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Virtual Research Presentation Conference

The Development of Advanced High Voltage, High Specific Energy and High Power Li-ion Cells with Improved Low Temperature Performance

Principal Investigator: Marshall C. Smart (3463)
Co-Is: Name(s) Charlie Krause (3463), John-Paul Jones (3463)
Program: (Topic R&TD)

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Jet Propulsion Laboratory
California Institute of Technology

Tutorial Introduction

Abstract

Rechargeable batteries with high specific energy, good power capability, and the ability to operate effectively at low temperatures are desired for many NASA applications. The key innovative element of this proposed effort is the design of Li-ion electrolytes tailored to support high voltage and very low temperature battery operation which will be incorporated into small format (18650-size) Li-ion cells. The electrolytes will feature mixtures of organic carbonates, organic esters, lithium conducting salts and electrolyte functional additives intended to improve the properties of the anode and cathode surface films. The developed advanced Li-ion rechargeable batteries will provide high specific energy (175-225 Wh/kg at - 40^{o}C at a C/5 rate), good rate capability (up to C/2 rates), and the capability to operate over a wide temperature range (-60^{o}C to +50^{o}C, including charging at temperatures down to -40^{o}C). The innovation will represent a major technical advance enabling high specific energy and power at low temperature, whereas commercially available chemistries have negligible performance at -40^{o}C.

Problem Description

a) Context:

- Li-ion batteries configured in a small cell format (similar to SMAP or the Europa Clipper) are becoming more attractive compared to large cell formats, due to enhanced safety characteristics and improved specific energy. However, the currently available cells perform very poorly at temperature < -30^{o}C.

b) SOA (Comparison or advancement over current state-of-the-art):

- Current state-of-practice (SOP) Li-ion batteries, such as the large format InSight Chemistry consisting of Graphite/$LiNiCoAlO_2$, can operate from -30^{o}C to +35^{o}C. [Ref. 1,2,3] At - 40^{o}C, the cells can deliver 105 Wh/kg at a C/5 rate when charged at room temperature. In contrast, commercial 18650 cells perform very poorly at temperatures of -30^{o}C and below, providing negligible capacity at -40^{o}C.

Technology	Mission/ Program	Operating Temperature Range (^{o}C)	Cell Specific Energy at +20^{o}C (Wh/kg)	Cell Specific Energy at -20^{o}C (Wh/kg)	Cell Specific Energy at -40^{o}C (Wh/kg) (RT Charge)	Low Temperature Charge Limit
SOP Li-Ion	MSL	-20^{o}C to +30^{o}C	135	100	75	-20^{o}C
SOP Li-Ion	InSight	-30^{o}C to +30^{o}C	145	118	105	-30^{o}C
Proposed High Voltage Lithium-Ion	**RTD Program**	**-60^{o}C to +50^{o}C**	> 250	> 225	> 175	-40^{o}C

c) Relevance to NASA and JPL (Impact on current or future programs)

- Upon successfully meeting the program objectives, a number of future applications that would benefit from the developed technology include: (i) future Mars landers, (ii) future Mars rovers, including the Mars Sample Return mission, and (iii) future planetary aerial vehicles, where high specific energy, high power and wide operating temperature range is desired. Furthermore, the developed technology will have promise for future mission to the Icy Moons of Jupiter and Saturn, which require high specific energy and wide operating temperature range.

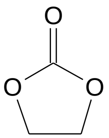
Methodology

a) Technical Approach and Implementation Plan:

