MCMB-$LiNiCoAlO_2$-Based Li-Ion Cells with Methyl Propionate-Based Electrolytes for Very Low Temperature Applications

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PRiME 2016

230th Meeting of the Electrochemical Society (ECS)

Honolulu, Hawaii

October 3, 2016

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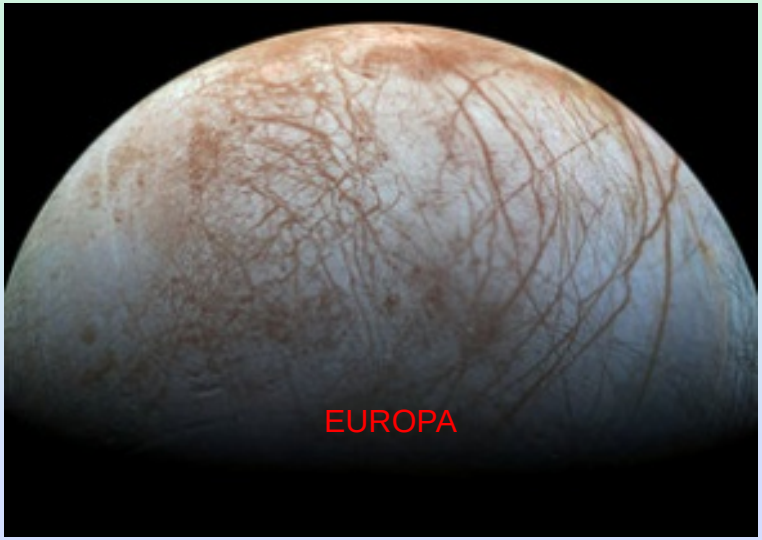
Background: Mission Concept Needs

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 missions 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

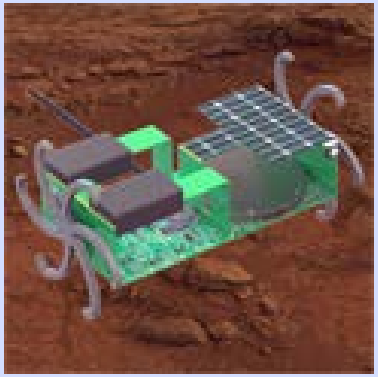
- Benchmark state of practice (SOP) aerospace quality Li-ion cells at low temperatures.
- Further develop JPL low temperature electrolytes to support charging and discharging down to low temperatures (- 40°C).
- Work with vendors to infuse electrolytes into flight qualifiable-cell designs optimized for 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.

Objective:

- Assess viability of using Quallion BTE Li-Ion cells for the Pop Up Flat Folding Explorer Robot (PUFFER) program.
- Evaluate the performance capability of Quallion BTE Li-Ion cells to operate at very low temperatures (-40°C to -70°C)
- Determine the capabilities of the Quallion BTE Li-ion cells to meet preliminary mission requirements.

Preliminary Configuration and Tentative Requirements :

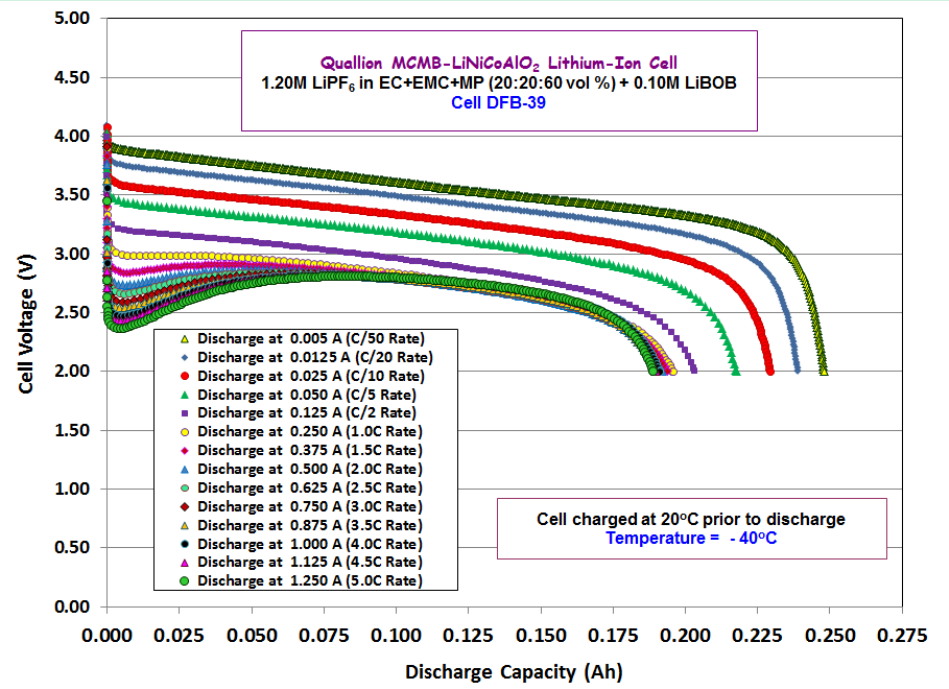
- Configuration: Two Li-ion cells connected in series
  - Currently baselining two Quallion QL0370B Li-Ion Cells
- Operating Temperature Range:
  - Maximum temperature = + 20°C
  - Minimum charge temperature = - 40°C
  - Minimum discharge temperature = - 70°C
  - Minimum survival temperature = - 120°C
- Energy and Power Requirements:
  - Nominal discharge current = 300 mA
  - Peak discharge current = 1500 mA
  - Nominal charge current = 55 mA
  - Peak charge current = 180 mA
  - Total discharge energy required per sol = 1 Wh
- Lifetime Requirements:
  - Operational lifetime on surface = > 10 sols
  - Operational time per sol = 1.33 hours per sol

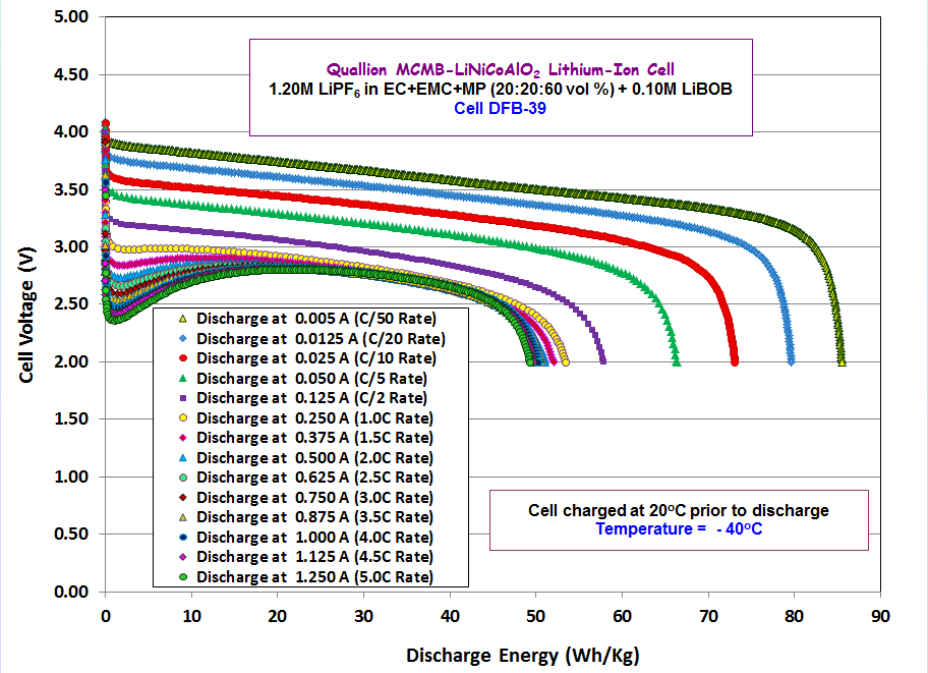


Performance of Quallion BTE Custom Cells

(Cells obtained under DOE program and NASA SBIR program)

