Low Temperature Lithium-Ion Electrolyte Development at JPL for Aerospace Applications

Marshall C. Smart

Ratnakumar Bugga

Larry D. Whitcanack

S. R. Narayanan

Subbarao Surampudi

Jet Propulsion Laboratory, California Institute of Technology

4800 Oak Grove Drive, Pasadena, CA 91109

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Outline

- Introduction
- Approach/Background
- Overview of Electrolyte Development
- Early Generation Ternary Electrolyte (-20 to +40°C)
- Quaternary Carbonate-Based Electrolytes (-50 to +40°C)
  - Conductivity Measurements
  - Cyclic Voltammetry Results
  - MCMB-$LiNiCoO_2$ experimental cell results
    - Charge/discharge characteristics of formation cycles (three electrode cells)
    - Discharge characteristics as a function of temperature
    - Electrochemical impedance spectroscopy (EIS) measurements
    - D.C. micropolarization measurements
    - Tafel polarization measurements
    - Electrochemical impedance spectroscopy (EIS) measurements
  - Prototype Cell Performance
- Ultra-Low Temperature Ester-Based Electrolytes (-80 to +40°C)
- Conclusions

Objective

- **The objective of our research is to develop low temperature lithium ion conducting non-aqueous liquid organic electrolytes, which will enable the operation of lithium-ion cells over a wide range of temperatures (– 80°C to +40°C) and enable future NASA missions.**

Approach

The program involves the following tasks:

- Identification of low viscosity, low melting point solvents
- Synthesis of novel co-solvents (if needed)
- Identification of candidate electrolyte salts
- Optimization of solvent and salt concentrations for low temperature conductivity
- Assessment of ionic conductivity and electrochemical stability
- Demonstration of low temperature performance capability of candidate electrolyte formulations in experimental rechargeable laboratory cells.
- Demonstration of low temperature performance capability of candidate electrolyte formulations in aerospace quality prototype Li-ion cells.

Ultra Low Temperature Lithium Batteries
Vision and Goal

Goal: To develop rechargeable lithium-based cells for future NASA applications which are capable of operation of operation over a large temperature range, especially at low temperatures (-80° to +40°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 II 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

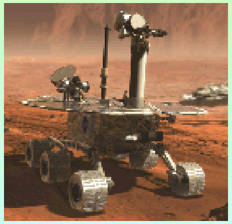
Operation –40 to +40°C

Operation –80 to +60°C

2000 2002 2004 2006 2008 2010 2020

Infusions:

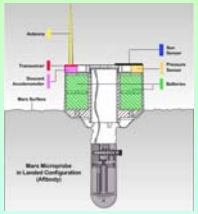
MSP01 Lander Battery



MER Rover Battery

2009 Smart Lander

Future Planetary Rovers and Landers



Future Planetary Penetrators and Probes

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 –80 to 40°C
- Wide liquid range (low melting point)
  - -80 to 75°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***
  - ***Good SEI characteristics on electrode***
  - Facile lithium intercalation/de-intercalation kinetics
- Good thermal stability
- Good low temperature performance throughout life of cell
  - Good resilience to high temperature exposure
  - Minimal impedance build-up with cycling and/or storage

Low Temperature Lithium Ion Electrolytes

Background

- Traditionally used electrolytes for ambient temperature applications are generally composed of binary EC-rich formulations:
  - 1.0M $LiPF_6$ EC+DMC (1:1) (50% EC v/v)
  - 1.0M $LiPF_6$ EC+DEC (1:1) (50% EC v/v)
  - Due to high solution viscosities, high melting points, and correspondingly poor conductivities at low temperatures negligible capacity observed at < –10^{o}C

- The use of lower EC-content coupled with using ternary and quaternary solvent mixtures has led to improved performance at low temperatures.
  - 1.0M $LiPF_6$ EC+DEC+DMC (2:1:2) (40% EC v/v)
  - 1.0M $LiPF_6$ EC+DEC+DMC (1:1:1) (JPL) (33% EC v/v)
  - 1.0M $LiPF_6$ EC+EMC+DMC (1:1:1) (ARMY) (33% EC v/v)
  - 1.0M $LiPF_6$ EC+EMC (1:3) (Covalent) (25% EC v/v)
  - 1.0M $LiPF_6$ EC+DEC+DMC+EMC (1:1:1:2) (JPL) (20% EC v/v)
  - 1.0M $LiPF_6$ EC+DEC+DMC+EMC (1:1:1:3) (JPL) (17% EC v/v)
  - $LiPF_6$, LiBOB and $LiBF_4$ in PC+EC+EMC (ARL) (20% EC v/v, 20% PC)
  - Good performance generally observed at – 20^{o}C (some perform well at –40^{o}C)
  - Electrolytes tend to perform poorly at temperature < - 40^{o}C

Low Temperature Lithium Ion Cells and Batteries

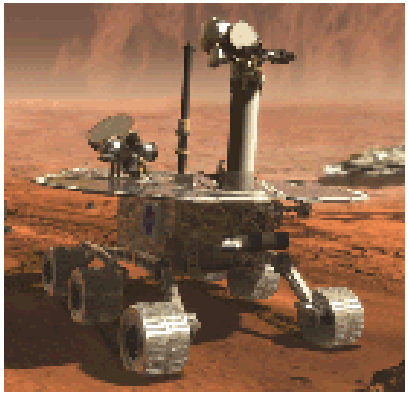
Performance Summary of Advanced Low Temperature Li-Ion Electrolytes Developed at JPL

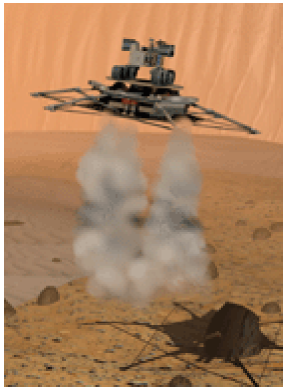
Electrolyte Type	- 20°C Enabling 1.0M $LiPF_6$ EC+DEC+DMC (1:1:1 v/v %) GEN 1 ('96-'00)	- 40°C Enabling 1.0M $LiPF_6$ EC+DEC+DMC+EMC (1:1:1:2 v/v %) GEN 2 ('97-'01)	- 60°C Enabling 1.0M $LiPF_6$ EC+DEC+DMC+EMC (1:1:1:3 v/v %) and Ester-Based GEN 3 ('00-'03)	- 80°C Enabling Ester-Based (i.e. 1.0M $LiPF_6$ EC+EMC+MB (1:1:8 v/v %) GEN 4 ('04-'05)
Operating Temperature at C/5	- 20 to + 40°C	- 40 to +40°C	-60 to + 40°C	-80 to + 25 C (Goals)
Specific Energy (Wh/kg)				
25 C	125	125	125	125
-20 C	75	95	105	110
-40 C	< 40	75	85	90
-60 C	NA	NA	50-65	70
-80 C	NA	NA	NA	50
100 % DOD Cycle Life	>1500	>1500	>1500	TBD
NASA Application	MSP'01 Lander MER '03 Rover	B2 Bomber Future Landers	Future Mars Landers and Rovers	Future Mars Surface Operations

- ***Specific energy values dependent upon prototype cell type and size***

Mars Technology Program-Past, Present and Future Missions

Low Temperature Lithium-Ion Batteries





Mars '01 Surveyor Program

- **Mars 2001 Program required two 25 AHr, 8-cell batteries which can operate over a wide range of temperatures (developed by Yardney)**
- Successful operation demonstrated over wide temperature range (-20 to +40^{o}C)
- **Battery space qualified prior to mission cancellation**
- **Battery incorporated early generation JPL electrolyte**

[1.0 M $LiPF_6$ EC+DEC+DMC (1:1:1)]

2003 Mars Exploration Rovers (MER)

- **MER Program requires high energy density secondary battery which can operate over a wide range of temperatures**
- Mission Requirements:
- Operation from - 20 to +30^{o}C
- Cycle Life > 90 SOLS
- Shelf Life > 2.5 Years
- **Battery incorporates early generation JPL electrolyte**

[1.0 M $LiPF_6$ EC+DEC+DMC (1:1:1)]

Future Mars Landers/Rovers

- **Future planetary Landers and Rovers will likely require high energy density secondary batteries which can operate over a wide range of temperatures and display long life.**

Mission Projections

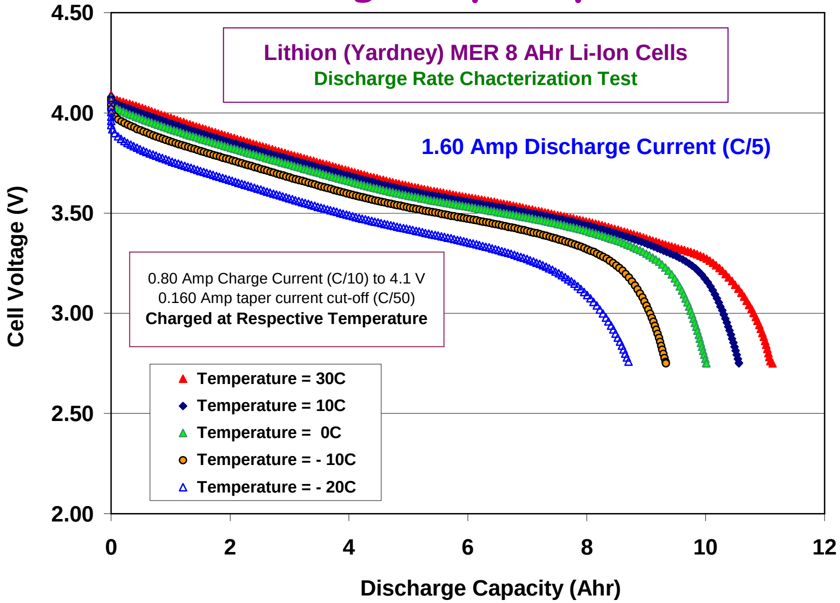
- Operation from - 40 to +40^{o}C
- Cycle Life > 1000 SOLS
- Wet Life > 5 Years
- **Batteries will most likely require next generation low temperature electrolytes.**

Lithion 8 Ah Li-Ion Cells for Mars Exploration Rover (MER)