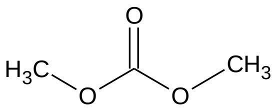
- *The approach of the proposed effort will consist of designing wide operating temperature range lithium-based organic electrolytes that contain electrochemically stable solvents and functional additives, which are targeted at stabilizing the electrode interfaces to achieve enhanced voltage stability and improved kinetics.*
- *Use of solvent mixtures (ternary and quaternary) enables one to optimize the physical properties of the electrolyte such that operation over a wide temperature range is possible.*
- *These advanced electrolytes will be coupled with high voltage cathodes (i.e., $LiNi_xMn_yCo_zO_2$ (NMC), $LiCoPO_4$, $LiCoO_2$) to achieve high specific energy, which will ultimately be incorporated into prototype cells that will be manufactured by a vendor (i.e., E-One Moli Energy and/or Hydro-Quebec).*
- *The research program involves the following tasks: (1) Identification of low viscosity, low melting point solvents compatible with Li-ion chemistry, (2) Identification of candidate Li-ion electrolyte salts and optimization of salt concentrations, (3) Electrochemical characterization in three-electrode experimental cells and (4) Demonstration in prototype lithium-ion cells (manufactured by a vendor).*

b) Innovation, Advancement:

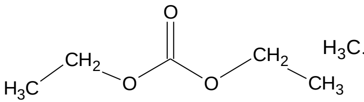
- *Currently, there is very little work in progress external to JPL to develop high voltage, high specific energy lithium-ion batteries that operate at very low temperature (< -20^{o}C).*
- *The developed technology will extend the operational capability of small format 18650-size Li-ion cells, resulting in the delivery of high specific energy down to -60^{o}C.*



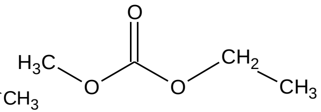
Ethylene carbonate (EC)



Dimethyl carbonate (DMC)

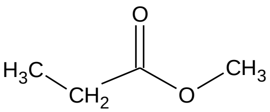


Diethyl carbonate (DEC)

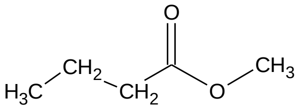


Ethyl methyl carbonate (EMC)

- **Carbonate-based solvents that possess high dielectric constant, high donor number, and good electrode filming characteristics are key electrolyte components.**



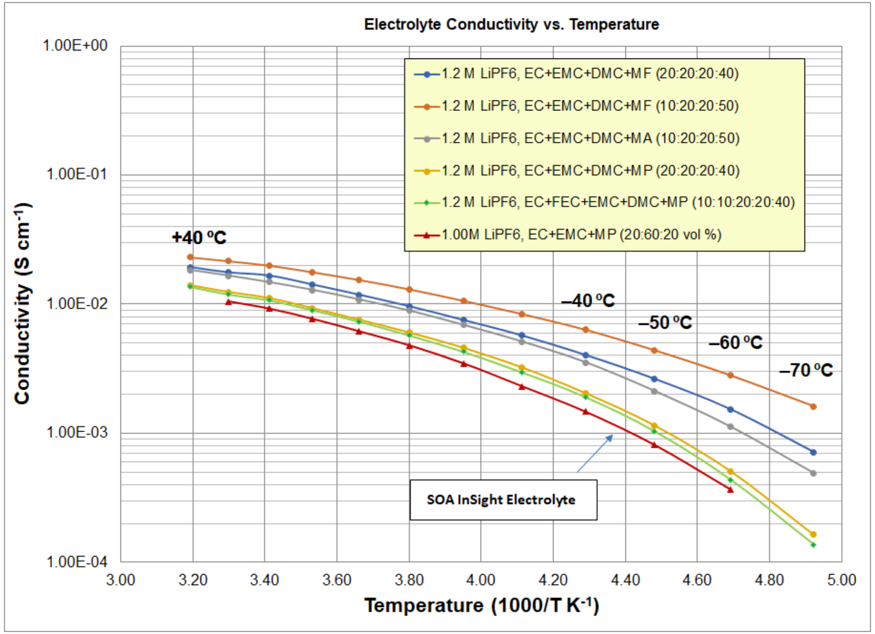
Methyl propionate (MP)



Methyl butyrate (MB)