Discharge Rate Capability at -40°C





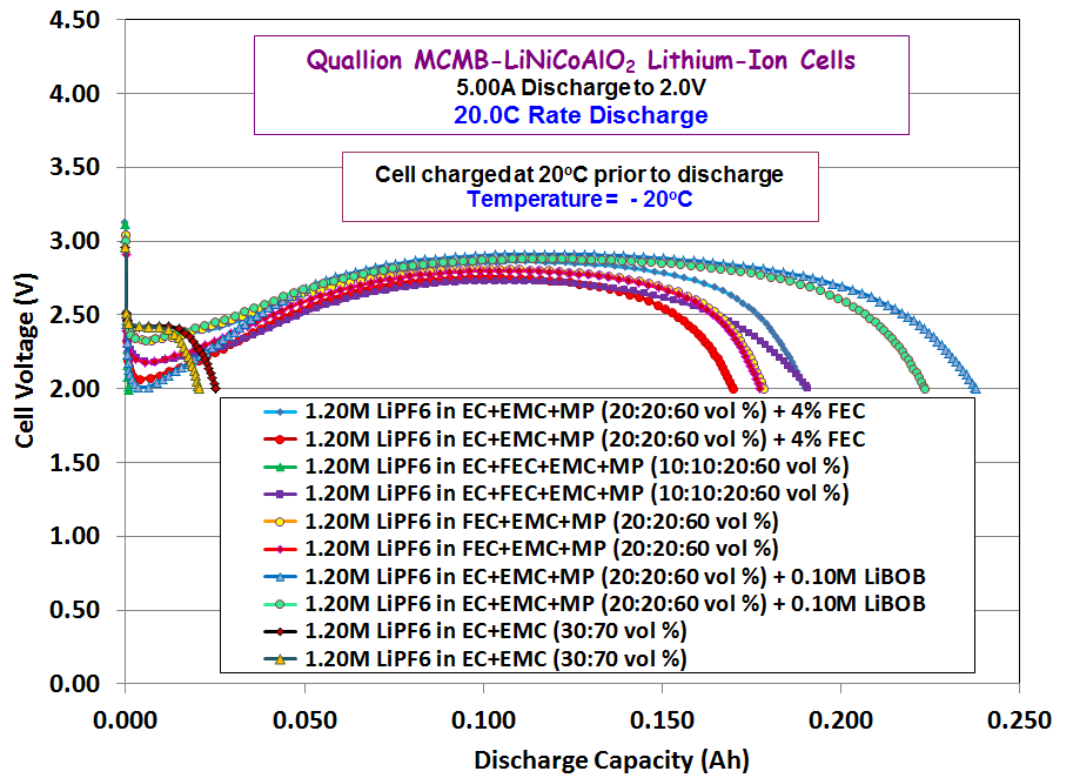
- Quallion cells have been demonstrated to provide excellent low temperature characteristics, with the ability to support high power discharge. Excellent retention of room temperature performance.
- Electrolyte selection of new generation of cells based on results of initial assessment.

- **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 Methyl Propionate-Based Electrolytes in Prototype Cells

Discharge Performance at - 20°C

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



- **Demonstration of high power capability of methyl propionate-based electrolytes in Quallion 0.25 Ah Li-ion cells.**
- **A number of MP-based electrolytes have been further developed that contain FEC and LiBOB as additives.**
- ***Cells observed to support 20C discharge rates 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).**
  - ***However, how do these systems behave when required to be charged at -40°C or lower ??***

Advanced Li-Ion Prototypes Cells Under Evaluation

➢ 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**
  - ➢ **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**
  - ➢ **A number of all carbonate and ester-based electrolytes have been evaluated:**
    - ➢ **1.2M $LiPF_6$ in EC+EMC+MP (20:20:60 vol %)**
    - ➢ **1.2M $LiPF_6$ in EC+EMC+MP (20:20:60 vol %) + 0.10M LiFSI**
    - ➢ **1.2M $LiPF_6$ in EC+DMC+MP (20:20:60 vol %)**
    - ➢ **1.4M $LiPF_6$ in EC+EMC+MP (10:10:80 vol %)**

    - ➢ **1.0M $LiPF_6$ in EC+DMC+EMC (15:35:50 vol %)**
    - ➢ **1.0M $LiPF_6$ in EC+DMC+EMC (25:35:40 vol %)**
    - ➢ **1.0M $LiPF_6$ in EC+DMC+DEC+EMC (1:1:1:2 vol %)**
    - ➢ **1.0M $LiPF_6$ in EC+DMC+DEC+EMC (1:1:1:3 vol %)**

  - ➢ **These JPL developed low temperature Li-ion electrolytes that have previously been demonstrated to have good performance in NCO[1,2] and NCA[2,3] systems.**

(1) M. C. Smart, B. V. Ratnakumar, K. B. Chin, and L. D. Whitcanack, *J. Electrochem. Soc.*, **157 (12)**, A1361-A1374 (2010).
(2) M. C. Smart, B. L. Lucht, S. Dalavi, F. C. Krause, and B. V. Ratnakumar, *J. Electrochem. Soc.*, 159 (6), A739-A751 (2012).
(3) M. C. Smart, B. V. Ratnakumar, L. Whitcanack, K. Chin, and S. Surampudi, H. Croft, D. Tice and R. Staniewicz, *J. Power Sources*, **119-12**, 349-358 (2003).
(4) M. C. Smart, B. V. Ratnakumar, M. R. Tomcsi, M. Nagata, V. Visco, and H. Tsukamoto, 2010 Power Sources Conference, Las Vegas, NV, June 16, 2010.

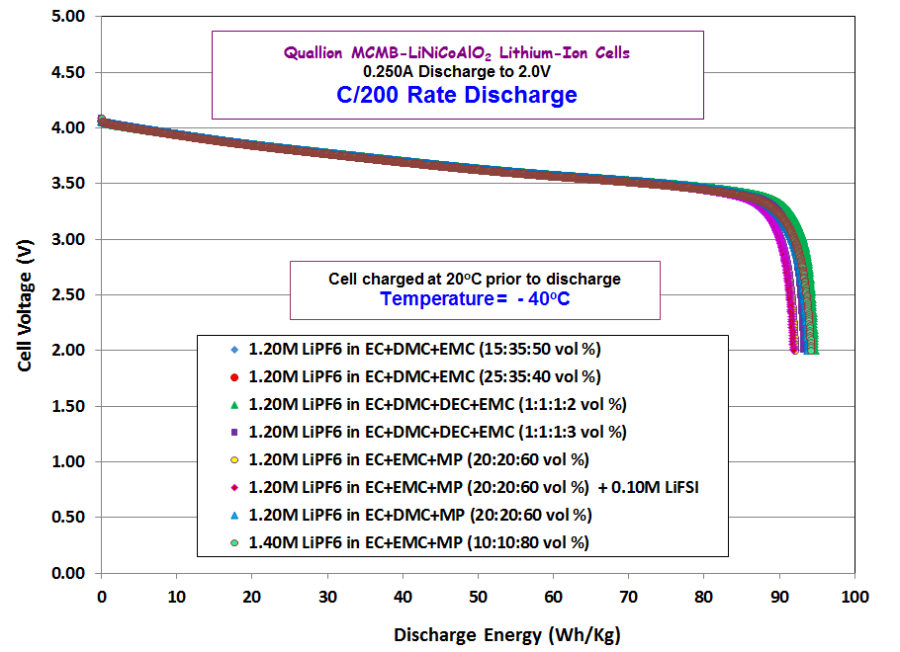
Low Temperature Performance Evaluation of Custom Quallion BTE Biomedical Prismatic Li-Ion Cells

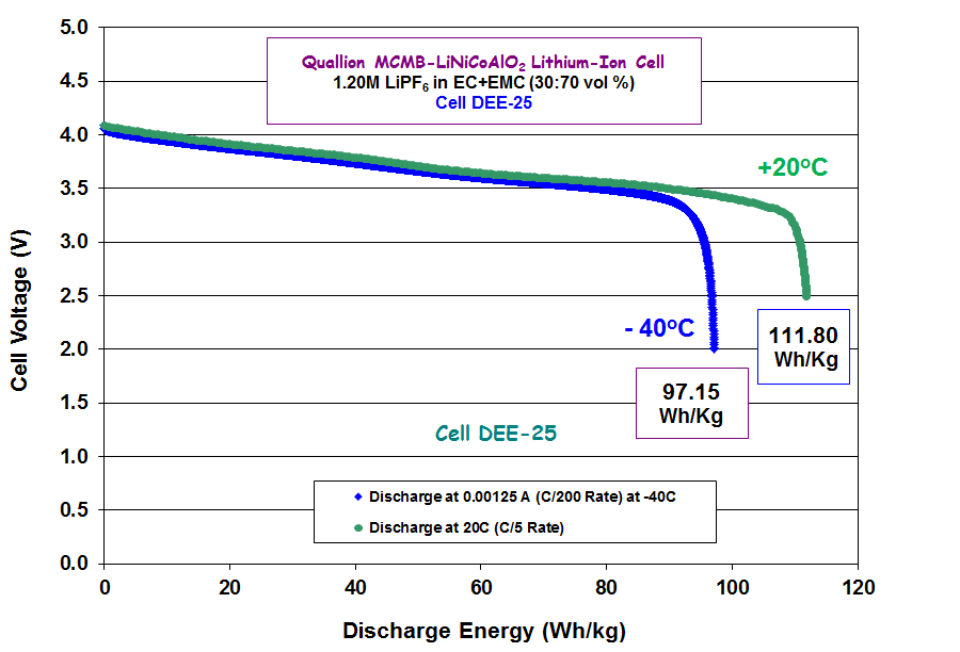
Overview of Test Plan

- Performed initial capacity and impedance characterization
  - Temperature = +20°C (voltage range = 3.0V to 4.10V) (C/5 Rates)
- Performed discharge rate characterization (with charging at room temperature)
  - Temperature Range = - 40°C to -70°C
  - Range of Discharge Rate Evaluated = C/200 to 1.20C
  - Evaluated ultra-low temperature discharge capability at -90°C
- Performed ultra-low temperature survivability testing
  - Evaluated ultra-low temperature discharge capability at -90°C
  - Evaluated ultra-low temperature survivability at -135°C
- Performed charge rate characterization at various temperatures
  - Temperatures evaluated = -20°C, -25°C, -30°C, -35°C, and -40°C
  - Charge rate utilized = 0.40C rate (100 mA)
- Continuous cycling tests at -40°C

