Low Temperature Electrolytes in High Specific Energy 18650 Li-Ion Cells for Future NASA Missions

M. C. Smart*, F. C. Krause*, J. –P. Jones*, L. D. Whitcanack*, B. V. Ratnakumar*, E. J. Brandon*, and M. Shoesmith‡

** Jet Propulsion Laboratory, California Institute of Technology*
4800 Oak Grove Drive, Pasadena, CA 91109-8099, USA
‡ E-One Moli Energy, Canada, Ltd.
20 000 Stewart Crescent, Maple Ridge, BC, V2X 9E7, Canada

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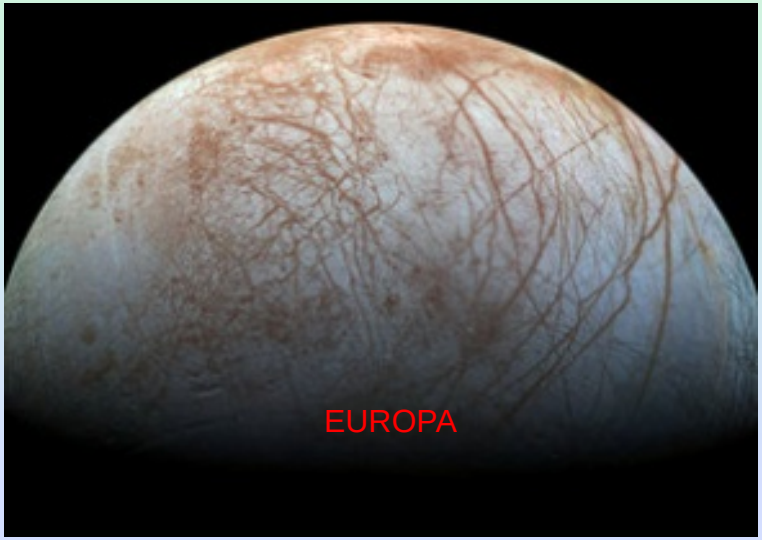
Background: Mission Concept Needs

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.

Advanced Li-Ion Prototypes Cells Under Evaluation

➢ E-One Molicel Custom 18650 Li-Ion Cells (~ 2.80 Ah)

- **18650-Size Cylindrical Li-Ion Cells (~ 2.50 Ah capacity over range of 3.00 to 4.10V)**
  - ➢ **Early generation prototypes evaluated under the Europa Clipper program (chemistry similar to ICR-M)**
  - ➢ **Excellent low temperature has been demonstrated previously (down to -50°C)**
  - ➢ **Cells display very high specific energy**
  - ➢ **The Moli custom cells were incorporated with JPL developed low temperature Li-ion electrolytes that have previously been demonstrated to have good performance in NCO[1,2], NCA[2,3], and LFP[5] systems.**
    - ➢ **Ester-Based Electrolytes Evaluated in E-One Moli Custom 18650 Cells :**
      - **1.0M $LiPF_6$ in EC+EMC+MP (20:60:20 vol %)**
      - **1.0M $LiPF_6$ in EC+EMC+MP (20:20:60 vol %)**
      - **1.0M $LiPF_6$ in EC+EMC+MP (20:20:60 vol %) + 2% VC**
      - **1.2M $LiPF_6$ in EC+EMC+MP (20:20:60 vol %) + 2% FEC**
      - **1.2M $LiPF_6$ in EC+EMC+MB (20:20:60 vol %)**
    - ➢ **All Carbonate-Based Electrolytes Evaluated in E-One Moli Custom 18650 Cells :**
      - **1.0M $LiPF_6$ in EC+EMC (10:90 vol %)**
      - **1.0M $LiPF_6$ in EC+DEC+DMC+EMC (1:1:1:3 vol %)**
      - **1.2M $LiPF_6$ in EC+DMC+EMC (15:35:50 vol %)**

(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.
(5) M. C. Smart, B.V. Ratnakumar, A. S. Gozdz, and S. Mani, 214th Meeting of the Electrochemical Society, Honolulu, HI, Oct. 12-17, 2008.

Low Temperature Performance Evaluation of E-One Molicel Custom Prototype 18650 Cells

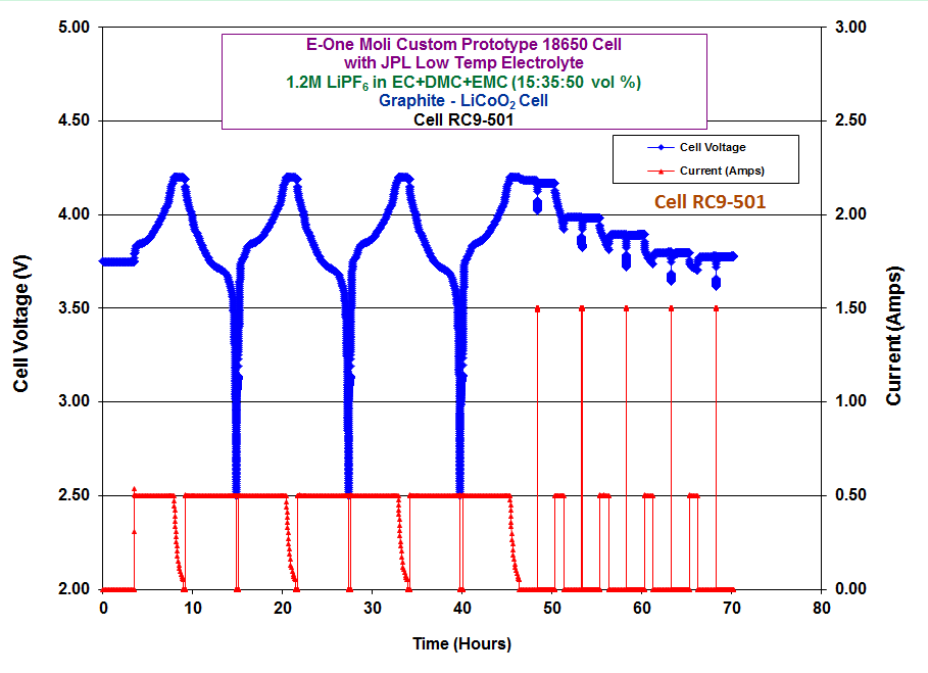
Overview of Test Plan

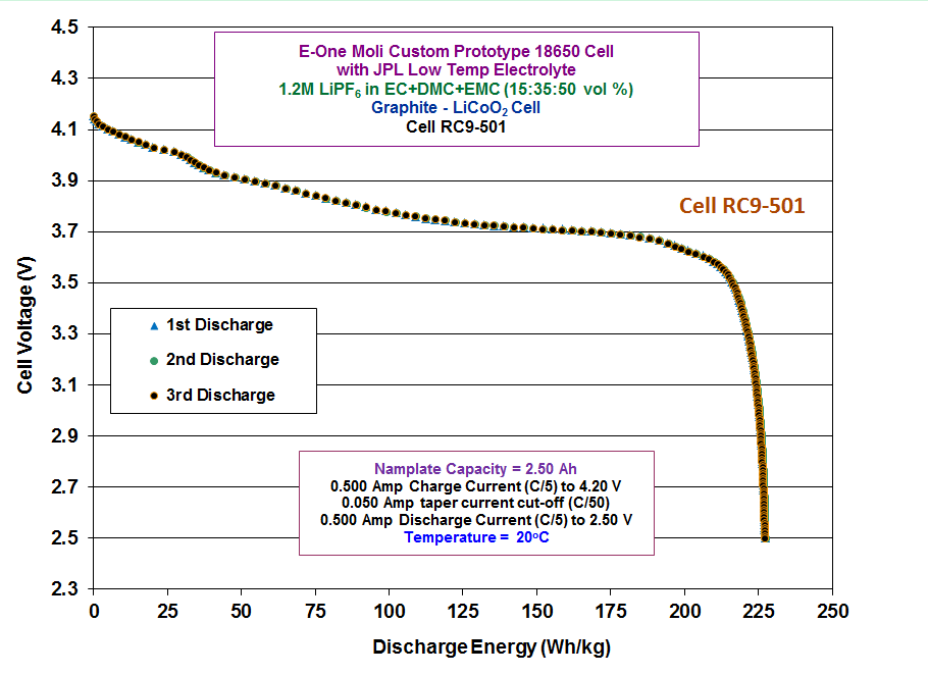
- Performed initial capacity and impedance characterization
  - Temperature = +20°C (voltage range = 3.0V to 4.10V and 3.0V to 4.20V) (C/5 Rates)
  - Temperature = 0°C (voltage range =3.0V to 4.10V) (C/5 Rates)
  - Temperature = - 20°C (voltage range = 2.5V to 4.10V) (C/10 Charge and C/5 Discharge)
  - Temperature = - 25°C (voltage range = 2.5V to 4.10V) (C/10 Charge and C/5 Discharge)
  - Temperature = - 30°C (voltage range = 2.5V to 4.10V) (C/10 Charge and C/5 Discharge)

- Performed discharge rate characterization (with charging at room temperature)
  - Temperature = - 40°C; Rates = C/200, C/100, C/50, C/20, C/10, C/5, C/2, 1.0C
  - Temperature = - 50°C; Rates = C/200, C/100, C/50, C/20, C/10, C/5, C/2
  - Temperature = - 60°C; Rates = C/200, C/100, C/50, C/20, C/10,
  - Temperature = - 70°C; Rates = C/100, C/50, C/20,
  - Low rate discharge with periodic high rate pulsing (at -40oC, -50°C, and -60°C).
- Continuous cycling tests at -40°C
  - Incrementally increasing charge and discharge rate and charge voltage
    - C/100 rates increasing to C/25 rates
    - Charge voltage = 4.10V, 4.15V, and 4.20V
  - Continuously cycling at C/50 charge and discharge rates and 4.20V charge

- The nameplate capacity of the cells has been set to 2.50Ah for the test program, corresponding to the capacity obtained over the voltage range of 3.0V to 4.10V which is adopted to preserve life for extended operation.