- **Use of low viscosity, low melting ester-based co-solvents results in improved low temperature ionic conductivity.**
- **$LiPF_6$ electrolyte salt exhibits desirable properties.**
- **Functional additives that serve to improve SEI, such as LiFSI, LiBOB, $LiPO_2F_2$, ethylene sulfite, propane sultone, and $CsPF_6$, will be investigated.**

Results



Ionic Conductivity Measurements

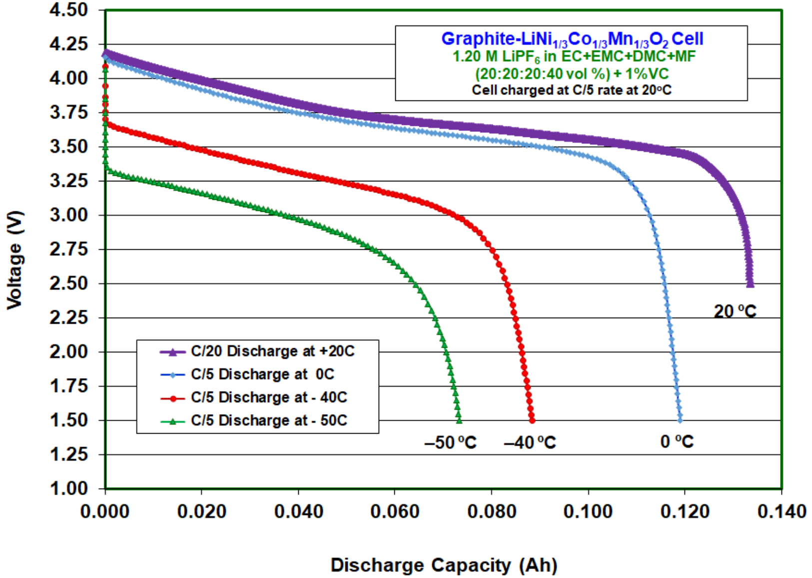
- ***Programmatic Objective:***
  Develop electrolyte formulations that exhibit > 1 mS/cm down to -60°C

- ***Approach:***
  Develop multi-component electrolyte formulations that contain low viscosity, low melting co-solvents.

- *Dramatic improvement in the conductivity is observed with the use of methyl formate (MF) and methyl acetate (MA), especially at very low temperatures.*
- *A number of formulations have been shown to have dramatically higher conductivity than SOA InSight electrolyte.*
  - Demonstrated > 6.4 mS/cm at -40°C (SOA heritage = 1.46 mS/cm)
  - Demonstrated > 2.8 mS/cm at -60°C (SOA heritage = 0.37 mS/cm)

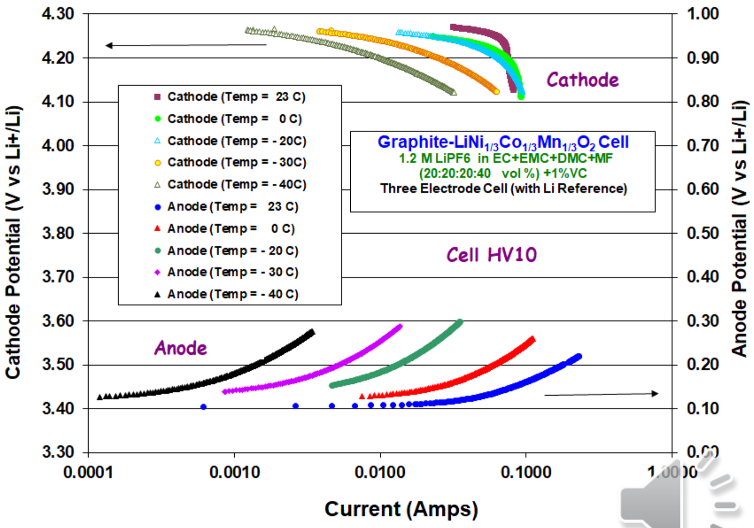
Results: Experimental Three-Electrode Cell Studies

Discharge Characterization of 3-Electrode Cells



- ***Experimental Graphite – $LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$ Li-Ion Cells***
- Good performance was obtained with the methyl formate (MF)-based electrolyte over a wide range of temperatures, with high voltage operation over much of the discharge.