Performance of Quallion BTE Custom Li-Ion Cells

C/200 Discharge Rate at -40°C



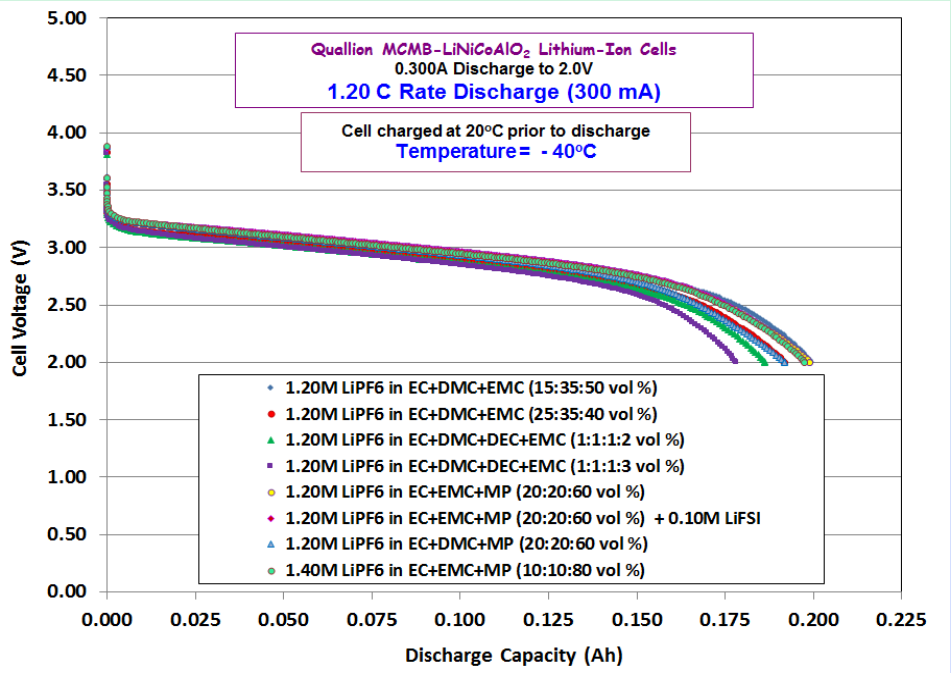


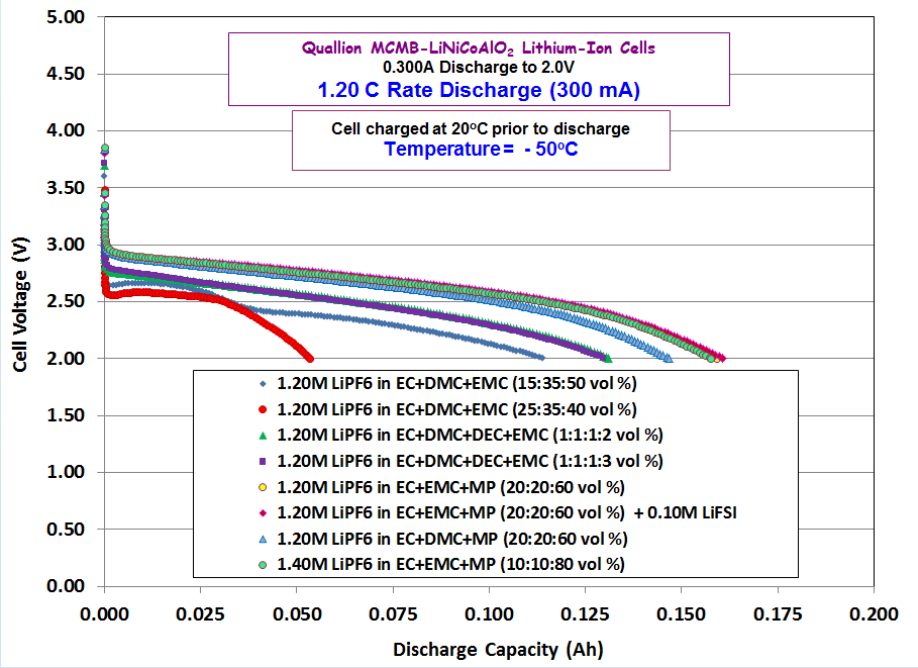
- **Quallion cells have been demonstrated to provide consistent low temperature performance at -40°C at low rate, with the little impact of electrolyte type when charge at room temperature.**
- **Excellent retention of room temperature performance is observed.**

➢ **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 Li-Ion Cells

1.20 C Rate Discharge Rate at -40°C and -50°C

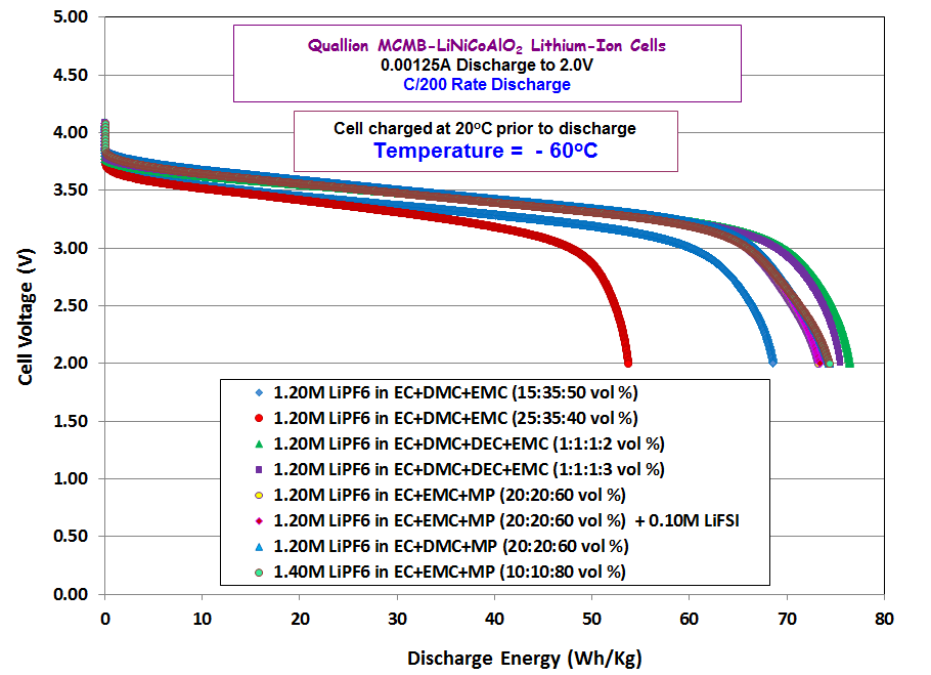


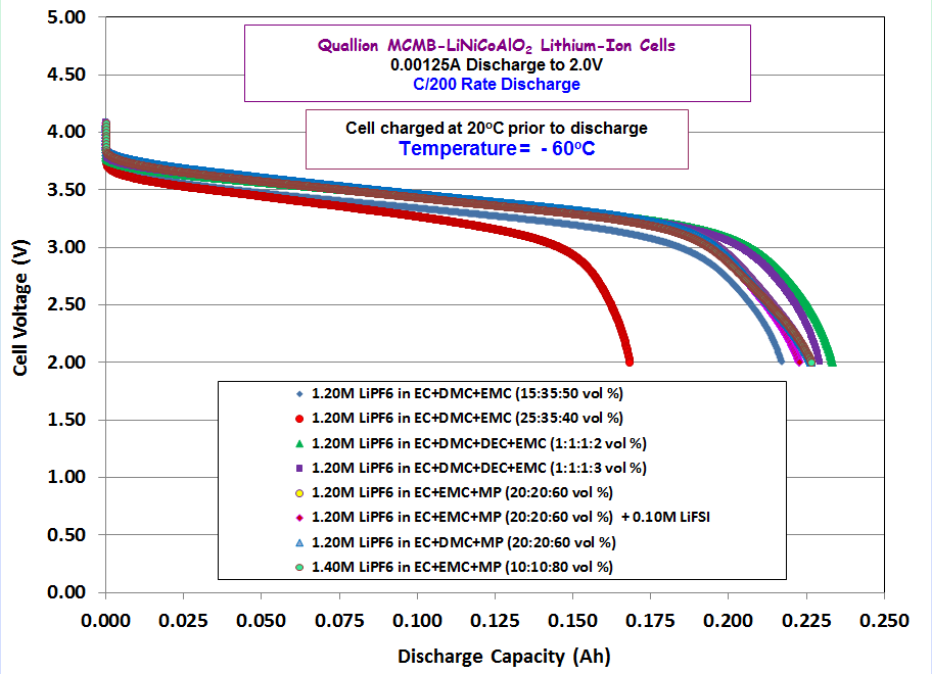


- Quallion cells have been demonstrated to provide excellent high rate capability at -40°C and -50°C rate, with the best performance being observed with methyl propionate containing electrolytes.
- The electrolytes 1.20M $LiPF_6$ in EC+EMC+MP (20:20:60 vol %) + 0.10M LiFSI was observed to display the best performance over the range of temperatures invested (-40° to -70°C)