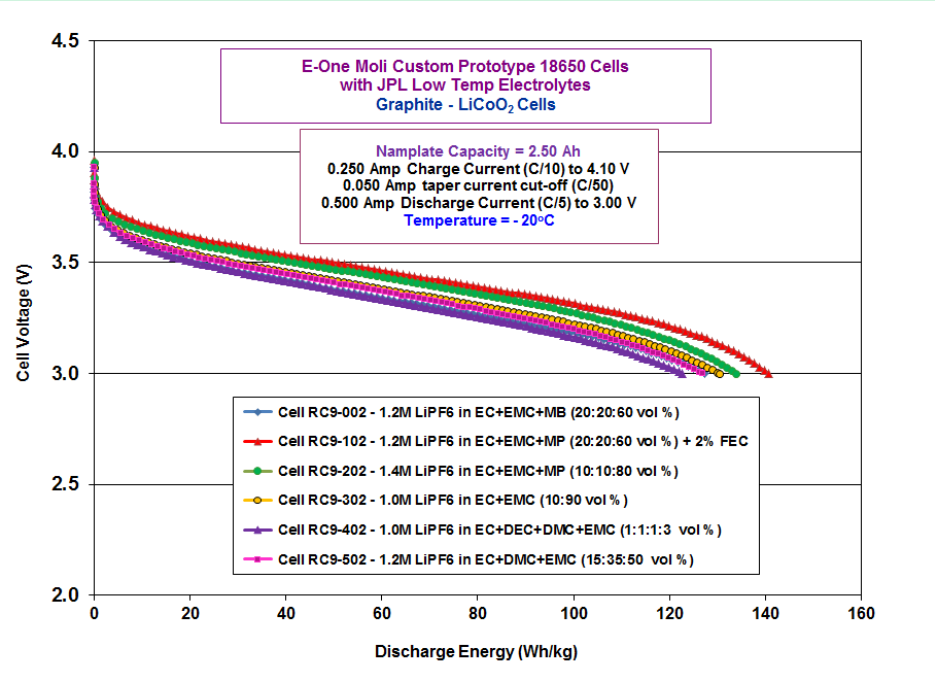
Performance of E-One Moli Custom Prototype 18650 Cells at Room Temperature:
Characteristization at +20°C (2.50V to 4.20V)

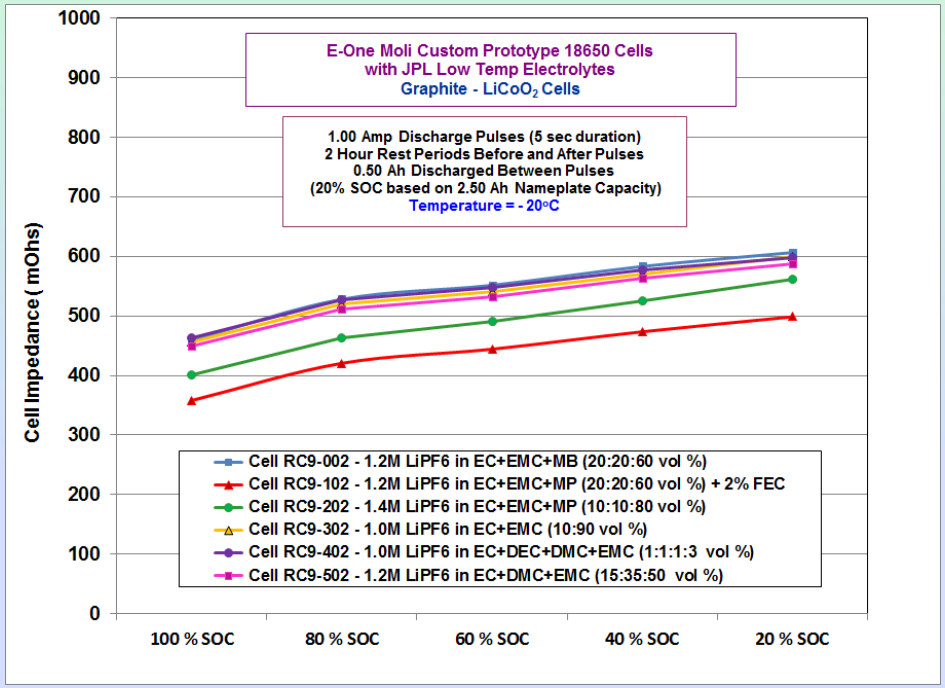




- Excellent specific energy at +20°C observed using C/5 rates over the voltage range of 2.50V-4.20V (> 220 Wh/kg).
- Cell containing methyl propionate delivered the lowest impedance.
- Of the all carbonate-based electrolytes, the 1.20M $LiPF_6$ in EC+DMC+EMC (15:35:50 vol %) resulted in cells with the lowest impedance.

Performance of E-One Moli Custom Prototype 18650 Cells at Room Temperature:
Characteristization at -20°C (3.00V to 4.10V)

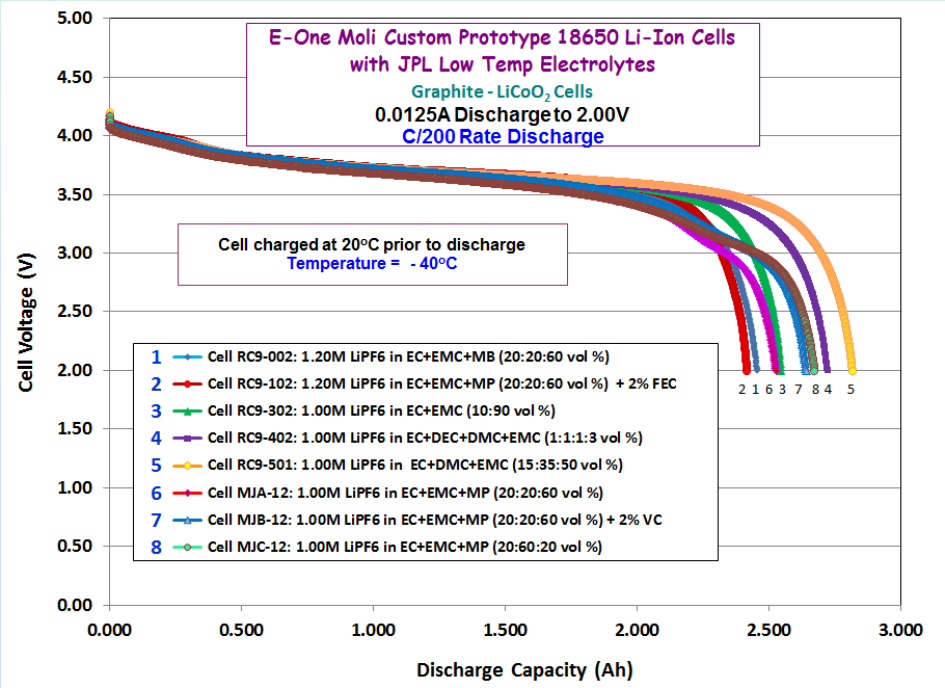




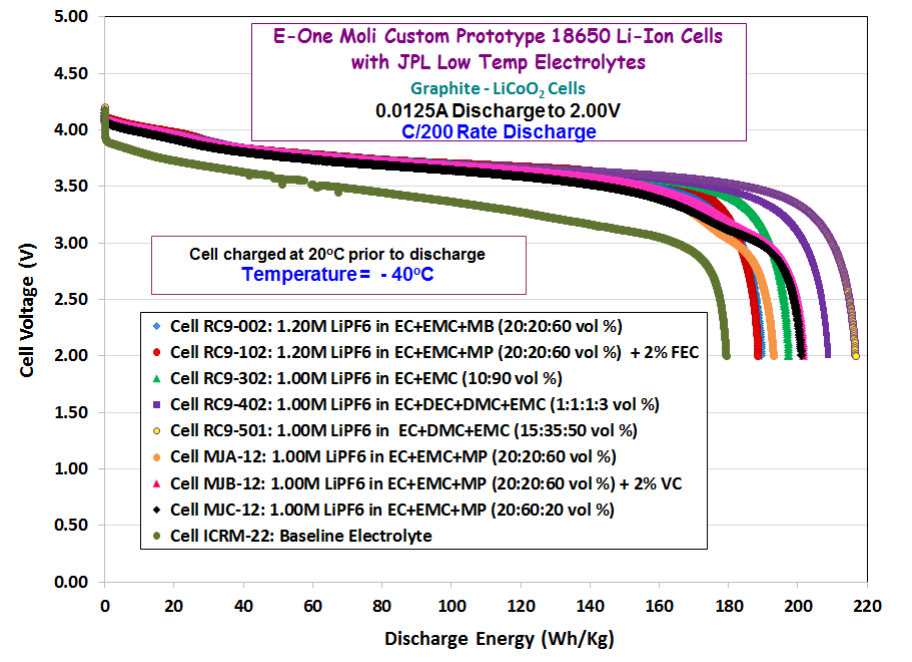
- Initial characterization testing was performed with an intent to avoid the possibility of lithium plating at low temperature, so low charge voltage and moderate charge rates were employed.
- A range of ~ 120-140 Wh/kg was observed over the voltage range of 3.00V-4.10V.
- Cells containing methyl propionate delivered the lowest impedance and highest capacity when evaluated at -20°C, using a C/10 charge and C/5 discharge rate.

