The Use of Low Temperature Electrolytes in High Specific Energy Li-Ion Cells for Future NASA Missions to Icy Moons

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229th Meeting of the Electrochemical Society (ECS)
San Diego, California
June 1, 2016

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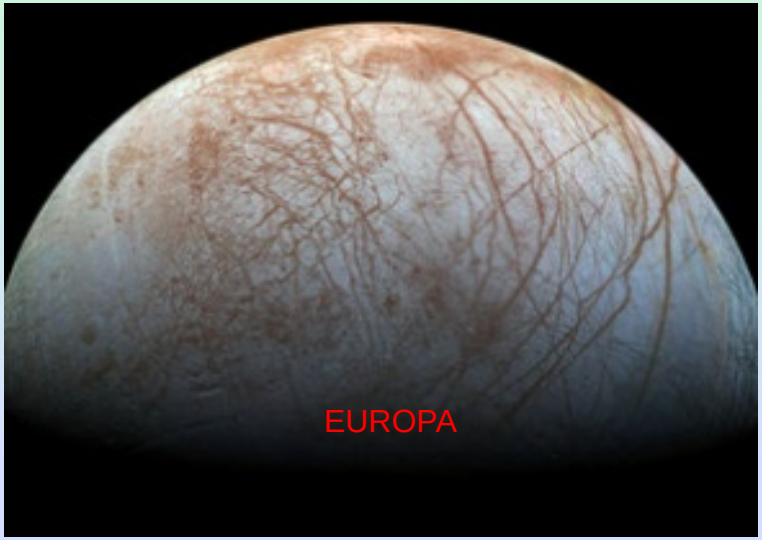
Background: Mission Concept Needs

Potential Europa Lander Power System Needs

- **Power: ~ 100 W**
- **Voltage ~ 28 V**
- **Operational Life on Surface: 7-14 days**

  (2 - 4 Europa days)
- **Mission Survivability/Shelf Life: 15 years**
- **Operating Temperature: - 60ºC to 40ºC**
- **Radiation Tolerance: > 2-4 Mrad**
- **Planetary Protection: Required**



- **A potential mission to Europa could benefit significantly from a low temperature rechargeable battery with full operational capability when coupled with solar arrays, enabling a means to meet a 14 day requirement:**
  - If RHU's or RTG's were not selected to provide heat, low temperature batteries would be desired
  - Improved low temperature performance **(down to -60ºC)** would reduce thermal power loads
  - Results in lower power sub-system and thermal power sub-system mass
  - Extended mission durations are possible (> 14 days)

Background: Technology Development Targets

- **Combined rechargeable Li-ion batteries/solar arrays could augment primary batteries for extended missions:**
  - Current technology limited to operation at temperatures above -30ºC.
  - One of the key challenges is *charging* at low temperatures, due to reduced charge acceptance.
  - Low temp charging and Li plating can lead to increased rate of cell degradation and premature cell failure.
  - Improved low temperature performance (-40 to -60ºC) will reduce required thermal management power and complexity, by bringing operational temperature limits in-line with primary batteries and avionics.

Performance Metrics	State-of-practice Rechargeable Batteries	Proposed Rechargeable Low Temperature Li-Ion Batteries	Proposed Rechargeable Low Temperature Li-Ion Batteries (stretch goal)
Cell Specific Energy at +20˚C (Wh/kg)	130-150	150-200	150-200
BOL Cell Specific Energy at Low Temperature (Wh/kg, discharge)	95-115 at -20˚C	≥100 at -40˚C	75-100 at -60˚C
Cycle Life	>500	300	300
Lower Temperature Charging Limit (˚C)	-20 to -30	-40	-60
Operational Temperature (˚C)	-30 to +35	-40 to +35	-60 to +35
Shelf Life (Years)	15	15	15
Heritage	Phoenix, InSight Li-ion		

- **Primary goal is to demonstrate > 100 Wh/kg at -40ºC (with both charging and discharging).**

Objective

- Develop rechargeable Li-Ion batteries that can operate at low temperatures for potential mission to Icy Moons
- Improve the specific energy of Li-ion batteries at low temperatures (increase the Wh/kg available)
- Extend the low temperature operating temp range (to -40°C or -60°C)
- Demonstrate continuous operation at low temperature

Approach

- Benchmark state of practice (SOP) aerospace quality Li-ion cells at low temperatures.
- Further develop JPL low temperature electrolytes to support charging and discharging down to low temperatures (- 40°C).
- Work with vendors to infuse electrolytes into flight qualifiable-cell designs optimized for low temperature operations.
- Demonstrate improved low temperature performance in prototype Li-ion cells.
- Utilize experimental three-electrode cells to elucidate the aspects of low temperature operation, including determining the kinetics as a function of temperature.

Advanced Li-Ion Prototypes Cells Under Evaluation

➢ Eagle-Picher Yardney Prototype Li-Ion Cells

- **MSL NCP-20-1 Prismatic Cells (~ 24Ah actual capacity)**
  - ➢ Represents baseline state of practice (SOP) aerospace Li-Ion Chemistry
  - ➢ Benchmarked cell chemistry over range of temperatures and rates
- **NCP-25-6 Prismatic Cells (~ 38Ah actual capacity) (InSight Cell)**
  - ➢ Represents state of art (SOA) Li-Ion Chemistry
  - ➢ Evaluated cell chemistry over range of temperatures and rates

➢ Quallion BTE Biomedical Prismatic Li-Ion Cells (0.25Ah actual capacity)

- **BTE Biomedical Prismatic Cells (0.25Ah actual capacity)**
  - ➢ Early generation prototypes evaluated under a NASA-SBIR program and a DOE program (> 30 Cells)
  - ➢ Excellent low temperature has been demonstrated previously (down to -60°C)
  - ➢ Quallion has provided a technical pathway to developing large capacity Li-ion cells that can provide high specific energy at -40°C

➢ E-One Molicel ICR-18650 M Custom Li-Ion Cells (~ 2.50 Ah actual capacity)

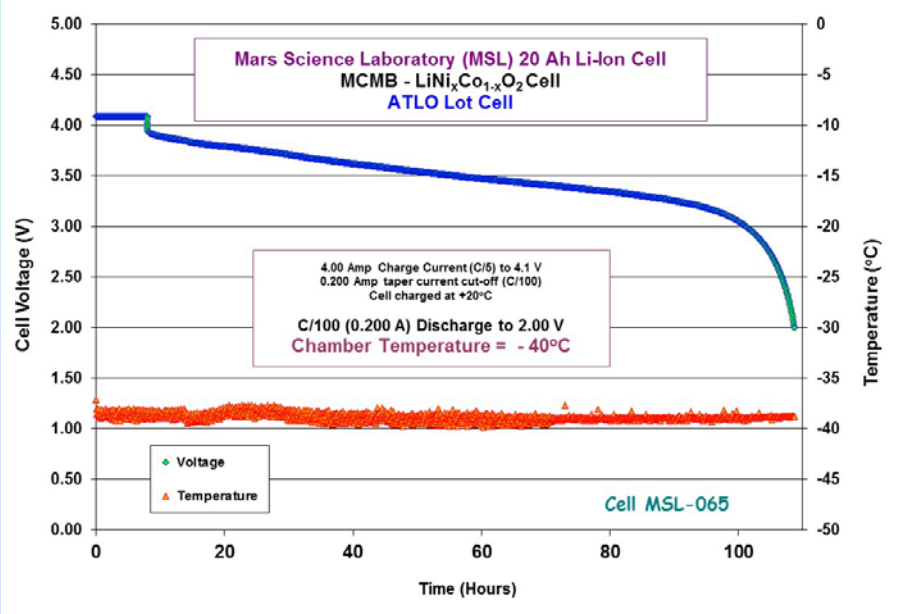
- **18650-Size Cylindrical Li-Ion Cells (2.50 Ah actual capacity)**
  - ➢ Early generation prototypes evaluated under the Europa Clipper program
  - ➢ Excellent low temperature has been demonstrated previously (down to -50°C)
  - ➢ Cells display very high specific energy

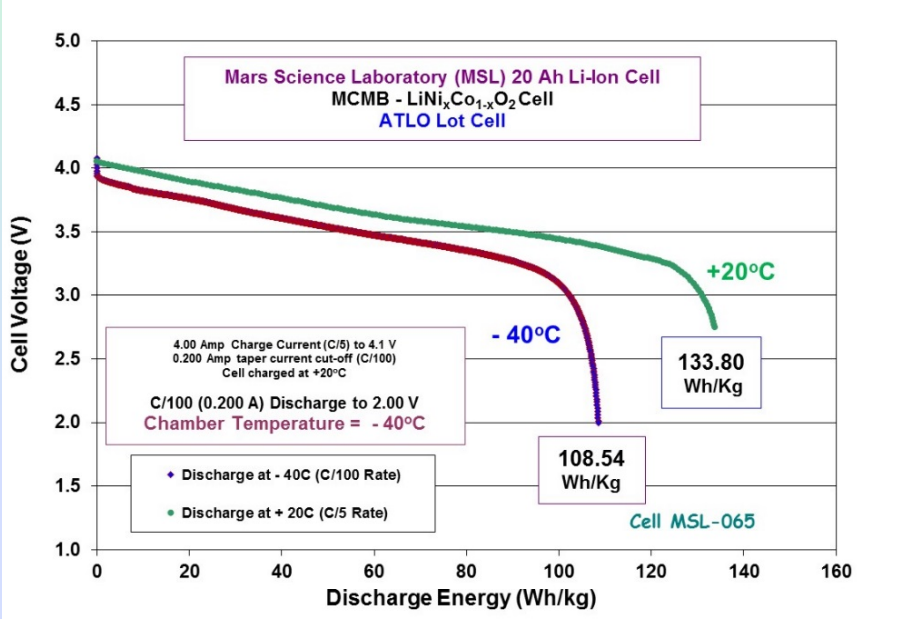
➢ **All cell designs incorporate JPL developed low temperature Li-ion electrolytes.**

Performance of MSL 20 Ah (Yardney NCP-20-1 Design) Li-Ion Cells:

