Low Temperature Rechargeable Li-ion Batteries for Potential Mars Sample Return and Small Robotic Missions

Marshall C. Smart, Frederick C. Krause, John–Paul Jones, Christine L. Fuller, Joel A. Schwartz,
and Ratnakumar V. Bugga

Jet Propulsion Laboratory, California Institute of Technology
4800 Oak Grove Drive, Pasadena, CA 91109-8099

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Outline

- ***Background***
- ***Objectives*** **and** ***Approach***
- ***JPL Low Temperature Electrolyte Development***
- ***Development and Demonstration of Heritage Carbonate-Based Electrolyte***
    - ***MSP'01Mission, MER Mission, MSL Mission***
- ***Development and Demonstration of Ester-Containing Electrolytes***
    - ***InSight Mission***
- ***Development of Electrolytes for Future Mars Robotic Missions***
    - ***Quallion Prototype BTE Cells***
    - ***PUFFER Application***
    - ***Mars Orbiting Sample (OS) Canister Beacon Application***
- ***Conclusions***

Development of Low Temperature Lithium Batteries

Vision and Goal

Goal: To develop rechargeable lithium-based cells for future NASA applications which are capable of operation over a large temperature range, especially at low temperatures (-60° to +60°C).

Technology Development:

- Improved Low Temperature Li-Ion Electrolyte Technology
- Gen I Electrolyte Incorporated into MSP01 and MER Batteries

- Further optimization of carbonate-based electrolytes
- Demonstrated improved capabilities of Gen II and Gen III electrolytes

- Development of improved electrolytes with aggressive solvents and salts and modified cell design.
- Will result in improved temperature range of operation

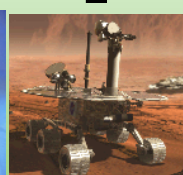
Capabilities:

Operation –20 to +40°C	Operation – 40 to +40°C	Operation –60 to +60°C

2000 2002 2004 2006 2008 2010 2012 2014 2016 2018 2020 2022

Infusions:

2001 MSP'01 Lander Battery (Phoenix Battery)

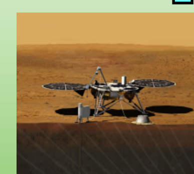


2003 MER Rover Battery

2007 Mars Phoenix Mission

2009 Mars Science Laboratory

2011 Juno Mission



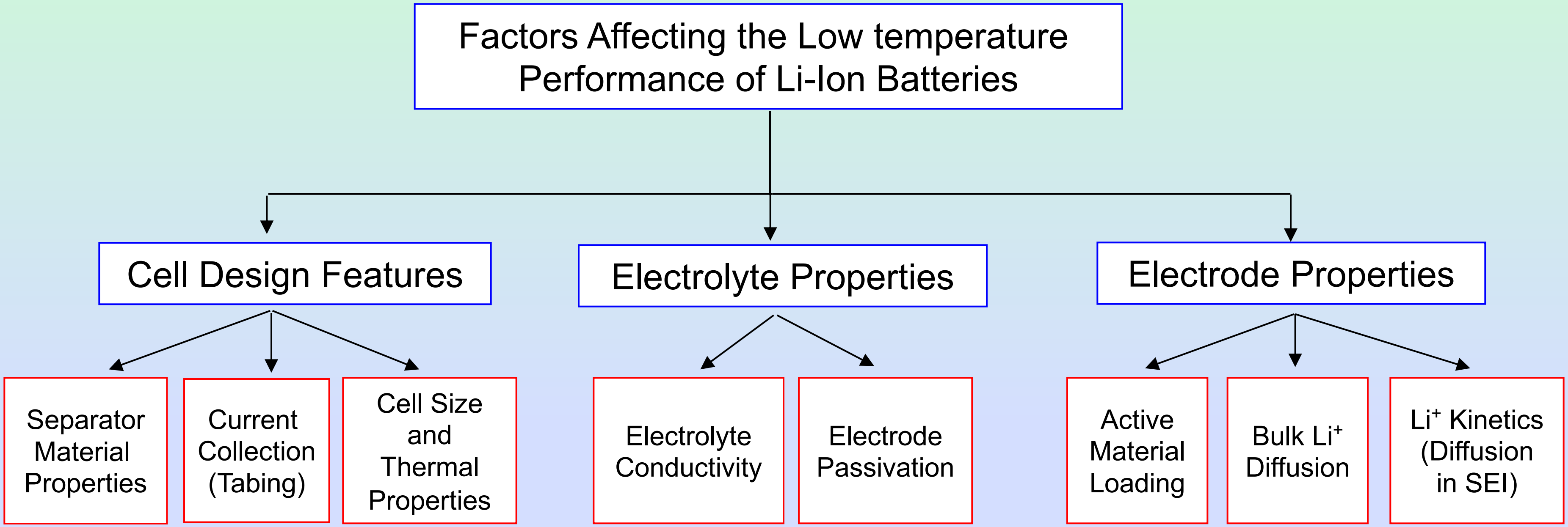
2018 InSight Lander

Mars 2020 Mission

Future Ocean Worlds Missions

Low Temperature Lithium Ion Electrolytes

Electrolyte Development: Approach/Background



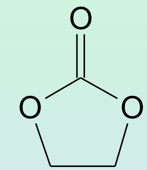
- *Of these factors, the electrolyte properties have the most dramatic impact on low temperature performance (i,e., if the the electrolyte is frozen the cell/battery will not operate).*
- *Sufficient electrolyte conductivity at low temperature is not sufficient to ensure efficient operation due to potential reactivity leading to poor kinetics and/or inadequate life aspects.*
- *To enable very low temperature operation (< - 40°C), high diffusivity electrode materials must be identified coupled with improved cell design.*

Low Temperature Lithium Ion Electrolytes
Electrolyte Development: Approach/Background

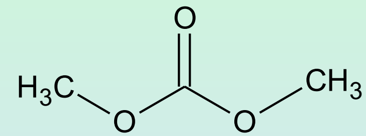
• ***Low Temperature Electrolyte Selection Criteria***

- High conductivity over a wide range of temperatures
  - 1 mS cm-1 from –60 to 40^{o}C
- Wide liquid range (low melting point)
  - -60 to 75^{o}C
- Good electrochemical stability
  - Stability over wide voltage window (0 to 4.5V)
  - Minimal oxidative degradation of solvents/salts
- Good chemical stability
- Good compatibility with chosen electrode couple
  - Formation of solid electrolyte interface “SEI” critical
  - SEI film properties prevents further electrolyte reaction
  - SEI impacts lithium intercalation/de-intercalation kinetics
  - Electrolyte additives can assist in SEI formation
- Good thermal stability
- Good low temperature performance throughout life of cell
  - Good resilience to high temperature exposure
  - Minimal impedance build-up with cycling

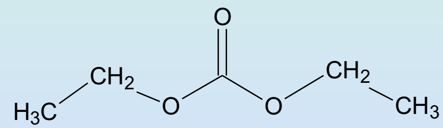
Use of solvent mixtures (ternary and quaternary) enables one to optimize the physical properties of the electrolyte such that operation over a wide temperature range is possible.