Performance of Quallion BTE Custom Li-Ion Cells

C/200 Discharge Rate at - 60°C



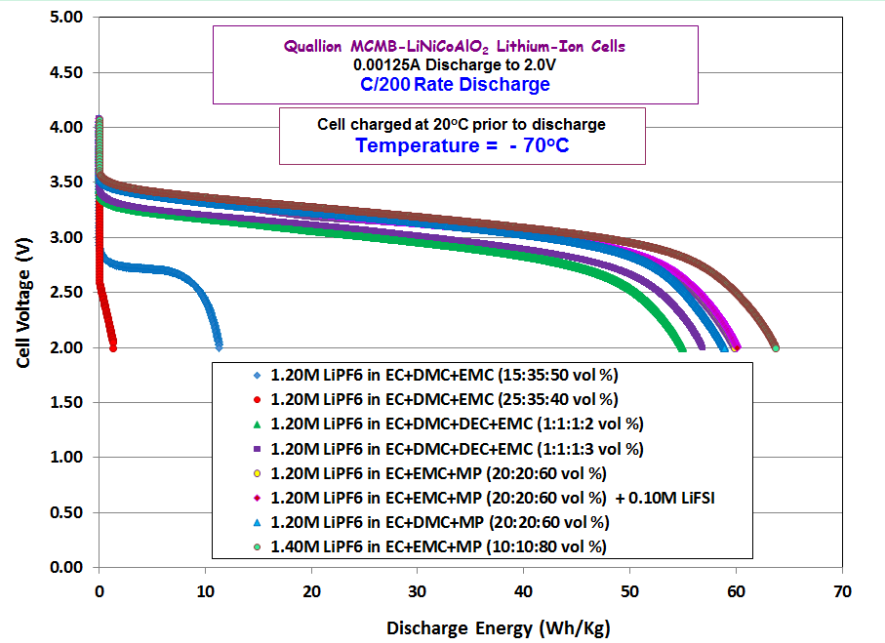


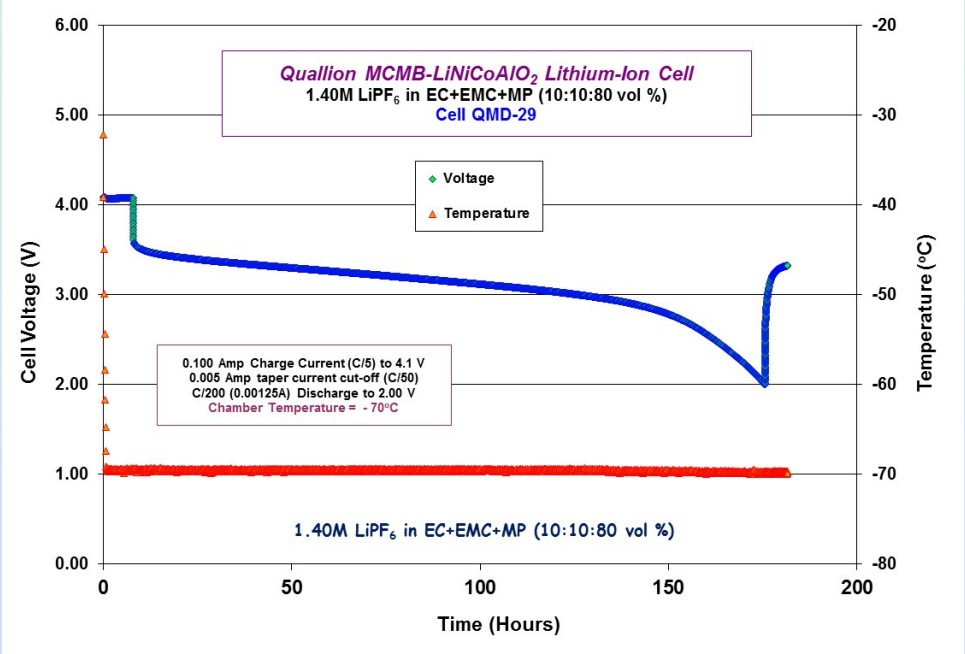
- **Quallion cells have been demonstrated to provide excellent low temperature performance at -60°C at low rate, with the ester-containing electrolyte blends delivering the highest specific energy.**
- **Of the all-carbonate-based blends, the best performance was obtained with the electrolytes containing low ethylene carbonate (EC) content.**

➢ **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

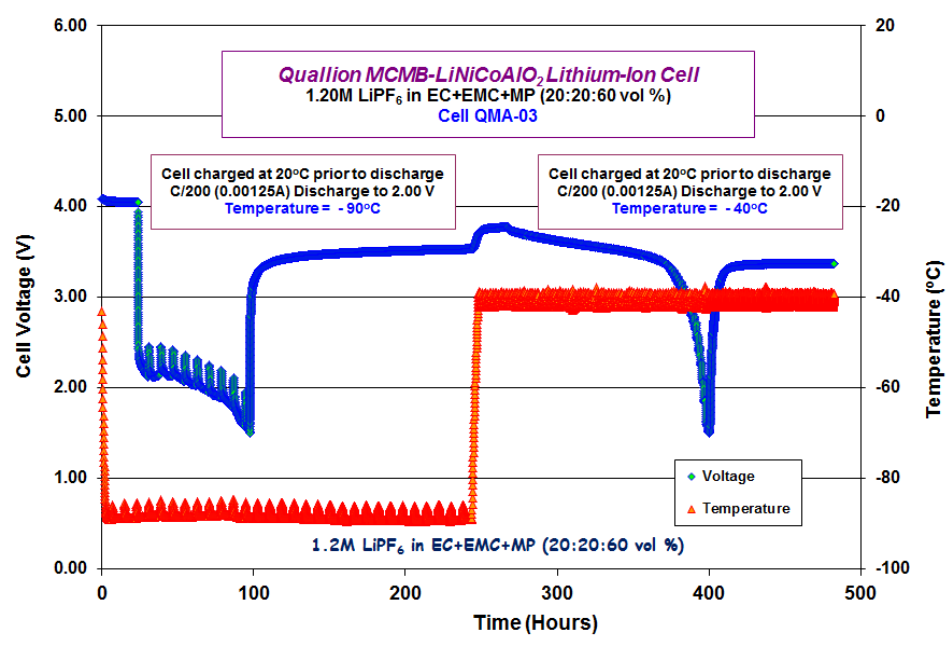


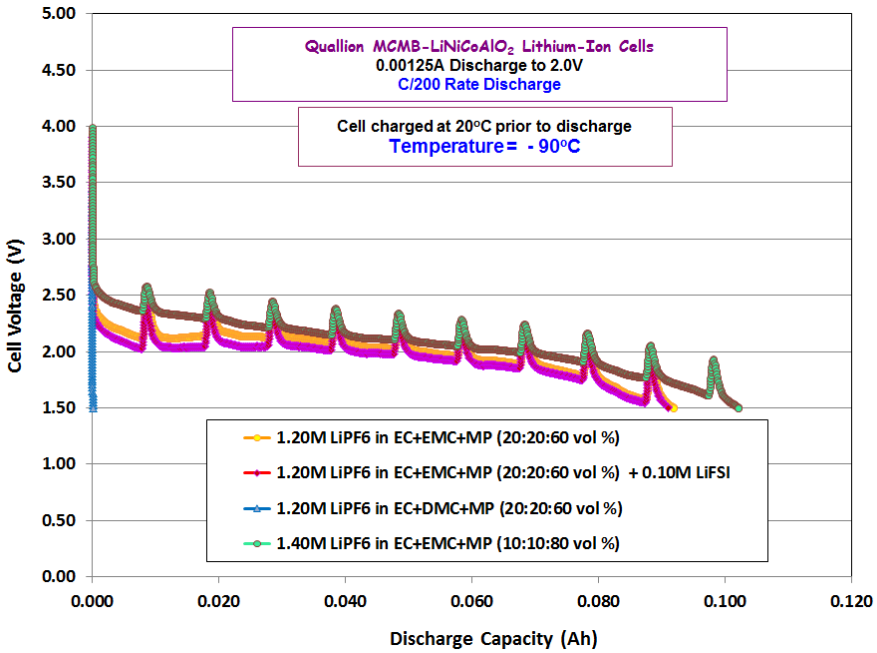


- Quallion cells have been demonstrated to provide excellent low temperature characteristics, with the ability to support discharge at -70°C (with over 165 hours of operation).
- Electrolyte selection of new generation of cells based on results of initial assessment.