Mars Science Laboratory (MSL or Curiosity) Heritage Chemistry

C/100 Discharge Rate at -40°C





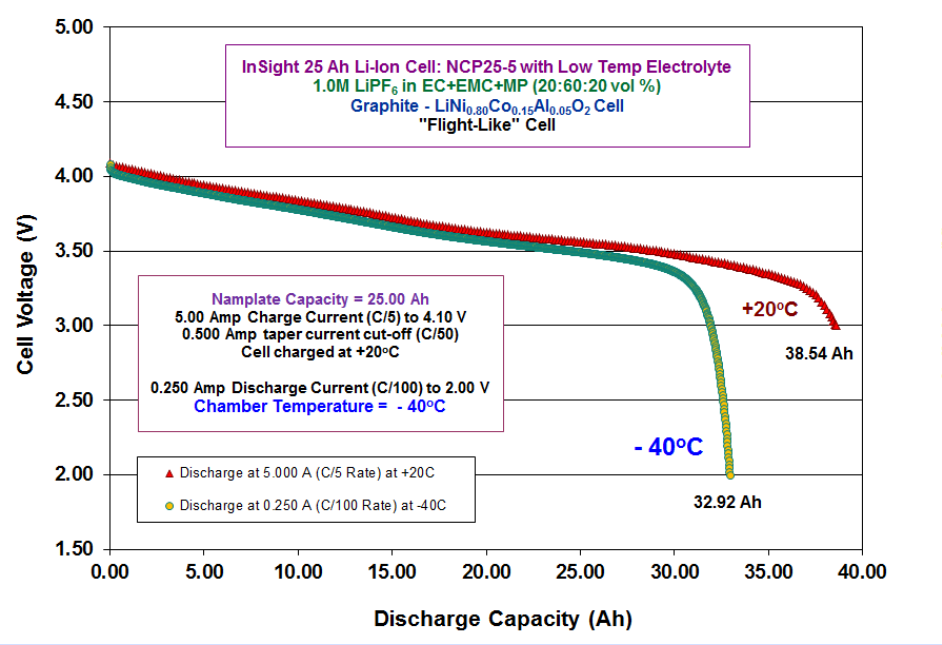
- The MSL heritage chemistry (i.e., first generation cell) delivers ~ 108 Wh/kg at -40°C using a low rate discharge (C/100 rate), compared with ~ 134 Wh/kg delivered at room temperature.
- This cell is also anticipated to have robust charge characteristics at -40°C. However, the specific energy will be low.

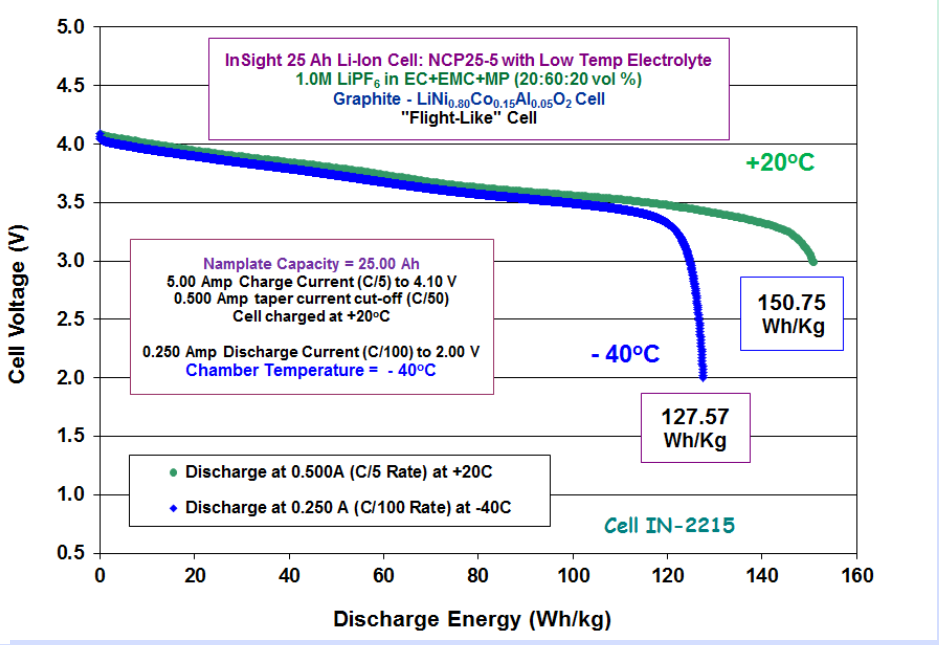
➢ The baseline heritage Li-ion battery technology has been benchmarked under relevant potential Europa Lander conditions.

Performance of InSight 36 Ah (Yardney NCP-25-1 Design) Li-Ion Cells:

(Next Generation NCA Chemistry + Low Temperature Electrolyte)

C/100 Discharge Rate at -40°C





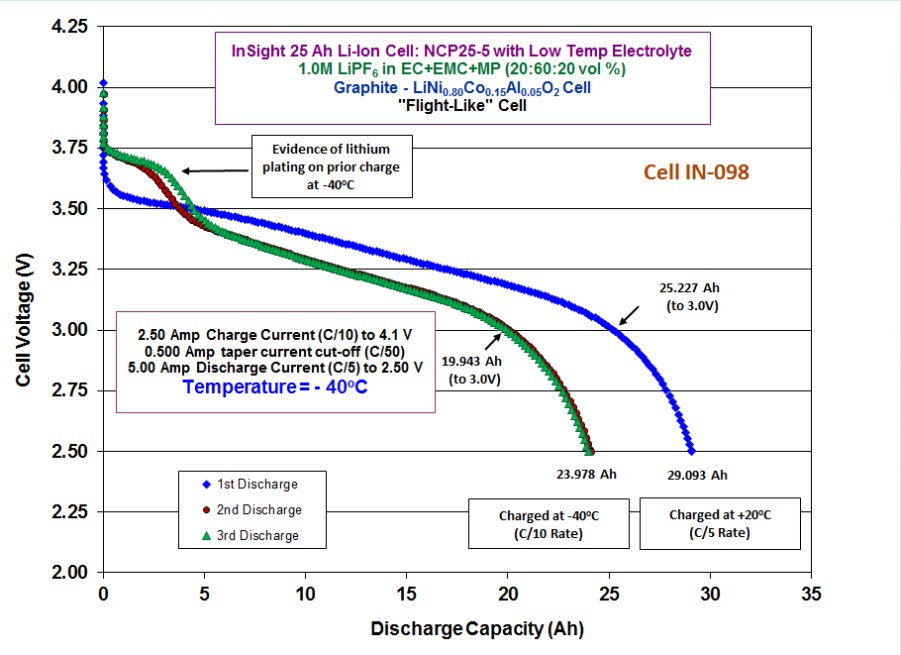
- The next generation InSight chemistry containing the MP-based low temperature electrolytes deliver improved performance compared with the MER/MSL heritage chemistry (i.e., it delivers ~ 127 Wh/kg at -40°C using a low rate discharge (C/100 rate), compared with ~ 150 Wh/kg delivered at room temperature.

- **The state of art (SOA) Li-ion battery technology has been benchmarked under relevant Europa Lander conditions.**

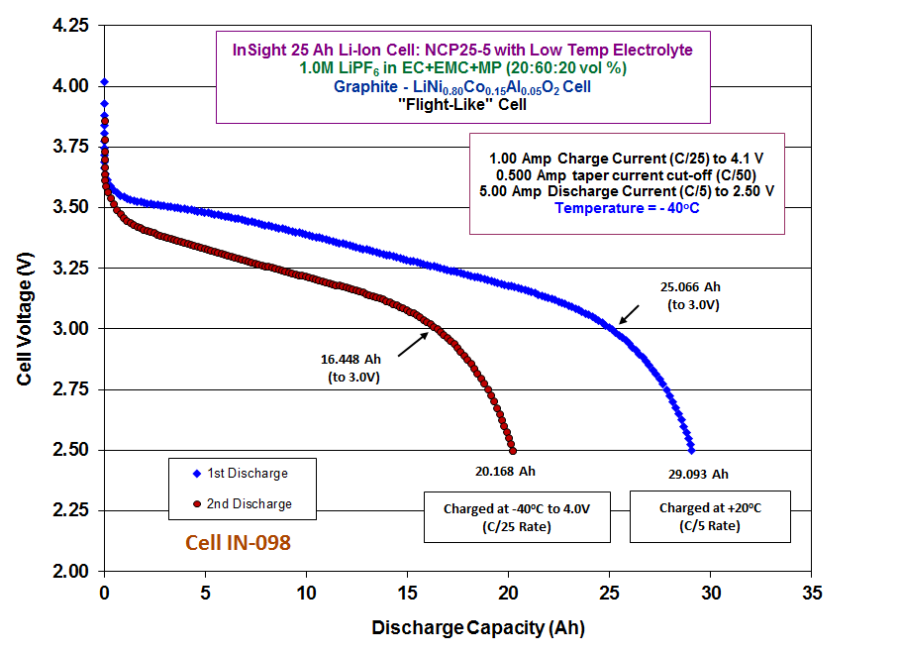
Performance Testing in Support of InSight Project