Discharge Rate Characterization at Various Temperatures

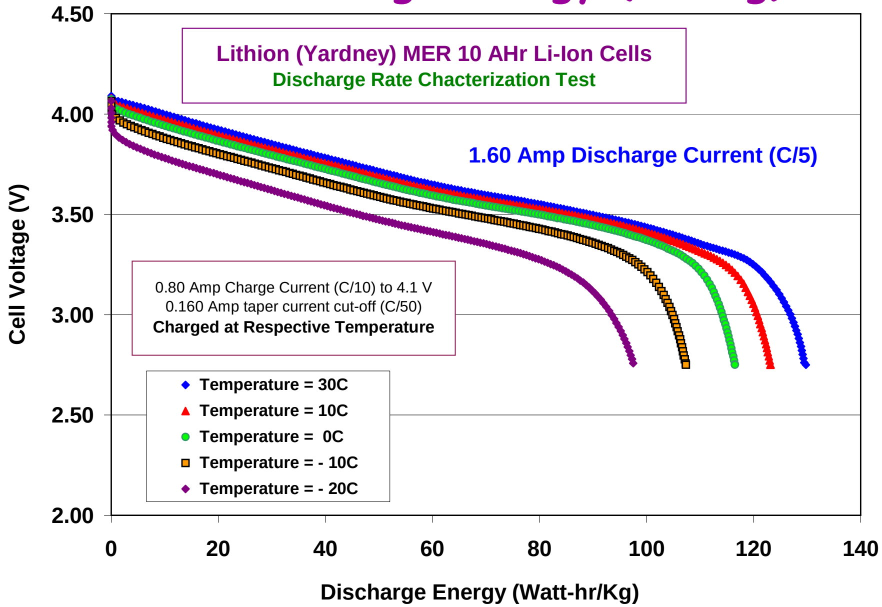
(C/5 Discharge Rate = 1.60 Amps)

Discharge Capacity (Ah)



	Capacity (AHr)	% of RT
30 C	11.122	100.00
10 C	10.561	94.95
0 C	10.012	90.01
-10 C	9.332	83.91
-20 C	8.700	78.22

Discharge Energy (Wh/kg)



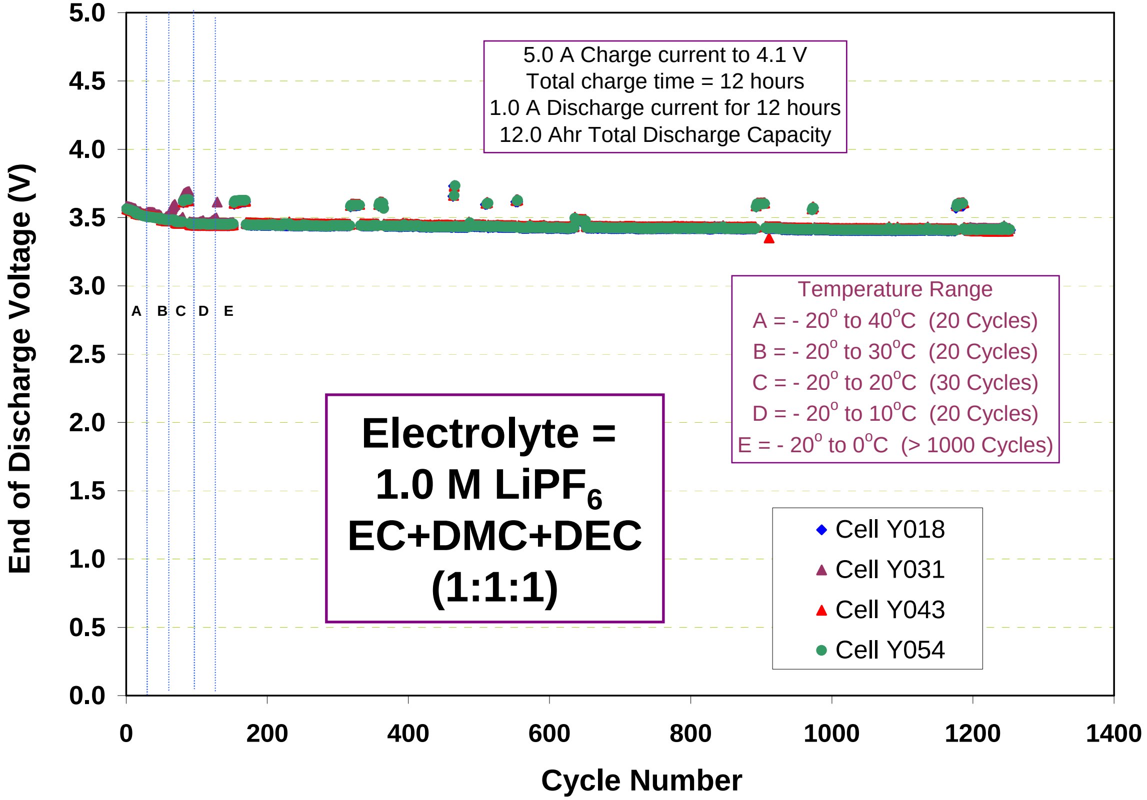
	Energy (WHr/Kg)	% of RT
30 C	129.77	100.00
10 C	123.61	95.25
0 C	116.50	89.77
-10 C	107.35	82.72
-20 C	97.50	75.13

- ***Cells contain 1.0M $LiPF_6$ +EC+DMC+DEC (1:1:1) (Range of operation –30 to +40°C)***
- ***Performance reflects charging at low temperate***

Yardney 25 Ah Lithium-Ion Cells for Mars Lander Applications

Mission Simulation Profile-MSP01 Design Cells

Cells Stored at 10ºC on the Buss for 11 Months Prior to Test



- **Initial acceptance test performed 4-13-1999 prior to cruise storage test (~ 5.1 years ago)**
- **Surface Operation Test started 4-17-2000 (total test duration = > 4.0 years)**
- **Data suggests that the chemistry/technology possesses excellent life characteristics with the potential to support multi-year missions.**

Experimental MCMB-$LiNi_{0.8}Co_{0.2}O_2$ Carbon Cells and Electrochemical Characterization of Electrolytes

Evaluation of Low-EC Content Electrolytes in Experimental Cells

Electrolyte Type

- 1.0 M $LiPF_6$ EC+DMC (1:1)
- 1.0 M $LiPF_6$ EC+DMC (30:70)
- 1.0 M $LiPF_6$ EC+DEC+DMC (1:1:1 v/v)
- 1.0 M $LiPF_6$ EC+DMC+EMC (1:1:1: v/v)
- 1.0 M $LiPF_6$ EC+DMC+DEC (4:4:2: v/v)

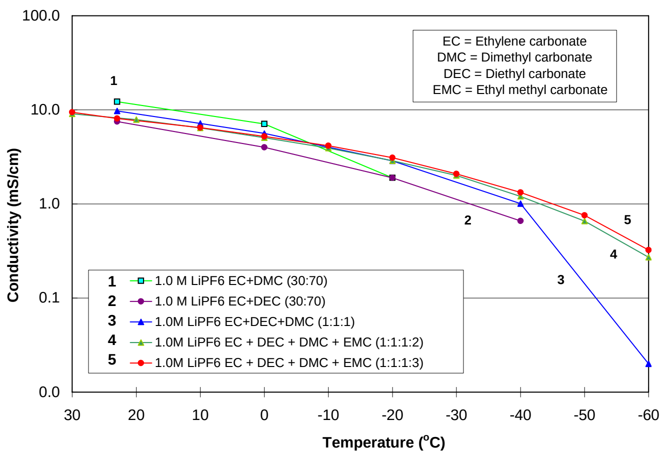
- 1.0 M $LiPF_6$ EC+DEC+DMC+EMC (1:1:1:2 v/v)
- 1.0 M $LiPF_6$ EC+DEC+DMC+EMC (1:1:1:3 v/v)
- 1.0 M $LiPF_6$ EC+DEC+DMC+EMC (1:1:1:4 v/v)
- 1.0 M $LiPF_6$ EC+ DMC+EMC (15:15:70 v/v)
- 0.6 M $LiPF_6$ EC+DEC+DMC+EMC (1:3:3:3 v/v)

- **MCMB Carbon-$LiNiCoO_2$ Cells**
  - 400-450 mAh Size Cells
- All Cells equipped psuedo **Li metal reference electrodes**
  - Flooded electrolyte design (cylindrical cells)

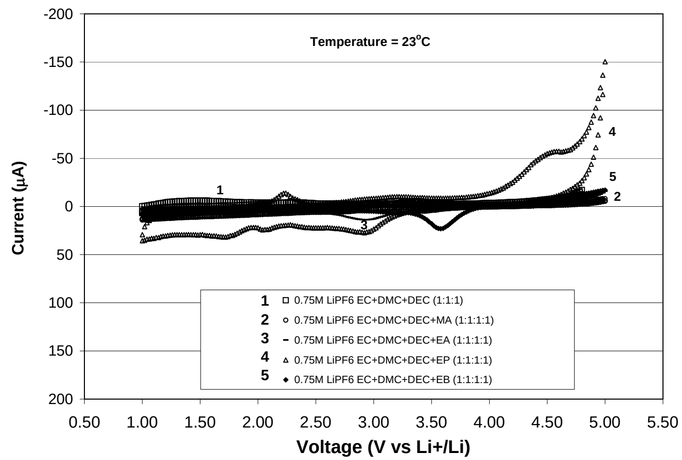
Techniques Used to Study the Low Temperature Characteristics

- Charge/discharge behavior at various temperatures
- Electrochemical Impedance Spectroscopy (EIS)
- DC Polarization Techniques

