Development of low-temperature electrolytes for Lithium-ion batteries

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Outline

- Introduction
- Approach/Background
- Overview of Electrolyte Development
- Wide Operating Temperature Electrolytes
  - Early Generation Ternary Electrolyte (-20 to +40°C)
  - Quaternary Carbonate-Based Electrolytes (-40 to +40°C)
  - Use of High Proportions of Ester-Based Co-Solvents (-80 to +40°C)
  - Use of Low Proportions of Ester Co-Solvents (-60 to +40°C)
  - Use of Medium Proportions of Ester Co-Solvents with Electrolyte Additives to Improve the High Temperature Resilience (-60 to +60°C)
  - Development of High Temperature Electrolytes
- Conclusions

Outline

- DOE desires Li-ion batteries than can operate over a wide temperature range *(i.e., -30 to +60°C)*. and provide good life characteristics for HEV and PHEV applications
- NASA also desires Li-ion batteries than can operate over a wide temperature range for future planetary lander and rover applications.

Objectives and Approach

- *Develop advanced Li-ion electrolytes that enable cell operation over a wide temperature range (i.e., -60 to +60°C).*
- Improve the high temperature stability and lifetime characteristics of wide operating temperature electrolytes.
- Define the performance limitations at low and high temperature extremes, as well as, life limiting processes.
- Demonstrate the performance of advanced electrolytes in large capacity prototype cells.

Why Battery Performance Degrades at Low Temperatures?

- Increased cell and electrode polarizations in general
  - Ohmic, kinetic as well as mass transfer
- Increased Ohmic polarization
  - Mainly contributed by the electrolyte
    - Reduced Ionic mobility in electrolyte.
      - Slow diffusion of ions mainly due to increased viscosity of solvent components
    - Reduced ionic strength due to lower solubility at low temperatures.
- Slower electrode kinetics
  - Slower charge transfer at the electrodes governed by Arrhenius dependence.
  - Charge-transfer over film-covered electrodes?
- Enhanced mass transfer polarization
  - Slow diffusion of (Li^+) ion in solution caused by increased electrolyte viscosity
  - Slower diffusion of reactant/product species in the electrode lattices (bulk diffusion).
  - Surface films complicating the charge transfer and diffusion process.
- Likelihood of lithium plating is possible at high charge rates at low temperatures

Low Temperature Lithium Ion Electrolytes
Electrolyte Development: Approach/Background
General Approaches to Improve Low Temperature Performance of SOA Electrolytes

- Optimization of linear carbonate type and concentration
- Optimization of cyclic carbonate concentration (i.e., EC content)
- Use of aggressive low viscosity co-solvents
- Optimization of electrolyte salt type and concentration
- Use of "SEI promoting" additives

- These approaches are often used in conjunction to achieve desired result.
- In addition, the specific application can influence low temperature electrolyte selection (i.e., low temperature requirement, life requirement, or the need for high temperature resilience, etc.).

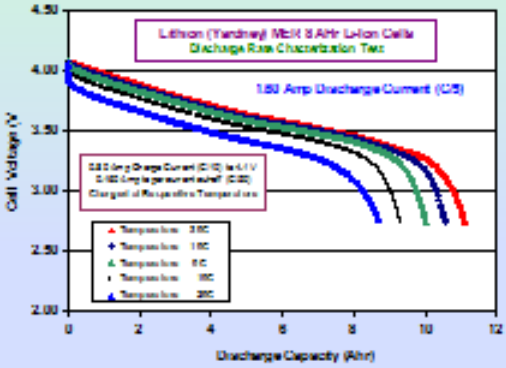
Low Temperature Lithium Ion Cells and Batteries
Performance Summary of Early Generation Low Temperature Li-Ion Electrolytes Developed at JPL

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)	-50°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 Specific Energy (Wh/kg)	-20 to +40°C	-40 to +40°C	-60 to +40°C	-80 to +25 C (Goals)
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 2001 Lander MER 2003 Rover Phoenix 2007 Lander 2011 Grail Mission 2011 Juno Mission MSL 2011 Lander	Future Mars Landers and Rovers	Future Mars Landers and Rovers	Future Mars Surface Operations