Performance of E-One Moli Custom Prototype 18650 Cells at Room Temperature:
Characteristization at - 40°C (C/200 Discharge to 2.0V)

Discharge Capacity (Ah)



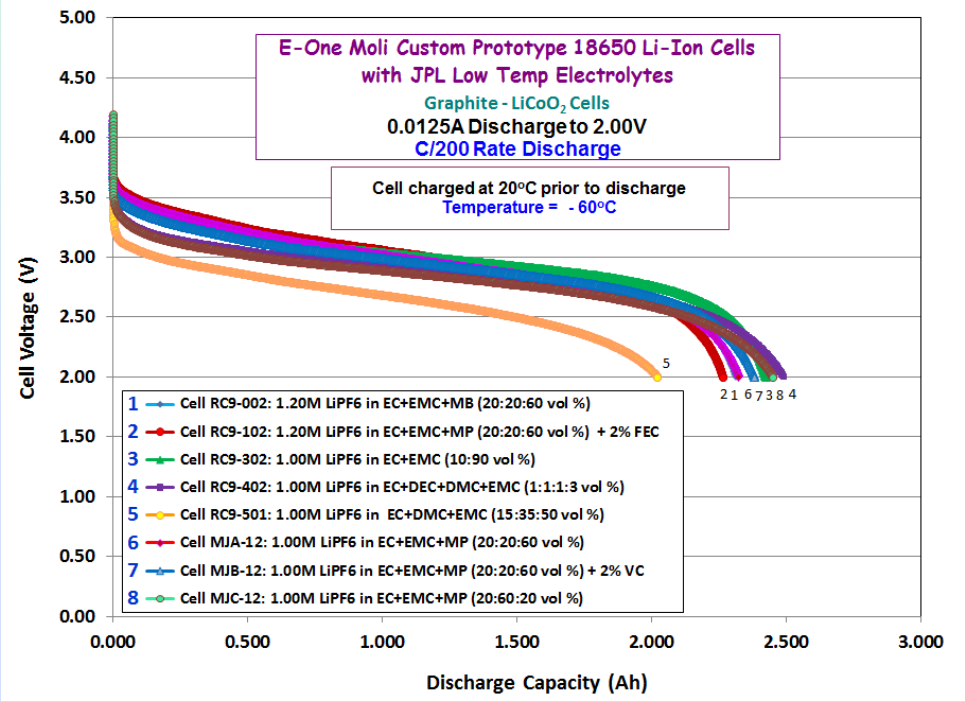
Discharge Energy (Wh/Kg)



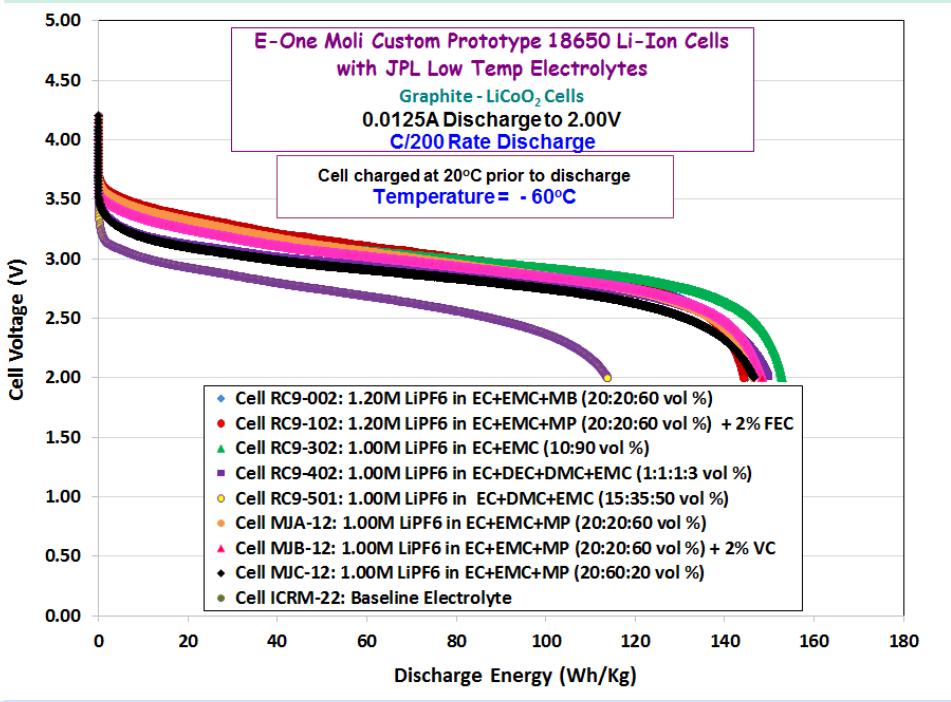
- With charging at room temperature, excellent specific energy can be observed at low rate (C/200) at -40°C.
- Over 200 Wh/kg was observed for many electrolyte variations.
- At these low rates, the all carbonate-based electrolyte systems provided the highest specific energy.

Performance of E-One Moli Custom Prototype 18650 Cells at Room Temperature:
Characteristization at - 60°C (C/200 Discharge to 2.0V)

Discharge Capacity (Ah)



Discharge Energy (Wh/Kg)



- **With charging at room temperature, excellent specific energy can be observed at low rate (C/200) at -60°C .**
- **Over 150 Wh/kg was observed for many electrolyte variations.**

Performance of E-One Moli Custom Prototype 18650 Cells at Low Temperature

Discharge Characteristics at -40°C to -70°C

			Cell RC9-001				Cell RC9-101				Cell RC9-301				Cell RC9-401				Cell RC9-501			
			1.20M $LiPF_6$ in EC+EMC+MB (20:20:60 vol %)				1.20M $LiPF_6$ in EC+EMC+MP (20:20:60 vol %) + 2% FEC				1.00M $LiPF_6$ in EC+EMC (10:90 vol %)				1.00M $LiPF_6$ in EC+DEC+DMC+EMC (1:1:1:3 vol %)				1.20M $LiPF_6$ in EC+DMC+EMC (15:35:50 vol %)			
Temperature (°C)	Rate	Current (A)	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	Capacity (Ah)	Watt-Hours (Wh)	Energy (Wh/Kg)	% of Room Temp
20°C	C/5	0.500	2.8093	10.539	224.22	100	2.8199	10.629	225.35	100	2.8175	10.579	224.38	100	2.8224	10.607	225.02	100	2.8275	10.645	226.98	100
- 40°C	1.0 C	2.500	0.0116	0.0242	0.52	0.41	2.1713	5.5625	117.93	77.00	0.0030	0.0065	0.14	0.11	0.0022	0.0048	0.10	0.078	0.0035	0.0076	0.16	0.12
	C/2	1.250	1.2264	3.1283	66.56	43.65	1.9716	5.2803	111.95	69.92	0.1387	0.3432	7.28	4.92	0.6911	1.6770	35.58	24.48	0.9435	2.3502	50.11	33.37
	C/5	0.500	2.0749	5.6072	119.30	73.86	2.3863	6.8960	146.20	84.63	1.3291	3.4164	72.46	47.17	1.7253	4.6166	97.94	61.13	1.6974	4.5943	97.96	60.03
	C/10	0.250	2.4445	7.0696	150.41	87.01	2.5158	7.6930	163.10	89.22	2.3541	6.7634	143.46	83.55	2.3616	6.8122	144.52	83.67	2.3328	6.7055	142.98	82.50
	C/20	0.125	2.5900	7.9532	169.21	92.19	2.6067	8.4176	178.46	92.44	2.5650	7.8434	166.36	91.04	2.5692	7.8809	167.20	91.03	2.5673	7.8798	168.01	90.80
	C/50	0.125	2.6906	8.6577	184.20	95.77	2.6984	9.2644	196.41	95.69	2.6888	8.6013	182.44	95.43	2.6962	8.6714	183.97	95.53	2.6922	8.6590	184.63	95.21
	C/100	0.125	2.6795	9.5318	202.80	95.38	2.6312	9.5940	203.40	93.31	2.6571	9.4562	200.57	94.31	2.6744	9.4926	201.39	94.76	2.6879	9.5829	204.33	95.06
- 50°C	C/2	1.250	0.4639	1.0304	21.92	16.51	0.9215	2.1935	46.50	32.68	0.0445	0.0938	1.99	1.58	0.0533	0.1094	2.32	1.89	0.0001	0.0003	0.01	0.00
	C/5	0.500	0.9987	2.4014	51.09	35.55	1.6772	4.2365	89.82	59.48	0.1383	0.3386	7.18	4.91	0.4878	1.1346	24.07	17.28	0.4154	0.9205	19.63	14.69
	C/10	0.250	1.6694	4.2497	90.42	59.42	2.1839	5.8656	124.35	77.45	0.8971	2.1667	45.96	31.84	1.1968	3.0117	63.89	42.41	0.8525	2.0909	44.58	30.15
	C/20	0.125	2.2705	6.2011	131.93	80.82					2.1287	5.8125	123.29	75.55	2.0344	5.5173	117.05	72.08	1.5579	4.1451	88.38	55.10
	C/50	1.250	2.5473	7.7400	164.67	90.67	2.5664	8.1412	172.60	91.01	2.5487	7.7366	164.10	90.46	2.5264	7.6172	161.60	89.51	2.4364	7.1155	151.72	86.17
	C/100	0.500	2.5955	8.3849	178.39	92.39	2.5627	8.6232	182.82	90.88	2.5726	8.2932	175.91	91.31	2.5810	8.2642	175.33	91.45	2.5693	8.0463	171.57	90.87
- 60°C	C/10	0.250	0.4791	1.0493	22.32	17.06	1.0838	2.4912	52.82	38.43	0.0614	0.1415	3.00	2.18	0.0694	0.1529	3.24	2.46	0.0000	0.0001	0.00	0.00
	C/20	0.125	1.1308	2.6389	56.15	40.25	1.7737	4.3280	91.76	62.90	0.3027	0.6909	14.65	10.74	0.5724	1.2888	27.34	20.28	0.0011	0.0023	0.05	0.04
	C/50	1.250	1.9922	5.1270	109.08	70.91	2.2820	6.2687	132.90	80.93	1.8580	4.7810	101.41	65.95	1.6181	4.0869	86.70	57.33	0.6633	1.5140	32.28	23.46
	C/100	0.500	2.3942	6.7521	143.66	85.22	2.4084	7.1682	151.97	85.41	2.3684	6.5959	139.90	84.06	2.2796	6.2376	132.33	80.77	1.3988	3.5769	76.27	49.47
- 70°C	C/20	0.125	0.0073	0.0155	0.33	0.26	0.3719	0.7936	16.83	13.19	0.0087	0.0186	0.39	0.31	0.0002	0.0004	0.01	0.01	0.0000	0.0000	0.00	0.00
	C/50	1.250	0.6795	1.4895	31.69	24.19	1.3456	3.0780	65.26	47.72	0.1147	0.2546	5.40	4.07	0.0200	0.0446	0.95	0.71	0.0000	0.0000	0.00	0.00
	C/100	0.500	1.3132	3.0785	65.50	46.74	1.8574	4.5590	96.66	65.87	0.8464	1.9455	41.27	30.04	0.4598	0.9970	21.15	16.29	0.0000	0.0000	0.00	0.00