Conductivity Measurements



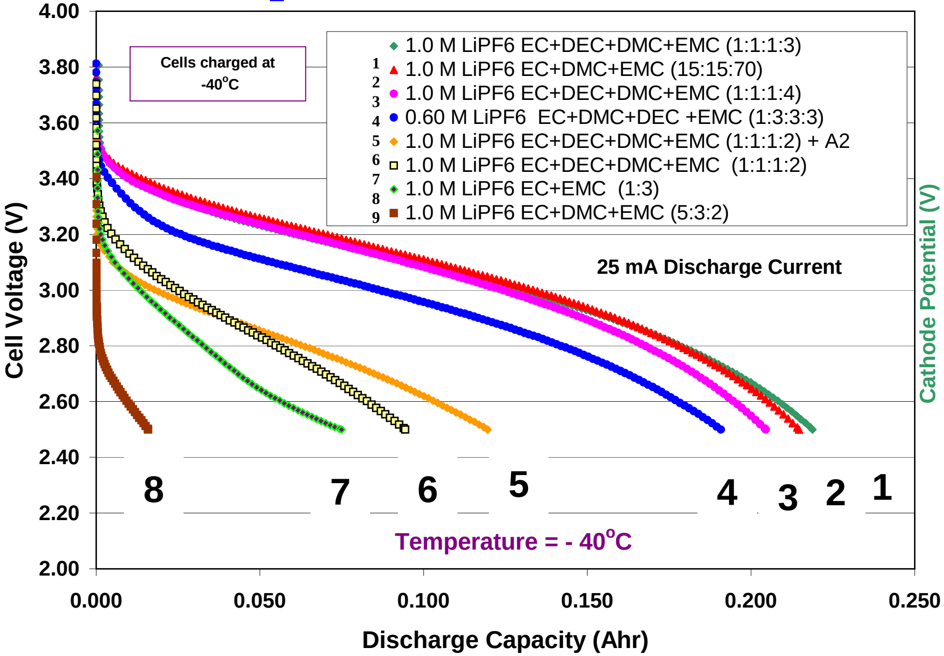
Cyclic Voltammetry Measurements



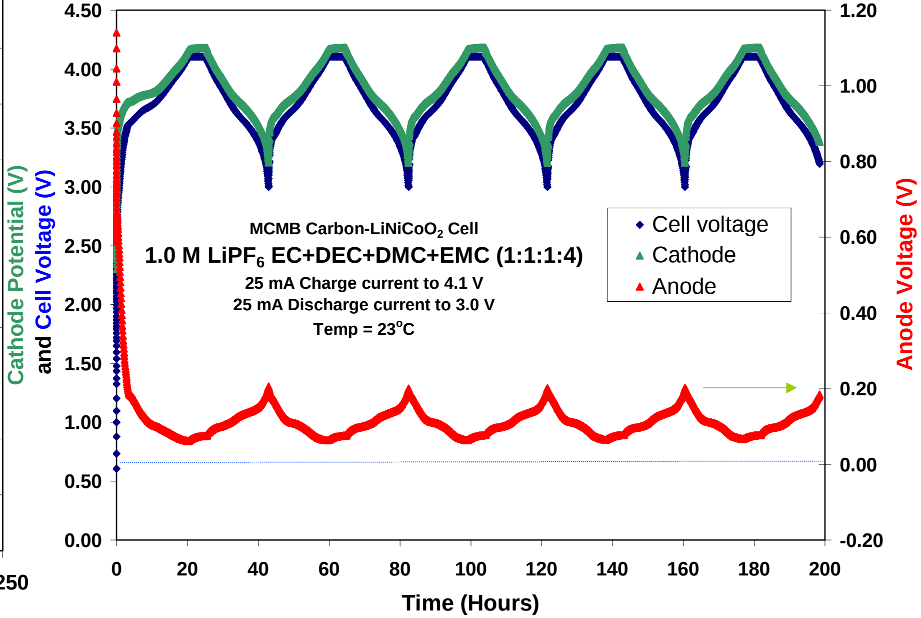
Operation of Li-Ion Cells Under Extreme Environmental Conditions

Development of Low Temperature Electrolytes

Experimental Cell Results



Formation Characteristics

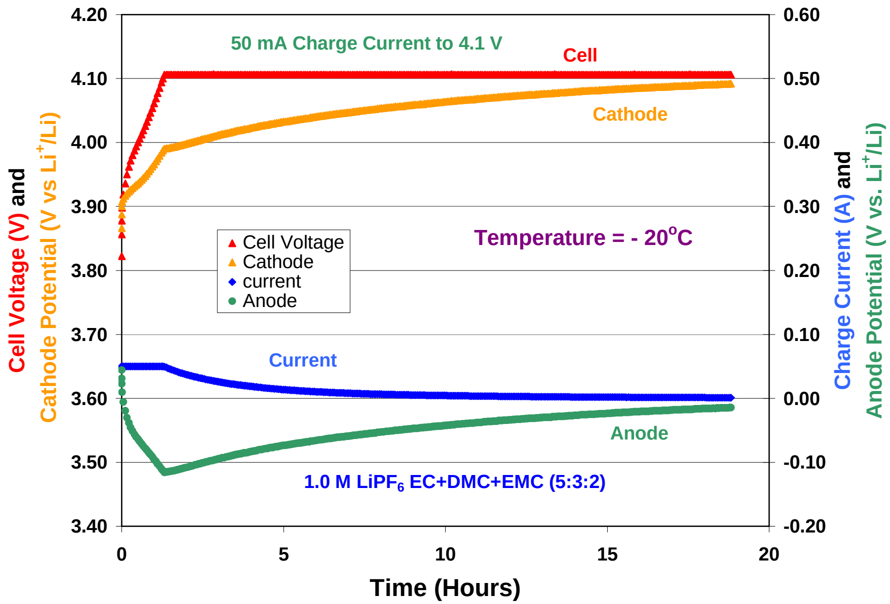


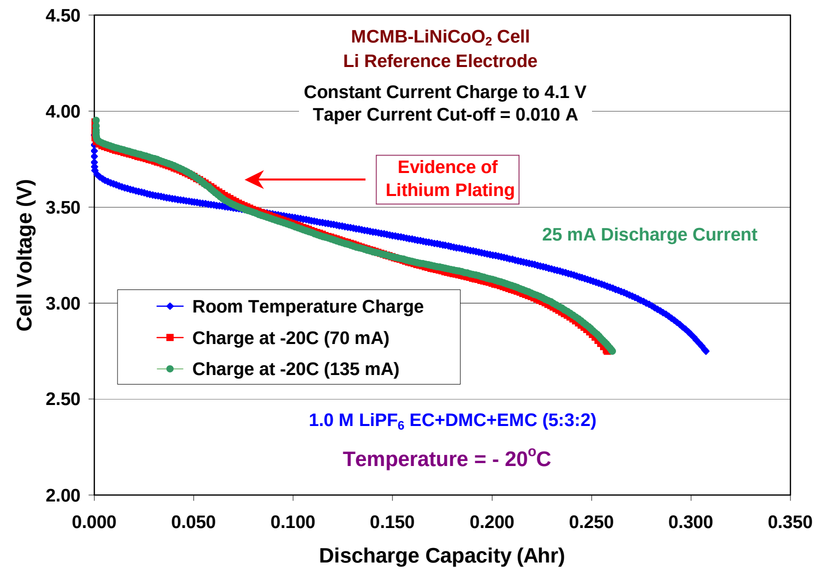
- ***At JPL, we have investigated a number of EC-based liquid electrolytes with the intent of improving the low temperature performance (especially at –40°C and below).***
- ***At - 40°C, the low EC-content electrolytes are superior with the cell containing 1.0M $LiPF_6$ EC+DEC+DMC+EMC (1:1:1:3) delivering the most capacity.***

- M. C. Smart, B. V. Ratnakumar, L. Whitcanack, K. Chin, and S. Surampudi, H. Croft, D. Tice and R. Staniewicz, “Improved Low Temperature Performance of Lithium Ion Cells with Quaternary Carbonate-Based Electrolytes”, *J. Power Sources*, **119-121**, 349-358 (2003).

Charge Characteristics of Experimental Lithium Ion Cells

Effect of Charging at Low Temperature (- 20°C)

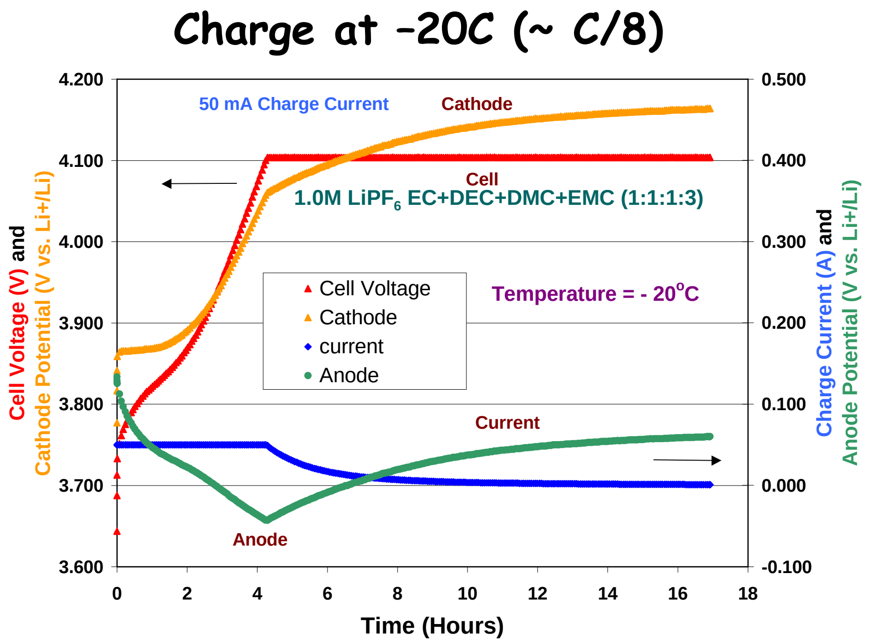


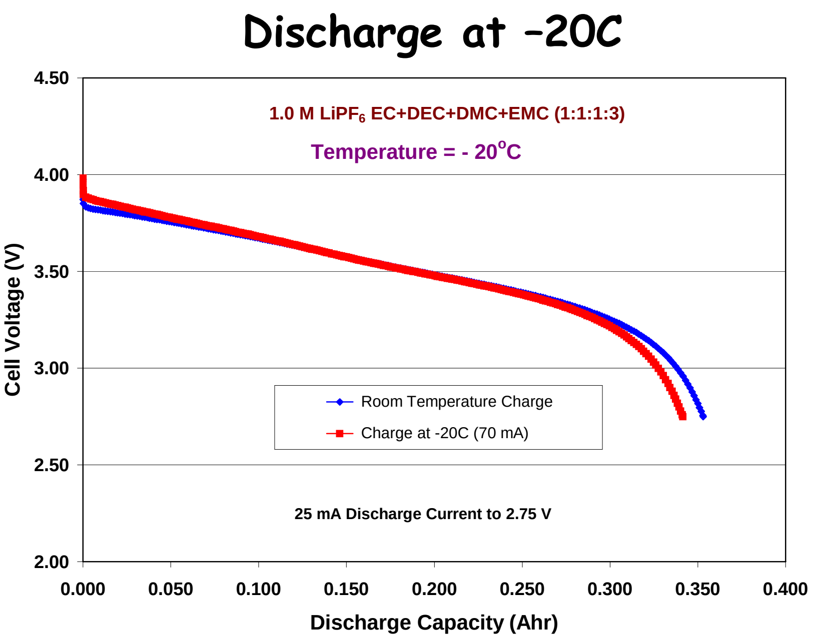


- In some cases, the anode can be excessively polarized in contrast to the cathode resulting in the possibility of lithium plating occurring.
- **In this example, the anode potential never becomes positive during entire charge.**

Charge Characteristics of Experimental Lithium Ion Cells

Effect of Charging at Low Temperature (- 20°C)





• As shown, the point at which the anode potential becomes the most negative (~ -70mV vs. Li^+/Li) is when the charge voltage and current are highest.