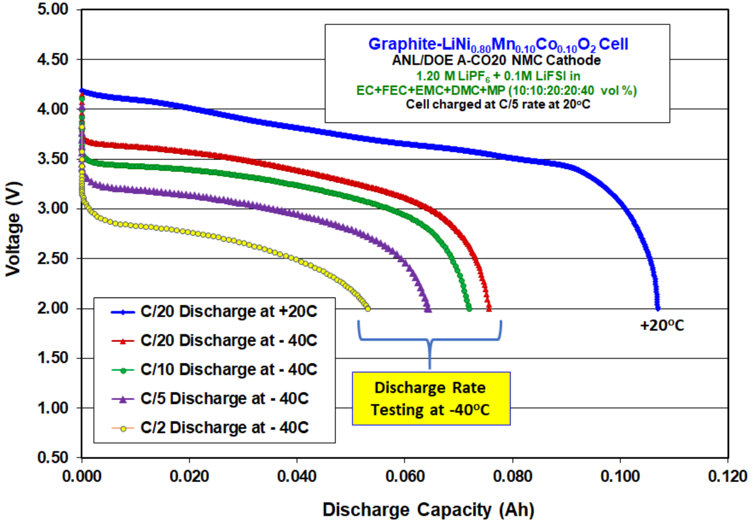
Tafel Polarization Measurements: Measurement of Li^+ Kinetics



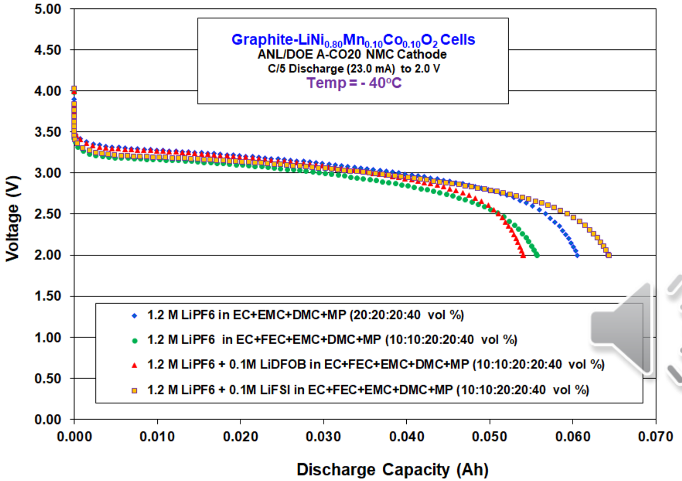
- At warmer temperatures, the cathode is the rate limiting electrode in this system.
- However, at temperatures of -20°C and below, the anode is the rate limiting electrode, suggesting that emphasis should be placed upon improving anode kinetics to improve performance.
- The use of electrolyte additives are being optimized to improve the low temperature charge and discharge performance.