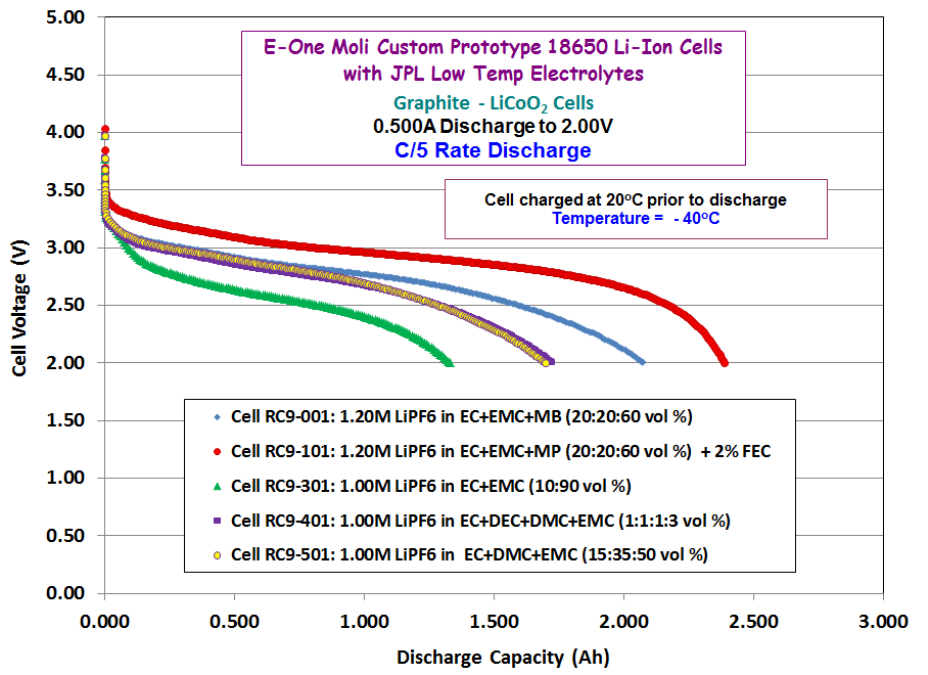
- **Excellent specific energy at -40°C observed using a low rate discharge (C/100) (i.e., > 200 Wh/kg).**
- **Methyl propionate yields improved discharge characteristics compared to methyl butyrate.**
- **Rate capability of cells with ester-based electrolytes at low temperatures is far superior to cells that contain the all carbonate-based electrolytes.**

Performance of E-One Moli Custom Prototype 18650 Cells at Low Temperature:

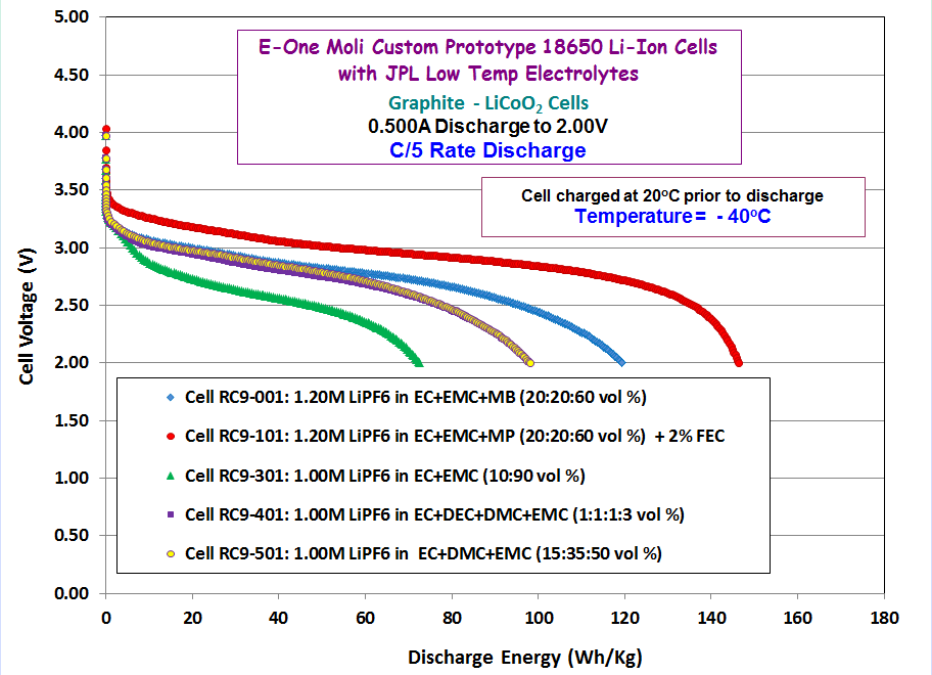
Discharge Characteristics at -40°C (Room Temperature Charge)

C/5 Discharge to 2.00V

Discharge Capacity (Ah)



Discharge Energy (Wh/Kg)

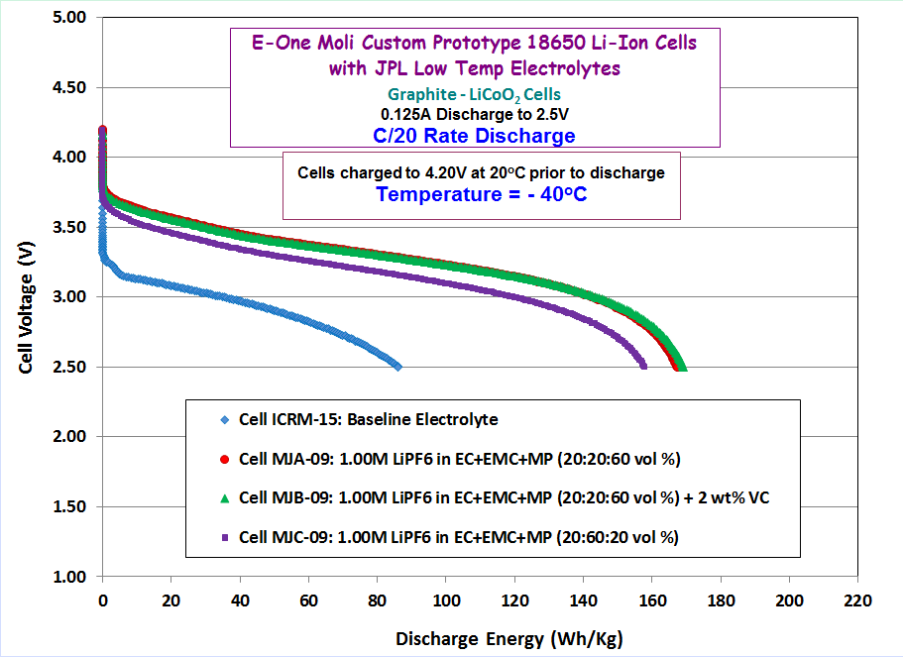


- Excellent specific energy at -40°C observed using a moderate rate discharge (C/5) with MP-based electrolyte (i.e., > 145 Wh/kg). Use of all carbonate-based electrolytes also lead to excellent discharge performance at low temperature (i.e., > 95 Wh/kg).
- Rate capability of cells with ester-based electrolytes at low temperatures is far superior to cells that contain the all carbonate-based electrolytes.