Specific energy values dependent upon prototype cell type and size

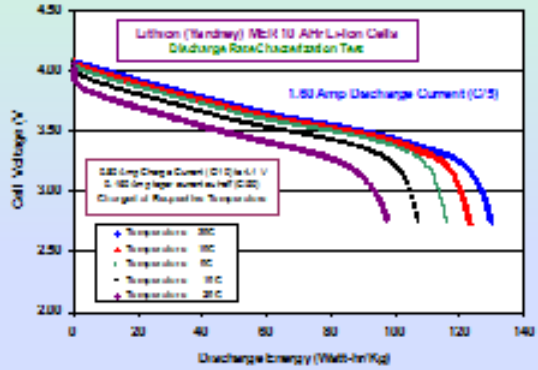
Lithion 8 Ah Li-Ion Cells for Mars Exploration Rover (MER)
Discharge Rate Characterization at Various Temperatures
(C/5 Discharge Rate = 1.60 Amps)

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)



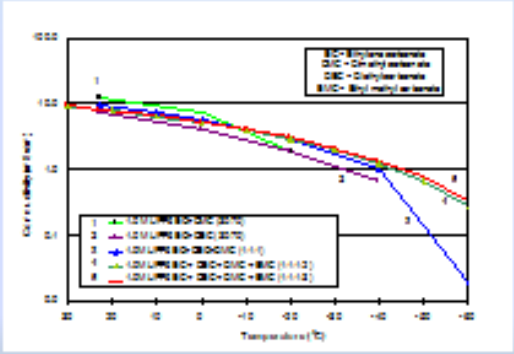
	Energy (WHr/Kg)	% of RT
30 C	129.77	100.00
10 C	123.81	95.25
0 C	118.60	89.77
-10 C	107.36	82.72
-20 C	97.60	75.13

Cells contain 1.0M $LiPF_6$-EC+DMC+DEC (1:1:1) (Range of operation –30 to +40°C)

- ***Low EC All Carbonate-Based Electrolytes***
  - *Robust electrolytes*
  - *Generally provide long life characteristics*
  - *Wide operating temperature range*
  - *Limited high rate capability at low temperatures*

1.0 M $LiPF_6$ EC+DEC+DMC (1:1:1 v/v) (JPL)
1.0 M $LiPF_6$ EC+DMC+EMC (1:1:1: v/v) (ARMY)
1.2 M $LiPF_6$ EC:EMC (30:70 v/v) (Covalent/DOE)

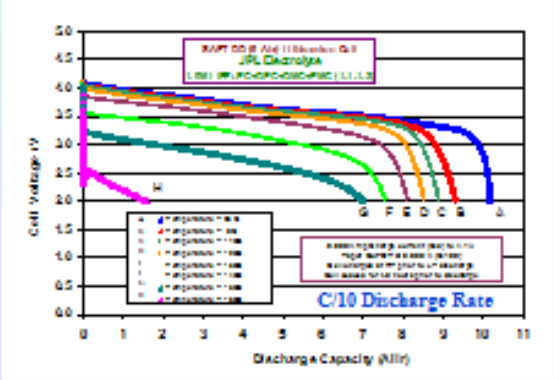
1.0 M $LiPF_6$ EC+DEC+DMC+EMC (1:1:1:2 v/v)
1.0 M $LiPF_6$ EC+DEC+DMC+EMC (1:1:1:3 v/v)
1.0 M $LiPF_6$ EC+DEC+DMC+EMC (1:1:1:4 v/v)
1.0 M $LiPF_6$ EC+ DMC+EMC (15:15:70 v/v)
0.6 M $LiPF_6$ EC+DEC+DMC+EMC (1:3:3:3 v/v)



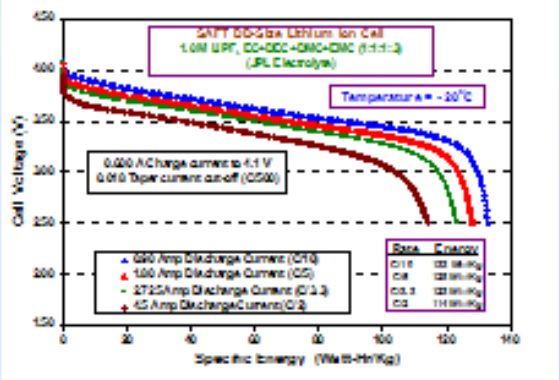
Performance Testing of SAFT DD-Size Lithium-Ion Cells