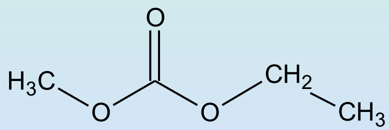
Ethylene carbonate (EC)



Dimethyl carbonate (DMC)

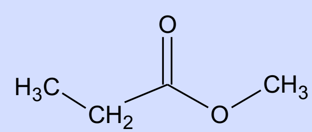


Diethyl carbonate (DEC)

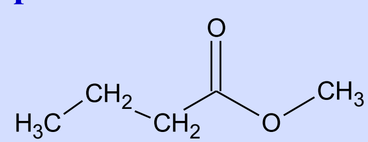


Ethyl methyl carbonate (EMC)

- **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.**

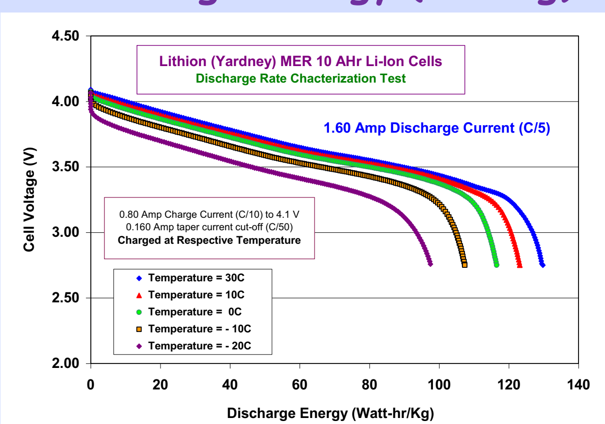
2003 Mars Exploration Rover- Rover Batteries

- **Lithium-ion technology was used for '03 MER Rovers**
- **Heritage chemistry, including electrolyte, adopted from MSP'01**
- **Opportunity has been operational since landing on Mars on 1/25/2004**
- **Battery fabricated by Yardney Technical Products, Inc.**

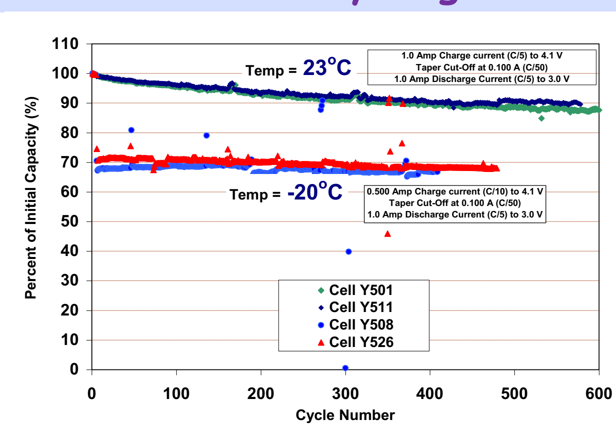
Rover Battery Requirements

- Voltage : 32-24 V
- Capacity: 16 Ah (BOL) at RT and 10 Ah at –20°C (BOL)
- Load : C/2 max at RT; Typical C/5
- Temperature : Charge at 0-25°C and discharge >-20°C
- Light weight and compact
- Long cycle life of over 300 cycles
- Long storage life of over 2 years

Discharge Energy (Wh/kg)



100% DOD Cycling Life



- *Aerospace quality large capacity Li-ion cells with good low temperature performance were not available in the mid-1990's.*
- *In collaboration with Yardney, JPL, NASA, and AFRL formed a partnership and initiated the early technology maturation to enable MSP'01 lander.*

Battery Contains Heritage JPL Low Temperature Electrolyte:

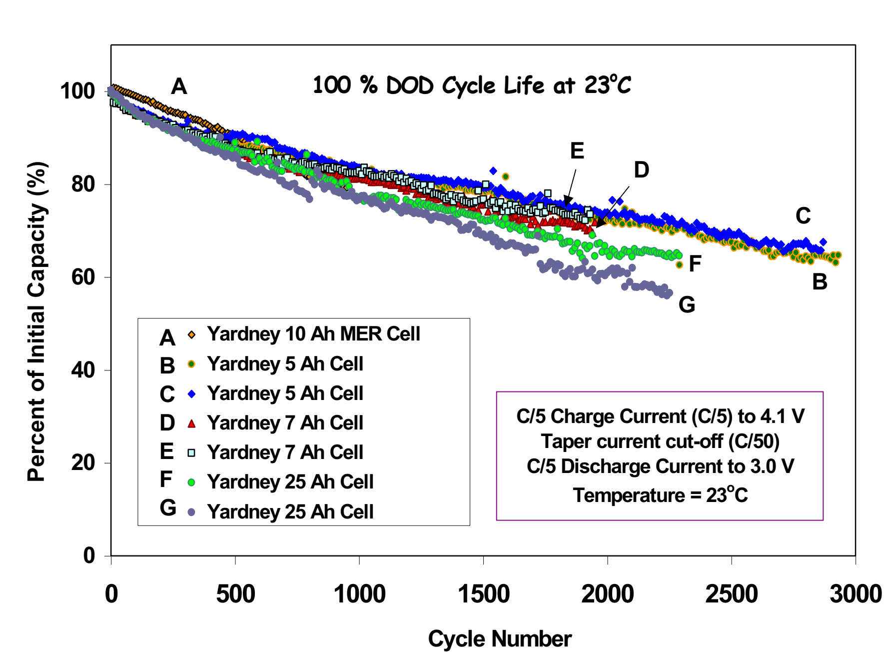
1.0M $LiPF_6$ EC+DMC+DEC (1:1:1) (Range of operation –20 to +40°C)

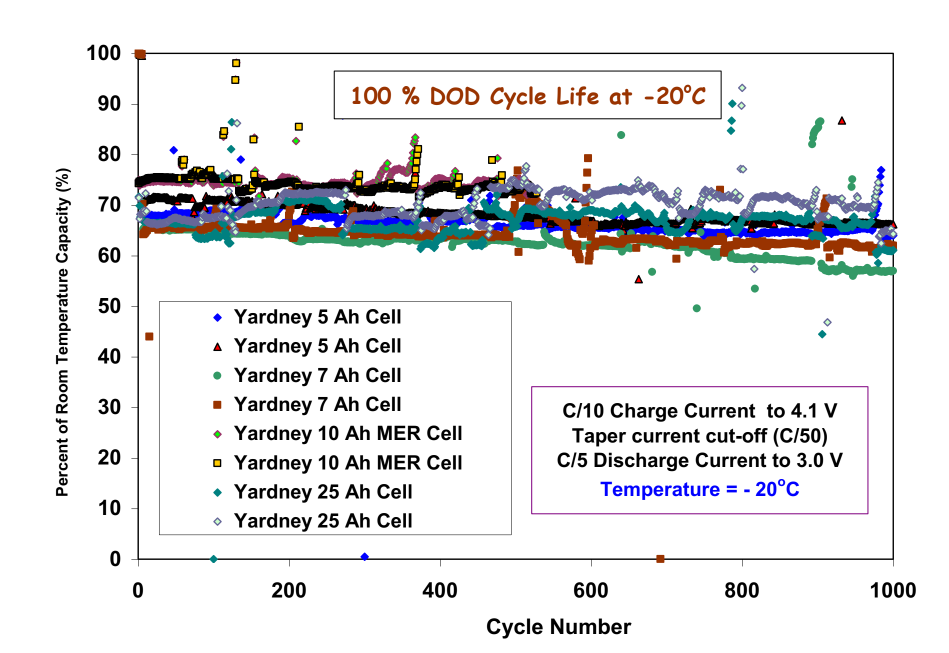
ELECTROCHEMICAL TECHNOLOGIES GROUP

Yardney Lithium-Ion Cells for Aerospace Applications

100% DOD Cycle Life Performance

Temp = 23°C **Temp = - 20°C**





- Comparable cycle life performance obtained with a range of cell sizes fabricated by Lithion, Inc. (from 5 to 25 Ahr).
- Stable performance displayed when continuous cycling is performed at – 20°C (lower capacity fade rate compared to room temperature).