Charging and discharging at -40°C

C/10 (2.5A) to 4.10V at -40°C



C/25 (1.0A) to 4.00V at -40°C

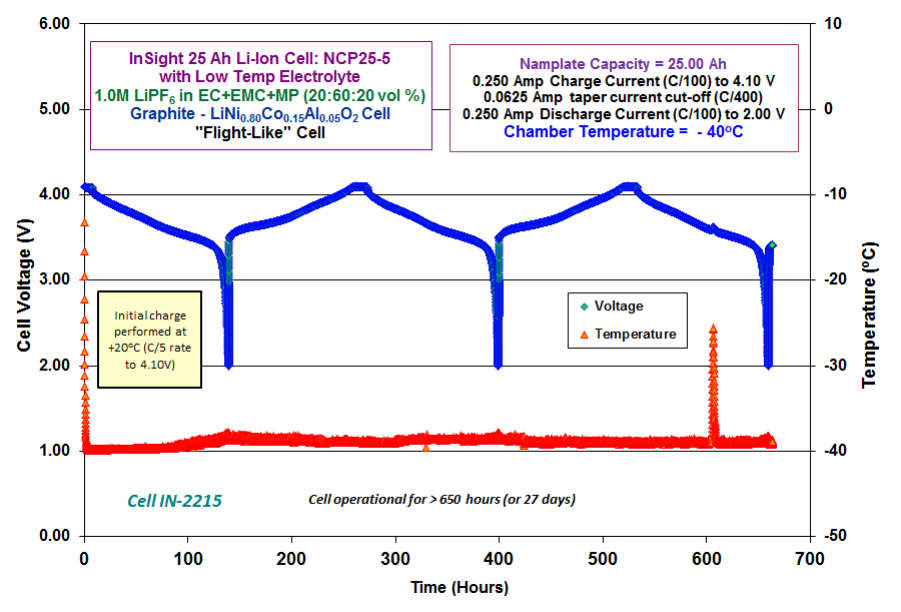


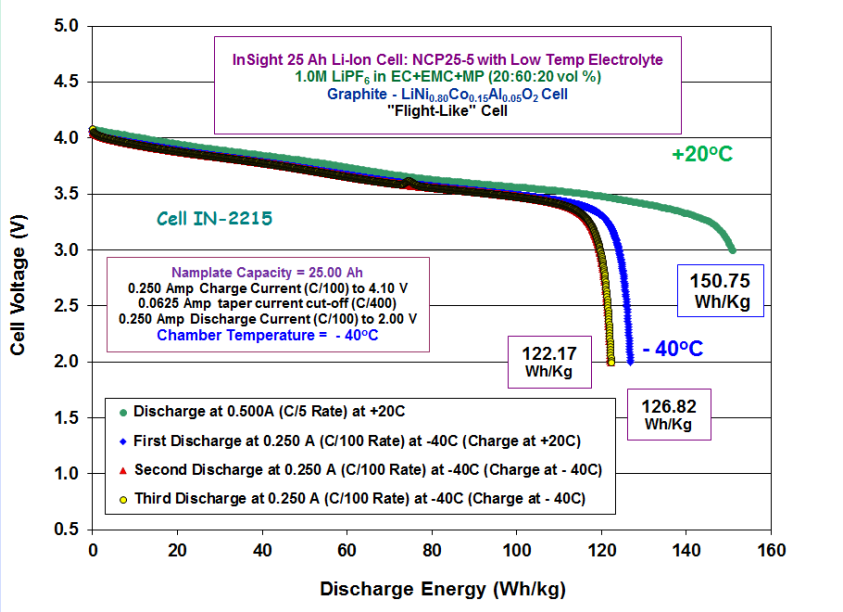
- When NCA/LTE cells were cycled at -40°C using C/10 charge rate, Li plating was observed on the anode
- This is indirectly observed by the higher voltage plateau on the subsequent discharge (i.e., the lower overpotential of lithium stripping compared to Li+ de-intercalation from graphite).
- Results led to the evaluation of lower charge rates and charge voltage test at -40°C (i.e., C/25 charge rate to 4.00V), where no evidence was observed.
- Subsequent testing established only modest plating at -35°C (C/5 rates to 4.10V) and no plating evident at -30°C (using C/5 charge rates to 4.10V)

Performance of InSight 36 Ah (Yardney NCP-25-1 Design) Li-Ion Cells:

(Next Generation NCA Chemistry + Low Temperature Electrolyte)

Cycling Continuously at -40°C at C/100 Rates (both Charging and Discharging)





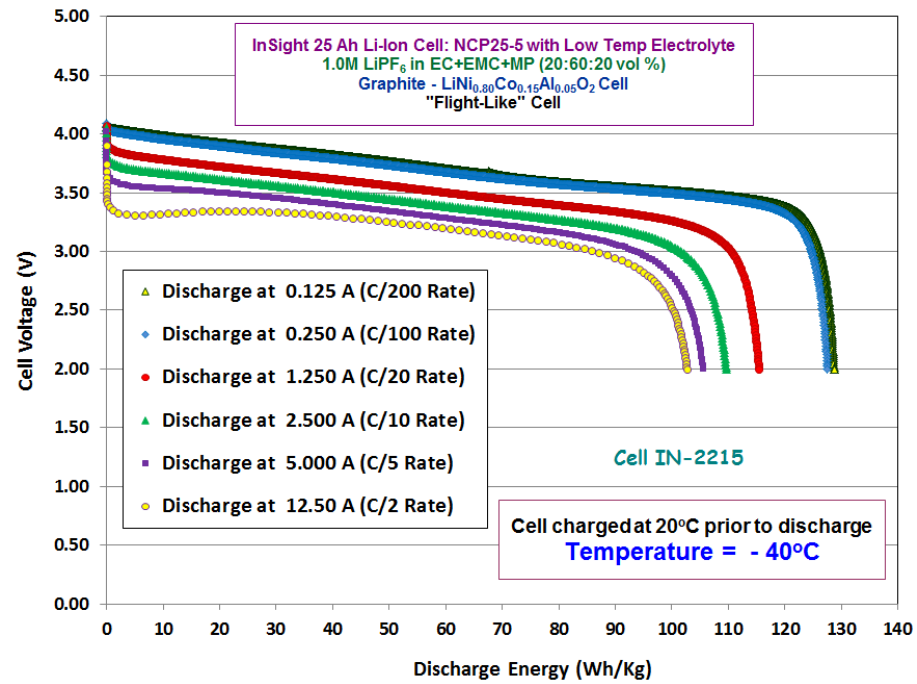
- The next generation InSight chemistry containing the MP-based low temperature electrolytes delivers good reversibility when cycled continuously at -40°C using low rates (i.e., delivering ~ 122 Wh/kg at -40°C).
- No evidence of lithium plating observed when cycled under these conditions.

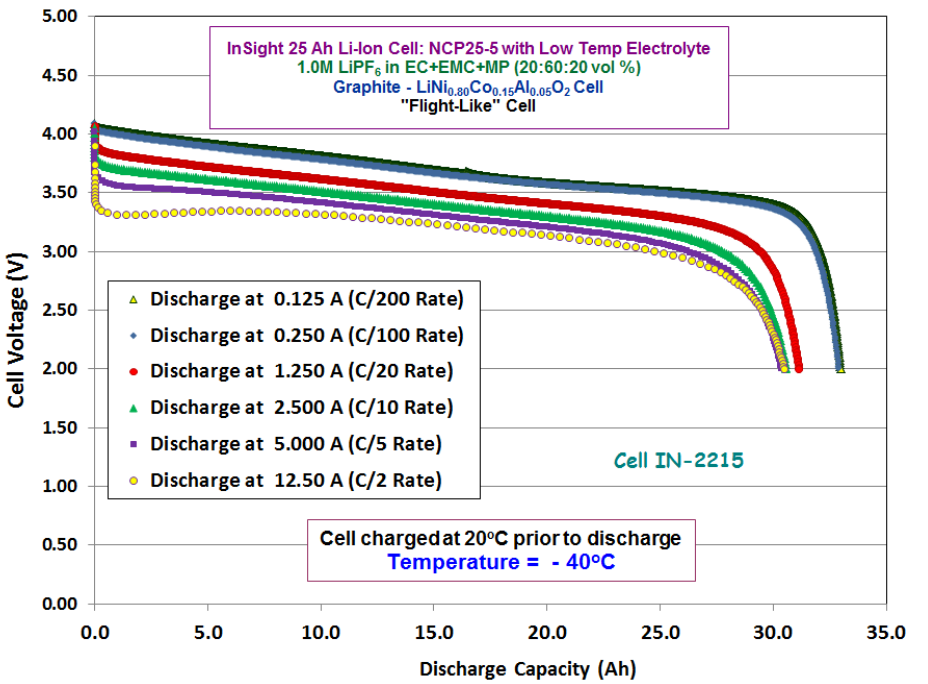
➢ Performance demonstration exceeds target of 100 Wh/kg at -40°C.

Performance of InSight 36 Ah (Yardney NCP-25-1 Design) Li-Ion Cells:

(Next Generation NCA Chemistry + Low Temperature Electrolyte)

Discharge Rate Capability at -40°C

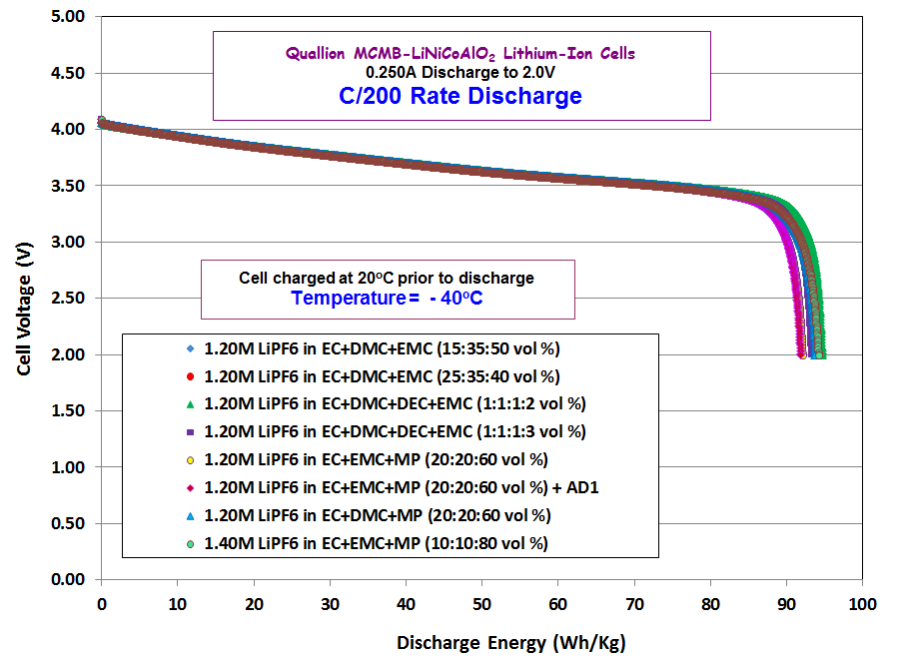


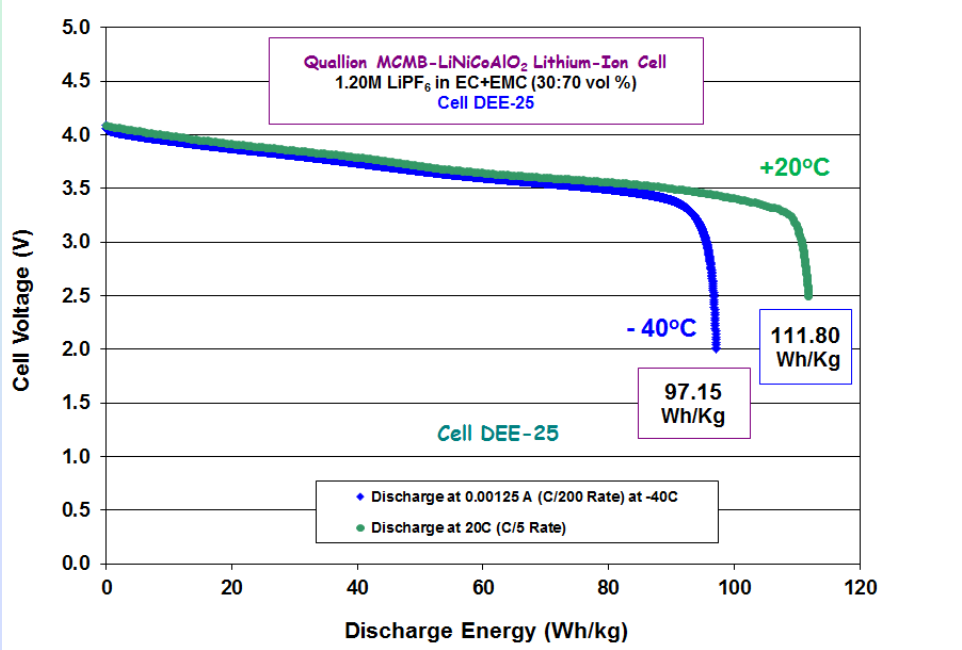


- The next generation InSight chemistry containing the MP-based low temperature electrolytes delivers good rate capability at -40°C , delivering over 102 Wh/kg at a C/2 rate (or 12.50A).
- Demonstrates that technology is well suited to support high power transmission events.