Cell Performance at Low Temperatures: JPL Electrolyte

Discharge Capacity (C/10 Rate)



Rate Capability at -20°C



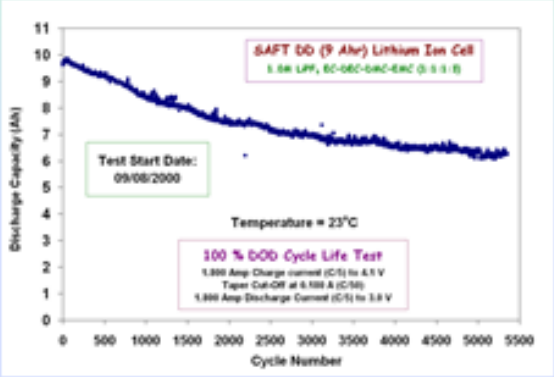
- Low ethylene carbonate-based electrolytes result in improved low temperature rate capability.

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).

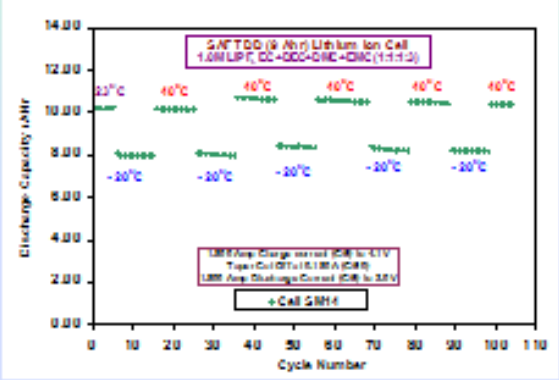
Performance Testing of SAFT DD-Size Lithium-Ion Cells

Prototype cells containing low temperature electrolytes

100% DOD Cycle Life Performance



Variable Temperature Cycling

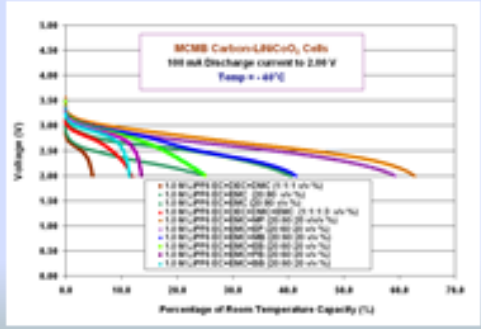


- Cell has been on test over 6 years !!
- Cell contains low EC-content electrolytes.
- Cells have been demonstrated to provide good low temperature performance (e.g., over 90 Wh/kg delivered at -40°C with a C/10 discharge rate)

- ***Low EC Electrolytes with Low Ester Content***
  - *20 % EC Content, 20% Ester Content*

  - *Improved conductivity at low temperature*
  - *Improved resilience to high temperature exposure compared to solutions with higher ester content*
  - *Wide operating temperature range*
  - *Good rate capability at low temperatures*

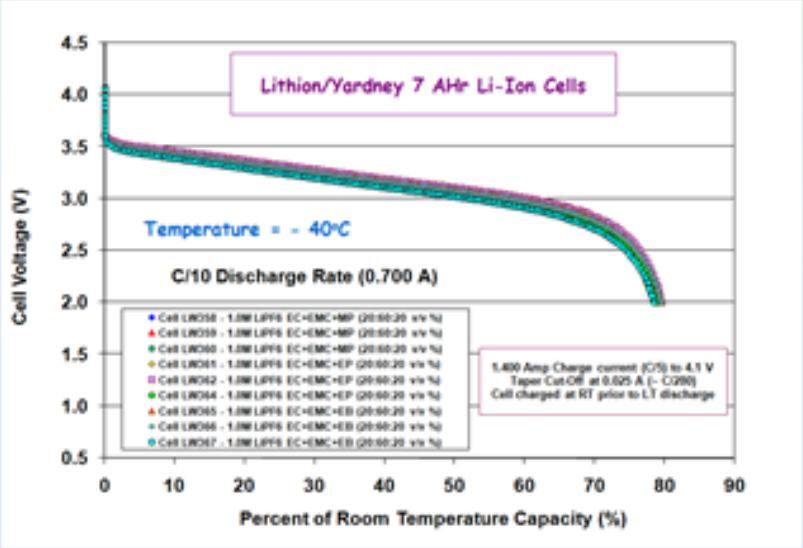
1.0 M $LiPF_6$ EC+EMC+MP (20:60:20 v/v) MP = methyl propionate
1.0 M $LiPF_6$ EC+EMC+EP (20:60:20 v/v) EP = ethyl propionate
1.0 M $LiPF_6$ EC+EMC+MB (20:60:20 v/v) MB = methyl butyrate
1.0 M $LiPF_6$ EC+EMC+EB (20:60:20 v/v) EB = ethyl butyrate
1.0 M $LiPF_6$ EC+EMC+PB (20:60:20 v/v) PB = propyl butyrate
1.0 M $LiPF_6$ EC+EMC+BB (20:60:20 v/v) BB = butyl butyrate