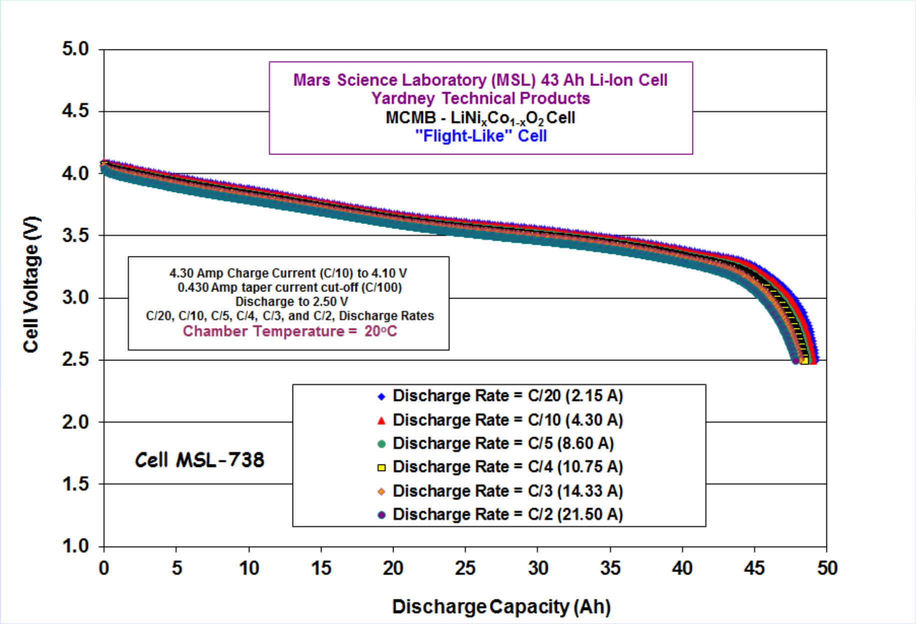
Cells contain 1.0M $LiPF_6$ EC+DMC+DEC (1:1:1) (Range of operation –20 to +40°C)

M. C. Smart, B. V. Ratnakumar, L. D. Whitcanack, F. J. Puglia, S. Santee, and R. Gitzendanner, "Life Verification of Large Capacity Yardney Li-ion Cells and Batteries in Support of NASA Missions", *Int. J. Energy Res*, **34**,116-134 (2010).

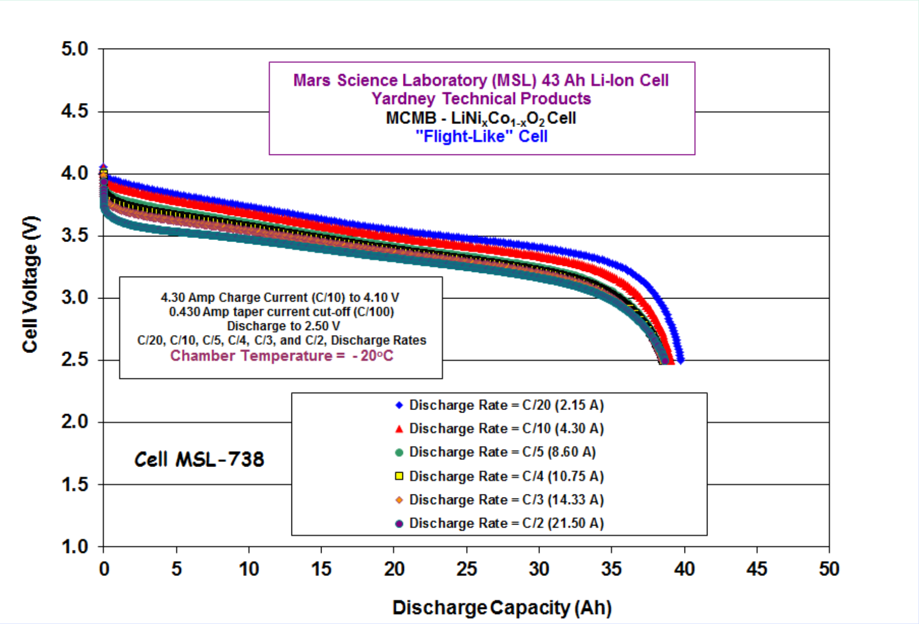
Yardney Li-ion MSL 43 Ah Li-Ion Performance Testing

Discharge Rate Characterization Testing at 20°C and -20°C

Temperature = +20°C

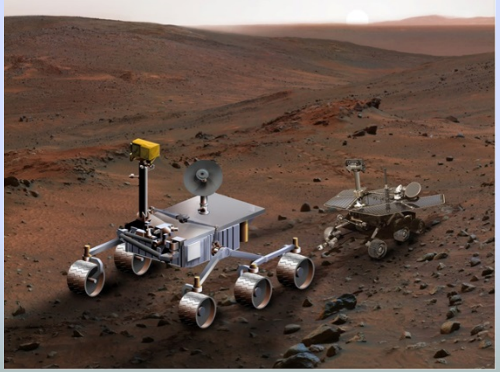


Temperature = - 20°C



- ***MER heritage chemistry was incorporated into larger 43 Ah cells that has been utilized on Mars Science Laboratory (MSL) Curiosity Rover***
- ***Operating Temperature Range: -20° to +30°C***
- ***Battery Contains Heritage JPL Low Temperature Electrolyte:***

1.0M $LiPF_6$ EC+DMC+DEC (1:1:1) (Range of operation –20 to +40°C)

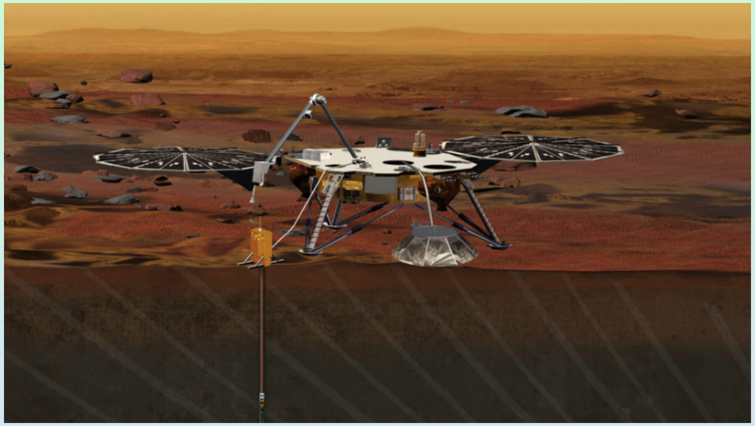


NASA's Mars InSight Lander

- **InSight (Interior Exploration using Seismic Investigations, Geodesy and Heat Transport) is a NASA Discovery Program mission that will place a single geophysical lander on Mars to study its deep interior.**
- **Mission will consist of a spacecraft built by Lockheed Martin Space Systems Company based on a design that was successfully used for NASA's Phoenix Mars lander mission**

- Science Goals:.
  - InSight is a terrestrial planet explorer that will address the processes that shaped the rocky planets of the inner solar system (including Earth) more than four billion years ago
  - InSight will probe beneath the surface of Mars, detecting the fingerprints of the processes of terrestrial planet formation