Performance of Quallion BTE Custom Li-Ion Cells

C/200 Discharge Rate at -40°C





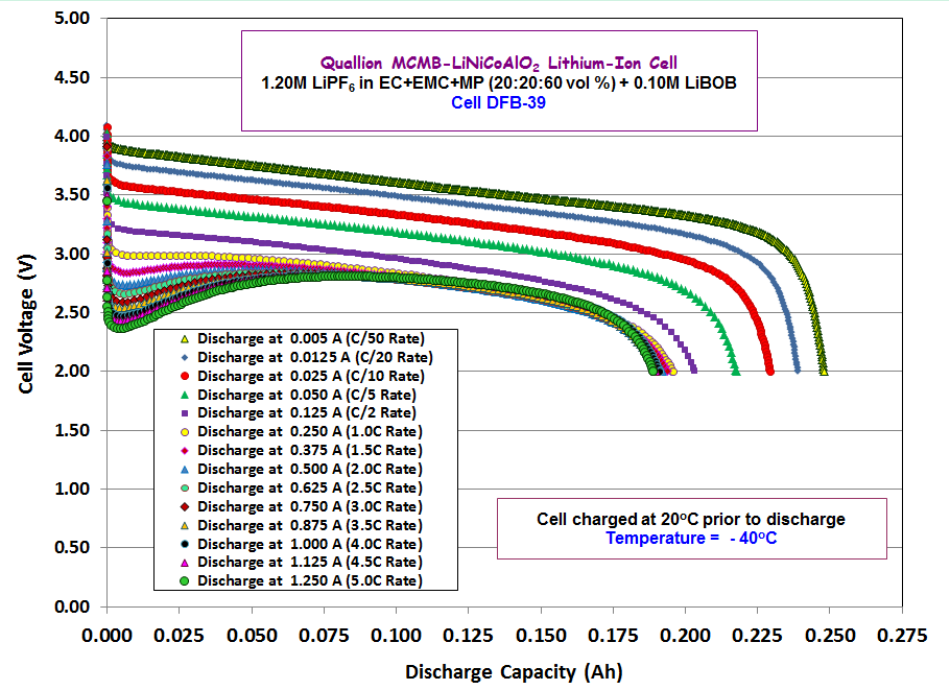
- Quallion cells have been demonstrated to provide consistent low temperature performance at -40°C at low rate, with the little impact of electrolyte type when charge at room temperature.
- Excellent retention of room temperature performance is observed.

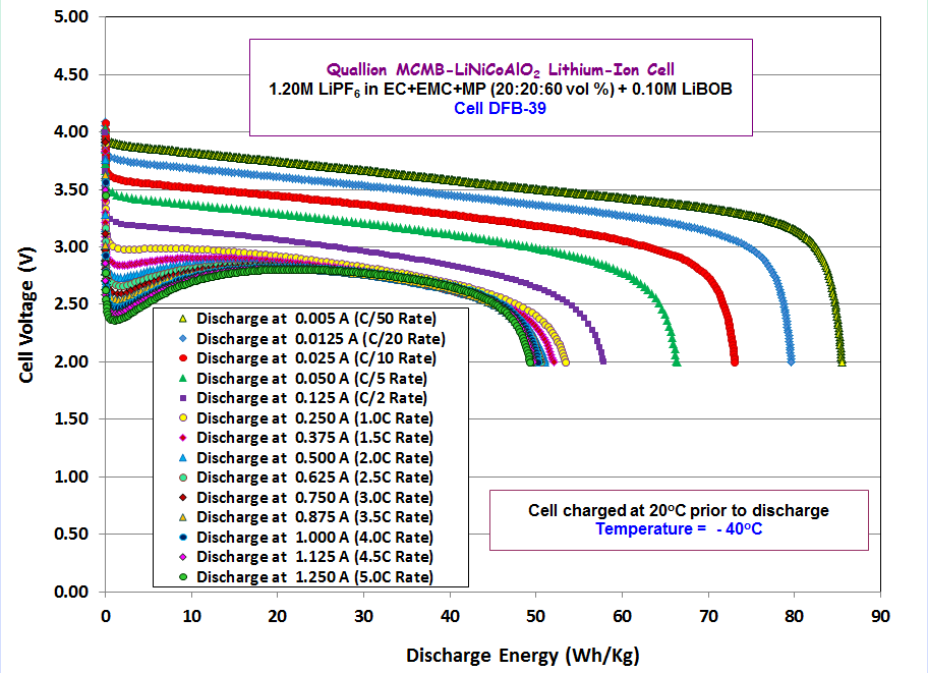
➢ **Larger cell designs provided by Quallion (up to 15 Ah) will result in higher specific energy at low temperatures compared to the small BTE cells (0.25 Ah).**

Performance of Quallion BTE Custom Cells

(Cells obtained under DOE program and NASA SBIR program)

Discharge Rate Capability at -40°C



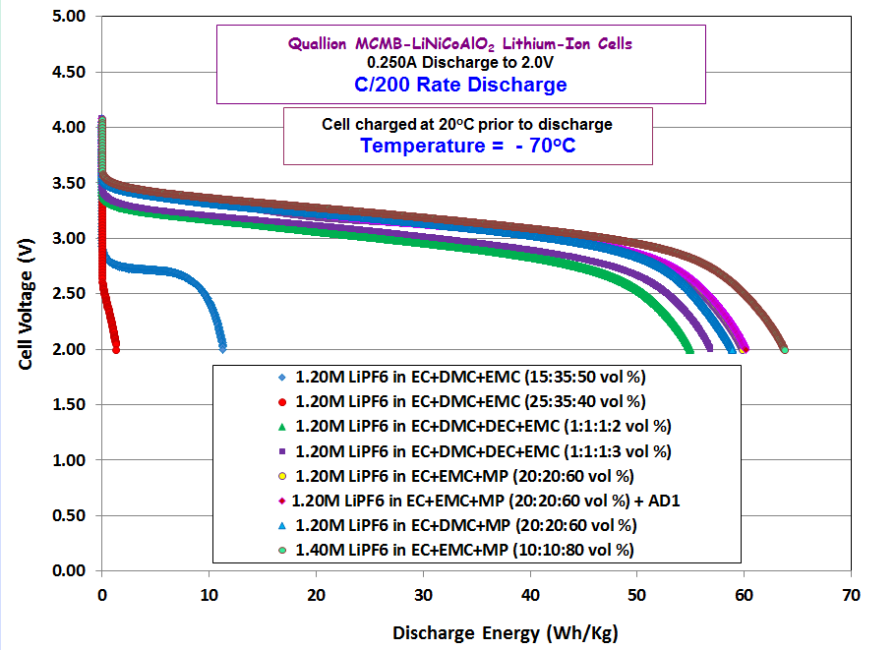


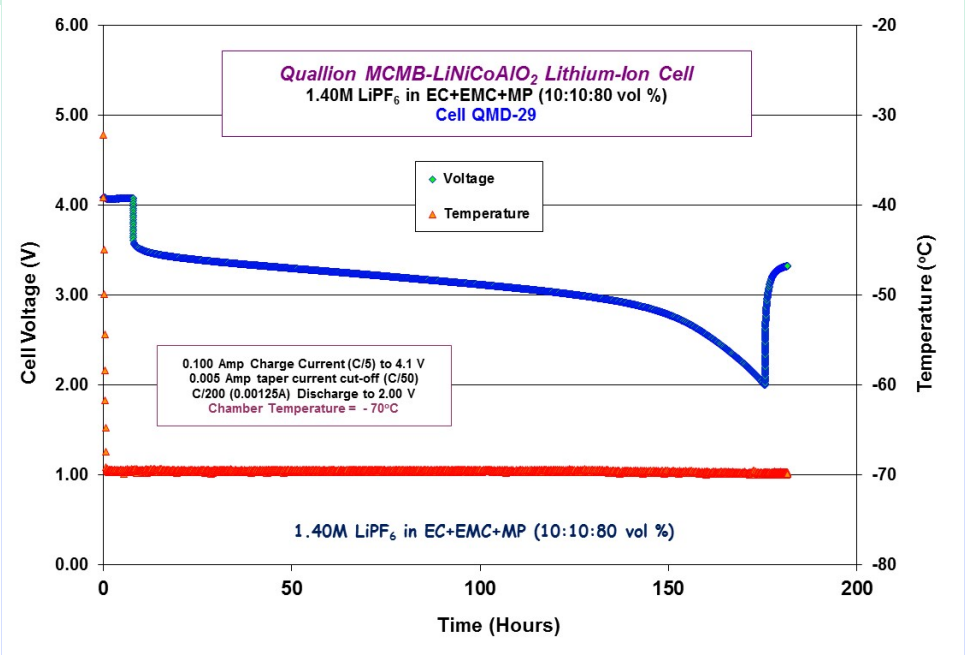
- Quallion cells have been demonstrated to provide excellent low temperature characteristics, with the ability to support high power discharge. Excellent retention of room temperature performance.
- Electrolyte selection of new generation of cells based on results of initial assessment.

- **Larger cell designs provided by Quallion (up to 15 Ah) will result in higher specific energy at low temperatures compared to the small BTE cells (0.25 Ah).**

Performance of Quallion BTE Custom Cells

C/200 Discharge Rate at -70°C



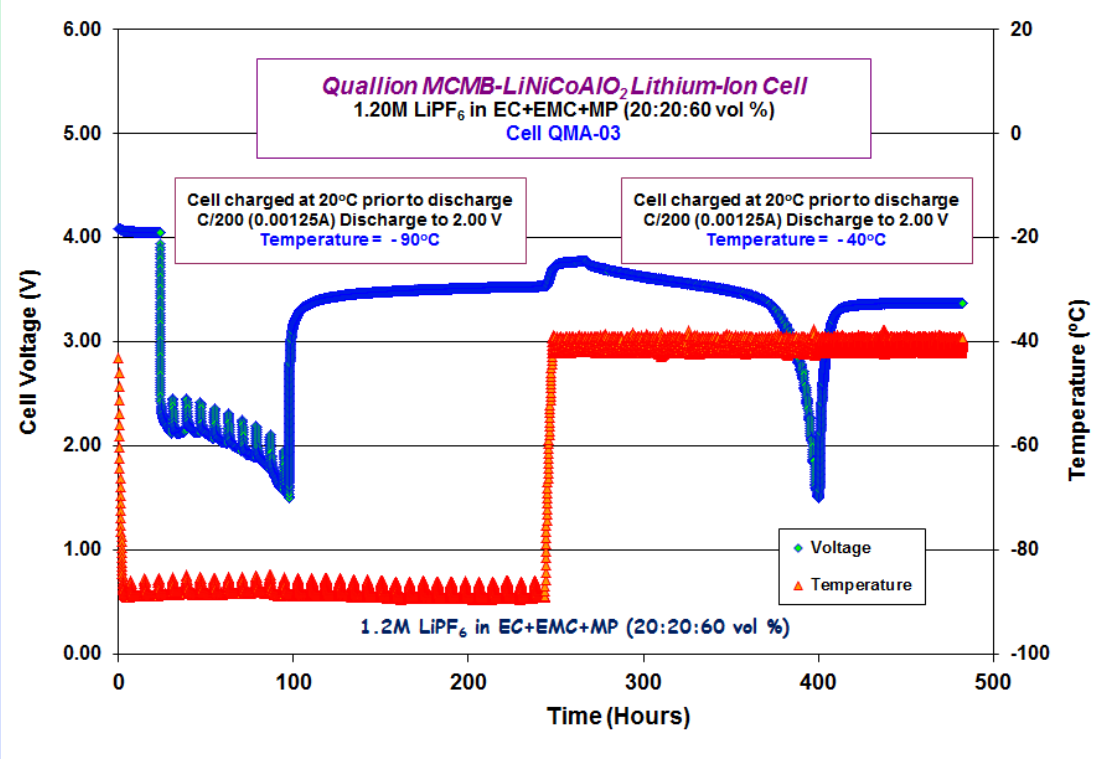


- Quallion cells have been demonstrated to provide excellent low temperature characteristics, with the ability to support discharge at -70°C (with over 165 hours of operation).
- Electrolyte selection of new generation of cells based on results of initial assessment.