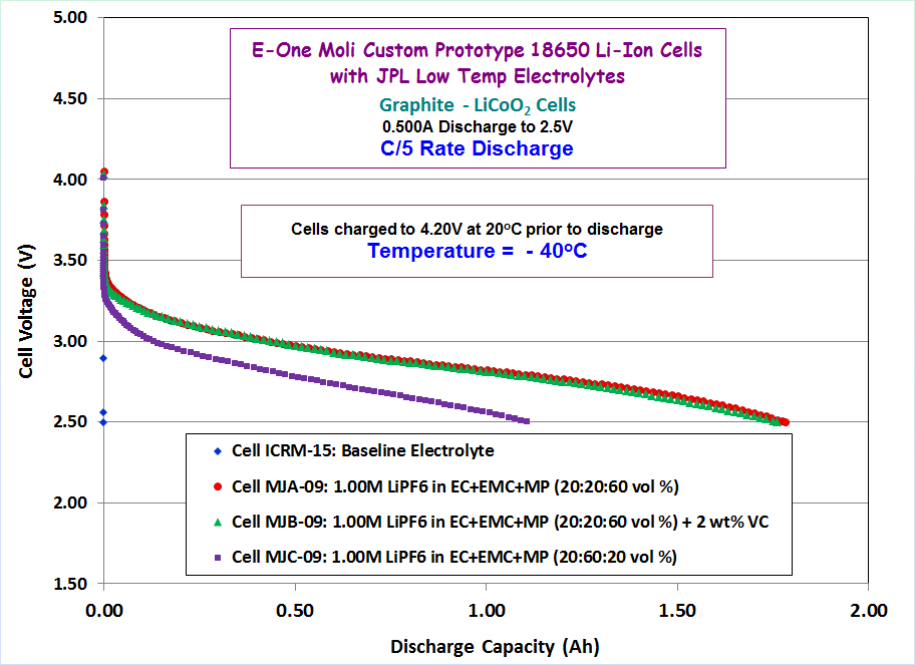
Performance of E-One Moli Custom Prototype 18650 Cells

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.**

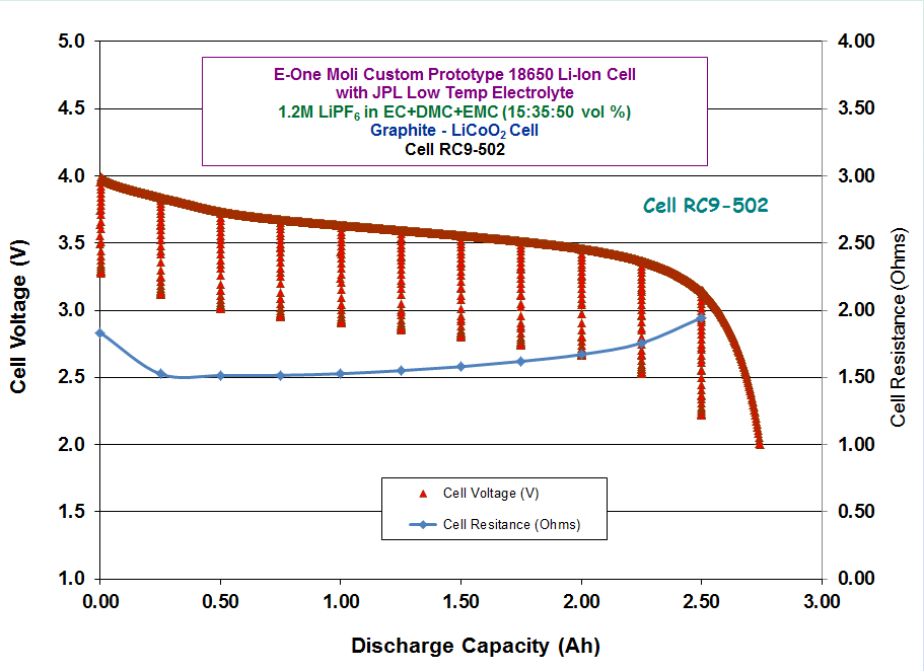
- **The custom Moli ICR-M cells with JPL electrolytes display improved low temperature discharge rate performance at -40°C compared to the baseline.**

Performance of E-One Moli Custom Prototype 18650 Cells at Low Temperature:

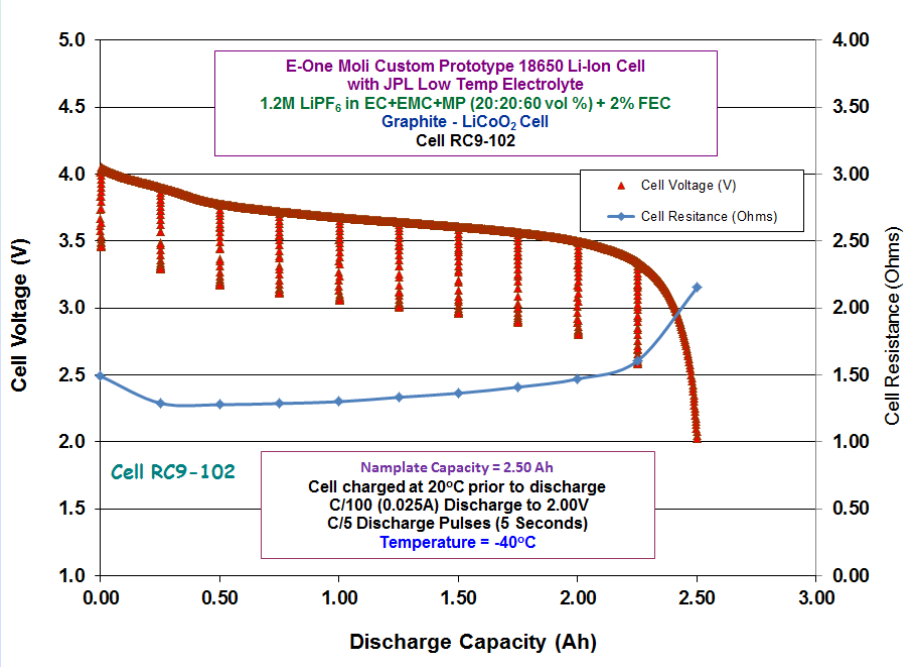
Discharge Characteristics at -40°C (Room Temperature Charge)

C/100 Discharge to 2.00V (with intermittent C/5 pulses)

All Carbonate Based Electrotye



Methyl Propionate-Based Electrolyte



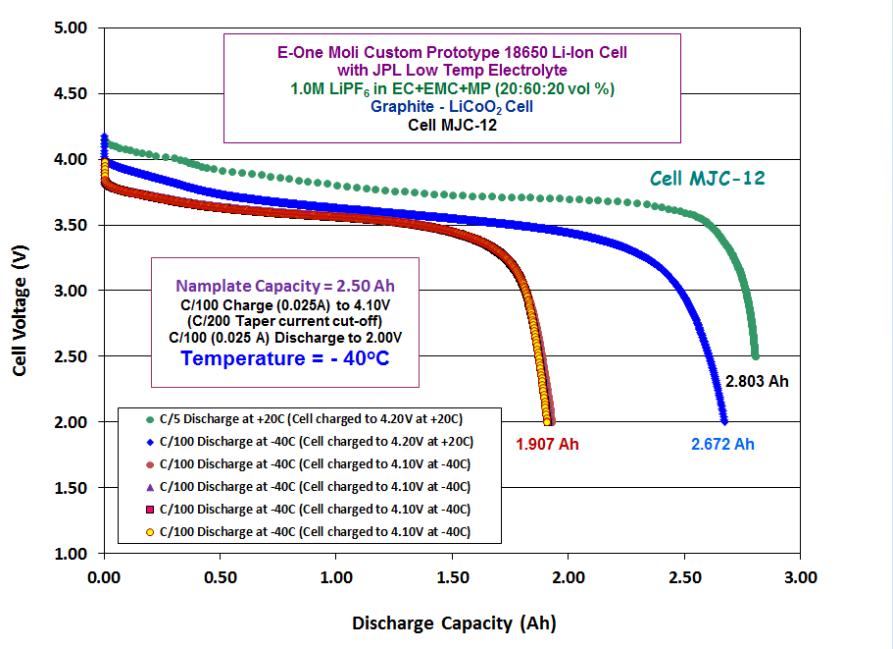
- **Cells containing ester-based electrolytes display lower cell impedance at -40°C, and the ability to support higher current pulses with less polarization.**
- **These trends become more pronounced at lower temperatures**

Performance of E-One Moli Custom Prototype 18650 Cells

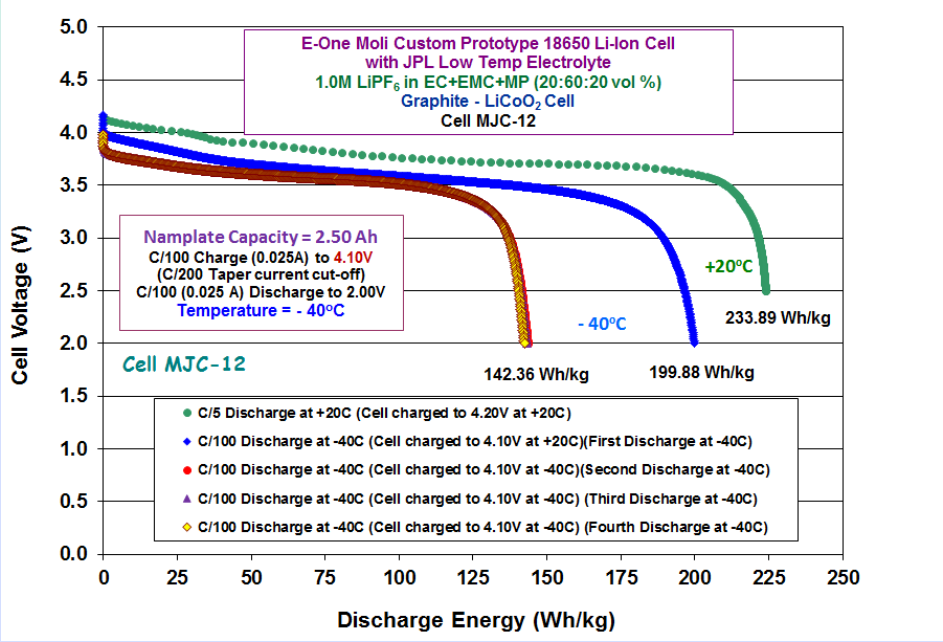
Charge and Discharge at -40°C (C/100 Rates)(Charge Voltage = 4.10V)

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 -40°C using low rate charge.