- **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 at -90°C





- **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 BTE Cells at Low Temperature:
Low Temperature Survivability Test at -90°C

				Cell QMA-03				Cell QMB-09				Cell QMC-17				Cell QMD-29			
				1.20M $LiPF_6$ in EC+EMC+MP (20:20:60 vol %)				1.20M $LiPF_6$ in EC+EMC+MP (20:20:60 vol %) + 0.10M LiFSI				1.20M $LiPF_6$ in EC+DMC+MP (20:20:60 vol %)				1.40M $LiPF_6$ in EC+EMC+MP (10:10:80 vol %)			
	Temperature (°C)	Rate	Current (mA)	Capacity (Ah)	Watt-Hours (Wh)	Energy (Wh/Kg)	% of Room Temp	Capacity (Ah)	Watt-Hours (Wh)	Energy (Wh/Kg)	% of Room Temp	Capacity (Ah)	Watt-Hours (Wh)	Energy (Wh/Kg)	% of Room Temp	Capacity (Ah)	Watt-Hours (Wh)	Energy (Wh/Kg)	% of Room Temp
	20°C	C/5	50	0.2991	1.091	105.65	100	0.2935	1.071	105.50	100	0.2990	1.090	107.19	100.00	0.2994	1.090	107.95	100
Prior Discharge Test at -40C	- 40°C	C/200	1.25	0.2620	0.9510	92.06	87.60	0.2568	0.9323	91.86	87.49	0.2628	0.9534	93.74	87.91	0.2629	0.9511	94.16	87.81
24 Soak Prior to Discharge	- 90°C	C/200	1.25	0.0911	0.1791	17.34	30.46	0.0919	0.1861	18.34	31.31	0.0002	0.0004	0.03	0.07	0.1022	0.2140	21.19	34.13
After -90C Discharge	- 40°C	C/200	1.25	0.1660	0.5639	54.59	55.51	0.1661	0.5644	55.60	56.60	0.2629	0.9383	92.26	87.95	0.1553	0.5219	51.68	51.88
Total Discharged				0.2571	0.7430	71.93	85.96	0.2581	0.7505	73.94	87.91	0.2632	0.9387	92.30	88.01	0.2575	0.7359	72.86	86.01

- **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 BTE Cells at Low Temperature:
Low Temperature Survivability Test (-135°C)

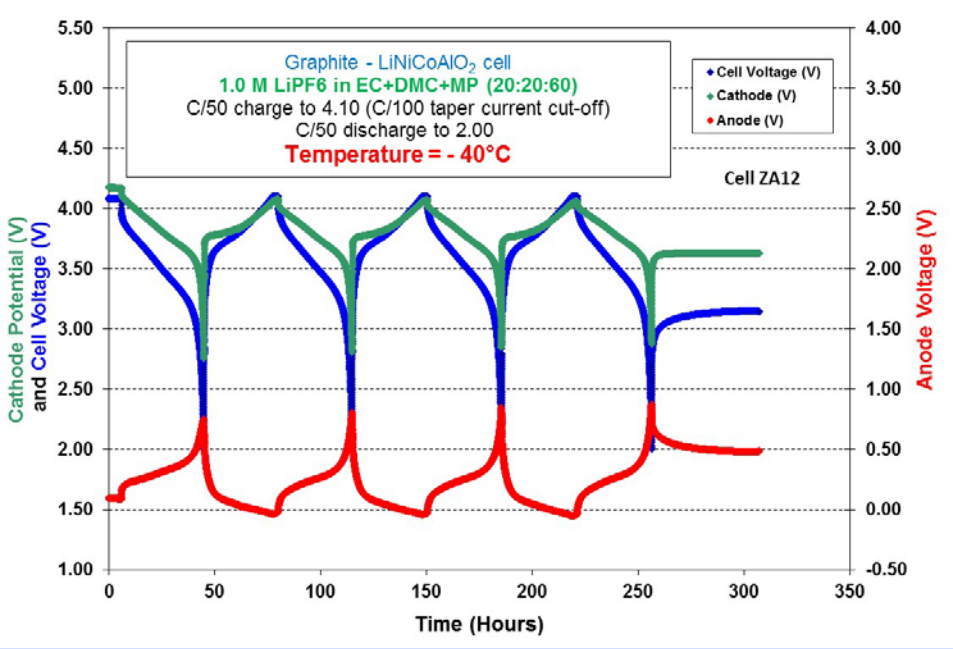
				Cell QMA-03				Cell QMB-09				Cell QMC-17				Cell QMD-29			
				1.20M $LiPF_6$ in EC+EMC+MP (20:20:60 vol %)				1.20M $LiPF_6$ in EC+EMC+MP (20:20:60 vol %) + 0.10M LiFSI				1.20M $LiPF_6$ in EC+DMC+MP (20:20:60 vol %)				1.40M $LiPF_6$ in EC+EMC+MP (10:10:80 vol %)			
	Temperature (°C)	Rate	Current (mA)	Capacity (Ah)	Watt-Hours (Wh)	Energy (Wh/Kg)	% of Room Temp	Capacity (Ah)	Watt-Hours (Wh)	Energy (Wh/Kg)	% of Room Temp	Capacity (Ah)	Watt-Hours (Wh)	Energy (Wh/Kg)	% of Room Temp	Capacity (Ah)	Watt-Hours (Wh)	Energy (Wh/Kg)	% of Room Temp
Initial Capacity	20°C	C/5	50	0.2991	1.0914	105.65	100	0.2935	1.0709	105.50	100	0.2990	1.0901	107.19	100.00	0.2994	1.0903	107.95	100
Performance Prior to Exposure at - 135C	20°C	C/5	50	0.2881	1.0485	101.50	96.32	0.2867	1.0438	102.84	97.66	0.2890	1.0523	103.47	96.66	0.2658	0.9703	96.07	88.77
Capacity Charged into Cells Prior to -135°C Exposure	20°C	C/5	50	0.1250	0.4406	42.65	41.80	0.1250	0.4406	43.41	42.58	0.1250	0.4410	43.36	41.81	0.1250	0.4417	43.74	41.75
Capacity Discharged from Cells After -135°C Exposure	20°C	C/5	50	0.1210	0.4183	40.50	40.46	0.1227	0.4243	41.81	41.81	0.1228	0.4245	41.74	41.06	0.1165	0.4036	39.96	38.90
Percentage of Storage Capacity Discharged After -135°C Exposure				96.80				98.20				98.21				93.17			
Performance After Exposure at - 135C	20°C	C/5	50	0.2866	1.0429	100.96	95.83	0.2865	1.0428	102.74	97.60	0.2892	1.0530	103.54	96.73	0.2678	0.9774	96.78	89.46
Total Irreversible Capacity Loss Due to - 135°C Exposure				0.0015	0.0056			0.0002	0.0010			-0.0002	-0.0007			-0.0020	-0.0071		

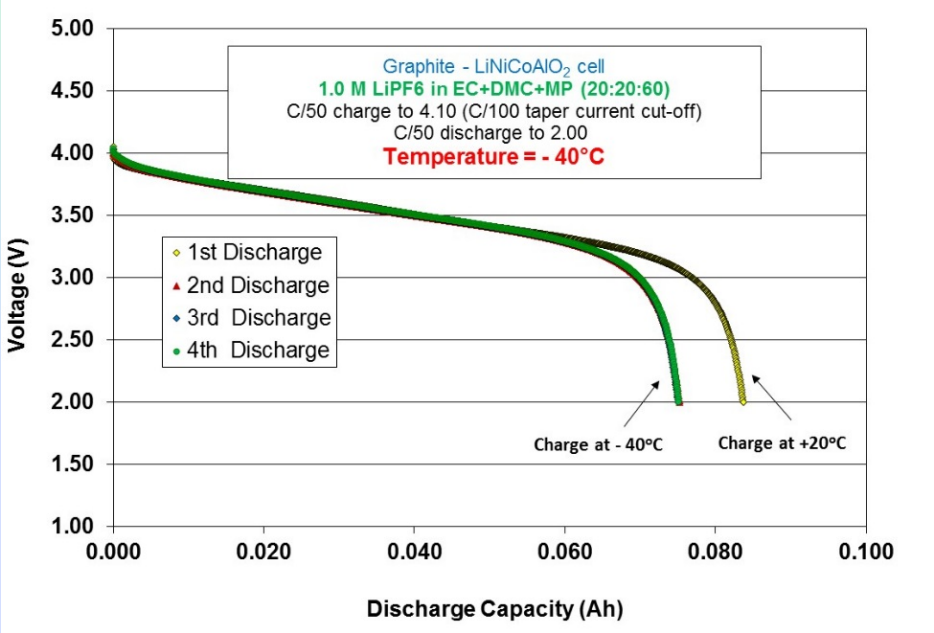
- **Quallion cells have been demonstrated to provide excellent low temperature survivability characteristics, being capable surviving exposure to -135°C and long term dwell periods.**
  - Cells soaked at -135°C for over 4 hours prior to discharge
  - Additional dwell periods of 0.5 hours at -90°C and -115°C
  - Cells impedance was recorded periodically during the ultra-low temperature testing
  - Cells characterized in terms of capacity and impedance before and after exposure

Performance of Quallion Experimental 3-Electrode Cells

(Electrodes obtained from Quallion)