➢ Although the anode potential became negative, no lithium plating was observed with this cell in the subsequent discharge profiles.

➢ This might be due to the fact that the potentials were not sufficiently negative and/or any lithium plated on the electrode surface had time to intercalate during the taper mode.

Linear Micropolarization Measurements

* At low overpotentials (<<RT/αnF) the electrochemical rate equation can be linearized resulting in a linear current-potential relation.

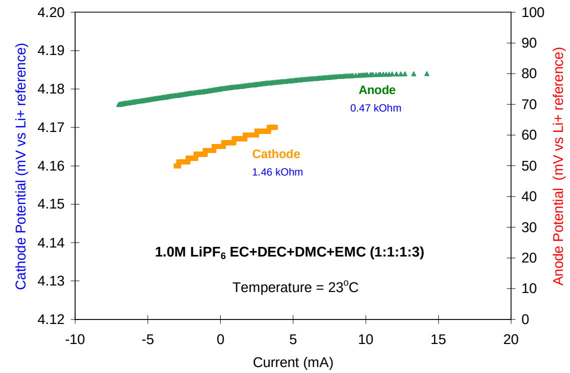
* The curves were obtained under potentiodynamic conditions conditions at scan rates of 0.02 mV/sec.

* The polarization resistance, or the exchange current density, can be calculated from the slopes of the linear plots.

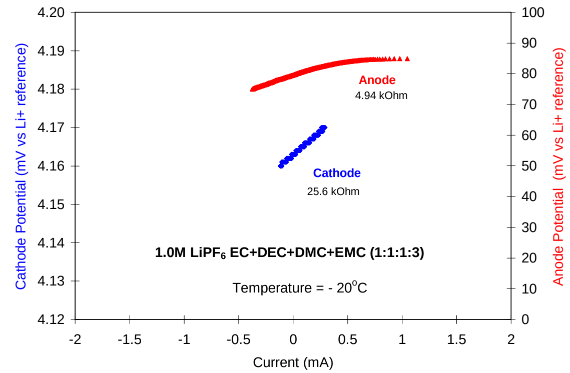
* The electrodes were tested in near full state of charge and biased over a 10 mV range.

* The resulting polarization resistance value is indicative of the facility of both the lithium inter-calation and de-intercalation processes in the material.

Measurements at 23°C



Measurements at - 20°C



▷ Polarization resistance is observed to be higher for the cathode with most systems.

▷ Good tool to investigate kinetics at different temperatures as a function of electrolyte type

Tafel Polarization Measurements of MCMB and $LiNiCoO_2$ Electrodes

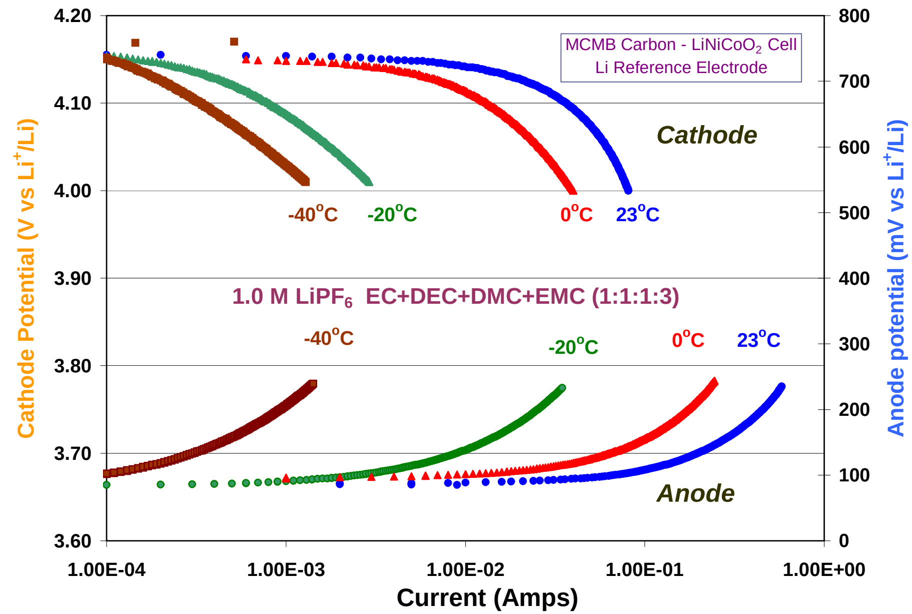
Effect of Electrolyte upon Polarization at Different Temperatures

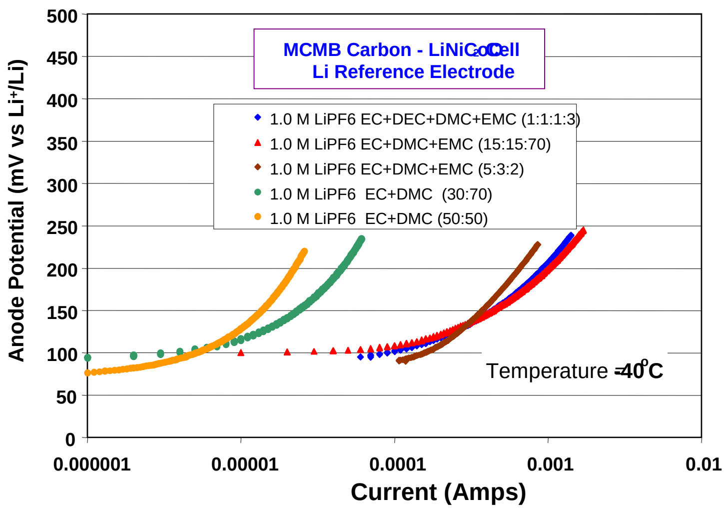
- Tafel polarization measurements allow further insight into the kinetics of lithium intercalation/de-intercalation on MCMB anodes and $LiNiCoO_2$ cathodes in these electrolytes.

- These measurements were made at scan rates slow enough (0.5 mV/s) to provide near-steady state conditions and yet with minimal changes in the state of charge of the electrode or its surface conditions.

- The cells were tested in near full state of charge and biased over a 150 mV range.

- Both anode and cathode polarization characteristics were measured at various different temperatures (23, 0, - 20 and – 40°C).





- **With electrolytes possessing favorable filming properties, the cathode usually displays poorer kinetics and is performance limiting.**

- **However, electrolytes which result in resistive SEI layers on the anode can dramatically limit low temp performance.**