Yardney 7 Ah Prototype Cells with Advanced Electrolytes

Low Temperature Discharge Performance at -40°C (C/10 Rate)

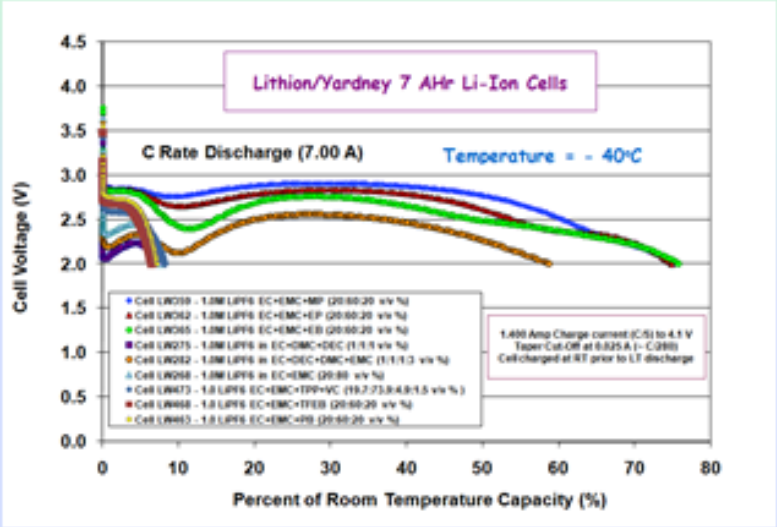
Discharge Capacity (Ah, % of Room Temperature)



M. C. Smart, B. V. Ratnakumar, K. B. Chin, and L. D. Whitcanack, *J. Electrochem. Soc.*, 157 (12), A1361-A1374 (2010).

Yardney 7 Ah Prototype Cells with Advanced Electrolytes

Low Temperature Discharge Performance at -40°C (C Rate)

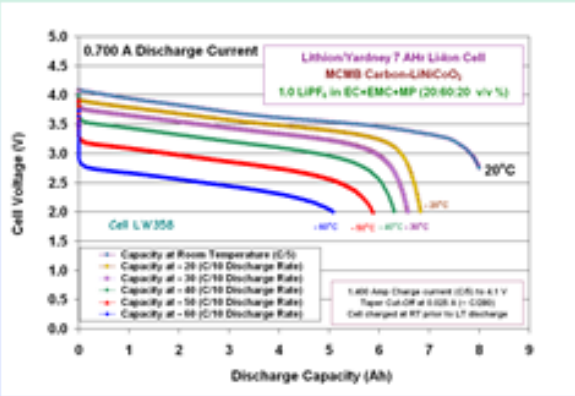


Discharge capacity (Ah) and discharge energy (Wh/Kg) at -40°C, using a C rate discharge (7 A), of prototype 7 Ah lithium-ion cells containing electrolytes consisting of 1.0M $LiPF_6$ EC+EMC+X (20:60:20 v/v%) (where X = MP, EP, EB, PB, TFEB), as well as cells with baseline all carbonate-based electrolytes.