- **In January 2016, the March 2016 launch date of InSight mission was suspended to allow the repair of a leak in a section of the prime instrument in the science payload.**
- **The InSight mission was launched successfully on May 5 and is scheduled to land on November 26, 2018.**



Battery Details

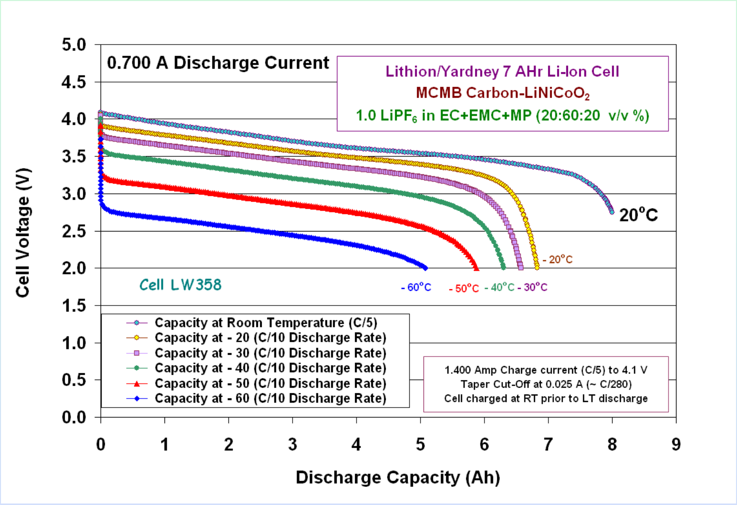
- Two 8-cell batteries (connected in parallel)
- Manufactured by Eagle-Picher Technologies / Yardney Division
- 24-32.8 V (Phoenix Battery Design)
- Qualification Temperature range: - 40°C to +50°C.
- **Operating Temperature Range: -30° to +35°C**
- **Required Life: ~ 4 years**
- **Surface Life: 709 Sols of operation.**
- **Fabricated by Yardney Technical Products, Inc**

Battery Contins Next Generation JPL Low Temperature Electrolyte:

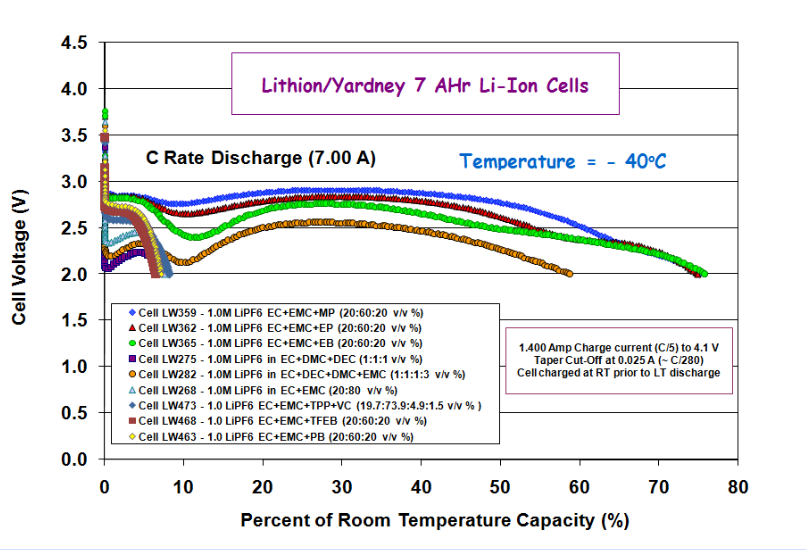
1.0M $LiPF_6$ EC+EMC+MP (20:60:20 v/v %) (Range of operation –30 to +35°C)

Development of Advanced Low Temperature Electrolytes

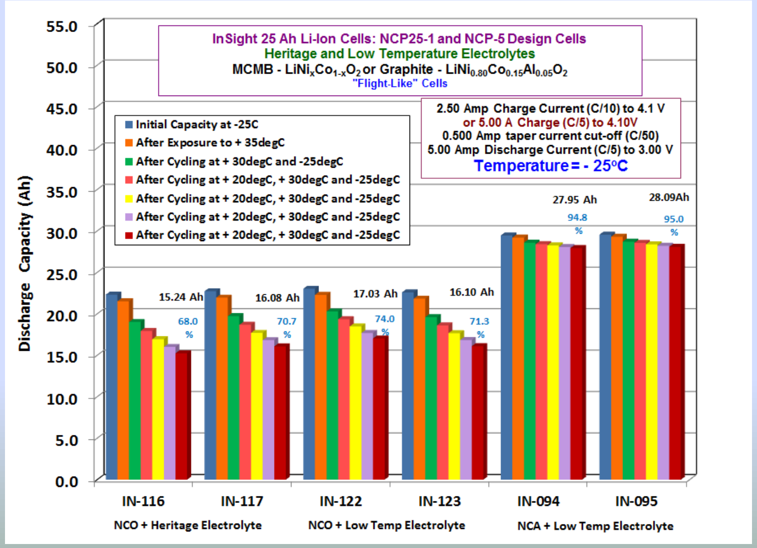
Demonstration of Ester-Based Electrolytes in Yardney Li-Ion Cells



Performance at -40°C (C Rate)



Performance at InSight Flight-like Cells at -25°C (C/5 Rate)



An electrolyte formulation containing methyl propionate, 1.0M $LiPF_6$ EC+EMC+MP (20:60:20 v/v %) was demonstrated to provide improved low temperature performance over baseline all carbonate-based electrolytes (including the heritage blend), while still providing reasonable high temperature resilience.

- M.C. Smart, and B.V. Ratnakumar, L.D. Whitcanack, K.A. Smith, S. Santee, R. Gitzendanner, V. Yevoli, *ECS Trans.* **11**, (29) 99 (2008).
- 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).
- M. C. Smart, S. F. Dawson, R. B. Shaw, L. D. Whitcanack, A. Buonanno, C. Deroy, and R. Gitzendanner, NASA Aerospace Battery Workshop, Huntsville, Alabama, November 18-20, 2014.

Technology Development Targets for Future Robotic Missions to Mars

➢ Technology need for future small robotic mission to Mars

- The performance of standard/commercial cells in low temperature environments are limited to operation at temperatures above -30ºC. Commercial cells display the following:
  - Poor rate capability at low temperatures
  - Reduced charge acceptance at low temperature
  - Concerns with low temperature charging (i.e., lithium plating on the anode)
- Small robotic missions will especially benefit from improved low temperature energy storage due to limited thermal management
  - Trade-off for designing cells with inherently low temperature performance vs. expending energy to heat the battery or use RTG waste heat