Results: Experimental Three-Electrode Cell Studies

Discharge Characterization of 3-Electrode Cells



Discharge Characterization of 3-Electrode Cells



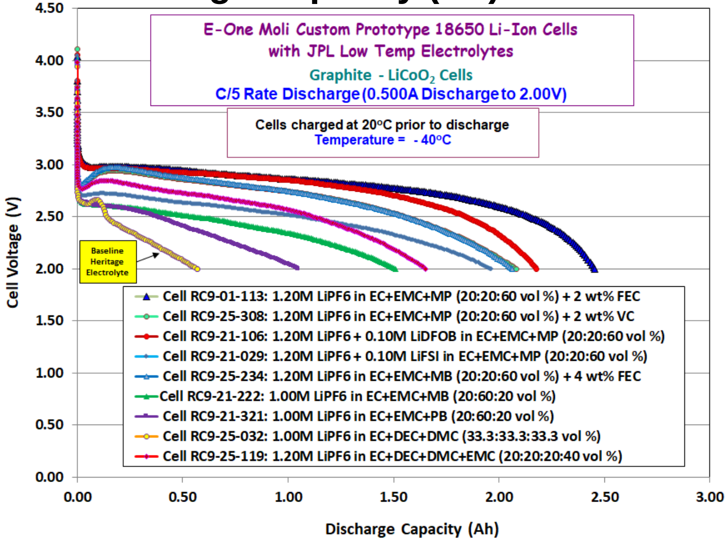
- ***Experimental Graphite – $LiNi_{0.80}Co_{0.10}Mn_{0.10}O_2$ (811) Li-Ion Cells***
- Although the NMC 811 system has higher energy design electrodes (higher loading), good low temperature performance was observed even at higher discharge rates.
- The electrolyte 1.20 M $LiPF_6$ + 0.1M LiFSI in EC+FEC+EMC+DMC+MP (10:10:20:20:40) displayed good performance over a range of temperatures and discharge rates, with over 70% of the room temperature capacity being delivered at -40°C using a C/20 rate

- The electrolyte 1.20 M $LiPF_6$ + 0.1M LiFSI in EC+FEC+EMC+DMC+MP (10:10:20:20:40) displayed the best low temperature performance of the electrolytes investigated in this system
- The presence of the LiFSI appears to beneficially influence the anode polarization during continuous discharge, which is not reflected in the linear or Tafel polarization measurements that are performed while the cell is at high SOC.

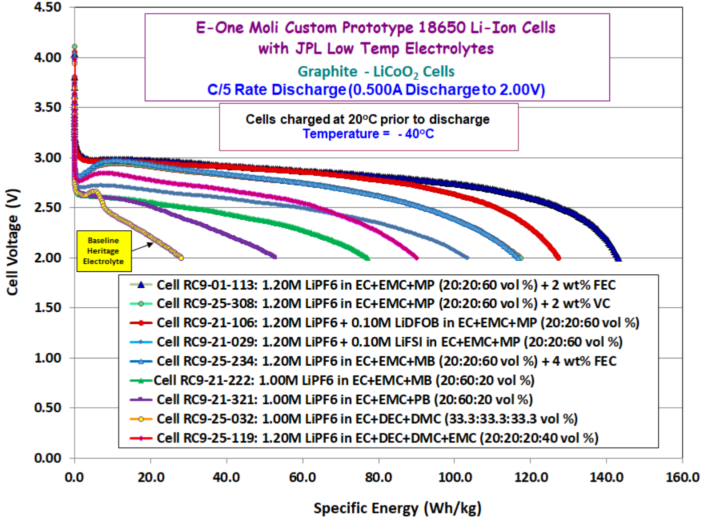
Results: Prototype High Specific Energy 18650 Li-Ion Cell Studies