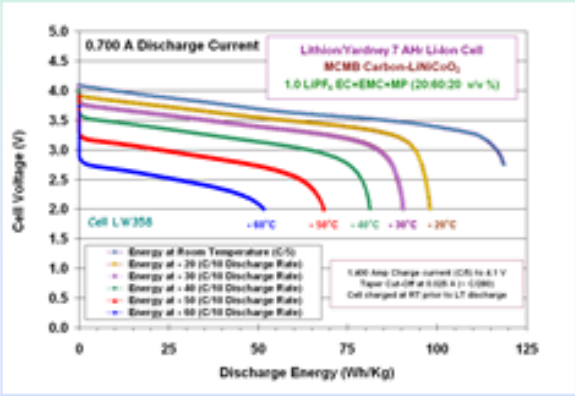
Yardney 7 Ah Prototype Cells with Advanced Electrolytes

Low Temperature Discharge Performance of Prototype Cells

Discharge Capacity (Ah)



Discharge Energy (Wh/Kg)



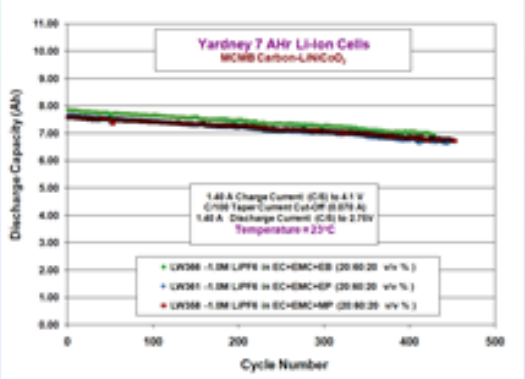
- Cells containing the methyl propionate-based electrolyte were observed to perform well down to -60°C using a C/10 discharge rate.

Yardney 7 Ah (NCP7) Prismatic Li-Ion Cells

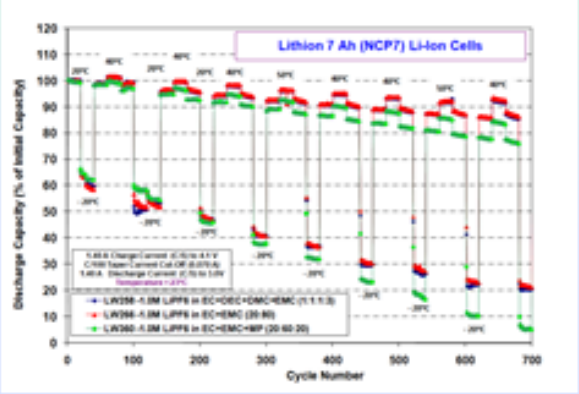
Characterization of Cells Containing Advanced Electrolytes

100 % DOD Cycle Life Testing

Discharge Capacity (Ah,%) at 20°C



Variable Temperature Cycling



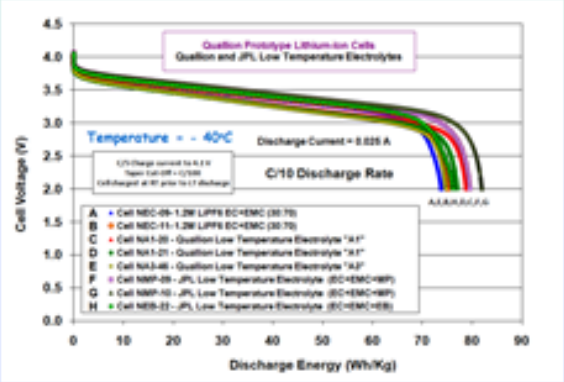
- Ester-based electrolytes have been observed to display generally good cycle life characteristics.
- Variable temperature cycling between a wide range of temperatures (i.e., +50°C to -20°C) represents a stressful test resulting in decreased low temperature capabilities.
- The ester-based solutions display decreased tolerance to high temperature excursions.

- ***Low EC Electrolytes with Medium Ester Content***
  - *20 % EC Content, 60% Ester Content*
  - *Excellent conductivity at low temperature*
  - *Reasonable resilience to high temperature exposure compared to solutions with higher ester content and lower EC content*
  - *Wide operating temperature range*
  - *Excellent rate capability at low temperatures*
  - *Solutions optimized to give high rate capability at low temperature without impacting life dramatically.*