- **Larger cell designs provided by Quallion (up to 15 Ah) will result in higher specific energy at low temperatures compared to the small BTE cells (0.25 Ah).**

Performance of Quallion BTE Cells at Low Temperature:

Low Temperature Survivability Test

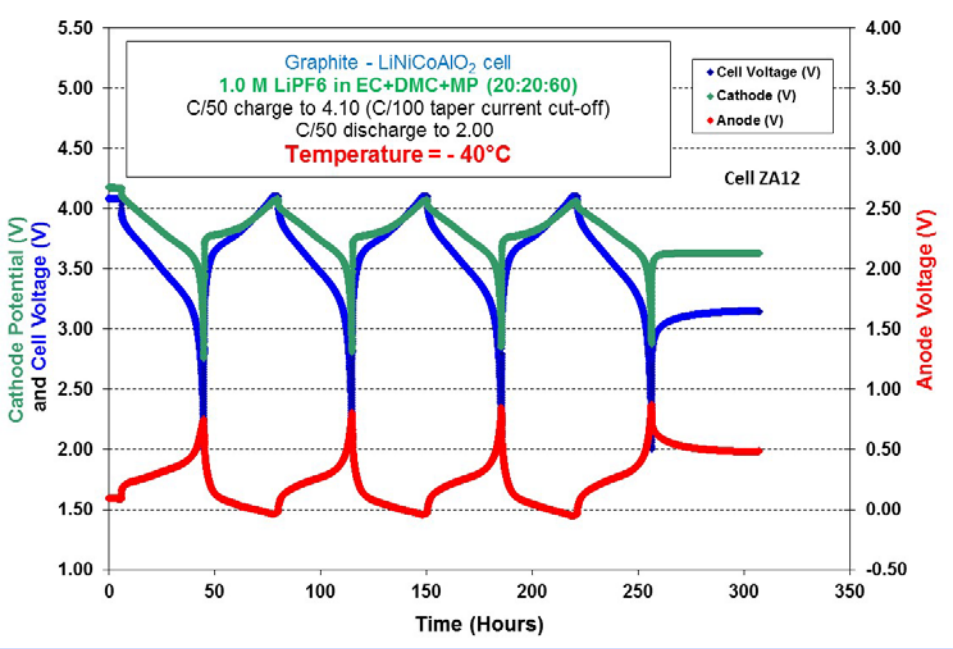


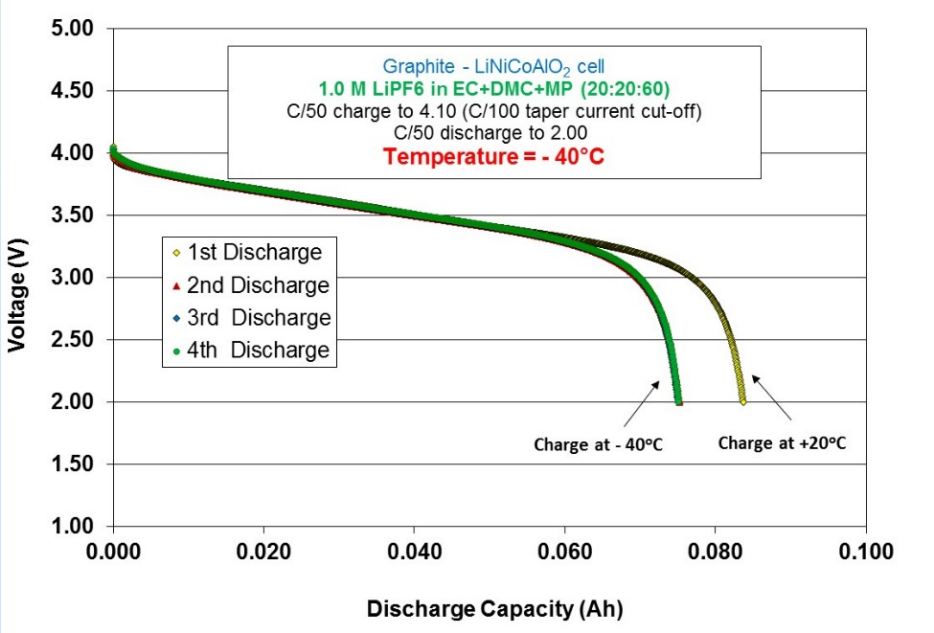
- **Quallion cells have been demonstrated to provide excellent low temperature survivability characteristics, being capable of supporting operation at -90°C and long term dwell periods.**
  - Cells soaked at -90°C for 24 hours prior to discharge
  - Cells discharged at C/200 rate at -90°C to 1.50V
  - Cells allowed to dwell at -90°C for > 5 days prior to warming to -40°C
  - Cells discharged at C/200 rate at -40°C to 1.50V
  - Cumulative capacity of discharge determined (-90°C + -40°C)
  - Capacity determined to be comparable with prior C/200 discharge testing at -40°C

Performance of Quallion Experimental 3-Electrode Cells

(Electrodes obtained from Quallion)

C/50 Rate Cycling at - 40°C

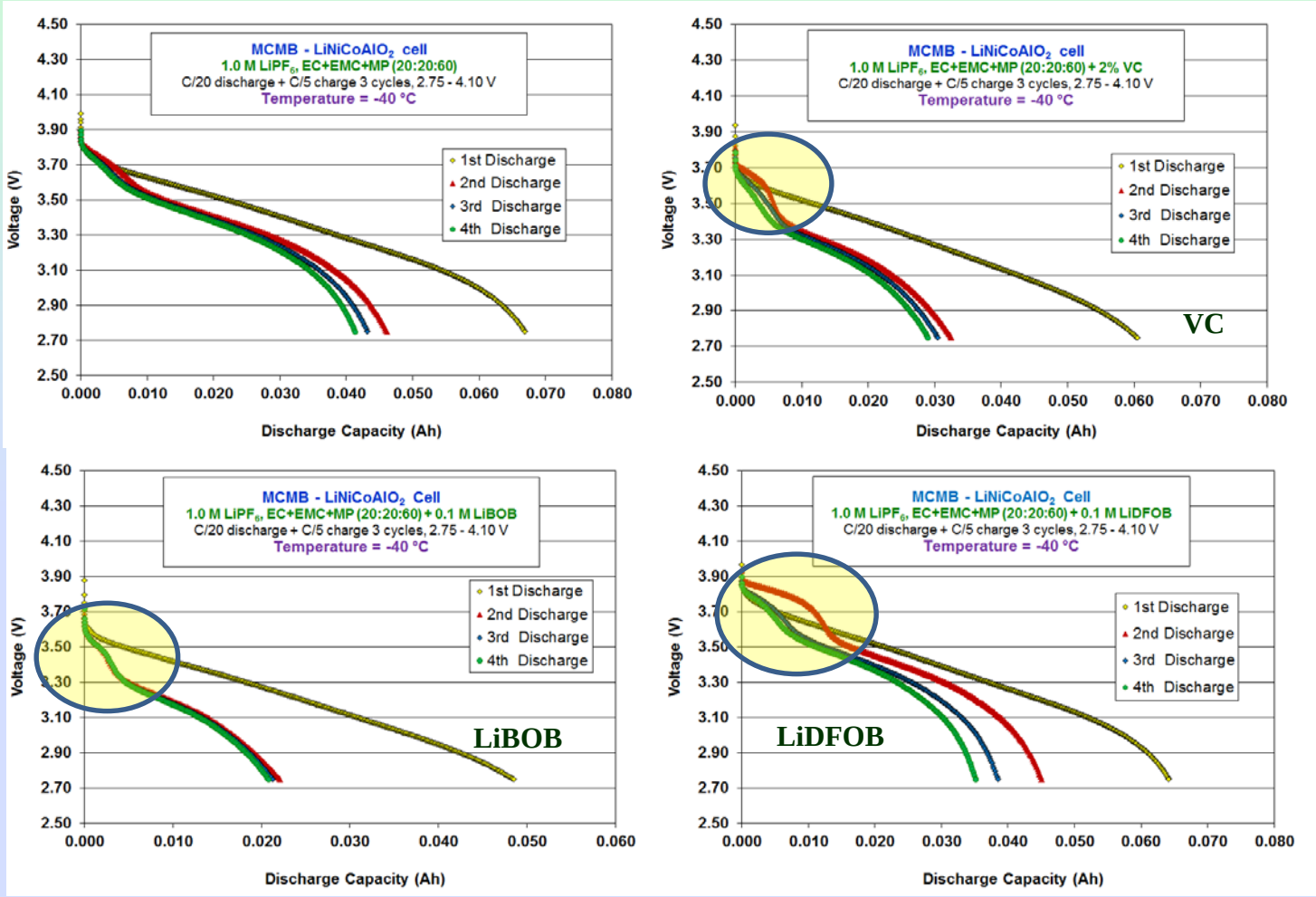




- Experimental 3-electrode cells with Quallion electrodes display reasonable robustness to charging at -40°C when low rates are employed.
- We are currently evaluating a number of electrolytes in these 3-electrode cells, and attempting to correlate the relative kinetics with the propensity of lithium plating.