Prototype Cells Manufactured by E-One Moli with JPL Electrolytes

Discharge Capacity (Ah) at -40ºC



Specific Energy (Wh/kg) at -40ºC

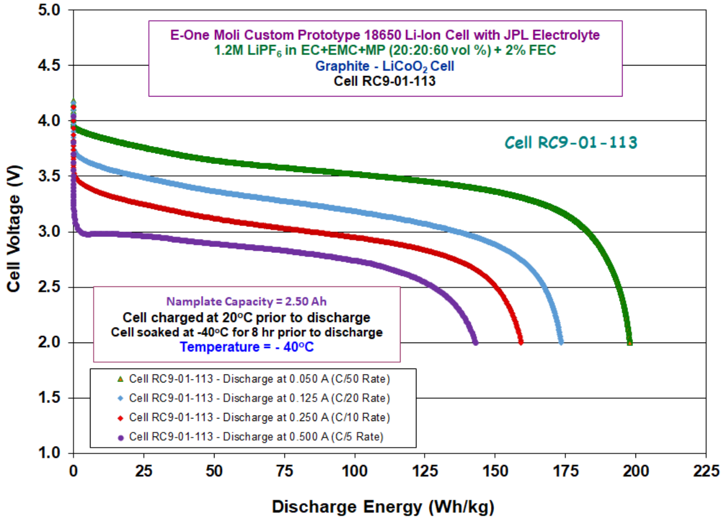


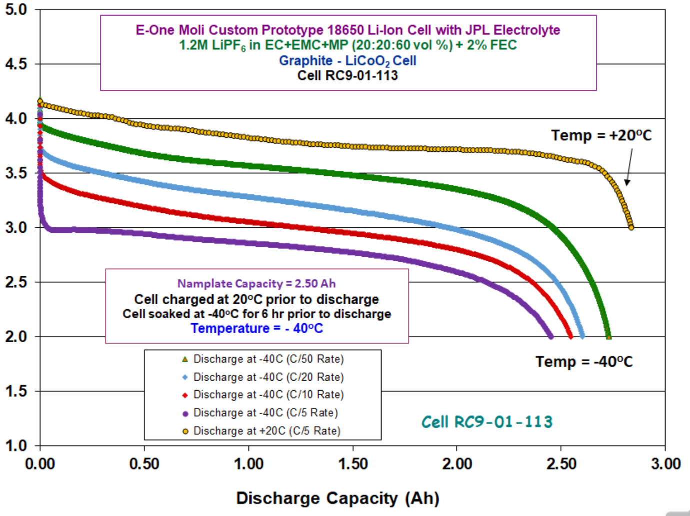
- A number of high specific energy prototype cells containing JPL developed electrolytes were subjected to discharge rate characterization at temperatures of -20ºC to -60ºC.
- The best performing electrolyte at lower temperatures and higher rates was the MP-based solution with FEC.
  - 1.20M $LiPF_6$ in EC+EMC+MP (20:20:60 vol %) + 2 wt% FEC
- ***Results represent a 5-fold improvement in energy over baseline heritage MER/MSL electrolyte.***

Results: Prototype High Specific Energy 18650 Li-Ion Cell Studies

Discharge Characterization of High Specific Energy Cells at -40°C

Prototype Cells Manufactured by E-One Moli with JPL Electrolytes



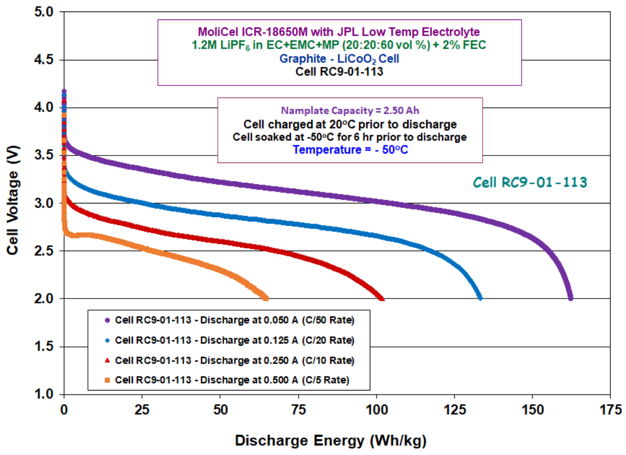


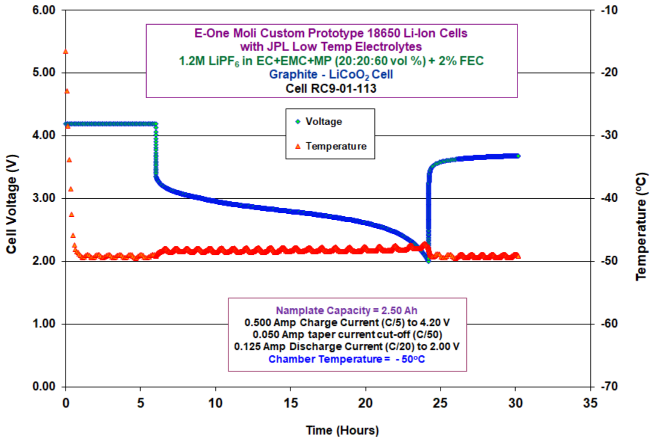
- Excellent performance was obtained with cells containing 1.20M $LiPF_6$ EC+EMC+MP (20:20:60 vol %) + 2% FEC.
- The high methyl propionate content and the addition of FEC to improve the interfacial kinetics results in good rate capability and high specific energy at -40°C.
- **Over 143 Wh/kg demonstrated at a C/5 rate and over 174 Wh/kg at a C/20 rate at -40°C *(Goal = 175 Wh/kg).***
- ***Results represent dramatic improvement over SOA of 105 Wh/kg at C/5 rate (InSight Electrolyte).***

