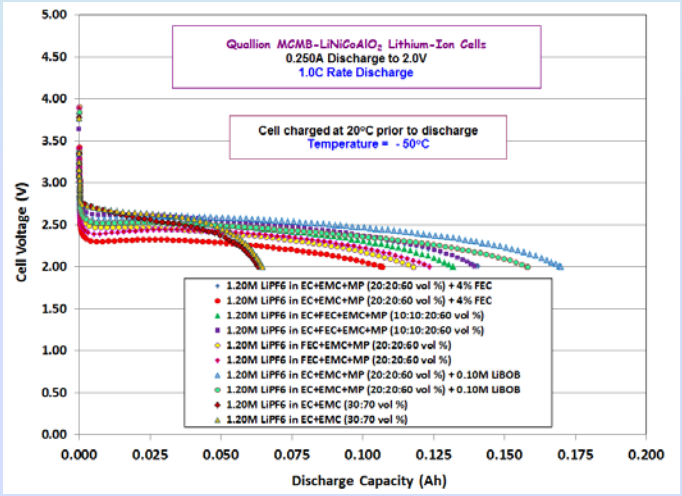
- When the cells were characterized at low temperature after cycling, the methyl propionate-based electrolytes were observed to deliver the highest capacities.
- The addition of FEC observed to improve the preservation of low temperature capability throughout life.
- Higher capacity seen in some cases compared to initially, which is attributed to internal cell heating on discharge associated with cell impedance increase.
- Based on data obtained on smaller prototype cells (0.25Ah size), the larger cells are anticipated to support much higher discharge rates at low temperature (discharge currents evaluated limited by channel capability of 25A).

Quallion Prototype 0.25 Ah Li-Ion Cells

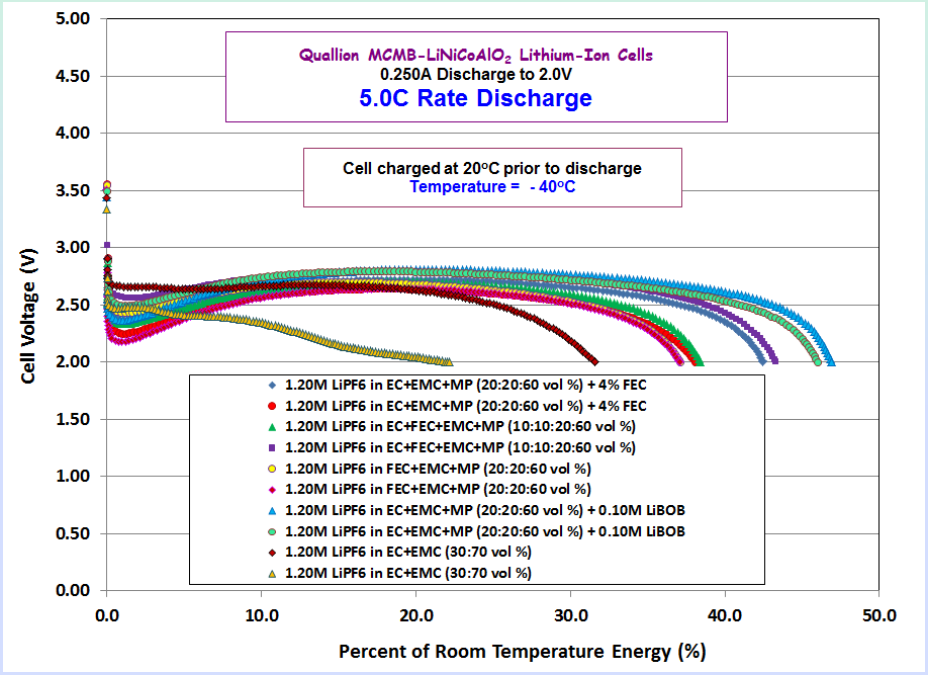
Discharge Characterization at Low Temperatures

- We are currently evaluating a number of 0.30 Ah Quallion cells with the following JPL electrolytes:
- **1.2M $LiPF_6$ in EC+EMC+MP (20:20:60) + 4% FEC**
- **1.2M $LiPF_6$ in EC+FEC+EMC+MP (10:10:20:60)**
- **1.2M $LiPF_6$ in FEC+EMC+MP (20:20:60)**
- **1.2M $LiPF_6$ in EC+EMC+MP (20:20:60) + 0.10M LiBOB**