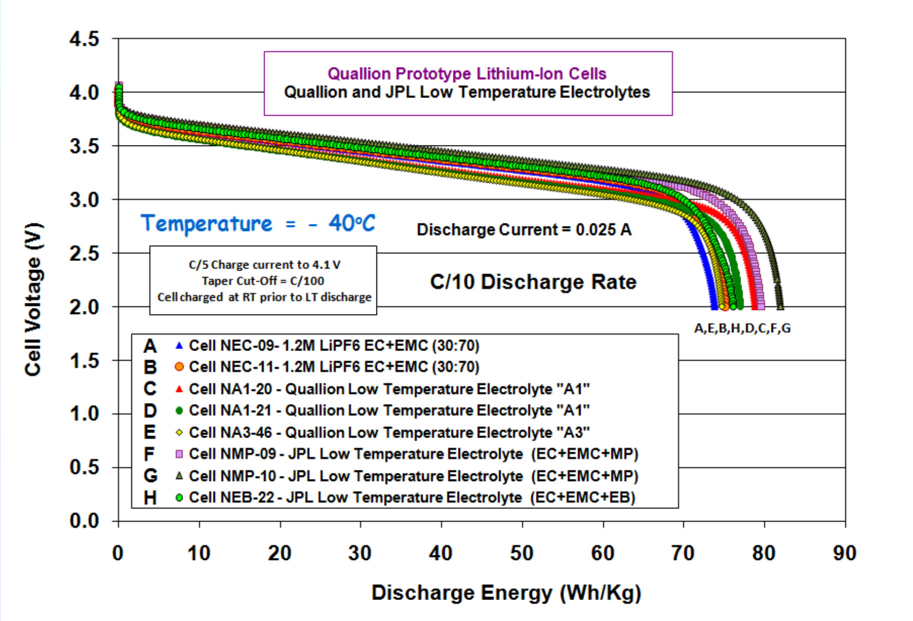
➢ Approach to enabling small robotic missions

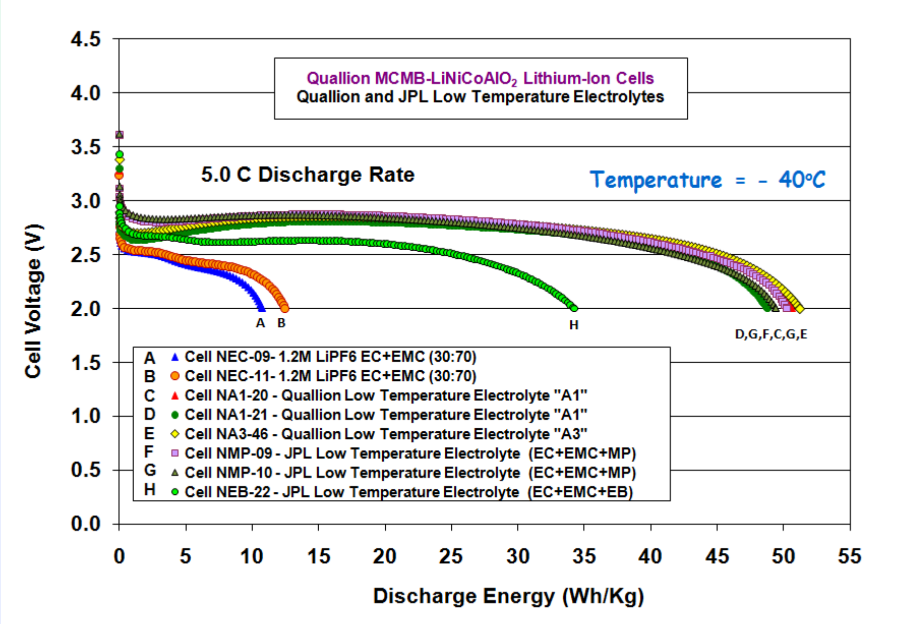
- The development of advanced rechargeable Li-ion cell with improved low temperature operational capability is desired (i.e., operation down to -60^{o}C).
- Survivability to very low temperatures may be critical (i.e., temperatures below -85^{o}C).
- Examples of Potential missions that would benefit from low temperature technology
  - **Pop Up Flat Folding Explorer Robot (PUFFER)**
  - **Mars Orbiting Sample (OS) Canister Beacon**

Quallion Prototype Li-Ion Cells

Wide Operating Temperature Electrolytes

Discharge Characterization at Various Temperatures





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

Quallion developed electrolytes also display impressive improvements at low temperatures.

- ***A JPL ester-containing wide operating temperature electrolyte developed under this DOE program has been infused into a JPL/CSUN Cubesat mission. Further developed formulations have been considered for use on future small robotic missions.***

M. C. Smart, Michael R. Tomcsi, L. D. Whitcanack, Ratnakumar V. Bugga, Mikito Nagata, and Vince Visco, "The Use of MP-Based Electrolytes with Additives to Improve the Low Temperature Performance of $LiNiCoAlO_2$-Based Li-Ion Cells", 224st Meeting of the Electrochemical Society, San Francisco, CA , October 30, 2013.

Objective:

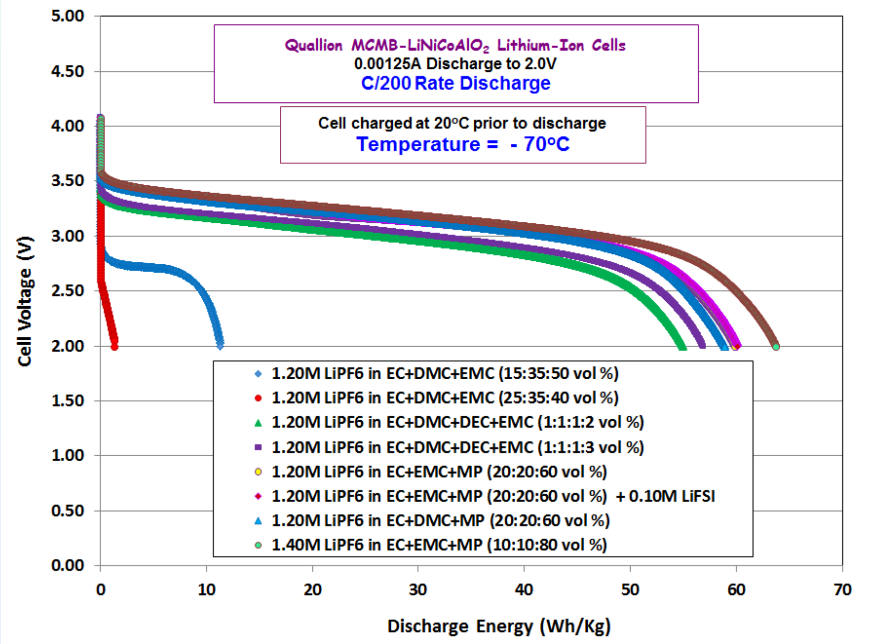
- Assess viability of using Quallion BTE Li-Ion cells for the Pop Up Flat Folding Explorer Robot (PUFFER) program.
- Evaluate the performance capability of Quallion BTE Li-Ion cells to operate at very low temperatures (-40^{o}C to -70^{o}C)
- Determine the capabilities of the Quallion BTE Li-ion cells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