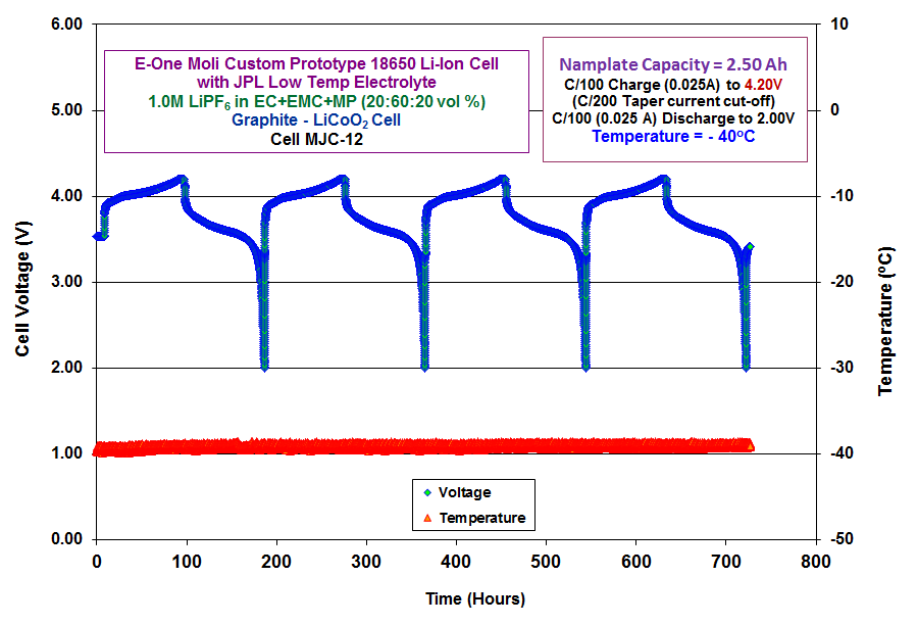
- **The custom Moli ICR-M cells with JPL electrolytes display improved cycling performance at -40°C compared to the baseline. A number of custom JPL electrolytes have been demonstrated to meet programmatic target of > 100 Wh/kg (both charge and discharge at -40°C).**

Performance of E-One Moli Custom Prototype 18650 Cells

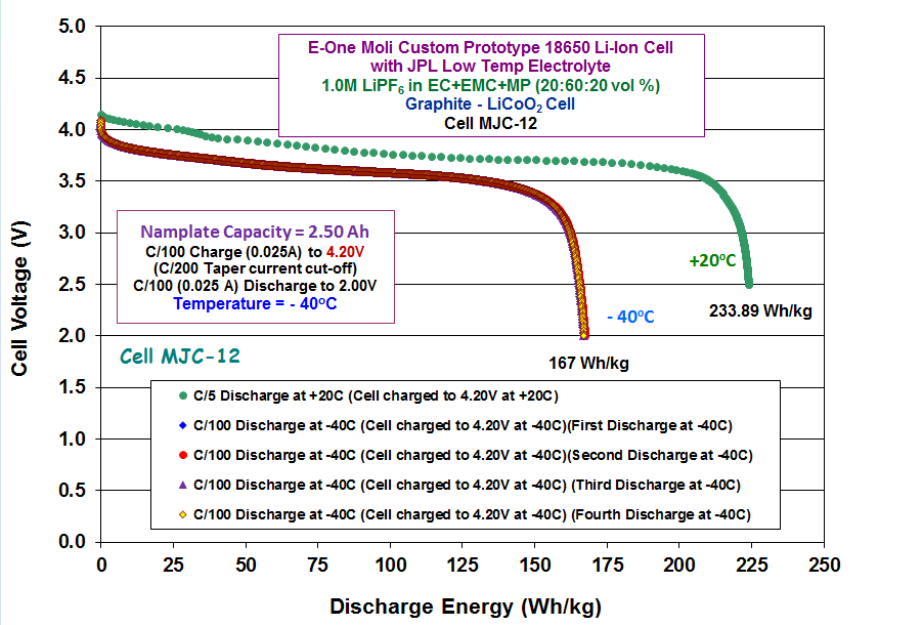
Charge and Discharge at -40°C (C/100 Rates))(Charge Voltage = 4.20V)

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



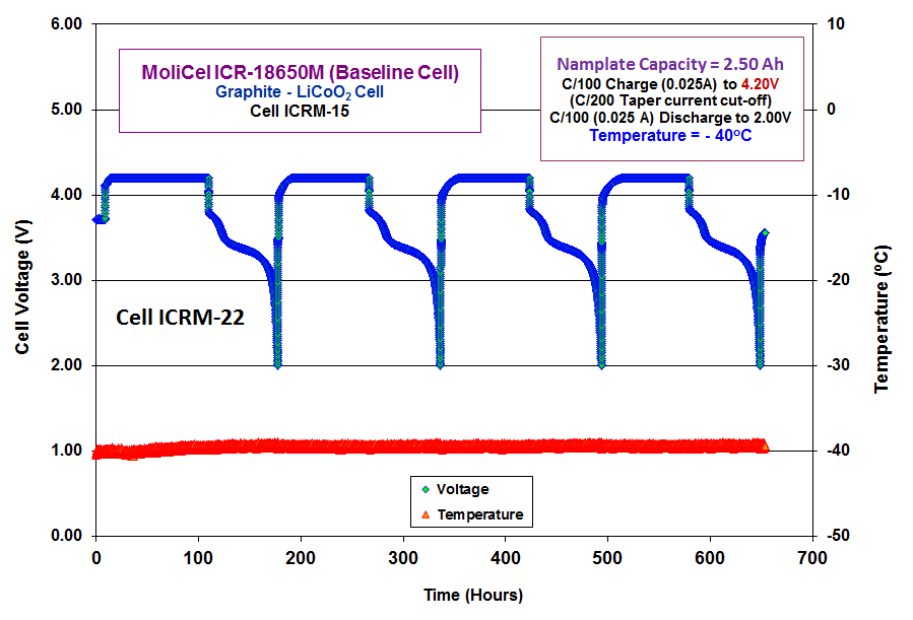
- **Excellent specific energy at -40°C observed using a low rate charge and discharge (C/100) (i.e., 167 Wh/kg).**
- **No lithium plating observed when charging to 4.20V at -40°C using low rate charge.**
- **The custom Moli ICR-M cells with JPL electrolytes display improved cycling performance at -40°C 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 Moli Custom Prototype 18650 Cells

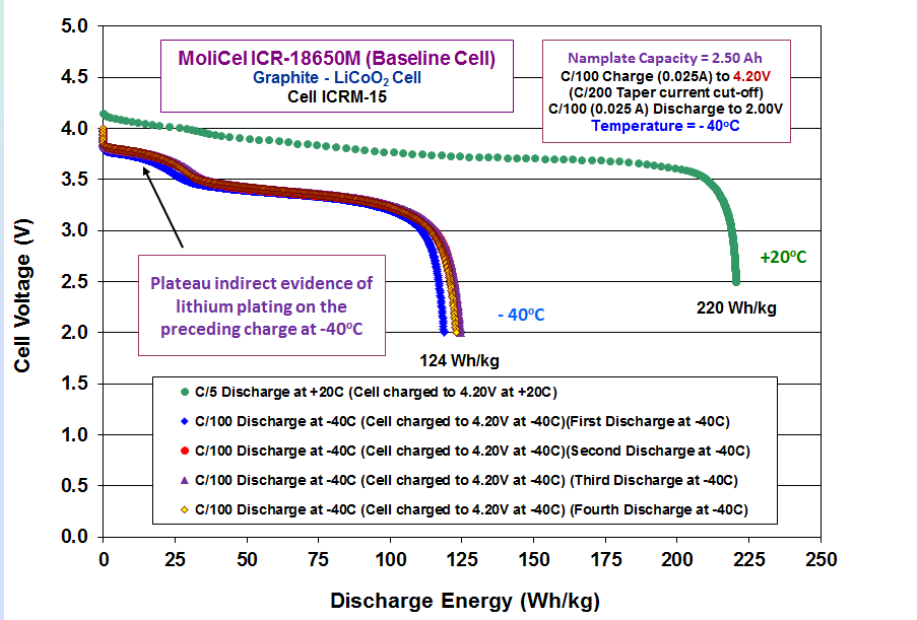
Charge and Discharge at -40°C (C/100 Rates))(Charge Voltage = 4.20V)

Baseline Commercial Off-the-Shelf Cell (COTS)