1C Rate Discharge at -50°C



5C Rate Discharge at -40°C



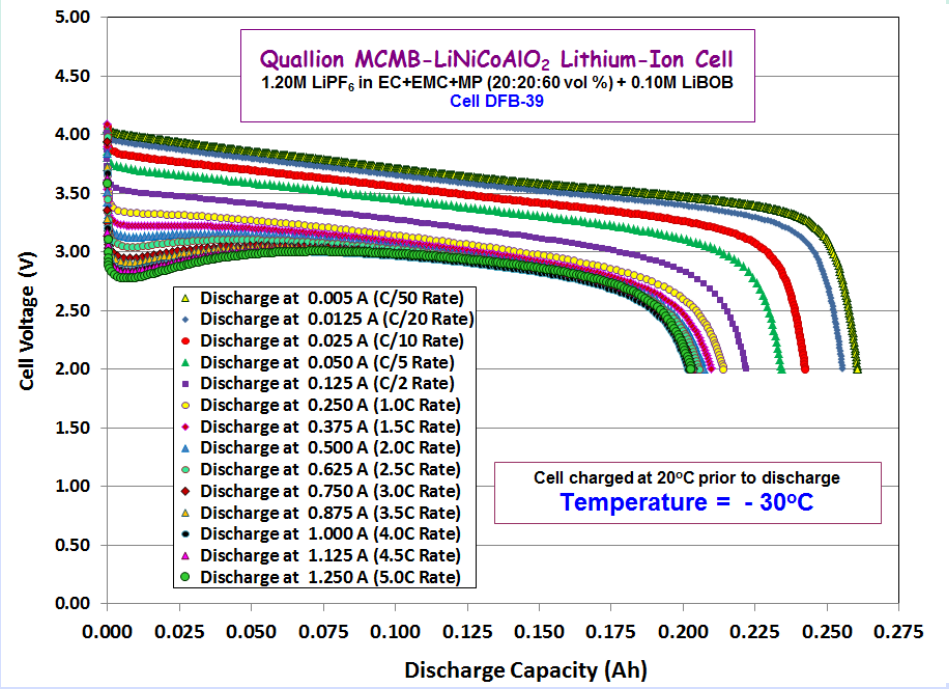
- **Electrolytes selected for evaluation include methyl propionate-based electrolytes with increasing FEC content and the use of LiBOB as an additive.**
- **All electrolytes are observed to provide improved performance at high rates at very low temperatures compared with the baseline electrolytes, with 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.**