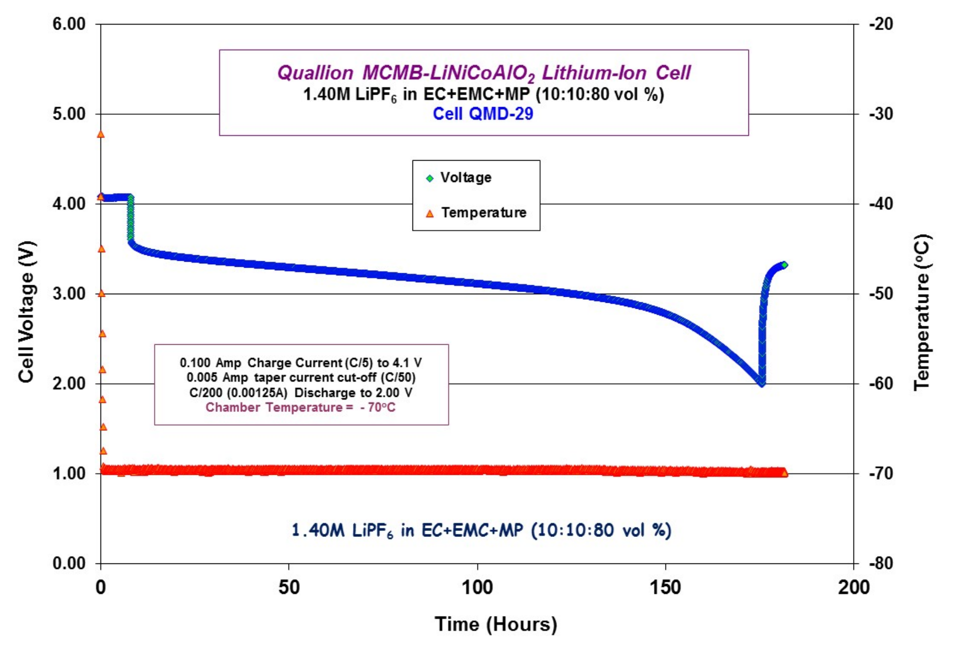
Preliminary Configuration and Tentative Requirements :

- Configuration: Two Li-ion cells connected in series
  - Currently baselining two Quallion QL0370B Li-Ion Cells
- Operating Temperature Range:
  - Maximum temperature = + 20^{o}C
  - Minimum charge temperature = - 40^{o}C
  - Minimum discharge temperature = - 70^{o}C
  - Minimum survival temperature = - 120^{o}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

C/200 Discharge Rate at -70°C

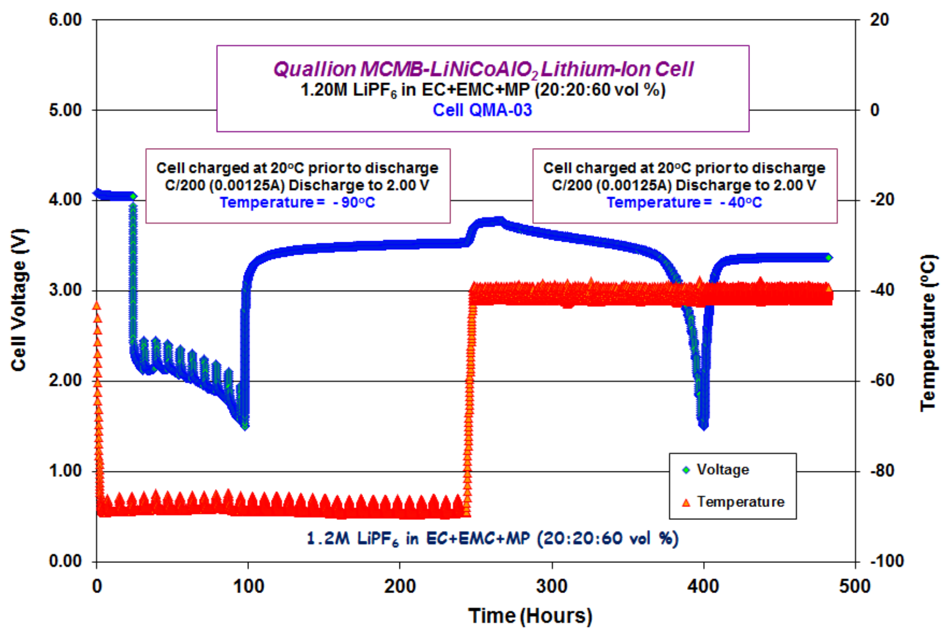


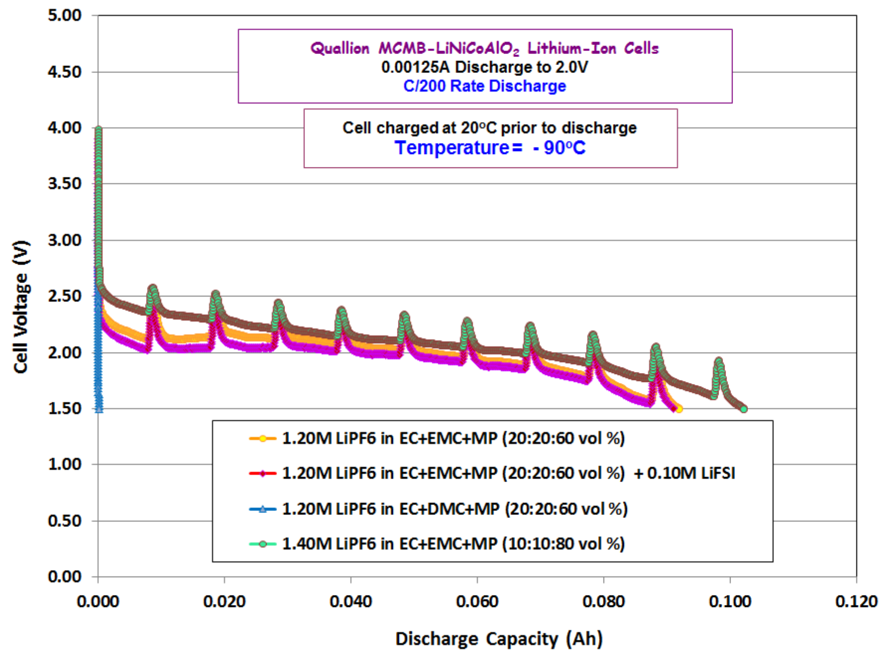


- Quallion cells have been demonstrated to provide excellent low temperature characteristics, with the ability to support discharge at -70°C (with over 165 hours of operation).
- Electrolyte selection of new generation of cells based on results of initial assessment.

> **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

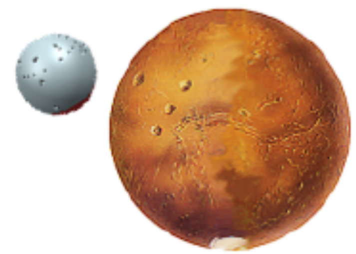




- **Quallion cells have been demonstrated to provide excellent low temperature survivability characteristics, being capable of supporting operation at -90°C and long term dwell periods.**
  - Cells soaked at -90°C for 24 hours prior to discharge
  - Cells discharged at C/200 rate at -90°C to 1.50V
  - 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
- **Quallion cells have been demonstrated to survive exposure to -135°C (> 4 hour soak) with no apparent performance loss observed.**

Mars Sample Return Advanced Development Team
OS Beacon Technology Development:
Low Temperature Li-Ion Battery Development

- **The Orbiting Sample cache (OS) is a key component of the current baseline Mars Sample Return architecture. The OS is the container that would store and protect the samples tubes on their ascent into Martian orbit, and on the journey back to Earth. OS design formulation is currently being done by the Mars Advanced Design Team (ADT). The objective of the ADT is to represent the potential Mars Sample Return (MSR) mission concepts and to provide an interface for the current mission studies to work with.**
- Summary of Technology Development Program:
  - Configured power system for Mars Orbiting Sample (OS) Canister Beacon
    - Developmental operational temperature requirement:
      - **- 60°C to +50°C**
    - Survival temperature requirement:
      - **- 85°C to +50°C**
    - Duty cycle consists of three possible states of operation:
      - Off; On - Transmitting; On - Not Transmitting
  - Compared two system designs:
    - Option 1: Solar cells + secondary battery
    - Option 2: Primary (non-rechargeable) battery
  - Trade results:
    - Solar cells + secondary battery offers longer operation, lower peak voltage, smaller volume and lower technical risk
    - Primary battery offers simplicity, ~20 g lower mass, but shorter operation (~6 days)
  - Completed battery cell demonstration testing for OS mission
    - **Successfully demonstrated Li-ion cell performance at -60°C using JPL developed low temperature electrolyte**
    - **Demonstrated 10 days operation at both hot and cold extremes, with worst-case eclipse and sun angle**