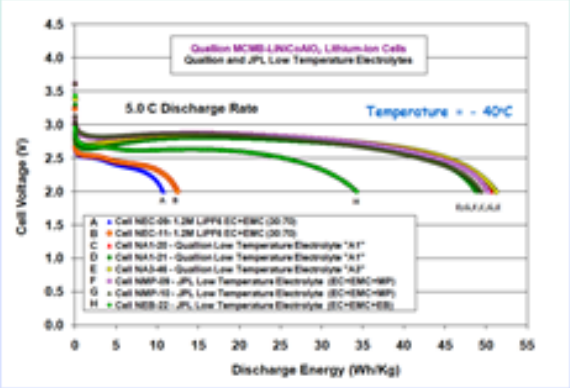
1.2 M $LiPF_6$ EC+EMC+MP (20:20:60 v/v) MP = methyl propionate
1.2 M $LiPF_6$ EC+EMC+EP (20:20:60 v/v) EP = ethyl propionate
1.2 M $LiPF_6$ EC+EMC+MB (20:20:60 v/v) MB = methyl butyrate

Quallion Prototype Li-Ion Cells
Wide Operating Temperature Electrolytes
Discharge Characterization at Various Temperatures

C/10 Discharge at -40°C



5C Discharge at -40°C !!



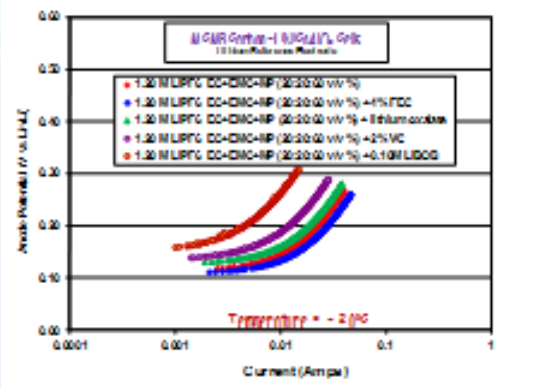
- In collaboration with Quallion, excellent low temperature rate capability has been demonstrated with advanced electrolytes.

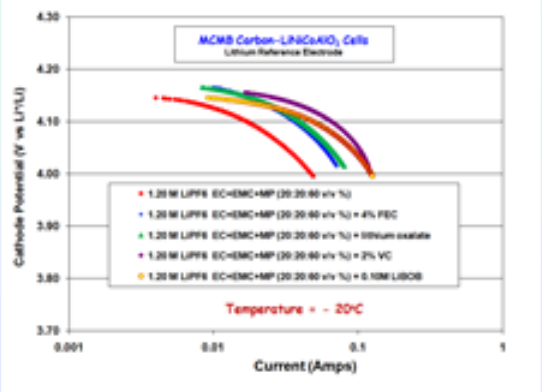
- ***Low EC Electrolytes with Medium Ester Content and the use of Electrolyte Additives***
  - *20 % EC Content, 60% Ester Content*
  - *Excellent conductivity at low temperature*
  - *Improved resilience to high temperature exposure compared to solutions with higher ester content and lower EC content*
  - *Wide operating temperature range*
  - *Improved rate capability at low temperatures*
  - *Solutions optimized to give high rate capability at low temperature without impacting life dramatically.*

1.2 M $LiPF_6$ EC+EMC+MP (20:20:60 v/v) + 2% FEC
1.2 M $LiPF_6$ EC+EMC+MP (20:20:60 v/v) + 4% FEC
1.2 M $LiPF_6$ EC+EMC+MP (20:20:60 v/v) + lithium oxalate
1.2 M $LiPF_6$ EC+EMC+MP (20:20:60 v/v) + 2% VC
1.2 M $LiPF_6$ EC+EMC+MP (20:20:60 v/v) + 0.10M LiBOB

1.2 M $LiPF_6$ EC+EMC+MB (20:20:60 v/v) + 2% FEC
1.2 M $LiPF_6$ EC+EMC+MB (20:20:60 v/v) + 4% FEC
1.2 M $LiPF_6$ EC+EMC+MB (20:20:60 v/v) + lithium oxalate
1.2 M $LiPF_6$ EC+EMC+MB (20:20:60 v/v) + 2% VC
1.2 M $LiPF_6$ EC+EMC+MB (20:20:60 v/v) + 0.10M LiBOB

Experimental lithium-ion cells (MCMB-$LiNiCoAlO_2$) fabricated with **methyl propionate**–based electrolytes containing various additives.