C/50 Rate Cycling at - 40°C



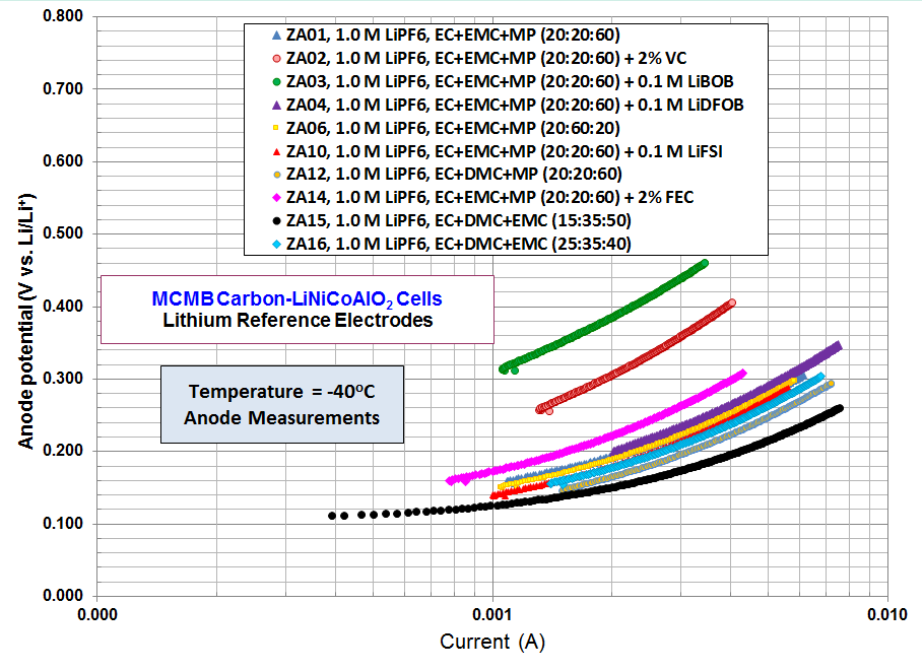


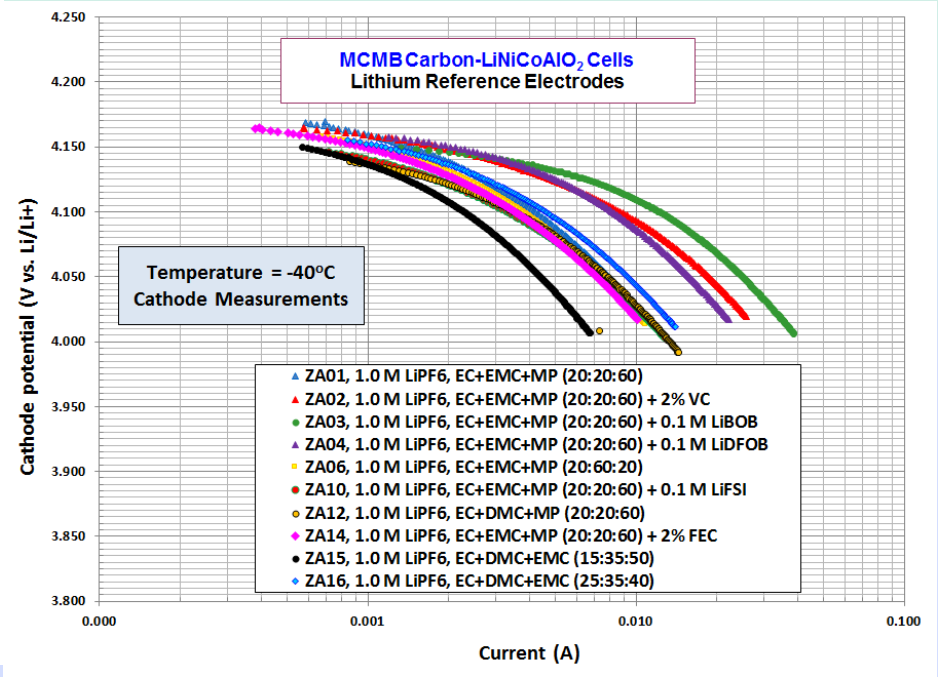
- Experimental 3-electrode cells with Quallion electrodes display reasonable robustness to charging at -40°C when low rates are employed.
- We are currently evaluating a number of electrolytes in these 3-electrode cells, and attempting to correlate the relative kinetics with the propensity of lithium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

Performance of Quallion Experimental 3-Electrode Cells

(Electrodes obtained from Quallion)

Tafel Polarization Measurements at - 40°C





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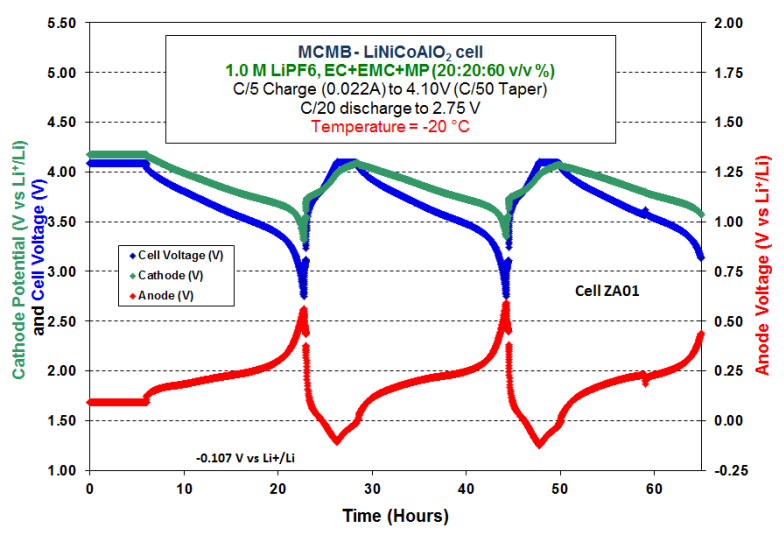
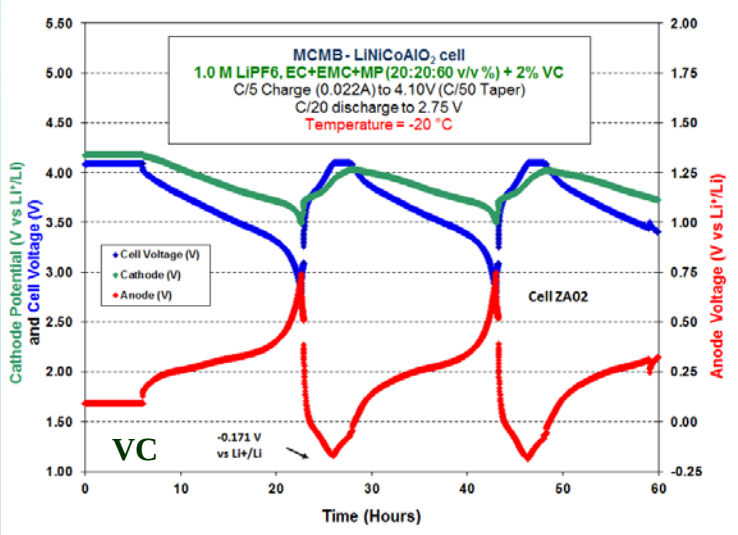
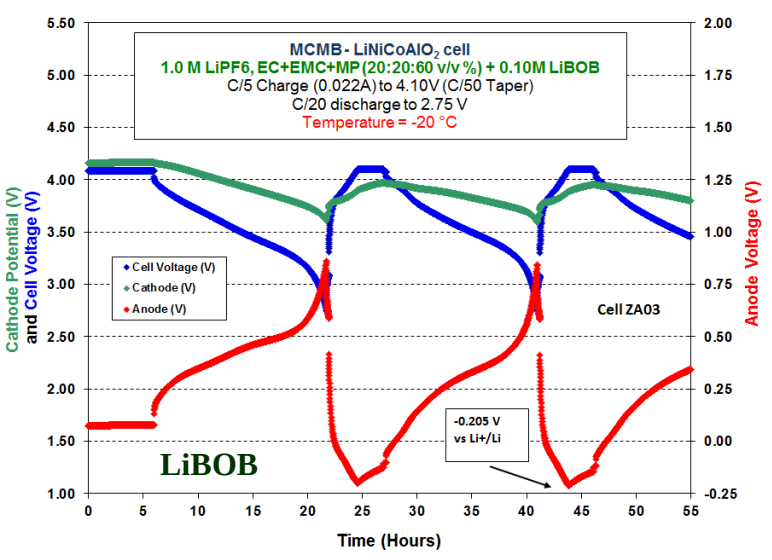
- We are currently evaluating a number of electrolytes in these 3-electrode cells, and attempting to correlate the relative kinetics with the propensity of lithium plating.

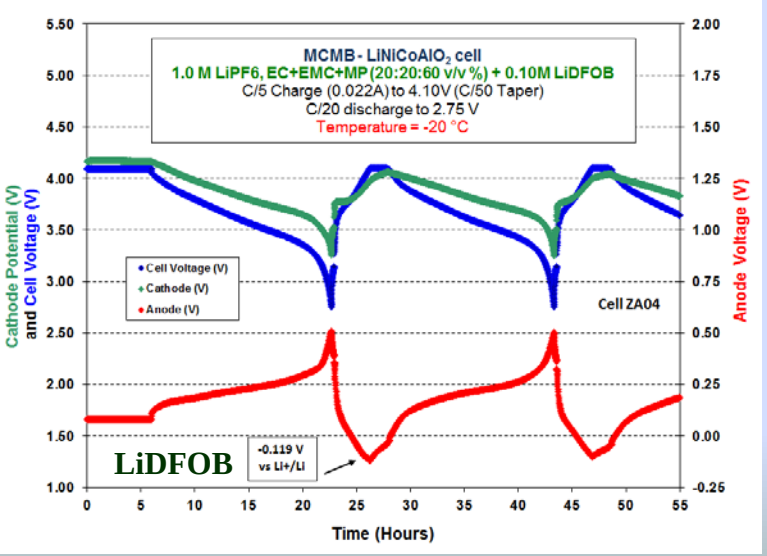
Charge Behavior of MCMB/$LiNiCoAlO_2$ Cells at Low Temperature

Charge at -20°C (C/5 Rates, 2.75V to 4.10V)