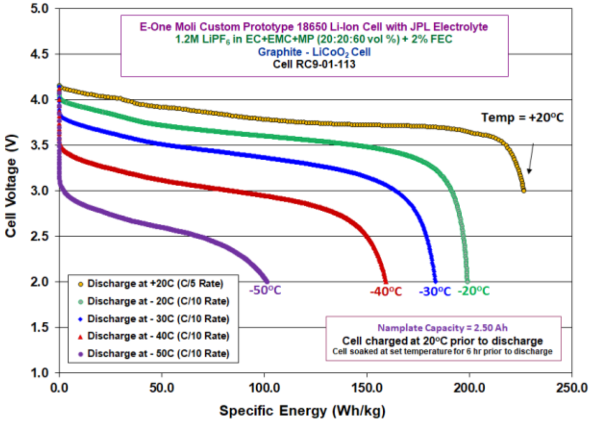
Results: Prototype High Specific Energy 18650 Li-Ion Cell Studies

Discharge Characterization of High Specific Energy Cells at -50°C

Prototype Cells Manufactured by E-One Moli with JPL Electrolytes





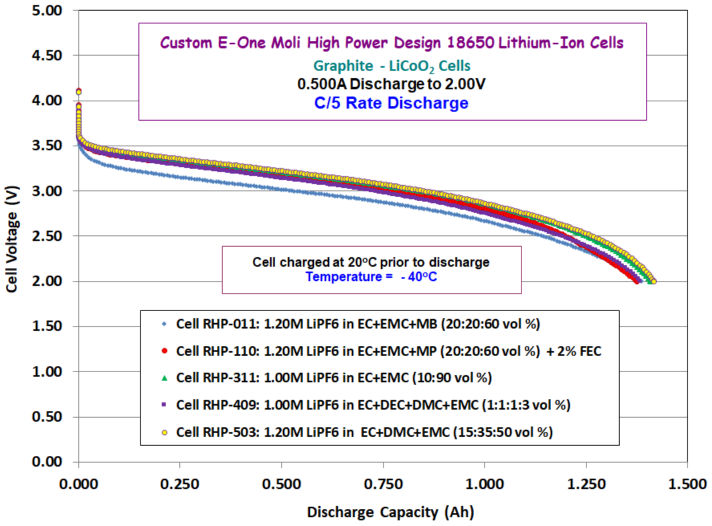


- Excellent performance was obtained with cells containing the electrolyte 1.20M $LiPF_6$ in EC+EMC+MP (20:20:60 vol %) + 2% FEC **at -50°C**.
- **Over 100 Wh/kg demonstrated at a C/10 rate and over 133 Wh/kg at a C/20 rate at -50°C.**