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



Specific Energy (Wh/kg) at -40°C

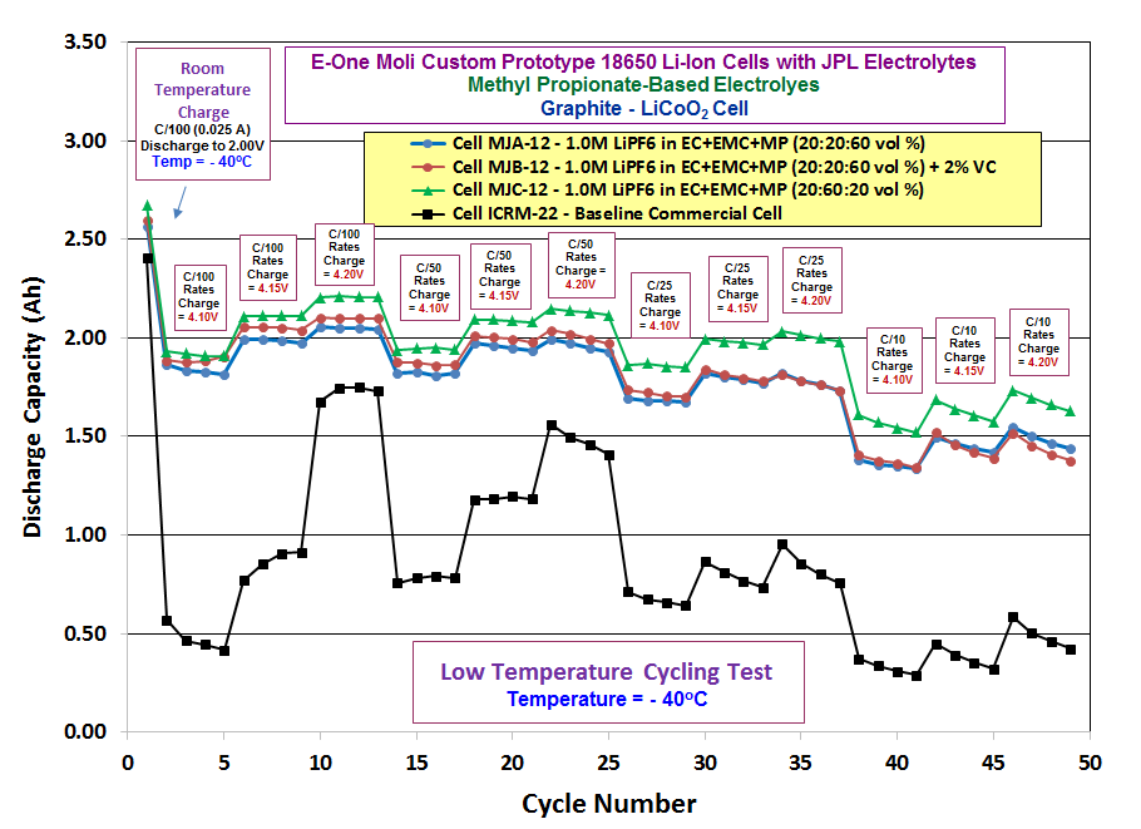


- **Although good specific energy at -40°C is observed with the baseline commercial cell when charging to 4.20V at -40 (C/100) (i.e., > 124Wh/kg), there is evidence of lithium plating which leads to cell degradation.**

- **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 Moli Custom Prototype 18650 Cells

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

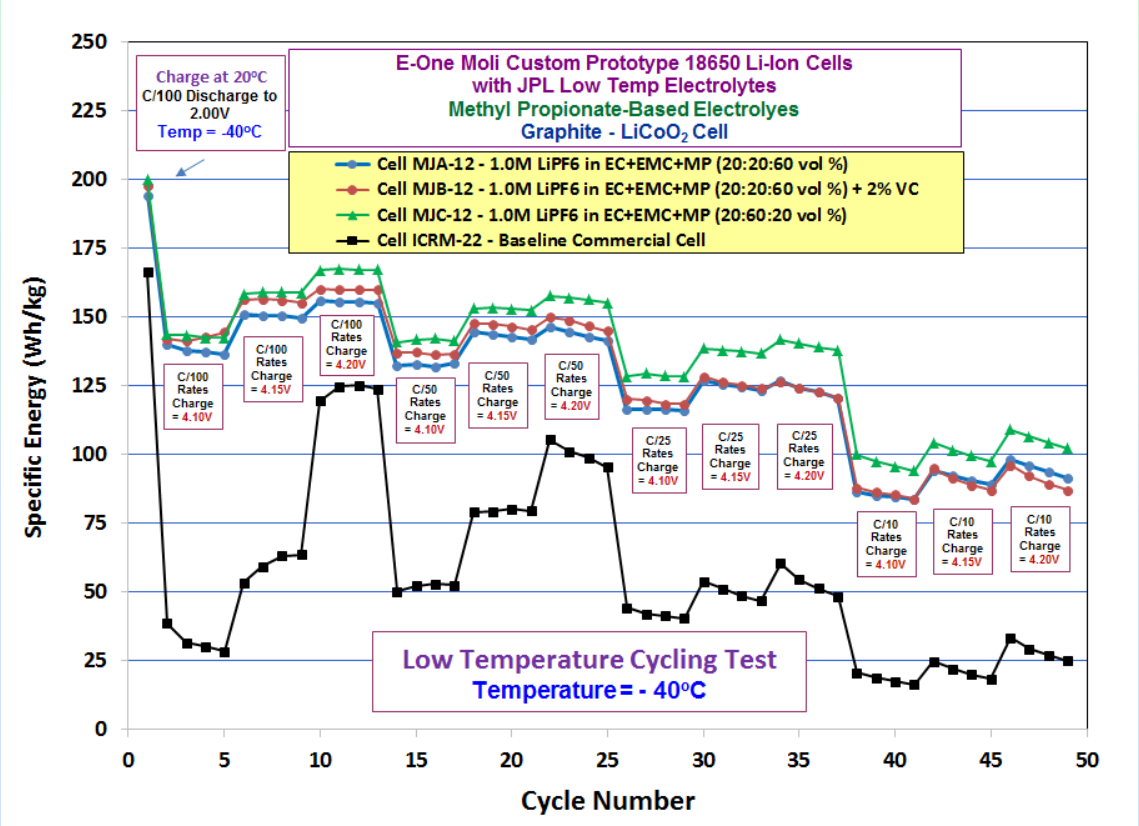


- Excellent discharge capacity at -40°C observed using a low rate charge and discharge (C/100) (i.e., > 2.1 Ah).
- At higher charge rates and charge voltage, there may be some lithium plating occurring, which may account for the higher capacity fade observed.

- **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 Moli Custom Prototype 18650 Cells

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

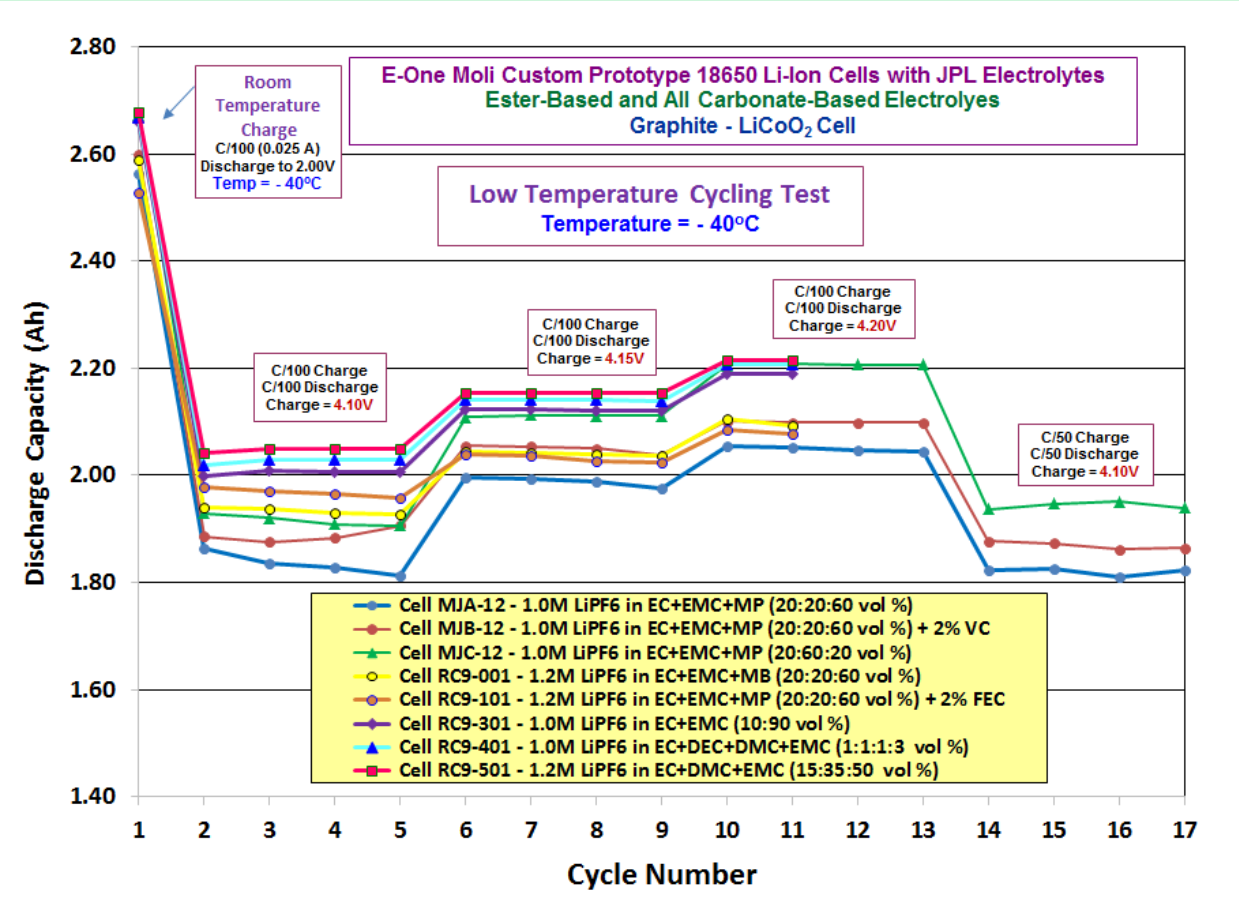


- Excellent specific energy at -40°C observed using a low rate charge and discharge (C/100) (i.e., > 167 Wh/kg).
- At higher charge rates and charge voltage, there may be some lithium plating occurring, which may account for the higher capacity fade observed.