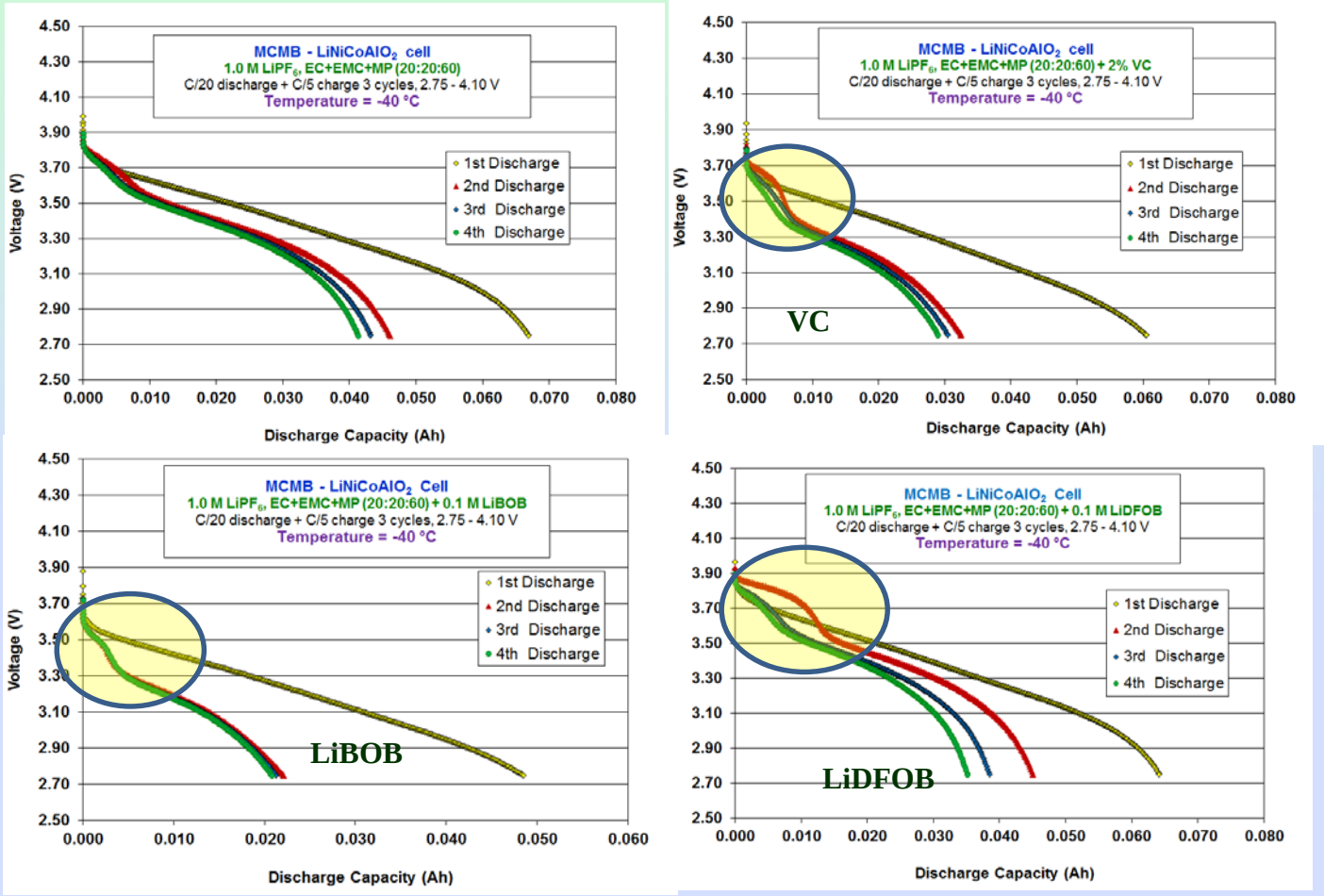






Charge Behavior of MCMB/$LiNiCoAlO_2$ Cells at Low Temperature

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

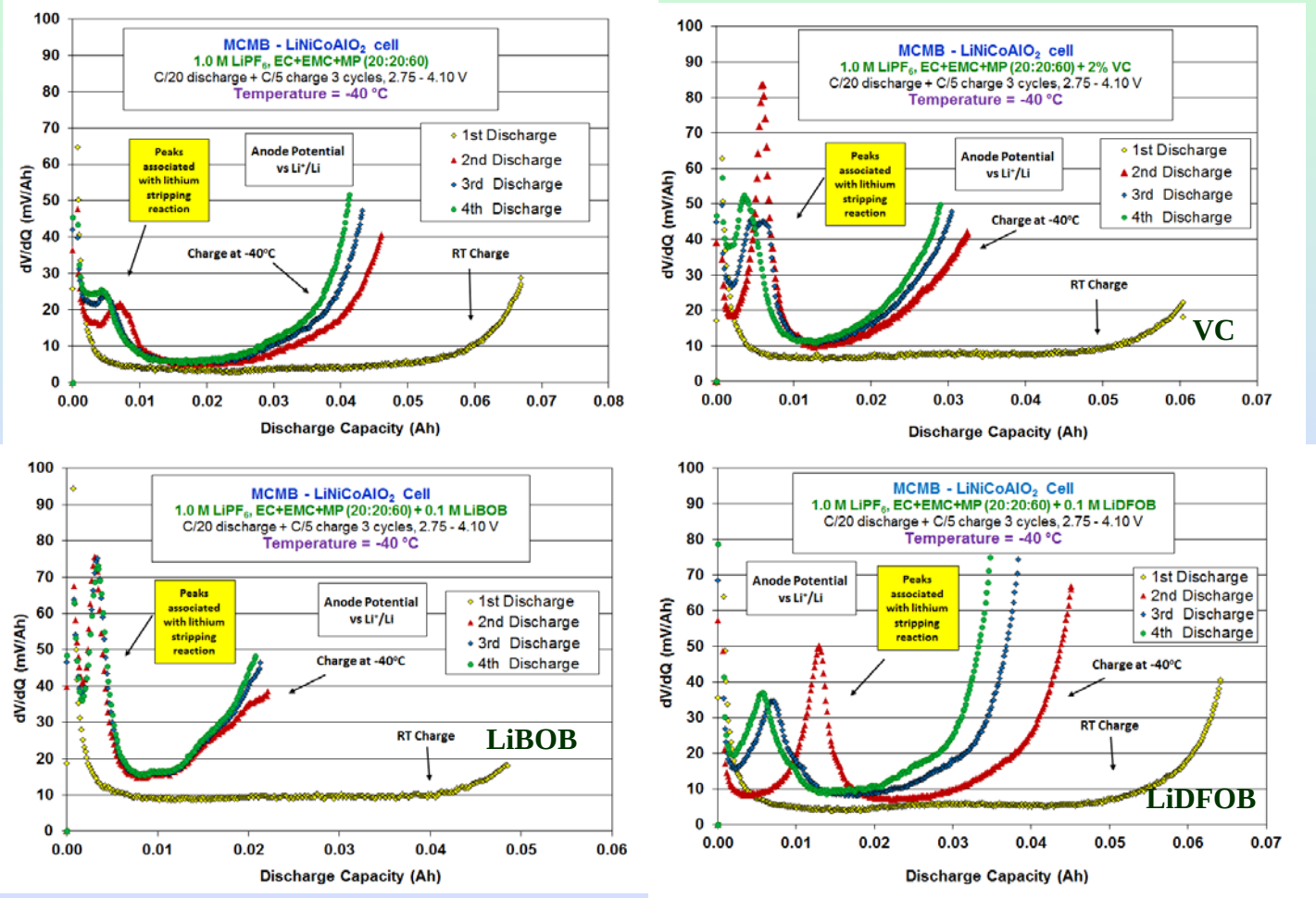


M. C. Smart. et al., 227th Meeting of the Electrochemical Society, Chicago, Illinois, May 25-29, 2015 (Abstract #47562).

- In experimental three electrode cells containing Quallion electrodes, the majority of additives appear to lead to increased lithium plating compared to the baseline solution at -40°C using C/5 charge rates.
- Please see our companion paper J.-P. Jones, et al, "The Effect of Electrolyte Composition on Lithium Plating During Low Temperature Charging of Li-Ion Cells", Abstract

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

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



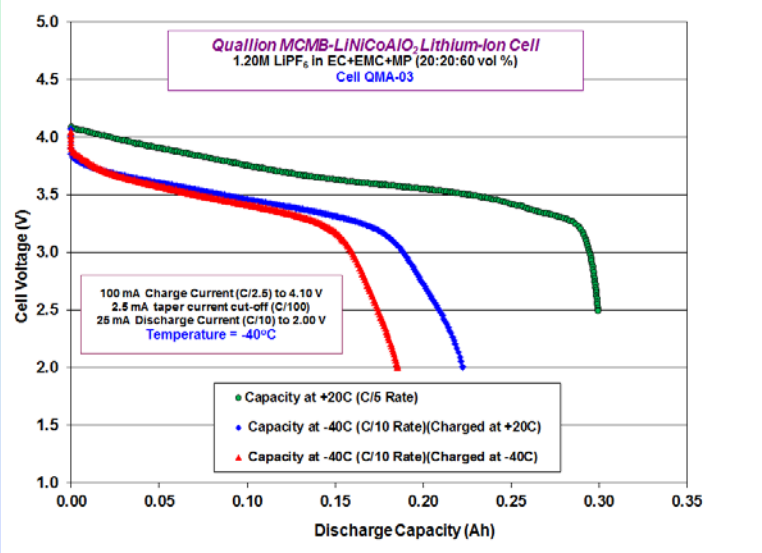
▷ **Differential voltage/capacity plots of the anode potential during cycling is insightful in determining which sample experiences the greatest amount of lithium plating/stripping.**