Orbiting Sample (OS)**
in Mars Orbit

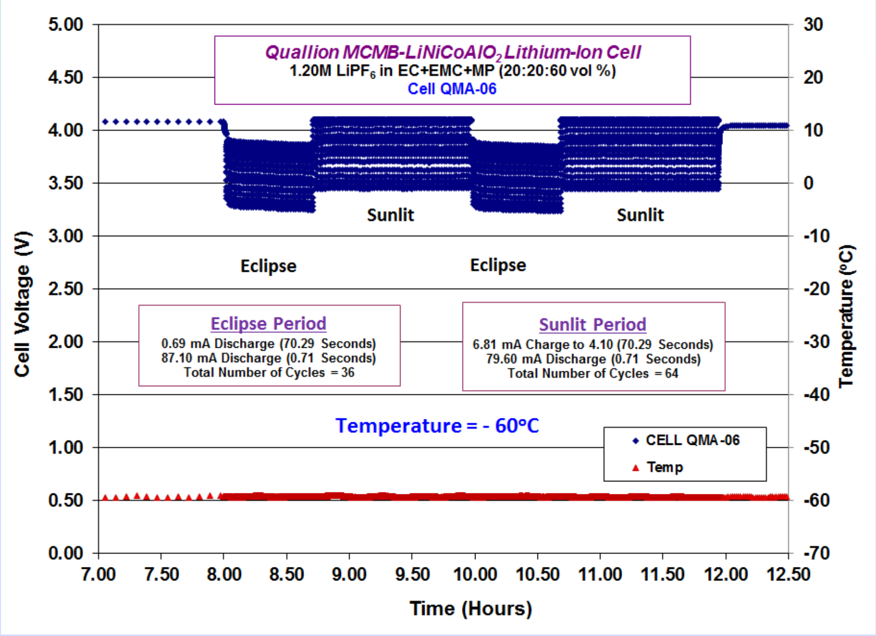
S. Perrino, *et al., "The Evolution of an Orbiting Sample Container for Potential Mars Sample Return"*, 2017 IEEE Aerospace Conference.

Mars Sample ReturnAdvanced Development Team
OS Beacon Technology Development:

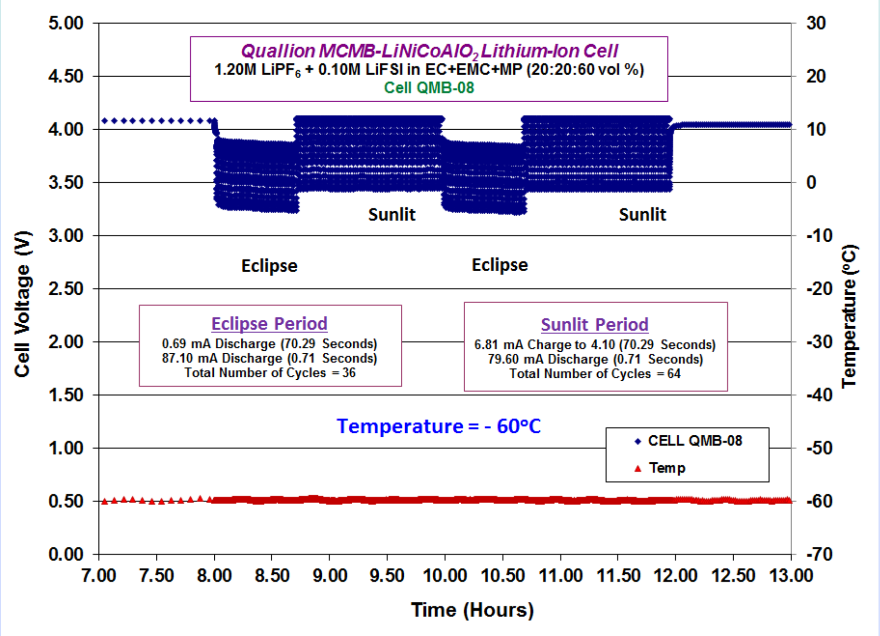
Cold Case On-Orbit Load Profile at - 60°C (after -80°C survival)

Cells at 100% SOC Prior to Testing

Cell QMA-06: 1.20M $LiPF_6$ in EC+EMC+MP (20:20:60 vol %)