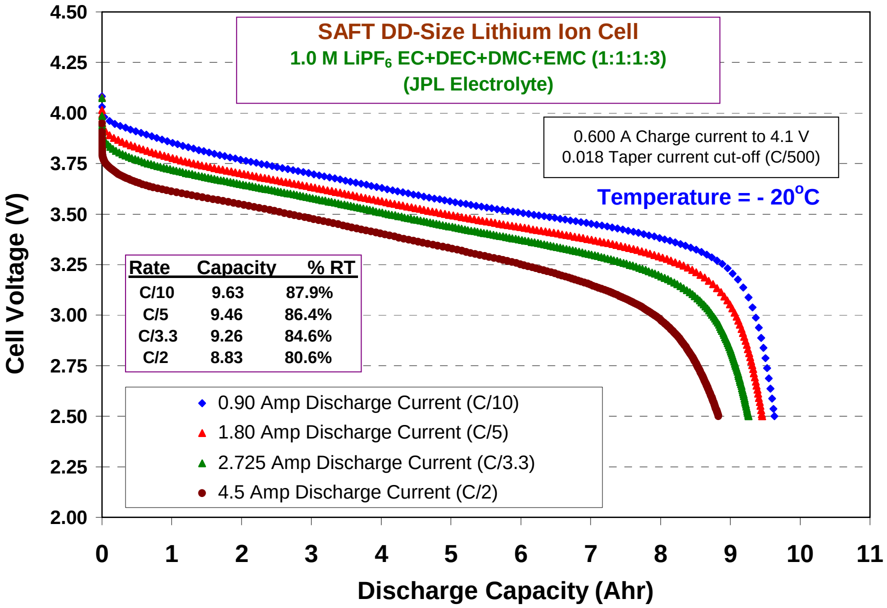
Prototype Cell Performance

- ***Prototype Cell Testing of Quaternary Low Temperature Electrolytes:***

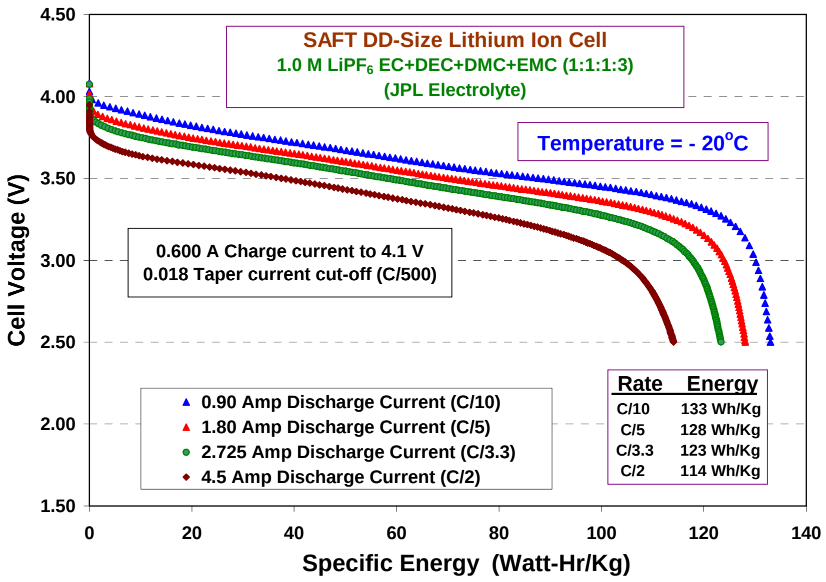
- ***SAFT DD-Size Cells (1.0M $LiPF_6$ EC+DMC+DEC+ EMC (1:1:1:2))***
  - *100 % DOD life testing at various temperature (-40, -20, 23 and 40^oC)*
  - *Discharge and charge rate characterization (low temperature charge)*
- ***SAFT DD-Size 9 Ah Cells (1.0M $LiPF_6$ EC+DMC+DEC+ EMC (1:1:1:3))***
  - *Performed 100 % DOD life testing at various temperature (-40, -20, and 23^oC)*
  - *Discharge and charge rate characterization (-70 to +30^oC)*
  - *Mission simulation cycling tests (-60 to 0^oC and –40 to 0^oC)*
- ***SAFT DD-Size 9 Ah Cells (1.0M $LiPF_6$ EC+DMC+DEC+ EMC (1:1:1:3))***
  - *Cells Contain Improved Anode Material*
  - *100 % DOD life testing at various temperature (-40, -20, and 23^oC)*
  - *Discharge and charge rate characterization (-70 to +30^oC)*
  - Pulse capability
- ***Compact Power Gel Polymer Electrolyte Cells***
  - ***1.0M $LiPF_6$ EC+DMC+DEC+ EMC (1:1:1:3)***
  - *High Power 7 Ah Cells and High Specific Energy 9 Ah Cells*
  - *Discharge and charge rate characterization (-70 to +30^oC)*
  - *Pulse capability including HEV “cold cranking” load profile*
- ***MER (LiTech, Inc.) Pouch Cells with Novel Anode Materials***
  - *1.0M $LiPF_6$ EC+DMC+DEC+ EMC (1:1:1:3)*
  - *1.0M $LiPF_6$ EC+EMC (1:3)*
  - *1.0M $LiPF_6$ EC+EMC (1:4)*

SAFT DD-Size Lithium-Ion Cells for Mars Rover Applications
Performance with Improved Anode Material and JPL Electrolyte
Discharge Rate Capability at - 20°C

Discharge Capacity (AHr)



Discharge Energy (WHr/Kg)



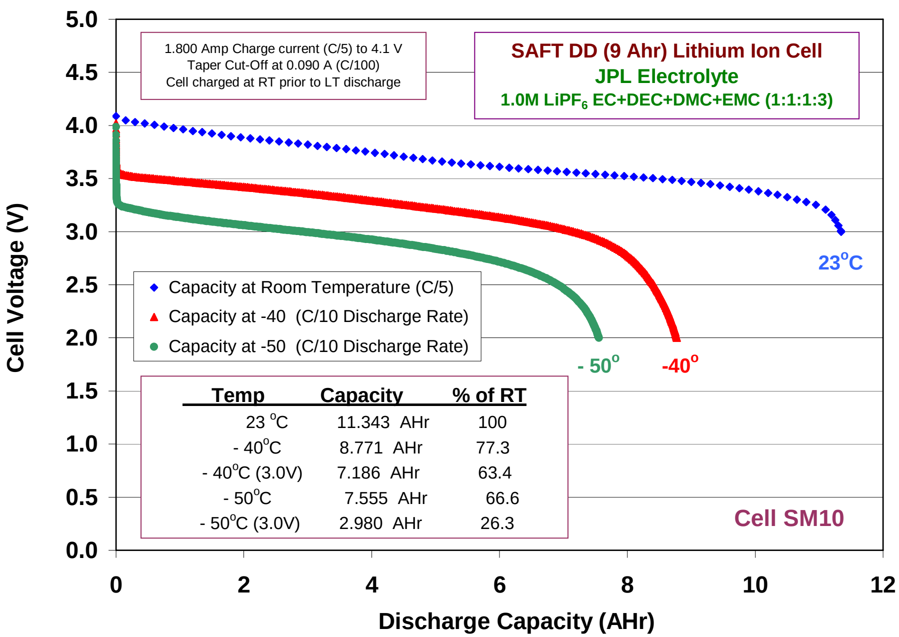
- 114 WHr/Kg delivered at – 20°C with a C/2 Rate (4.5A) (80.1% of RT C/10 capacity)

SAFT DD-Size Lithium-Ion Cells for Mars Rover Applications

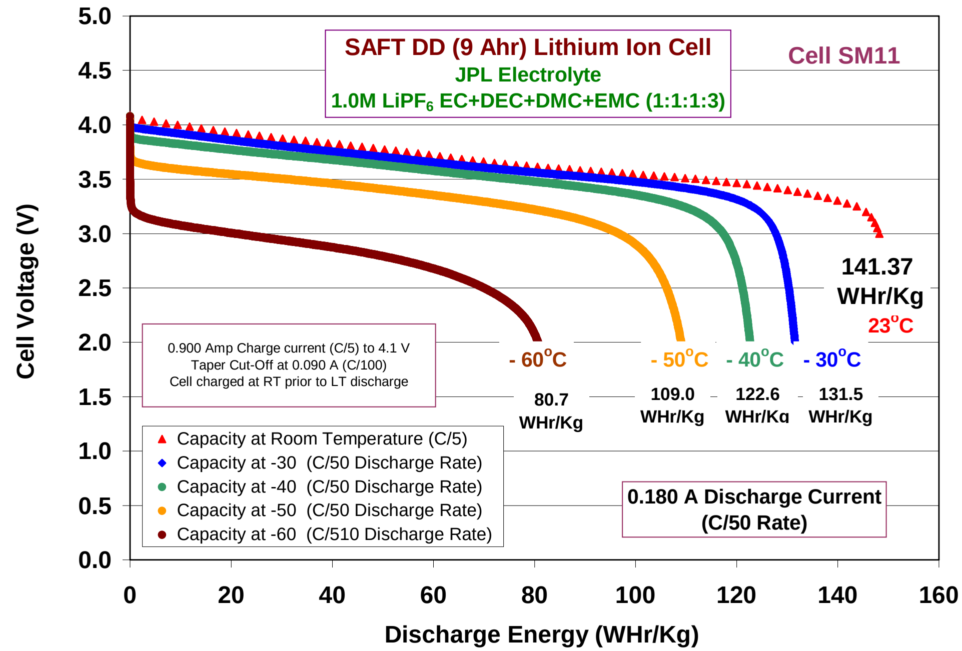
Performance with Improved Anode Material and JPL Electrolyte

Discharge Capacity at Various Temperatures (Room Temperature Charge)

Discharge Capacity at LT (C/10 Rate)



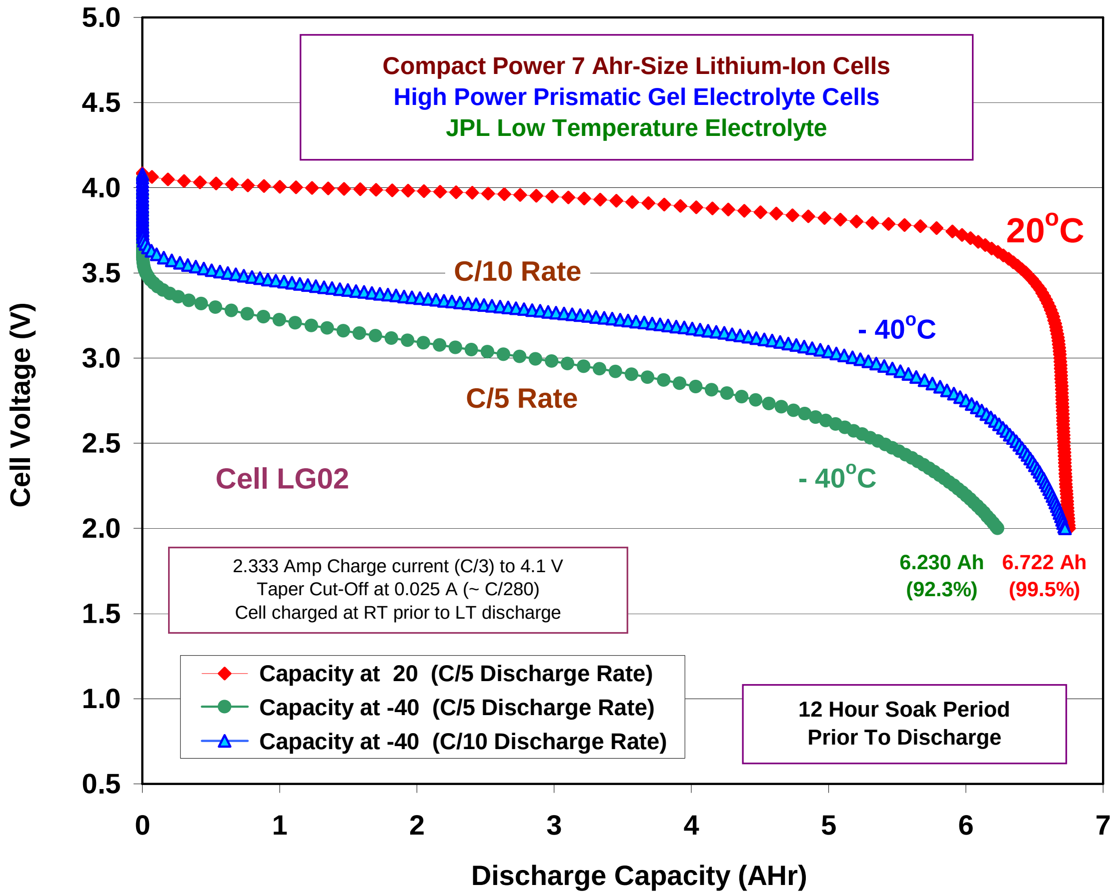
Discharge Energy at LT (C/50 Rate)



Performance Testing of High Rate, Gel Polymer Electrolyte Li-Ion Cells

Discharge Rate Performance of Compact Power Cells Containing JPL Electrolytes

Performance at –40°C (Room Temperature Charge)