Charge Behavior of MCMB/$LiNiCoAlO_2$ Cells at Low Temperature

Charge at - 40°C (C/5 Rates, 2.75V to 4.10V)

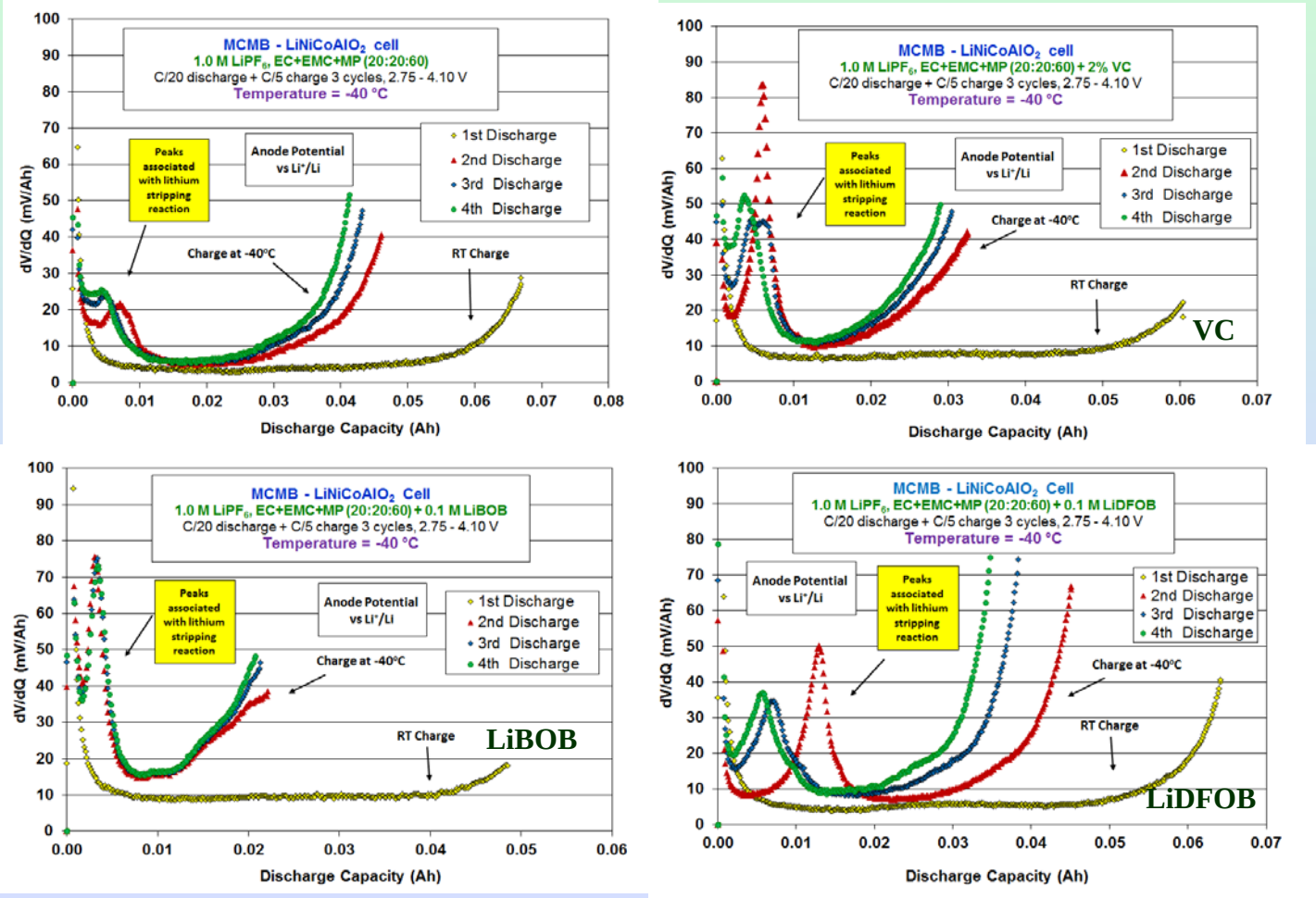


▷ **In experimental three electrode cells containing Quallion electrodes, all additives appear to lead to increased lithium plating compared to the baseline solution at -40°C using C/5 charge rates.**

M. C. Smart. et al., 227th Meeting of the Electrochemical Society, Chicago, Illinois, May 25-29, 2015 (Abstract #47562).

Charge Behavior of MCMB/LiNiCoAlO$_2$ Cells at Low Temperature

Charge at - 40°C (C/5 Rates, 2.75V to 4.10V) – Quallion Electrodes



▷ **Differential voltage/capacity plots of the anode potential during cycling is insightful in determining which sample experiences the greatest amount of lithium plating/stripping.**

▷ **When the discharges at -40°C are analyzed all of the cells with additives result in notable stripping peaks.**

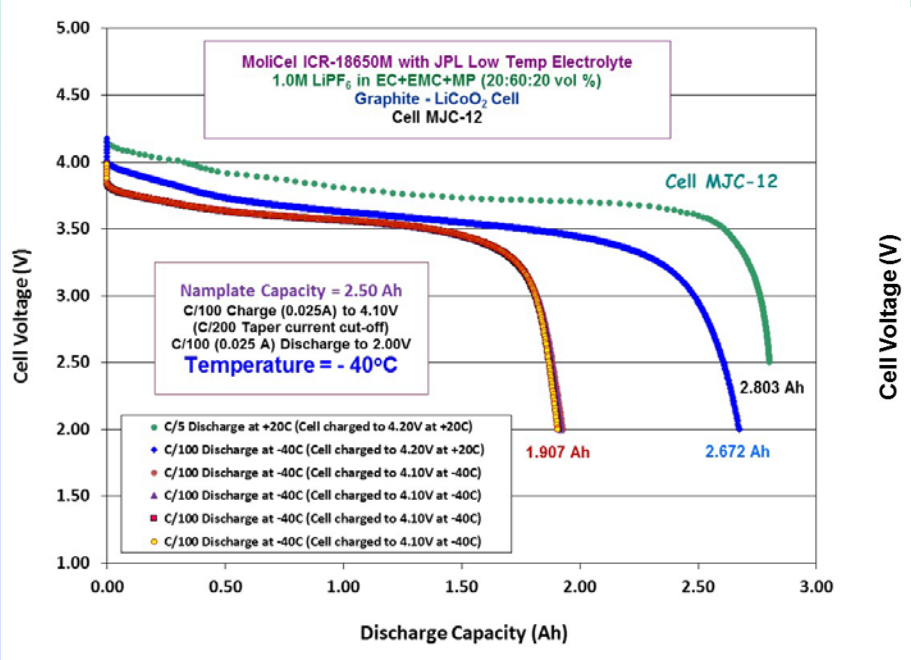
M. C. Smart. et al., 227th Meeting of the Electrochemical Society, Chicago, Illinois, May 25-29, 2015 (Abstract #47562).

Performance of E-One Molicel ICR-18650 M Custom Cells

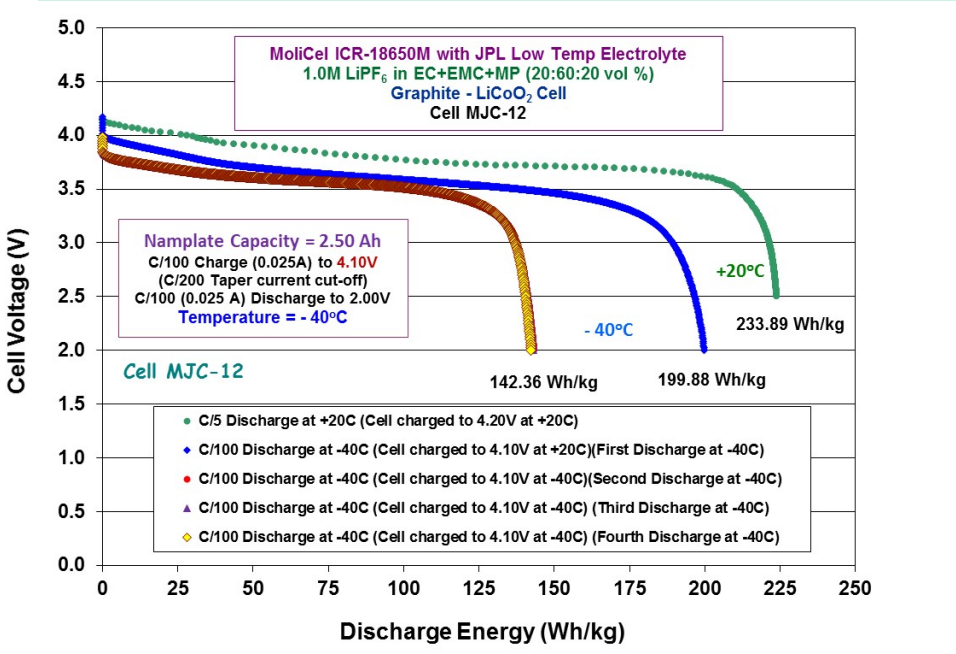
Charge and Discharge at -40°C (C/100 Rates)(Charge Voltage = 4.10V)

JPL Electrolyte = 1.0M $LiPF_6$ in EC+EMC+MP (20:60:20 vol %) [InSight Electrolyte]

Discharge Capacity (Ah) at -40°C



Specific Energy (Wh/kg) at -40°C



- **Excellent specific energy at -40°C observed using a low rate charge and discharge (C/100) (i.e., > 142 Wh/kg).**
- **No lithium plating observed when charging to 4.10V at -40oC using low rate charge.**

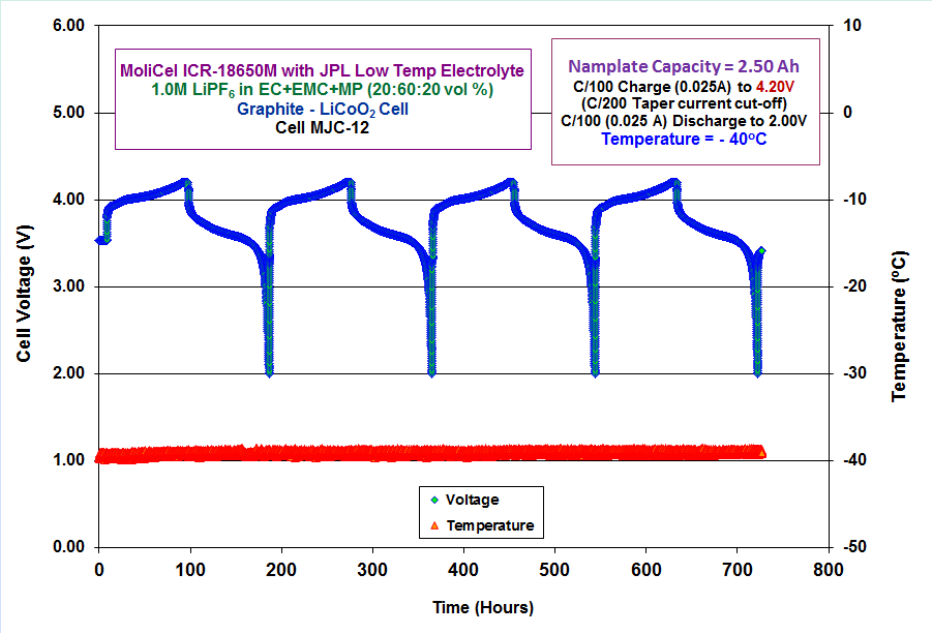
- **The custom Moli ICR-M cells with JPL electrolytes display improved cycling performance at -40°C compared to the baseline. A number of custom JPL electrolytes have been demonstrated to meet programmatic target of > 100 Wh/kg (both charge and discharge at -40°C).**