Quallion Prototype 0.25 Ah Li-Ion Cells

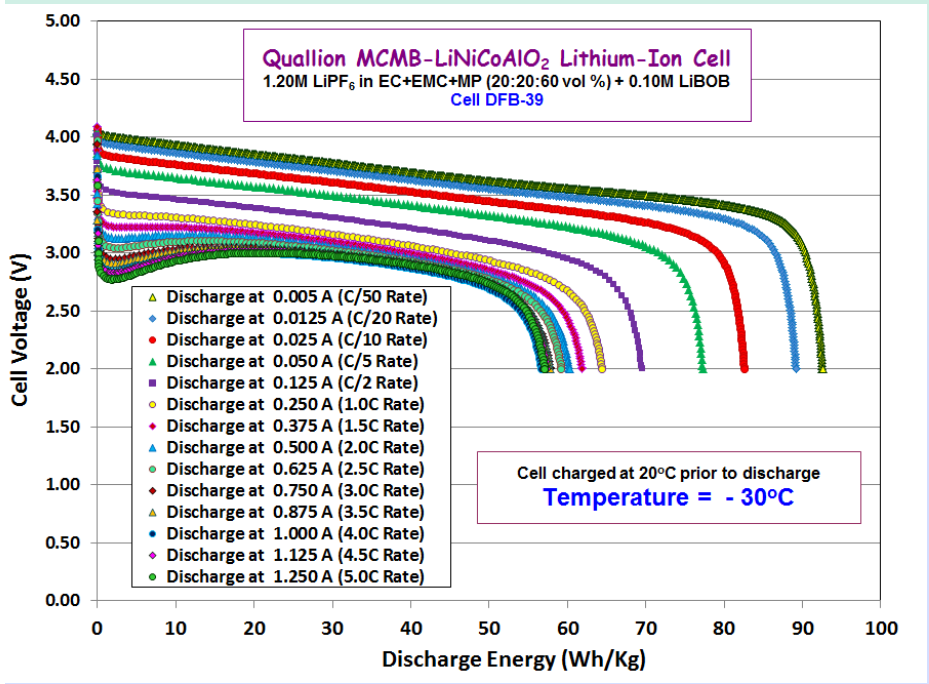
Discharge Performance at - 30°C

Electrolyte : 1.2M $LiPF_6$ + 0.10M LiBOB in EC+EMC+MP (20:20:60 v/v %)

Capacity (Ah)



Discharge Energy (Wh/Kg)



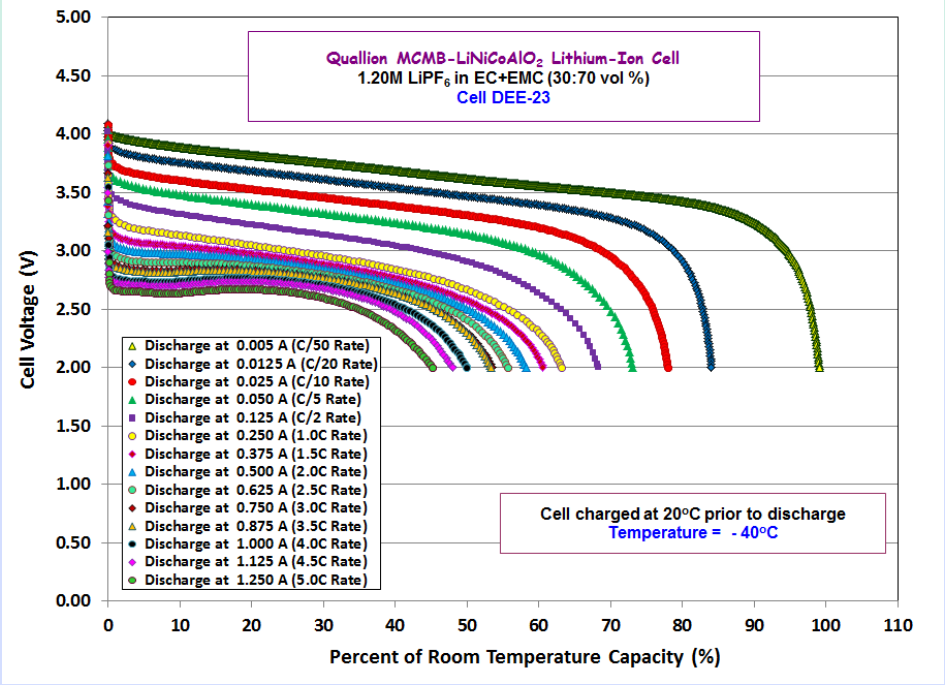
- The cell containing the electrolyte with methyl propionate and LiBOB has displayed excellent power capability at -30°C.
- The incorporation of LiBOB has been attributed to increase cathode kinetics at low temperatures, as determined by Tafel Polarization measurements performed on 3-electrode cells.