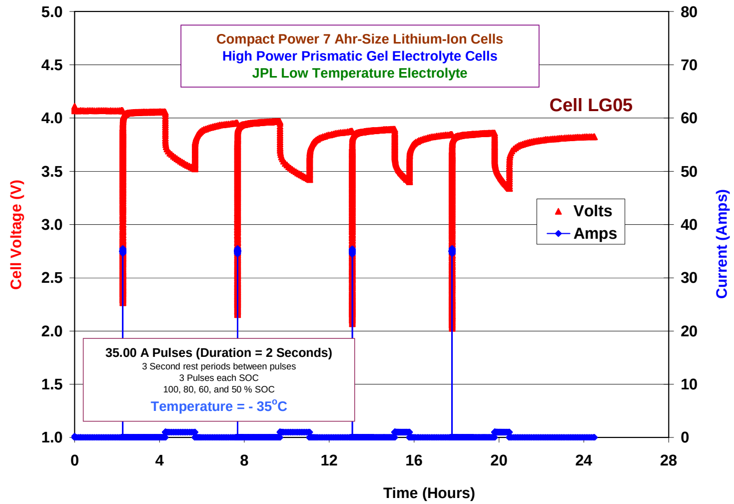
- ***At – 40°C, nearly full capacity (99.5%) was delivered when the cells were discharged to 2.0 V using C/10 discharge rate (94.6% @ 2.5 V cut-off)***

Performance Testing of High Rate, Gel Polymer Electrolyte Li-Ion Cells

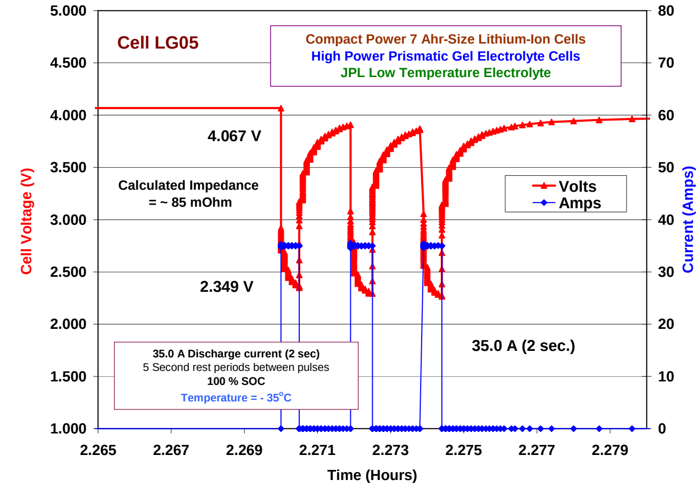
Pulse Capability at Low Temperature of Cells Containing Low Temperature Electrolyte

5C Discharge Pulsed (35.0 A – 3 Sec. Duration) at –35°C vs. SOC

Pulse Capability at –35°C



Pulse Capability at –35°C



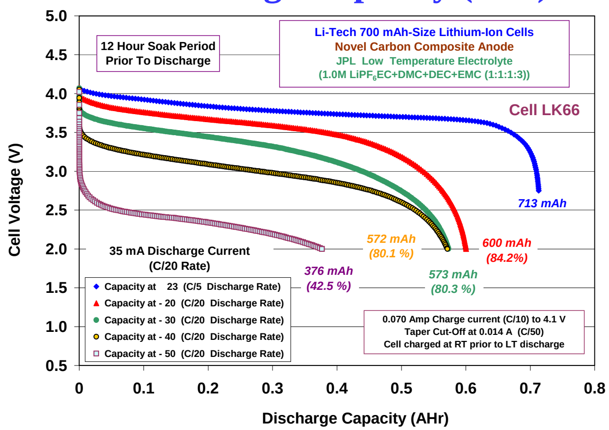
	100 % SOC		80 % SOC		60 % SOC		50 % SOC	
Time (Minutes)	Cell Voltage	Cell Impedance (Ohms)	Cell Voltage	Cell Impedance (Ohms)	Cell Voltage	Cell Impedance (Ohms)	Cell Voltage	Cell Impedance (Ohms)
Initial V	3.8697		3.7635		3.6866		3.6518	
Low V	2.2657		2.1540		2.0679		2.0246	
5	4.0320	0.0841	3.9191	0.0841	3.8428	0.0845	3.8129	0.0852
15	4.0455	0.0848	3.9362	0.0849	3.8642	0.0855	3.8300	0.0860
30	4.0491	0.0849	3.9466	0.0854	3.8703	0.0858	3.8379	0.0864
60	4.0528	0.0851	3.9564	0.0858	3.8819	0.0864	3.8477	0.0868
120	4.0565	0.0853	3.9673	0.0864	3.8953	0.0870	3.8593	0.0874

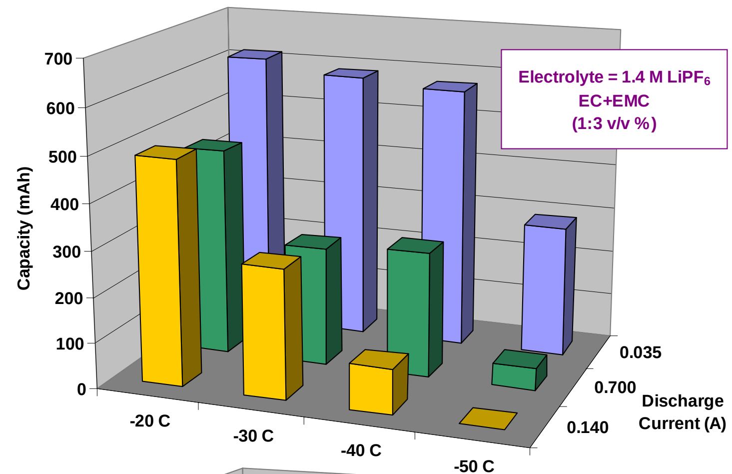
- **Cells observed to support 5C pulses (2 seconds in duration) at various SOCs at –35°C (35.0 Amps) (Cell voltage > 2.0V) (previously tested at –30°C).**
- **Observed the impedance to be relatively constant vs. SOC using current-interrupt method.**

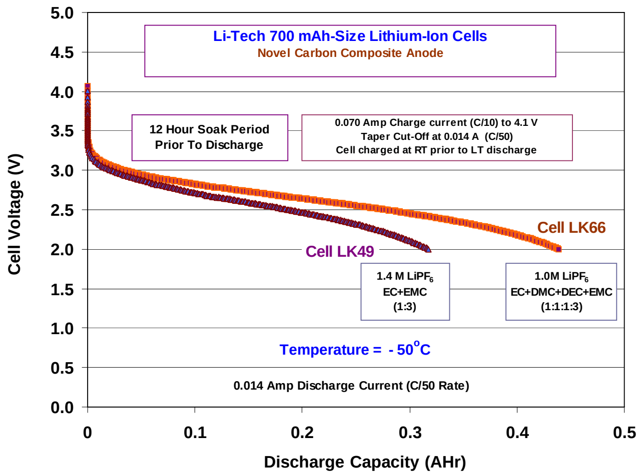
LiTech (MER) Prototype Cells with Low Temperature Electrolytes

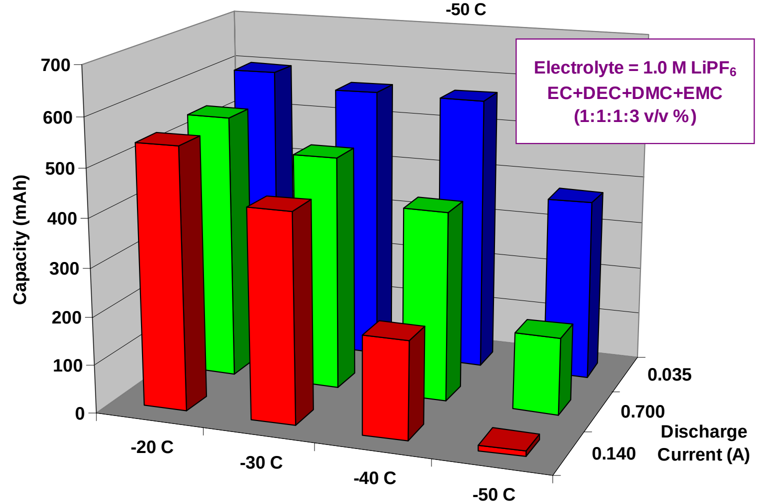
- The low temperature performance of JPL Gen III electrolyte was also evaluated in LiTech composite-carbon-based lithium-ion cells and compared to other low temperature electrolytes, including 1.0M $LiPF_6$ EC+EMC (1:3 v/v %), and 1.4 M $LiPF_6$ EC+EMC (1:3 v/v %)

Discharge Capacity (Ahr)









- **Superior performance was demonstrated by the JPL quaternary electrolyte compared with the binary EC+EMC mixtures. Findings communicated at the Power Sources Conference in Philadelphia.**

Low Temperature Lithium Ion Electrolytes

Ultra-Low Temperature Electrolyte Development: Approach/Background

- *The addition of low viscosity, low melting solvents to organic carbonate based electrolyte solutions proven approach:*
    - **Formates (i.e., methyl formate, ethyl formate)**
    - **Esters [i.e, methyl acetate (MA), ethyl acetate (EA), ethyl propionate (EP)]**
    - **Ethers (i.e., dimethoxy ethane (DME))**
    - **Lactones (i.e. γ-butyrolactone (GBL))**
    - ➢ High conductivity has been observed down to –60°C with some formulations
    - ➢ **Solutions often form resistive SEI layers (especially on carbon anodes)**
    - ➢ **Increased chemical reactivity observed in some cases (i.e., oligomerization)**
    - ➢ **Decreased electrochemical stability often observed (smaller voltage window)**
    - ➢ High vapor pressure associated with certain solvents

- ***Carbonate mixtures** generally display superior chemical and electrochemical stability and have found more widespread use.*
- *Use of mixtures (ternary and quaternary) enables one to optimize the physical properties of the electrolyte such that operation over a wide temperature range is possible.*
- Solvent mixtures also helps to create disorder in the ion solvation spheres resulting in higher conductivity and less tendency to precipitate

Low Temperature Lithium Ion Electrolytes
Background: Use of Ester-Based Solvents

- **Ohta, and coworkers (Matsushita): have investigated the use of MA-, EP-, and MP-based systems (i.e., EC+DEC+MP)**

(1) A. Ohta, H. Koshina, H. Okuno, and H. Murai, *J. Power Sources*, **54 (1)**, 6-10 (1995).

- **At JPL, we have previously studied MF-, EA-, MA-, EP-, and EB-based systems:**

(2) M.C. Smart, C.-K. Huang, B.V. Ratnakumar, and S. Surampudi, , Proceedings of the 37th Power Sources Conference, 239-242 (1996).

(3) M. C. Smart, B. V. Ratnakumar, S. Surampudi, Y. Wang, X. Zhang, S. G. Greenbaum, A. Hightower, C. C. Ahn, and B. Fultz., *J. Electrochem. Soc.*, **146**, 3963 (1999).