Performance of E-One Molicel ICR-18650 M Custom Cells

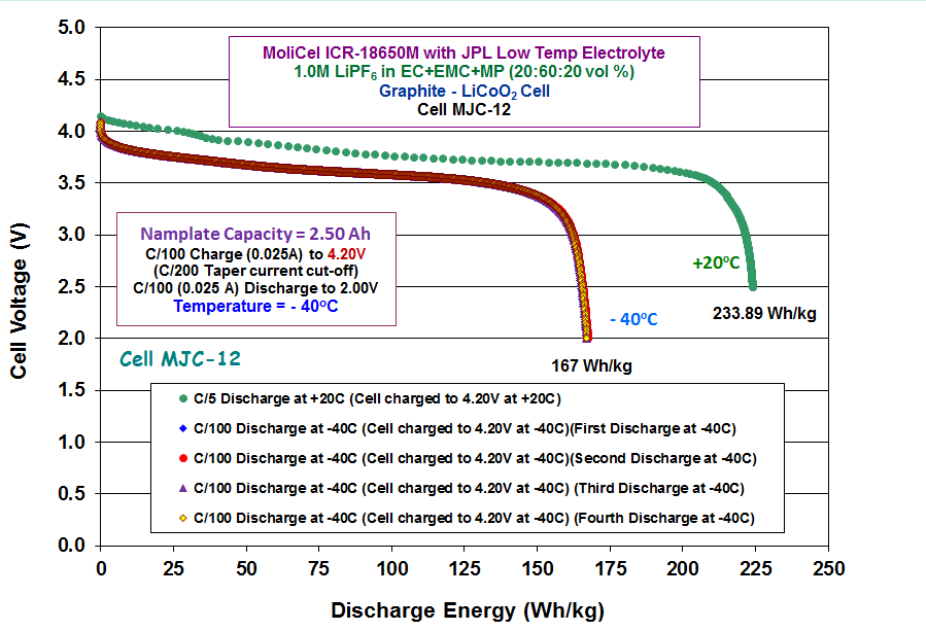
Charge and Discharge at -40°C (C/100 Rates))(Charge Voltage = 4.20V)

JPL Electrolyte "C" = 1.0M $LiPF_6$ in EC+EMC+MP (20:60:20 vol %) [InSight Electrolyte]

Continuous cycling at -40°C (4.20V Charge)



Specific Energy (Wh/kg) at -40°C



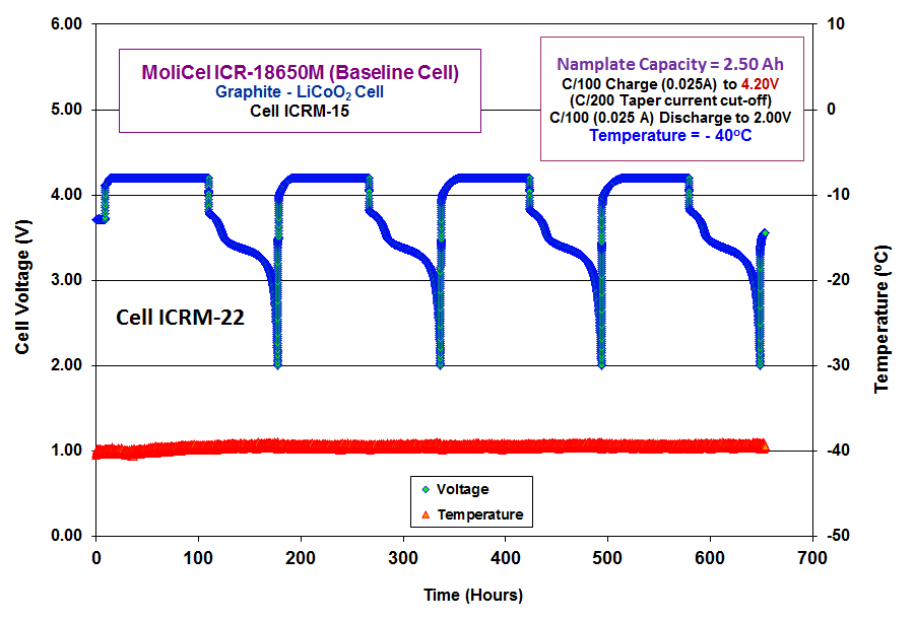
- Excellent specific energy at -40°C observed using a low rate charge and discharge (C/100) (i.e., 167 Wh/kg).
- No lithium plating observed when charging to **4.20V** at -40°C using low rate charge.
- **The custom Moli ICR-M cells with JPL electrolytes display improved cycling performance at -40°C compared to the baseline. A number custom JPL electrolytes have been demonstrated to meet programmatic target of >100 Wh/kg (both charge and discharge at -40°C).**

Performance of E-One Molicel ICR-18650 M Cells

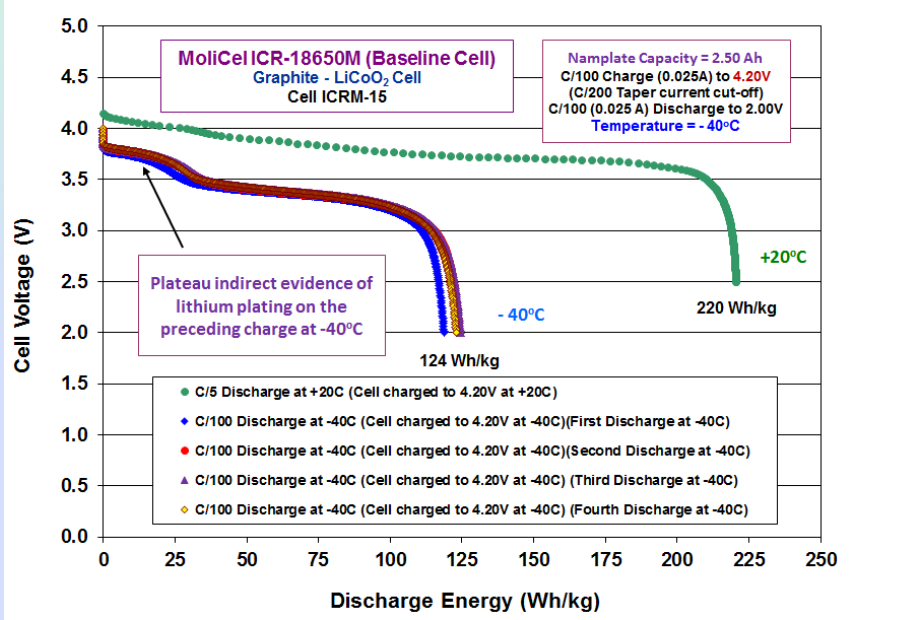
Charge and Discharge at -40°C (C/100 Rates))(Charge Voltage = 4.20V)

Baseline Commercial Off-the-Shelf Cell (COTS)

Continuous cycling at -40°C (4.20V Charge)



Specific Energy (Wh/kg) at -40°C

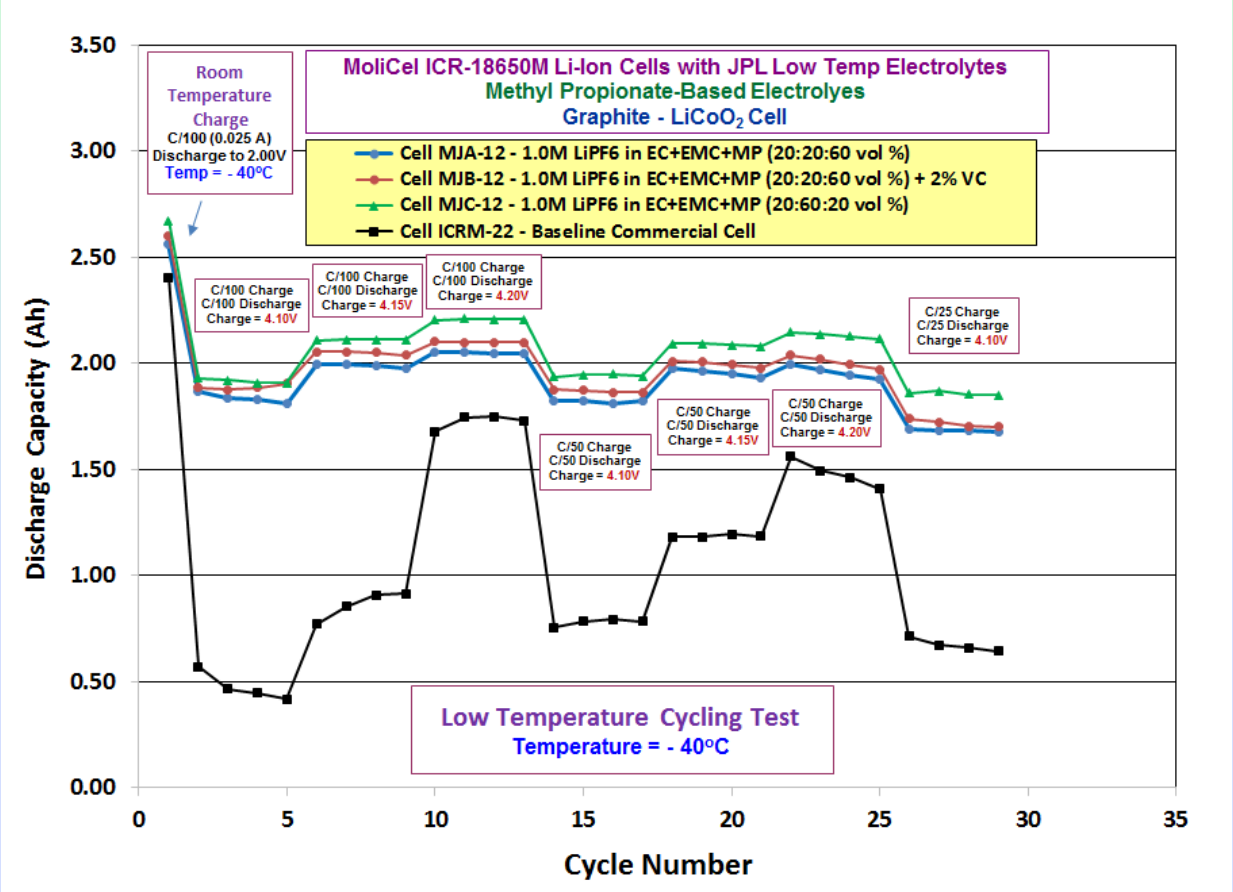


- **Although good specific energy at -40°C is observed with the baseline commercial cell when charging to 4.20V at -40 (C/100) (i.e., > 124Wh/kg), there is evidence of lithium plating which leads to cell degradation.**