Quallion Prototype 0.25 Ah Li-Ion Cells

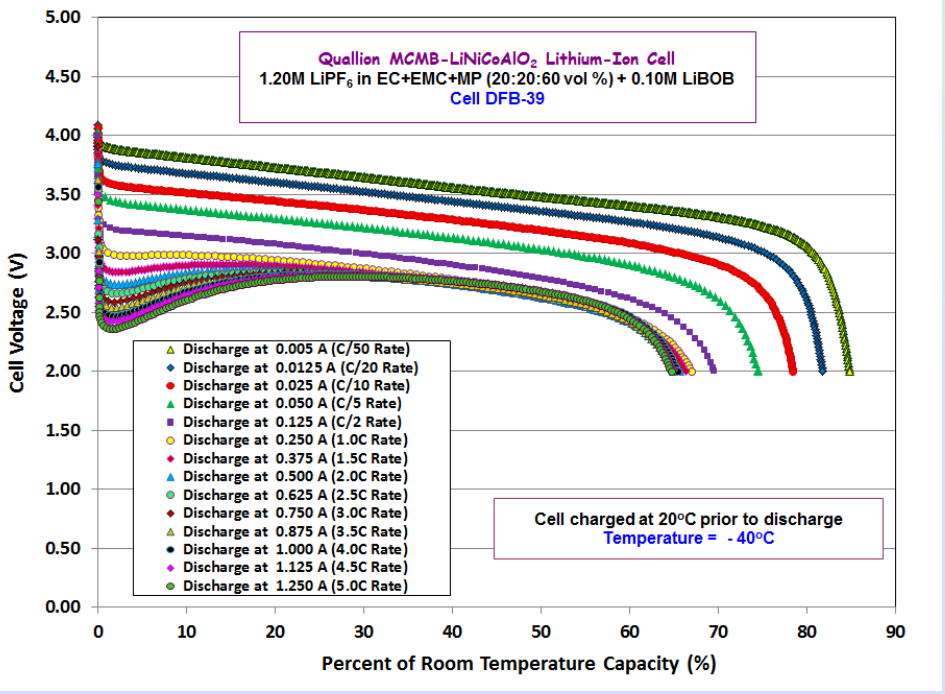
Discharge Characterization at Low Temperatures

High Rate Discharge at -40°C (Up to 5C Rates)

1.2M LiPF6 in EC+EMC (30:70) (Baseline)



1.2M LiPF6 in EC+EMC+MP (20:20:60) + 0.10M LiBOB



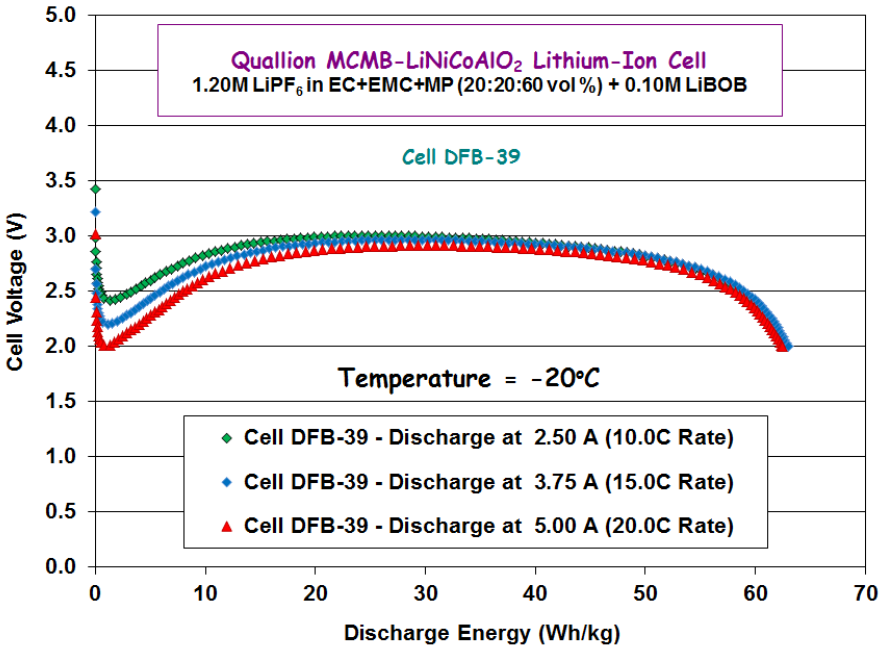
- All electrolytes are observed to provide improved performance at high rates at very low temperatures compared with the baseline electrolytes, with the LiBOB outperforming all formulations.
- The incorporation of LiBOB has been attributed to increase cathode kinetics at low temperatures, as determined by Tafel Polarization measurements performed on 3-electrode cells.