(4) M.C. Smart, B.V. Ratnakumar, S. Greenbaum, and S. Surampudi, 194th Electrochemical Society Meeting, Abst. # 159, Boston, Mass, Nov. 4, 1998.

(5) M. C. Smart, B. V. Ratnakumar, and S. Surampudi, *J. Electrochem. Soc.*, **149 (4)**, A361-A370 (2002)

- **Herreyre and coworkers have studied EA- and MB-based systems (SAFT):**
  (EC+DMC+EA, EC+DMC+MB, PC+DMC+MB)

(6) S. Herreyre, O. Huchet, S. Barusseau, F. Perton, J. M. Bodet, and Ph. Biensan, *J. Power Sources*, **97-98**, 576 (2001).

- **Shiao and coworkers have studied EA- and MA-based systems (Maxpower):**
  [EC+EMC+MA (1:1:1 v/v %) and EC+DMC+MA (1:1:1 v/v %)]

(7) H. –C. Shiao, D. Chua, H. –P., Lin, S. Slane, and M. Solomon, *J. Power Sources*, **87**, 167-173 (2000).

- **Sazhin and coworkers have studied EP- and MA-based systems (Samsung):**
  [EC–DEC–EP (30:35:35), and EC–EMC–EP (30:30:40)]

(8) S. V. Sazhin, M. Y. Khimchenko, Y. N. Tritenichenko, and H. S. Lim, *J. Power Sources*, **87**, 112-117 (2000).

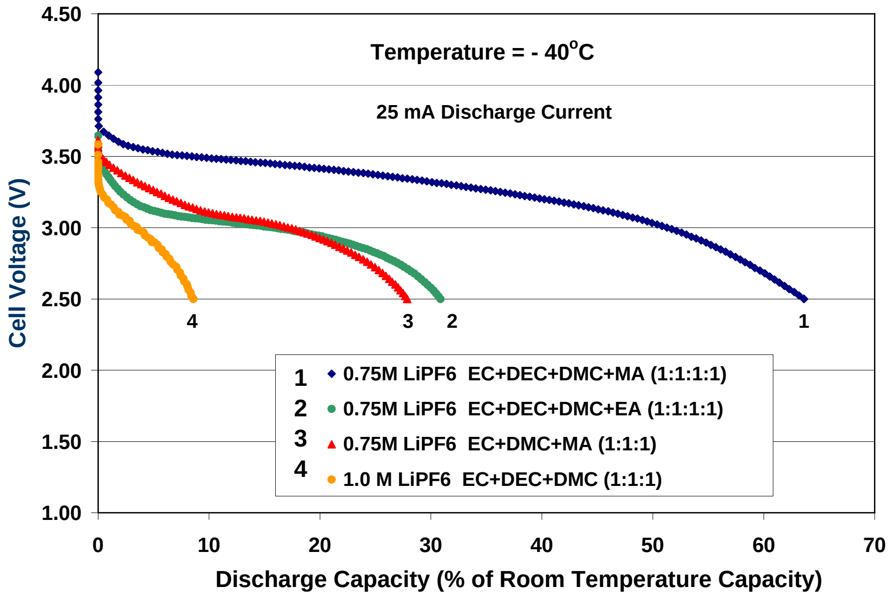
- **Jow and coworkers have studied EA- and GBL-based systems (Army Res. Lab.):**
  [LiBOB in EC–DMC-GBL–EA]

(9) T. R. Jow, K. Xu, M. S. Ding, S. S. Zhang, J. L. Allen, and K. Amine, *Journal of The Electrochemical Society*, 151, A1702-A1706 (2004).

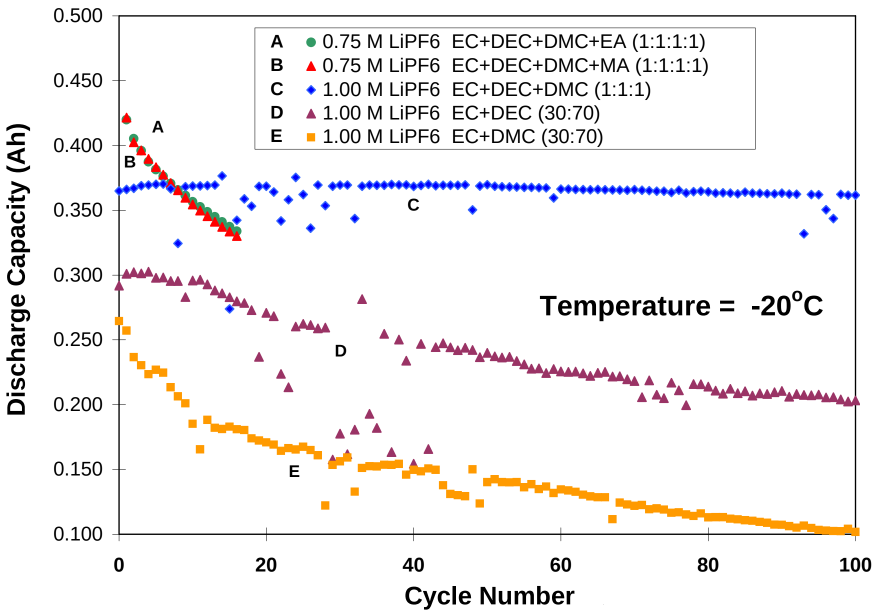
Low Temperature Performance of Ester-Based Electrolytes

Methyl Acetate and Ethyl Acetate-Containing Electrolytes

Discharge Performance at -40°C



Cycle Life Performance at -20°C



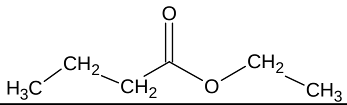
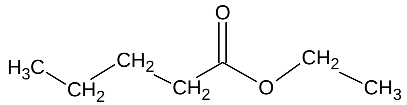
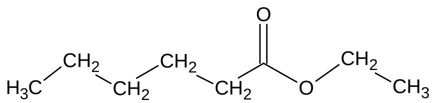
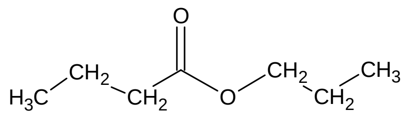
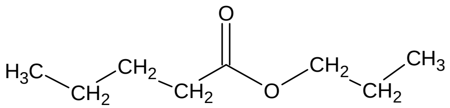
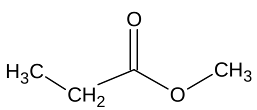
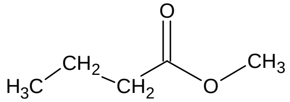
- **At very low temperatures (< - 30°C) the effect of adding a low viscosity co-solvent becomes more dramatic.**

  - **Low molecular weight ester-containing electrolytes (i.e., MA or EA) display better low temperature performance initially, however, exhibit rapid capacity fade.**

M. C. Smart, B. V. Ratnakumar, and S. Surampudi, *J. Electrochem. Soc.*, **149 (4),** A361-A370 (2002) .

Low Viscosity, Low Melting Electrolyte Co-Solvents

Candidate High Molecular Weight Ester-Based Co-Solvents

Chemical Structure	Name	m.p.	b.p	Viscosity (25°C)	Density	Dielectric Constant
	Ethyl butyrate	-93°C	120°C	0.639 cP	0.878	5.18
	Ethyl valerate	-91.2°C	145°C		0.875	4.71
	Ethyl caproate	-67°C	168°C		0.873	4.45
	Propyl butyrate	-95.2°C	143°C		0.873	4.3
	Propyl pentanoate	-70.7°C	167.5°C		0.870	4.0
	Methyl priopionate	-87.5°C	79.8°C	0.431 cP	0.915	6.200
	Methyl butyrate	-85.8°C	102.8°C	0.541 cP	0.898	5.48

Evaluation of Ester-Based Electrolytes

Experimental MCMB-$LiNi_{0.8}Co_{0.2}O_2$ Carbon Cells

- 1.0 M $LiPF_6$ EC+EMC+EV (1:1:8 v/v) EV=ethyl valerate
- 1.0 M $LiPF_6$ EC+EMC+MB (1:1:8 v/v) MB = methyl butyrate
- 1.0 M $LiPF_6$ EC+EMC+EB (1:1:8 v/v) EB = ethyl butyrate
- 1.0 M $LiPF_6$ EC+EMC+MP (1:1:8 v/v) MP = methyl propionate
- 1.0 M $LiPF_6$ EC+EMC (1:9 v/v) EMC = ethyl methyl carbonate

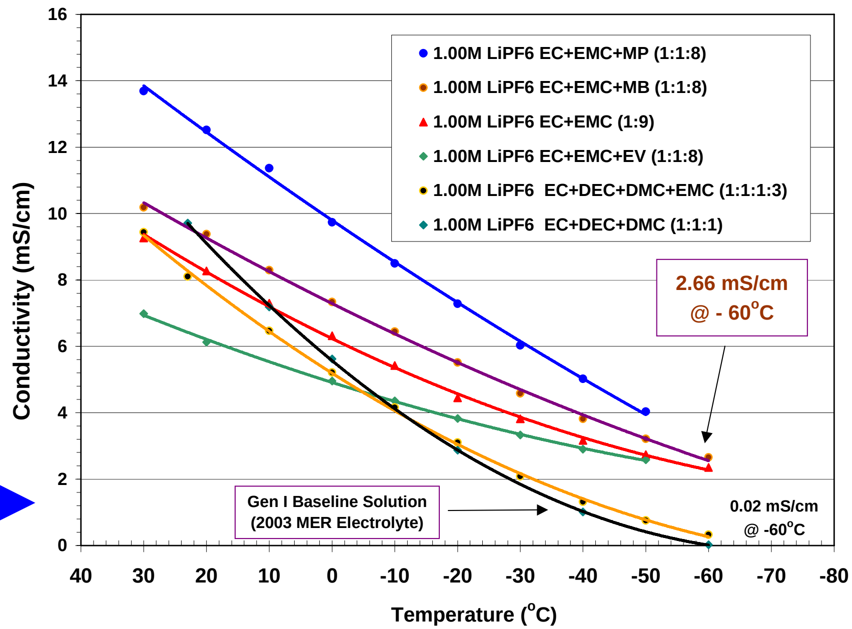
Baseline Electrolytes

- 1.0 M $LiPF_6$ EC+DEC+DMC (1:1:1 v/v) (2003 MER Baseline)
- 1.0 M $LiPF_6$ EC+DEC+DMC+EMC (1:1:1:2 v/v) (Adv. Gen)
- 1.0 M $LiPF_6$ EC+DEC+DMC+EMC (1:1:1:3 v/v) (Adv. Gen)

- MCMB Carbon-$LiNiCoO_2$ Cells
- 400-450 mAh Size Cells
- All Cells equipped psuedo Li metal reference electrodes
- Flooded electrolyte design (cylindrical cells)
- Electrochemical Characterization (EIS, Linear and Tafel Polarization)

> Demonstrated over 2 mS/cm^{-1} at –60°C with methyl propionate (MP)-based and methyl butyrate (MB)-based low temperature electrolytes.