- **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 Moli Custom Prototype 18650 Cells

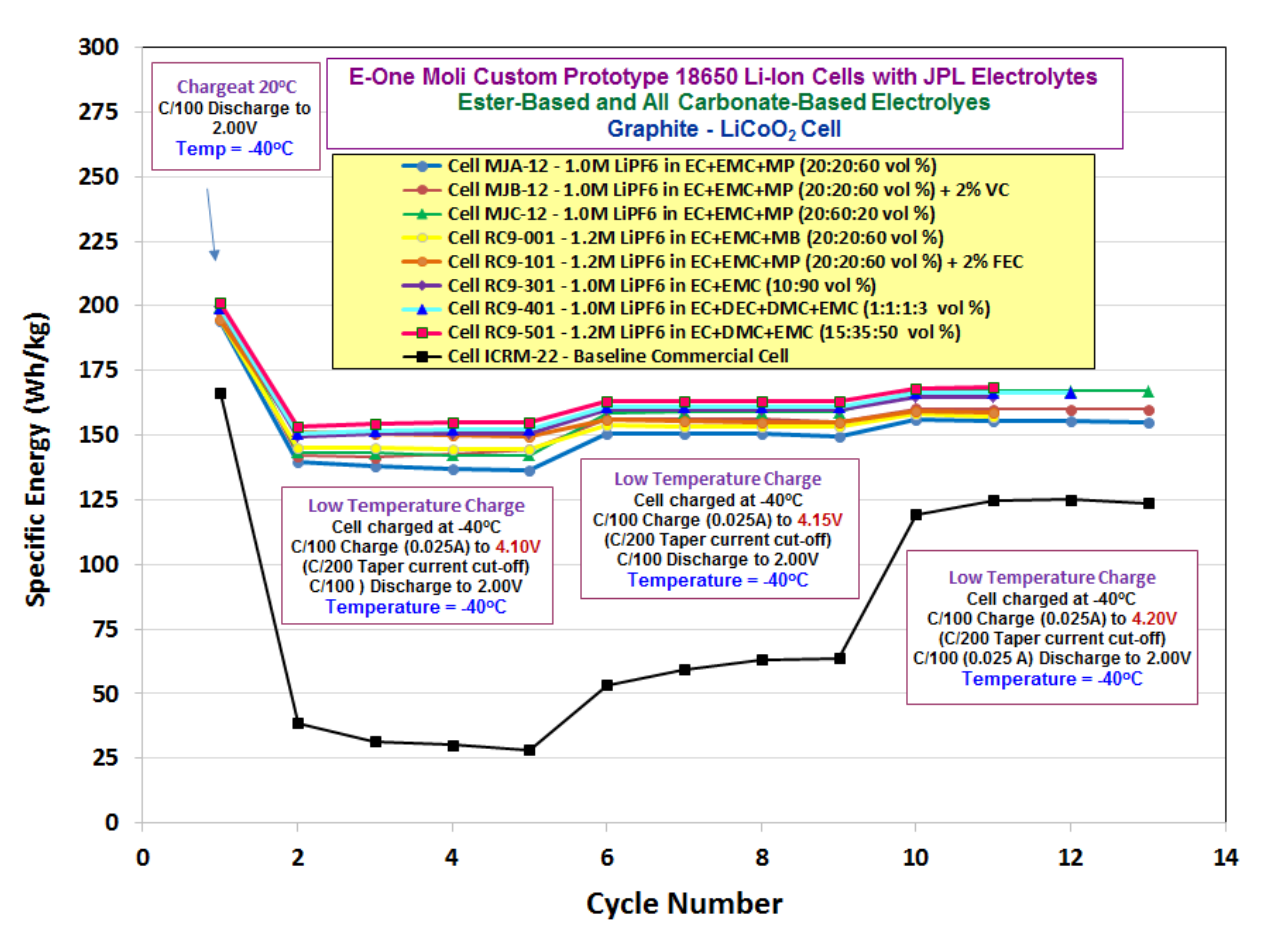
Continuous cycling at -40°C: Effect of charge voltage and charge rate



- Excellent specific energy at -40°C observed using a low rate charge and discharge (C/100) (i.e., > 167 Wh/kg).
- Cells containing all-carbonate-based electrolytes appear to display very stable performance and high specific energy when cycled at low rates.

Performance of E-One Moli Custom Prototype 18650 Cells

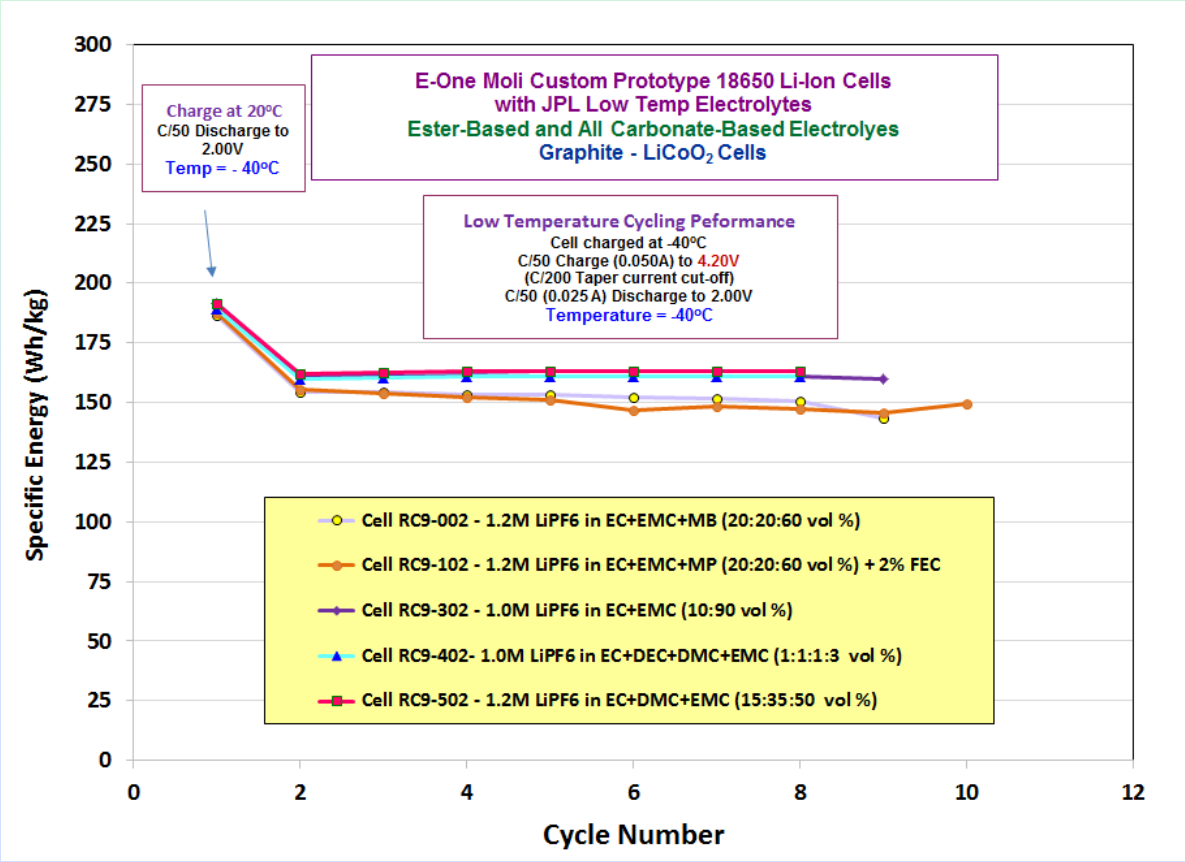
Continuous cycling at -40°C: Effect of charge voltage and charge rate



- Excellent specific energy at -40°C observed using a low rate charge and discharge (C/100) (i.e., > 167 Wh/kg).
- Cells containing all-carbonate-based electrolytes appear to display very stable performance and high specific energy when cycled at low rates.

Performance of E-One Moli Custom Prototype 18650 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/50) (i.e., > 160 Wh/kg).
- Cells charged to 4.20V. Prolonged life may be achieved with lower charge voltages.
- 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).

➢ *Summary and Conclusions*:

- **The custom Moli 18650 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 obvious signs of lithium plating observed when charging to 4.20V at -40°C using low rate charge.**

- **With charging at room temperature, excellent specific energy can be observed at low rate (C/200) at - 40°C with over 200 Wh/kg being delivered.**
  - **Both traditional all carbonate and ester-based electrolytes provide good performance.**
- **At - 60°C, over 150 Wh/kg was delivered with many permutations at low rate.**

➢ *Future Work*:

- **Evaluate the low temperature charge and discharge characteristics of next generation electrolytes in another cell build.**
- **Evaluate the cycling performance under various conditions and at various 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.