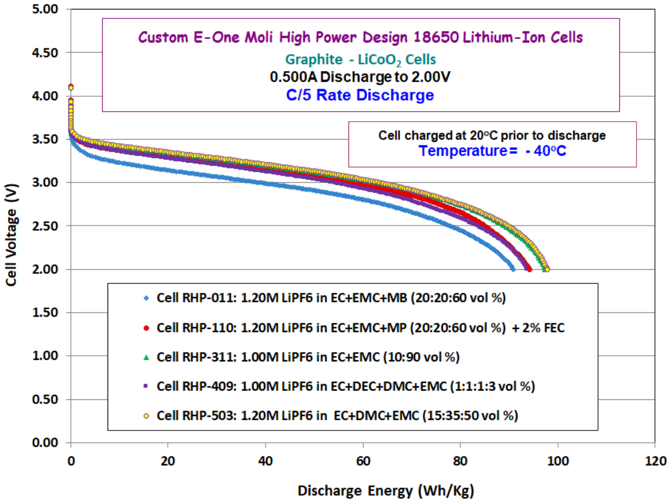
Results: Prototype High Power 18650 Li-Ion Cell Studies

Discharge Characterization of High Power Cells at -40°C

Discharge Capacity at -40°C (Ah)



Specific Energy at -40°C (Wh/kg)



- **High Power 186580-Size prototype cells were also manufactured by E-One Moli with JPL Electrolytes.**
- **Both carbonate-based and ester-based electrolytes provide good low temperature performance.**
- **Over 97 Wh/kg demonstrated at a C/5 rate and over 117 Wh/kg at a C/20 rate at -40°C.**
- **Higher operating voltage with high power cells compared to high energy design.**
- **High power cell designs are attractive for future planetary aerial vehicles.**

Future Work

a) Continue to develop next generation, multi-component wide operating temperature range electrolytes.

b) Continue to evaluate high voltage, high specific energy cathodes obtained from the Dept. of Energy (DoE) CAMP facility in experimental 3-electrode cells.

- Targray $LiNi_{0.80}Mn_{0.10}Co_{0.10}O_2$ (NMC 811)(~ 185 mAh/g)
- Targray $LiNi_{0.80}Mn_{0.10}Co_{0.10}O_2$ (NMC 622) (~ 179 mAh/g)
- Toda $LiNi_{0.50}Mn_{0.30}Co_{0.20}O_2$ (NMC 532) (~ 157 mAh/g)

c) Evaluate high voltage doped-$LiCoPO_4$ (LCP) electrodes from ARL/Hydro-Quebec.

- LCP electrodes display a desirable high voltage discharge profile.
- LCP systems have not been studied in conjunction with advanced low temperature electrolytes.

d) Procure additional high specific energy E-One Moli 18650-cells with next generation JPL wide operating temperature electrolytes. The ICRM cells are attractive for their high specific energy.

- Attempt to also procure high power (30A capability), high specific energy E-One Moli P26A cell design.

e) Procure Graphite/NCA-based18650-size cells from Quallion/Enersys.

- Cell specific energy is lower, but the NCA-based system is very robust over a wide temperature range.
- Cells display excellent rate capability at low temperatures.
- Cells have been optimized for long life aerospace applications.

Publications and References

- Publications:
  - Marshall C. Smart, F. C. Krause, J. -P. Jones, B. V. Ratnakumar and Mark Shoesmith, “Ester and Carbonate-Based Low Temperature Electrolytes in High Specific Energy and High Power 18650 Li-Ion Cells for Future NASA Missions,” ECS PRiME 2020 Joint International Meeting, (Virtual Meeting), Oct. 8, 2020.

- References:

1. M. C. Smart, B. V. Ratnakumar, R. C. Ewell, S. Surampudi, F. Puglia, and R. Gitzendanner, “The Use of Lithium-Ion Batteries for JPL’s Mars Missions”, *Electrochimica Acta,* **268**, 27-40 (2018).
2. M. C. Smart, B. V. Ratnakumar, K. B. Chin, and L. D. Whitcanack, “Lithium-Ion Electrolytes Containing Ester Co-solvents for Improved Low Temperature Performance”, *J. Electrochem. Soc.*, **157 (12)**, A1361-A1374 (2010).
3. M. C. Smart, and R. V. Bugga, “Lithium ion electrolytes and lithium ion cells with good low temperature performance”, United States Patent 8,920,981. (December 20, 2014). (InSight Electrolyte Patent)