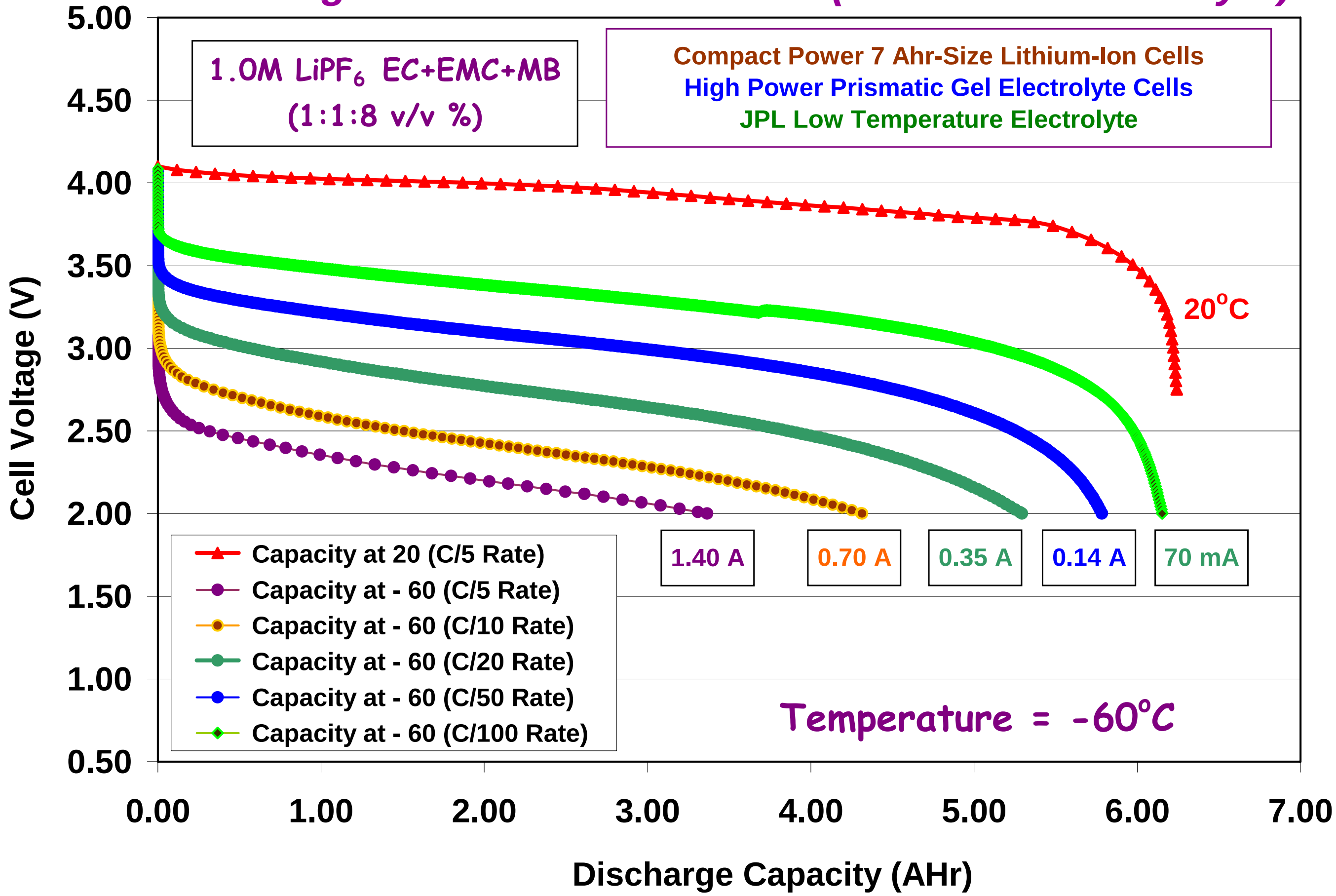
Conductivity Measurements



Performance Testing of High Rate, Gel Polymer Electrolyte Li-Ion Cells

Performance of Ester-Based Electrolytes at Low Temperatures

Discharge Performance at –60°C (MB-Based Electrolyte)



- *Nearly full capacity was delivered with the methyl-butyrate (MB)-containing electrolyte at –60°C using low rates (C/100) and still delivered ~ 85% of the room temperature capacity using higher rates (C/20).*

Other Li-Ion Electrolyte Related Research

- Development of fluorinated carbonates and carbamates
  - *Investigated a number of partially fluorinated and perfluorinated carbonates*
  - *Solvents synthesized by Prof. Surya Prakash (USC)*
  - *Solvents display good stability and enhanced safety aspects (low flammability)*
  - *Investigated in Li-MCMB and MCMB-LiNiCoO2 experimental cells*
  - *M.C. Smart, et.al. J. Power Sources, 119-121, 359-367 (2003).*
  - *M. C. Smart, et al.,11th International Meeting on Lithium Batteries (IMLB), Monterey, June 24-29, 2002.*
  - *M. C. Smart, et al., Ext. Abst. 198th Electrochemical Society Meeting, Phoenix, Arizona, , Oct. 22-27, 2000.*
- Investigation of electrolytes additives
  - *Investigated a number of electrolyte additives to improve low temperature performance*
  - *Observed improved interfacial properties and lithium intercalation/de-intercalation kinetics*
  - *Electrochemical evaluation as a function of temperature, cycling and/or high temp storage*
  - *Additives studied include: dimethl and dibutyl pyrocarbonates, vinylene carbonate, and vinyl ethylene carbonate*
  - *M. C. Smart, et. al, "The Effect of Electrolyte Additives Upon the Kinetics of Lithium Intercalation/De-Intercalation at Low Temperatures" 202nd Electrochemical Society Meeting, Salt Lake City, Utah, Oct. 20-25, 2002.*
  - *M. C. Smart, et al., "Akyl Pyrocarbonate Electrolyte Additives for Performance Enhancement of Li Ion Cells" Lithium Batteries; Proceedings of the International Symposium ,Proceedings Volume 99-25, The Electrochemical Society, 2000.*
- Effect of Electrolyte Type on High Temperature Storage Characteristics
  - *Subjected MCMB-$LiNiCoO_2$ cells to high temp. (55-75°C) with different electrolyte types*
  - *Performed electrochemical characterization in-situ (EIS, linear and Tafel polarization)*
  - *Reference electrode key to identifying performance limitations at high temperatures*
  - *Destructive physical analysis (DPA) easily performed with test cells yielding large samples*
  - *Performed ex-situ analysis of electrodes (i.e., ^{7}Li NMR…by Prof. Greenbaum at CUNY)*
  - *M. C. Smart et al. "The effect of high temperature exposure upon the performance of lithium-ion cells" J. Electrochem. Soc., In press.*
  - *M. C. Smart, et al., IEEE 17th Annual Battery Conference on Applications and Advances, Long Beach, CA, Jan. 15-18, 2002, p. 53-58.*

Conclusions

- **Developed an all carbonate ternary electrolyte enabling efficient operation over a wide temperature range.** (*1.0 M $LiPF_6$ EC+DEC+DMC (1:1:1) – GEN I)*
  - Operating temperature range = -30 to +40°C
  - *Incorporated into 2001 Mars Surveyor Lander (25 Ah battery, space qualified)*
  - *Incorporated into 2003 Mars Exploration Rover (10 Ah battery, space qualified)*

- **Developed all carbonate quaternary electrolytes enabling efficient operation over a wide temperature range.**
  - Operating temperature range = -50 to +40°C
  - *1.0 M $LiPF_6$ EC+DEC+DMC+EMC (1:1:1:2) – GEN II)*
  - *1.0 M $LiPF_6$ EC+DEC+DMC+EMC (1:1:1:3) – GEN III)*
  - *Demonstrated in a number of prototype designs (SAFT, Compact Power, MER)*
  - *Demonstrated over 114 Wh/kg at –20°C using a C/2 discharge rate (SAFT DD)*
  - *Demonstrated over 90 Wh/kg at –40°C using a C/2 discharge rate(SAFT DD)*
  - *Demonstrated over 98% of RT Capacity at –40°C (C/10) (Compact Power)*

- **Developed ester-based electrolytes enabling operation at ultra-low temperatures**
  - *1.0 M $LiPF_6$ EC+EMC+MB (1:1:8) – GEN III*
  - *1.0 M $LiPF_6$ EC+EMC+EB (1:1:8) – GEN III*
  - Operating temperature range = -80 to +40°C
  - *Demonstrated in a high power, gel polymer electrolyte cells (Compact Power)*
  - *Demonstrated over 85% of RT Capacity at –60°C using a C/20 discharge rate*
  - *Demonstrated operational capability down to –80°C*

Possible Areas of Collaboration Between JPL and DOE

- Prototype cell and battery testing
  - *JPL possesses five Maccor test systems, two Arbin test systems, and ~15 environmental chambers,*
  - *Capable of testing 0.100 Ah to 50 Ah cells/batteries*
  - *40 V, 45 A Testing capability*

- Electrochemical evaluation of DOE developed chemistries
  - Three electrode experimental cell fabrication (contains lithium reference electrodes)
  - Test vehicle = 300-400 mAh jelly roll design (also possess coin cell fabrication capability)
  - Electrochemical evaluation as a function of temperature, cycling and/or high temp storage
    - Electrochemical Impedance Spectroscopy (EIS)
    - Linear micro-polarization measurements
    - Tafel polarization measurements
    - Charge and discharge performance
  - Identify performance limitations and failure mechanisms
  - DPA performed easily with three electrode test vehicle yielding large samples

- Electrochemical evaluation of DOE developed electrodes with JPL electrolytes
  - Investigate use of previously developed electrolytes with DOE electrodes
  - Study the impact of high temperature exposure on performance.
  - Develop improved electrolytes with enhanced high temperature stability and life characteristics
  - Develop improved electrolytes with enhanced low temperature rate capability.

Acknowledgments

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