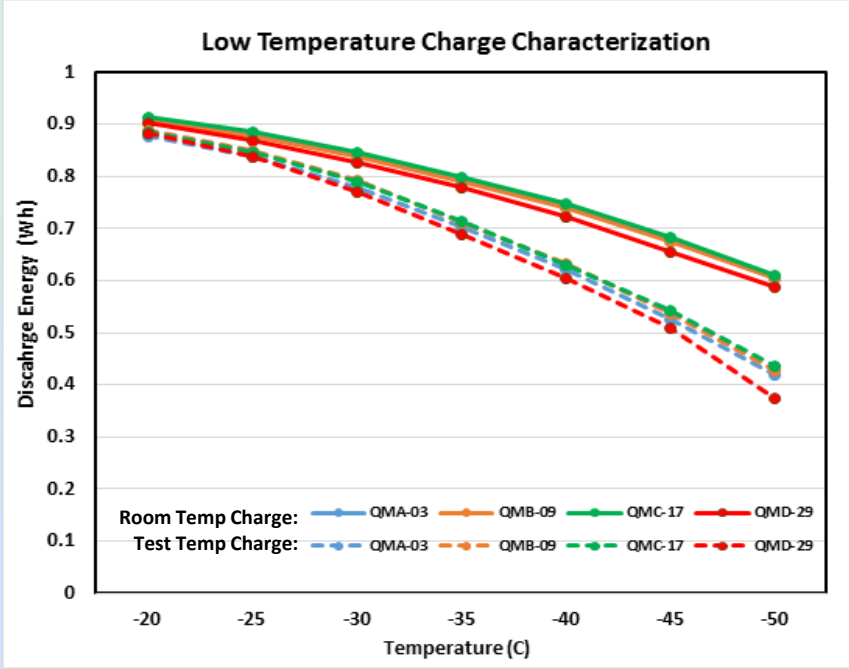
▷ **When the discharges at -40°C are analyzed all of the cells with additives result in notable stripping peaks.**

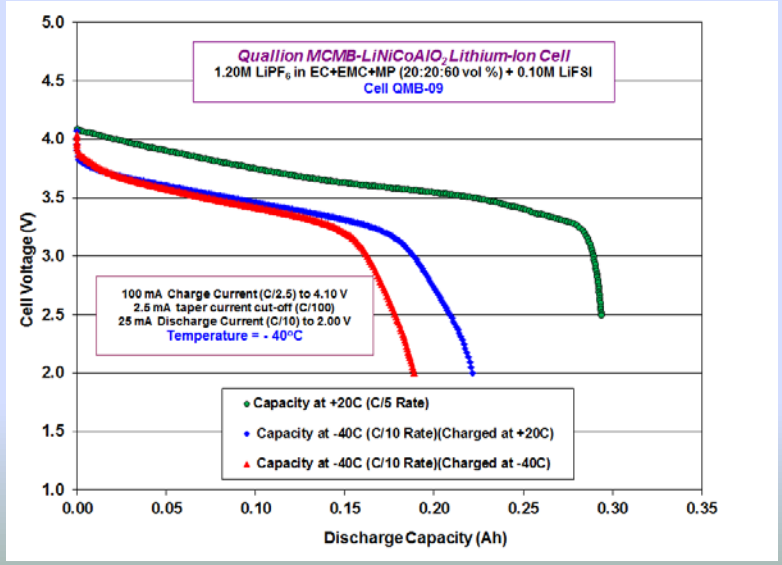
M. C. Smart. et al., 227th Meeting of the Electrochemical Society, Chicago, Illinois, May 25-29, 2015 (Abstract #47562).

Performance of Quallion BTE Custom Cells

C/2.5 Charge Rate Characterization at -20° to -50°C



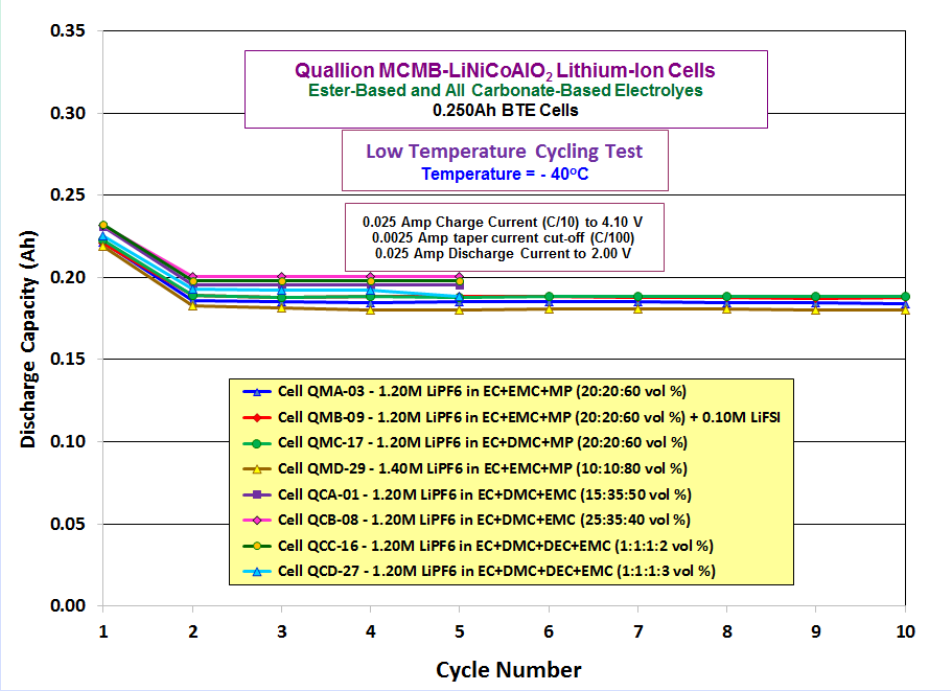


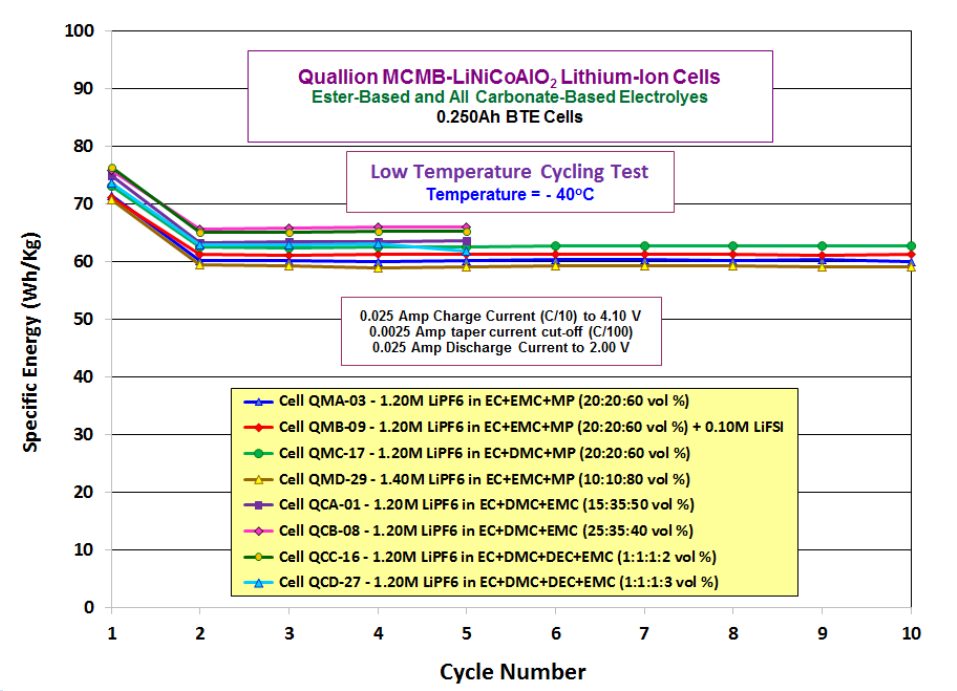


- Quallion cells have been demonstrated to provide reasonable robustness to charging at low temperatures, even when aggressive charge rates are used.
- Only low levels of lithium plating may have indirectly been detected, which may be acceptable given the modest life requirements of the PUFFER application.

Performance of Quallion BTE Custom Cells

Cycle Life Performance at -40°C using C/10 Charge and Discharge Rates





- **Quallion cells have been demonstrated to provide very stable cycle life performance at -40oC using C/10 charge and discharge rates over the voltage range of 2.0V to 4.10V.**
- **Low EC-content all carbonate-based solutions deliver the highest capacity and specific energy over the limited number of cycles performed.**

➢ *Summary and Conclusions*:

- **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 with long term dwell periods and good survivability to -135°C.**
- **The use of ester-based blends have led to the demonstration of high capacity at -60°C and -70°C when low rates are used.**
- **Stable cycle life performance at -40°C has been obtained when using C/10 charge and discharge rates.**
- **The electrolyte 1.20M LiPF6 in EC+EMC+MP (20:20:60 vol %) + 0.10M LiFSI has demonstrated excellent performance over a number of conditions at low temperature and has been selected for use for the PUFFER program development uses. .**

➢ *Future Work*:

- **Further investigate the impact of electrolyte type upon the charge acceptance when cycling at low temperatures.**
- **Evaluate the cycle life performance over a range of temperatures.**

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.