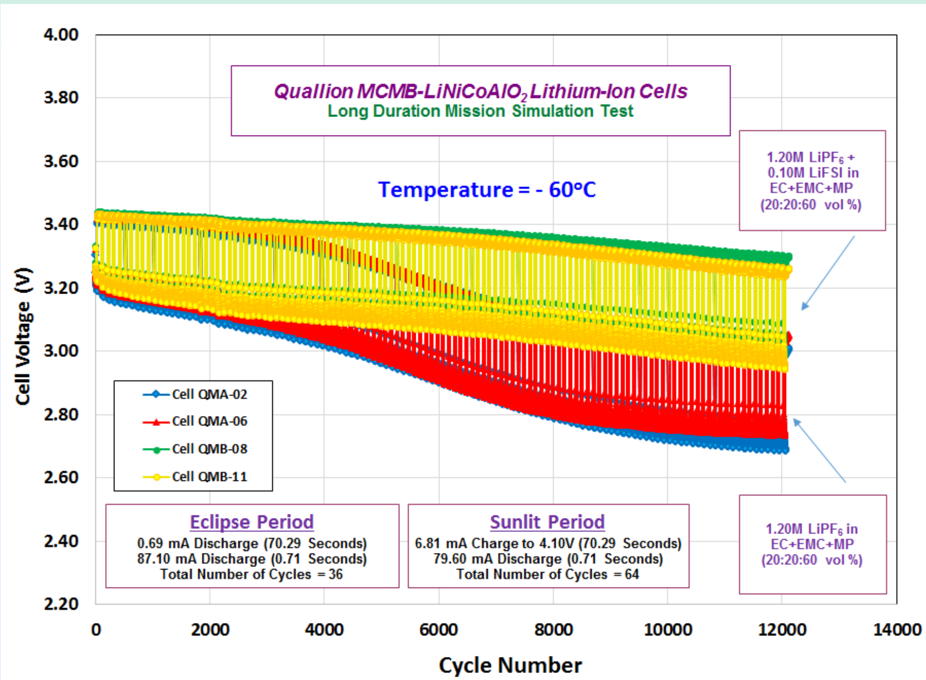


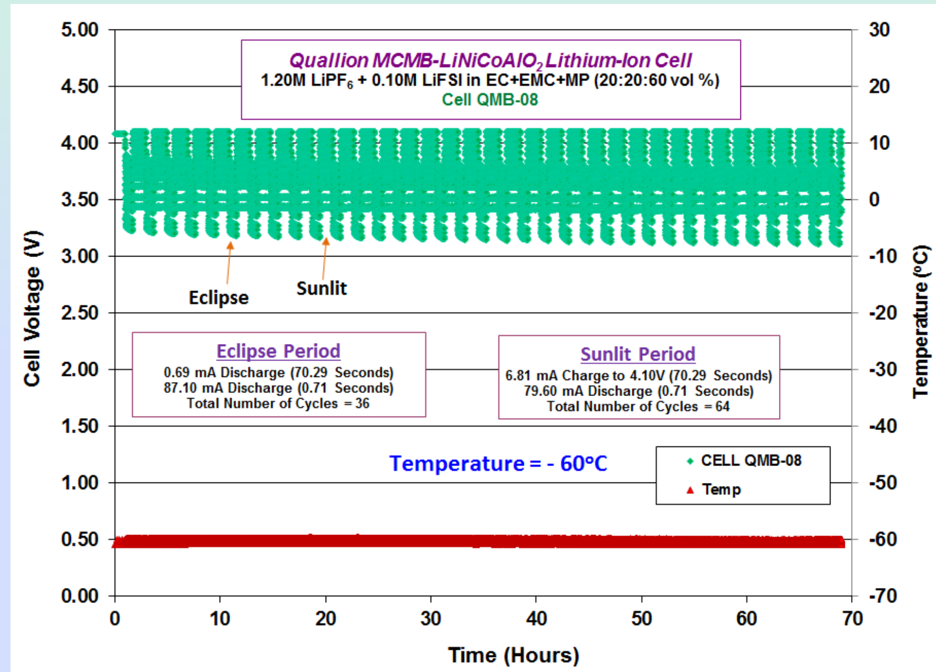
Cell QMB-11: 1.20M $LiPF_6$ + 0.10M LiFSI in EC+EMC+MP (20:20:60 vol %)



- After completing the low temperature survival test at -80°C, all cells were observed to perform well when subjected to the "cold case" mission profile at -60°C.
  - All cells displayed stable performance and voltages > 3.15V (cells were charged to 100% SOC prior to testing).

Mars Sample ReturnAdvanced Development Team
OS Beacon Technology Development:
Long Duration Mission Simulation Test at -60°C
End of Discharge Cell Voltage During Cycling





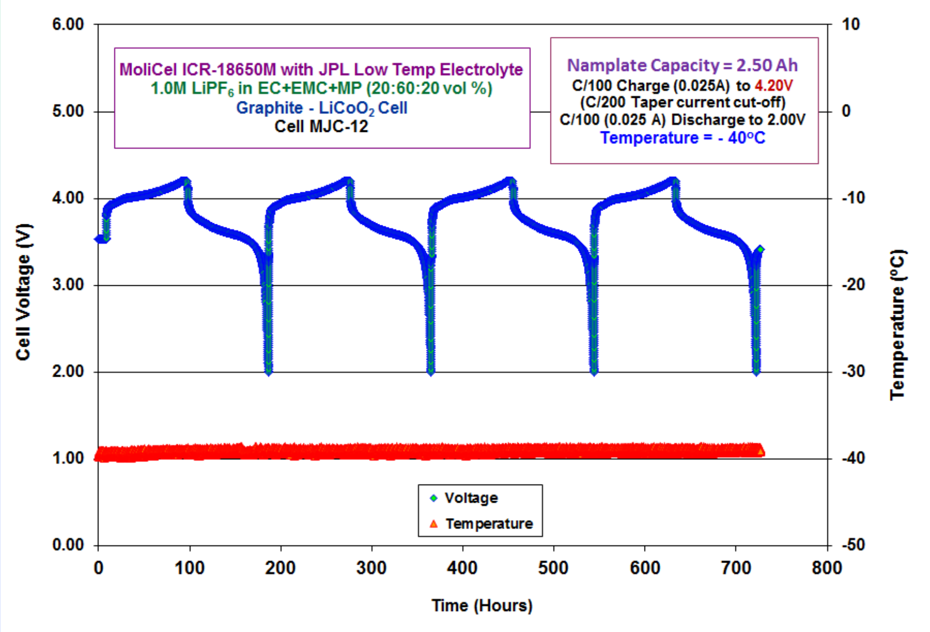
- The incorporation of LiFSI results in improved long term cycling performance at very low temperature (-60°C).
- It appears that the presence of LiFSI improves the charge characteristics of the cells, due to the formation of desirable solid electrolyte interphase (SEI) layers on the MCMB anodes.

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

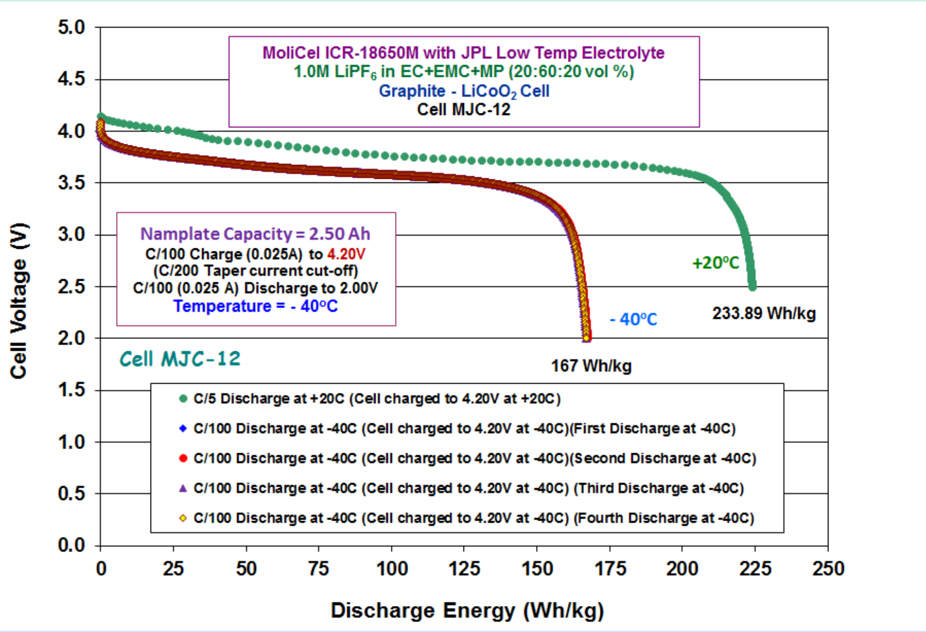
Charge and Discharge at -40°C (C/100 Rates)

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



- In support of the Oceans World Program Office and in collaboration with E-One Moli, developed high specific energy cells with good low temperature performance using JPL Li-Ion electrolytes.
- Technology attractive for future deep space missions.
- Excellent specific energy at -40°C observed using a low rate charge and discharge (C/100) (i.e., 167 Wh/kg).

> **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).**

Summary and Conclusions:

- The SOP heritage all carbonate-based low temperature Li-ion electrolyte has been infused into a number of Mars missions:
  - Electrolyte used on MER, Phoenix, Juno, Grail, and MSL

- The InSight project has selected the next generation JPL low temperature electrolyte for use coupled with NCA-based electrode chemistry.
  - 31% more capacity at -25°C compared to the NCO-based chemistries.

- Quallion BTE cells have been demonstrated to provide excellent low temperature characteristics, being viable for future missions.
  - Demonstrated operation at -90°C for PUFFER program
  - Demonstrated survivability down to -135°C.
  - Demonstrated operation from -60°C to +50°C for Mars OS
  - Continuous operation at -60°C demonstrated using JPL developed low temperature electrolyte (both charge and discharge).

- Demonstrated excellent low temperature performance and high specific energy in high TRL 18650-size Li-ion cells.
  - Over 167 Wh/kg demonstrated at -40°C with low rates
  - Operational capability down to -60°C

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