Quallion Prototype 0.25 Ah Li-Ion Cells

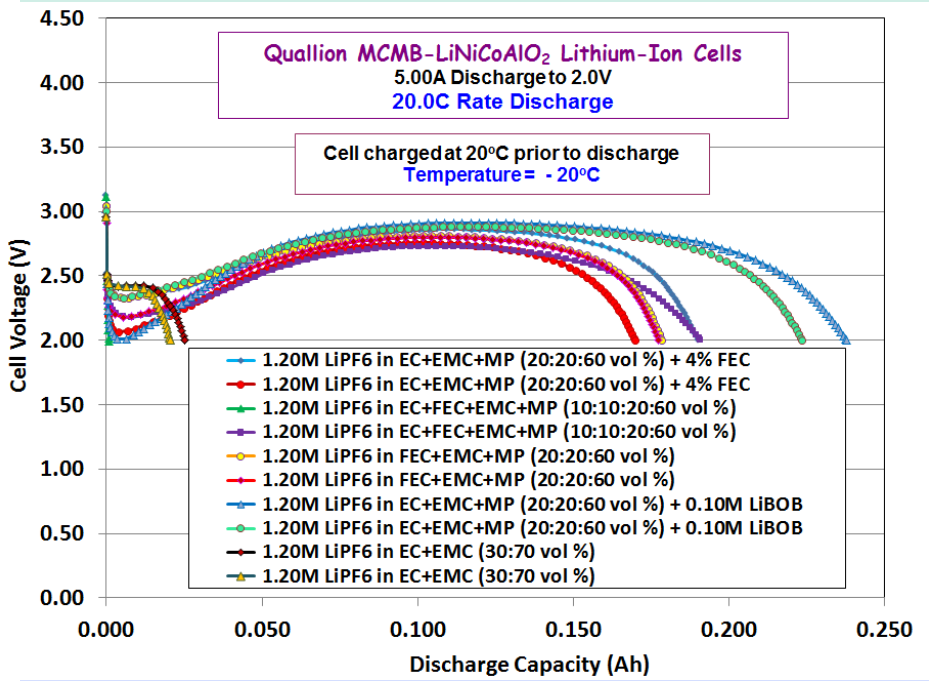
Discharge Performance at - 20°C

High Rate Discharge Performance at Low Temperature (up to 20C Rates)

MP + LiBOB Electrolyte



20C Discharge at -20°C



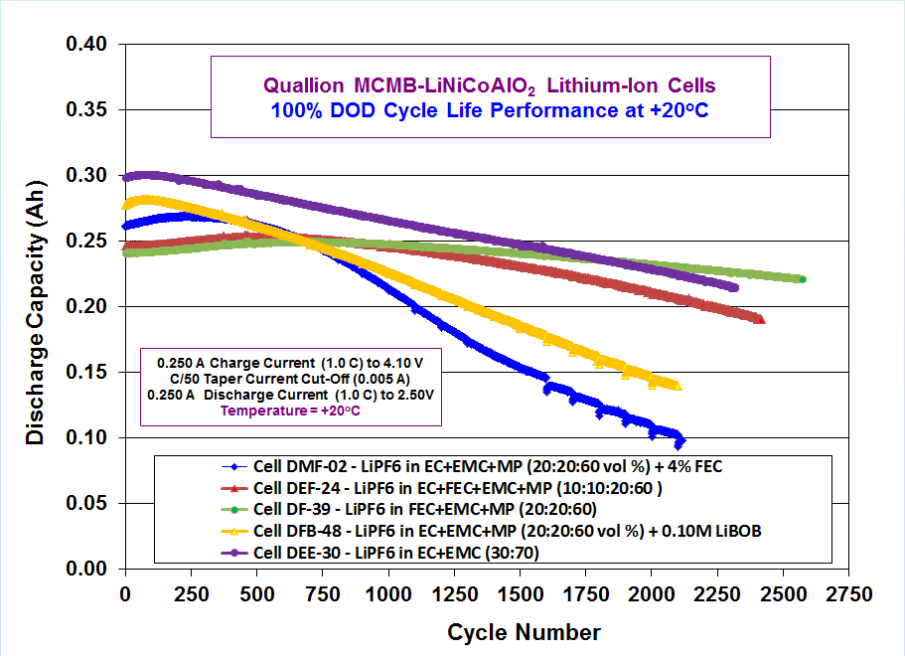
- The cell containing the electrolyte with methyl propionate and LiBOB has displayed very high power capability at -20°C, being able to provide over 60 Wh/kg at a 20C discharge rate.
  - All of the MP-based electrolytes displayed dramatically improved power capability.
- At a 20C discharge rate at -20°C, the cell containing the MP-based electrolyte delivered over 11 times greater discharge energy (i.e., 62.2 Wh/kg compared to only 5.5 Wh/kg for the baseline).