- **The custom Moli ICR-M cells with JPL electrolytes display improved cycling performance at -40°C compared to the baseline. A number of cells containing JPL electrolytes have been demonstrated to meet programmatic target of >100 Wh/kg (both charge and discharge at -40°C).**

Performance of E-One Molicel ICR-18650 M Custom Cells

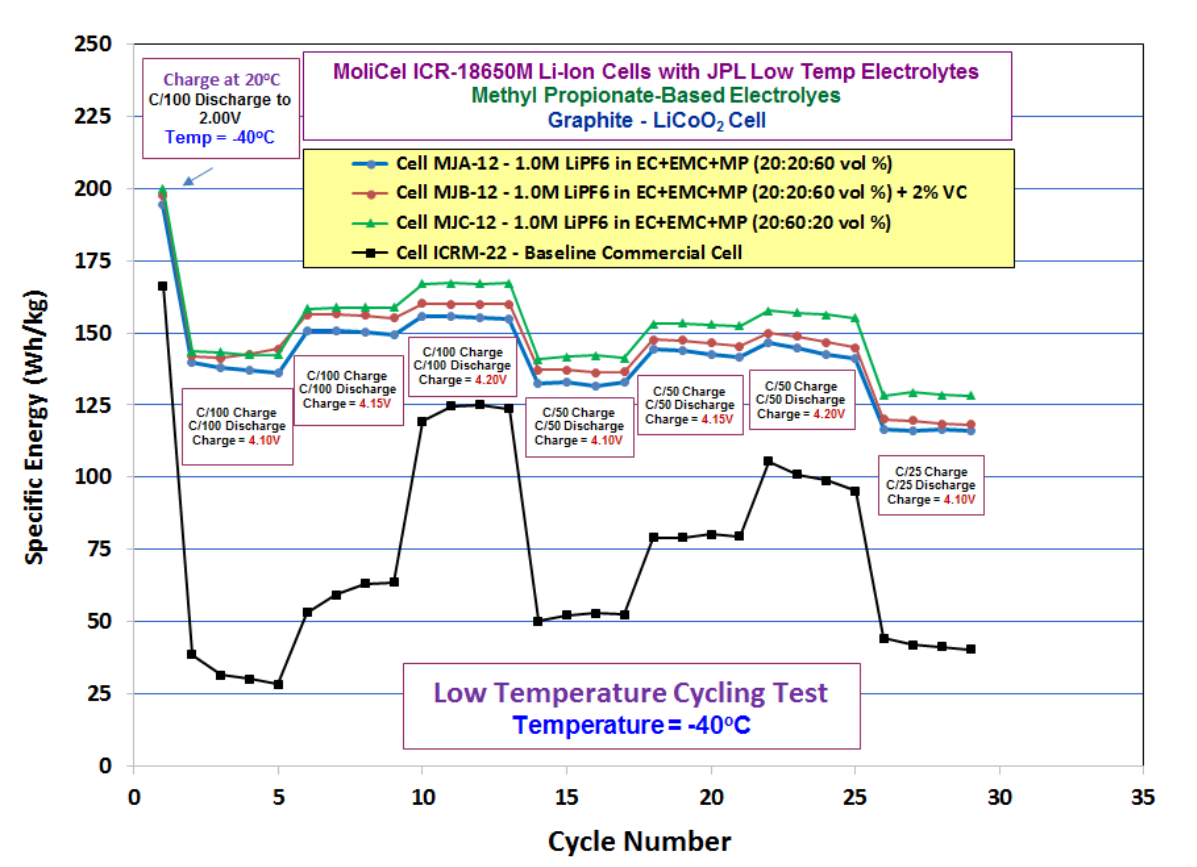
Continuous cycling at -40°C: Effect of charge voltage and charge rate



- Excellent discharge capacity at -40°C observed using a low rate charge and discharge (C/100) (i.e., > 2.1 Ah).
- Cells have been continuously cycled at -40°C since 10/22/2015 (over 5.5 months of operation)
- The custom Moli ICR-M cells with JPL electrolytes display improved cycling performance at -40°C compared to the baseline. A number of cells containing JPL electrolytes have been demonstrated to meet programmatic target of >100 Wh/kg (both charge and discharge at -40°C).

Performance of E-One Molicel ICR-18650 M Custom Cells

Continuous cycling at -40°C: Effect of charge voltage and charge rate

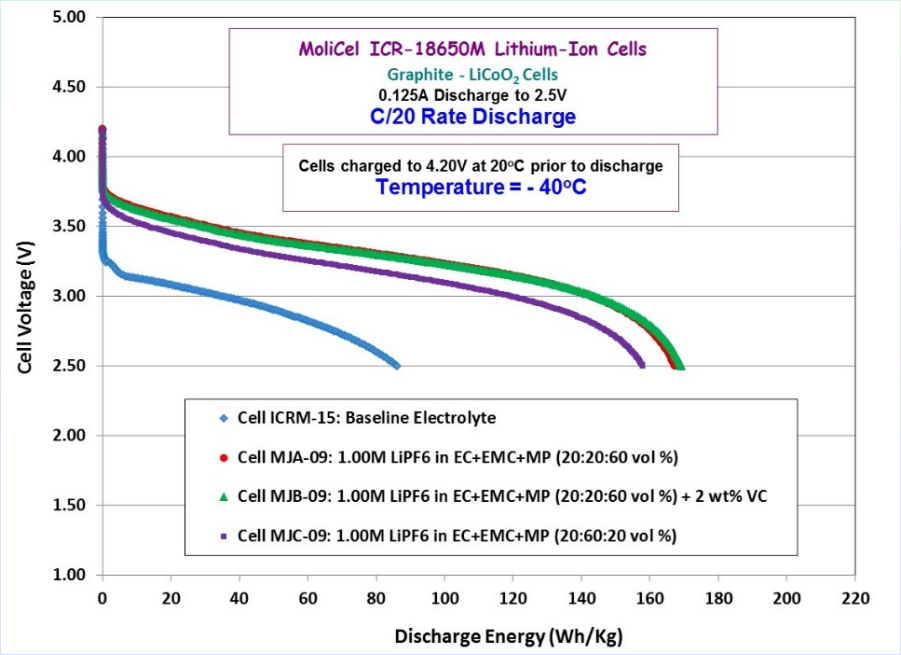


- Excellent specific energy at -40°C observed using a low rate charge and discharge (C/100) (i.e., > 167 Wh/kg).
- Cells have been continuously cycled at -40°C since 10/22/2015 (over 5.5 months of operation)
- **The custom Moli ICR-M cells with JPL electrolytes display improved cycling performance at -40°C compared to the baseline. A number of cells containing JPL electrolytes have been demonstrated to meet programmatic target of >100 Wh/kg (both charge and discharge at -40°C).**

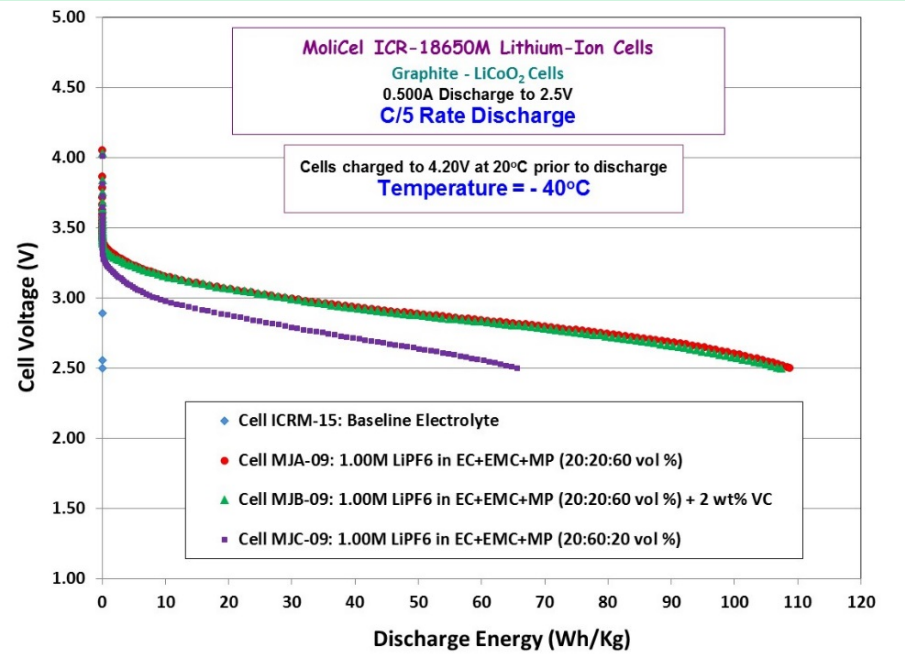
Performance of E-One Molicel ICR-18650 M Custom Cells

Discharge Rate Capability at -40°C

C/20 Discharge Rate at -40°C



C/5 Discharge Rate at -40°C



- **Excellent specific energy at -40°C observed using higher discharge rates (i.e., > 100 Wh/kg at C/5 rate).**
- **Demonstrates that technology is well suited to support high power transmission events.**

- **The custom Moli ICR-M cells with JPL electrolytes display improved low temperature discharge rate performance at -40°C compared to the baseline.**

➢ *Summary and Conclusions*:

- **The SOA aerospace Li-ion InSight chemistry containing a JPL developed MP-based low temperature electrolytes delivers good reversibility when cycled continuously at -40°C using low rates (i.e., delivering ~ 122 Wh/kg at -40°C).**
- **Quallion BTE cells have been demonstrated to provide excellent low temperature characteristics, with the ability to support high power discharge.**
- **Quallion cells have been demonstrated to provide excellent low temperature survivability characteristics, being capable of supporting operation at -90°C and long term dwell periods.**
- **The custom Moli ICR-M cells with JPL electrolytes display improved cycling performance at -40°C compared to the baseline. A number of cells containing JPL electrolytes have been demonstrated to meet programmatic target of >100 Wh/kg (both charge and discharge at -40°C).**
  - **Excellent specific energy at -40°C observed using a low rate charge and discharge (C/100) (i.e., 167 Wh/kg) when charging to 4.20V**
  - **No lithium plating observed when charging to 4.20V at -40°C using low rate charge.**

➢ *Future Work*:

- **Further investigate the impact of electrolyte type upon the charge acceptance of the various cells designs at low temperatures, using next generation formulations.**
- **Evaluate the charge characteristics of all three cells design using more aggressive charge rates and charge voltages.**

Acknowledgments

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), and supported by the Ocean Worlds Program Office.