Quallion Prototype 0.25 Ah Li-Ion Cells

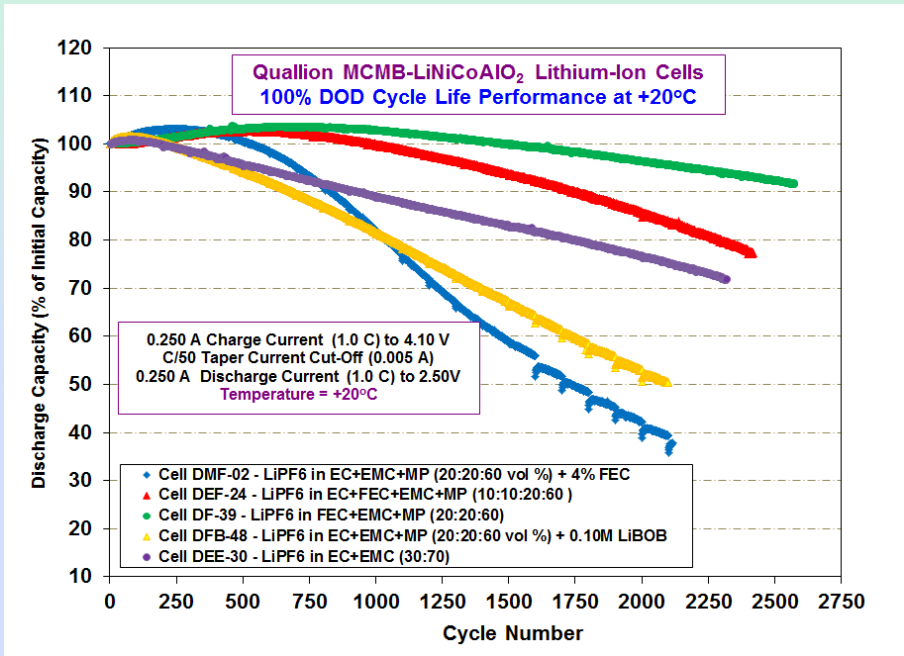
Methyl Propionate-Based Wide Operating Temperature Electrolytes

100% DOD Cycle Life at +20°C

Capacity (Ah)



Percent of Initial Capacity (Ah)



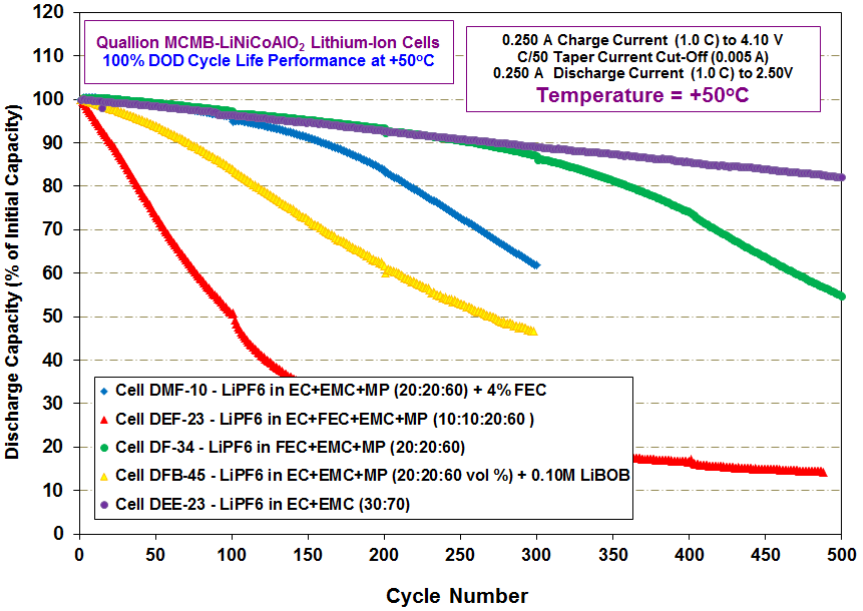
- **Thus far, the cells containing the MP-based wide operating temperature range electrolytes provide good life at 20°C, with somewhat lower capacity displayed initially.**
- **Unlike initial testing at high temperature (i.e. 50°C) , no degradation was observed when FEC was added to the electrolyte in high proportion (10 or 20%), even if present as the only cyclic carbonate.**
- **The cell containing LiPF6 in FEC+EMC+MP was observed to deliver > 91% of the initial capacity after completing 2,550 cycles (100% DOD).**

Quallion Prototype 0.25 Ah Li-Ion Cells

Methyl Propionate-Based Wide Operating Temperature Electrolytes

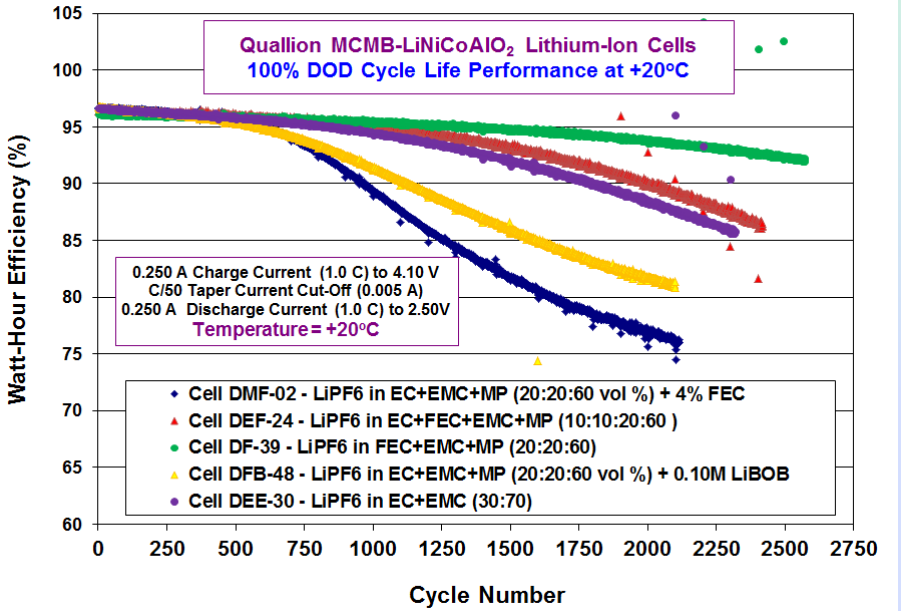
100% DOD Cycle Life at +50°C

Percent of Initial Capacity (Ah)



100% DOD Cycle Life at +20°C

Watt-Hour Efficiency (%)



- **Excellent retention of the watt-hour efficiency was observed with the cell containing $LiPF_6$ in FEC+EMC+MP when subjected to cycling at +20oC, suggesting minimal impedance growth.**
- **When the cells containing the MP-based wide operating temperature range electrolytes were cycled at 50°C, the electrolyte with FEC added in high proportion (20%), provided the best performance.**
- **Future efforts will be devoted to coupling additives targeted at improving the high temperature resilience with the FEC-rich methyl propionate blends.**

SUMMARY and CONCLUSIONS

- ***Demonstration of Methyl Propionate-Based 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. This represents over a 4-fold improvement over the baseline electrolyte system.***
  - ***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.***
  - ***At a 20C discharge rate at -20°C, a cell containing the MP-based electrolyte delivered over 11 times greater discharge energy (i.e., 62.2 Wh/kg compared to only 5.5 Wh/kg for the baseline).***
  - **A cell containing LiPF6 in FEC+EMC+MP was observed to deliver > 91% of the initial capacity after completing 2,550 cycles (100% DOD), outperforming the cells containing the baseline all carbonate-based blend.**
  - ***Demonstrated good performance in larger capacity (12 Ah) Quallion Li-ion cells with methyl propionate-based electrolytes. Good low temperature performance is preserved during the course of long term cycling.***

Acknowledgments

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