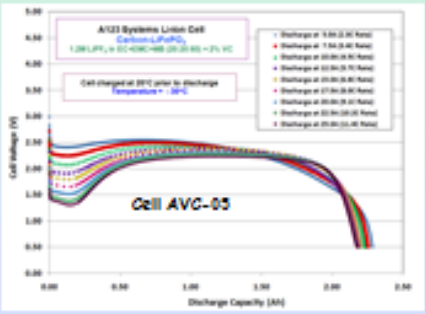
- **Promising electrolyte additives were explored in a wide operating temperature range solvent systems (EC+EMC+MP) with the intent of improving high temperature resilience**

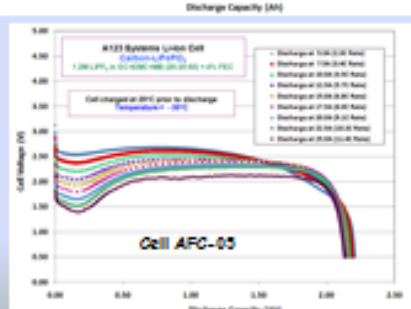
- *FEC was observed to enhance the lithium kinetics of the MCMB anode, whereas the other additives appeared to impede the kinetics (especially LiBOB).*
- *VC and LiBOB were observed to most dramatically enhance the kinetics of the cathode at low temperatures. All additives appeared to improve the kinetics somewhat.*

A123 2.20 Ah High Power Lithium-Ion Cells

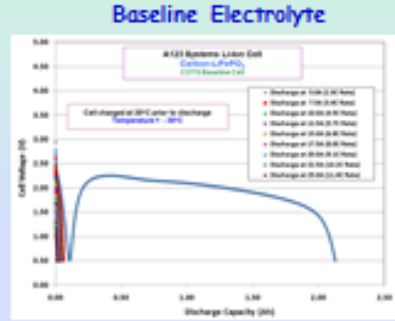
Discharge Rate Characterization Testing

Temperature = -30°C; Cells Discharged to 0.50V





Baseline Electrolyte



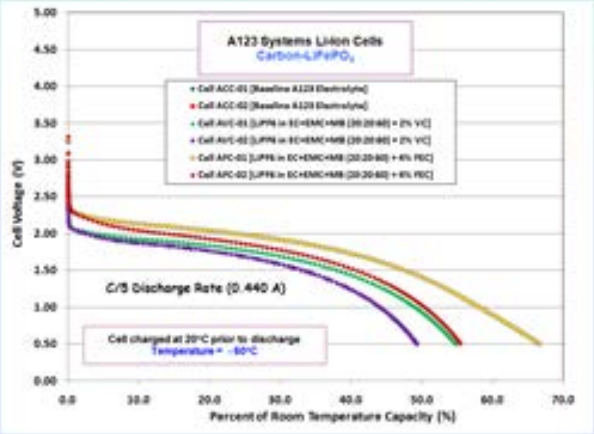
- The MB-based systems are capable of supporting greater than 11C discharge rates at -30°C, with over 90% of the room temperature capacity being delivered.
- Whereas, negligible capacity delivered with the baseline system under similar conditions.

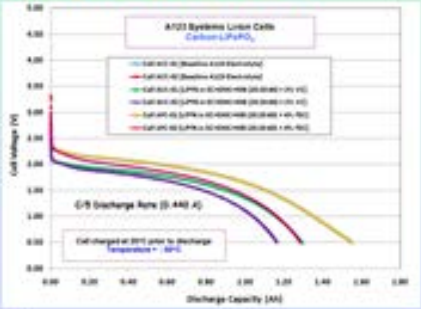
M. C. Smart, A. S. Gozdz, L. D. Whiteanack, and B. V. Ratnakumar, "Improved Wide Operating Temperature Range of High Rate Nano-Lithium Iron Phosphate Li-Ion Cells with Methyl Butyrate-Based Electrolytes", 220th Meeting of the Electrochemical Society, Boston, MA, October 11, 2011.

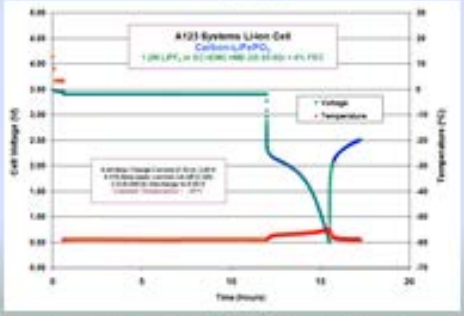
A123 2.20 Ah High Power Lithium-Ion Cells

Discharge Rate Characterization Testing

Temperature = -60°C; Rate = C/5; Cells Discharged to 0.50V







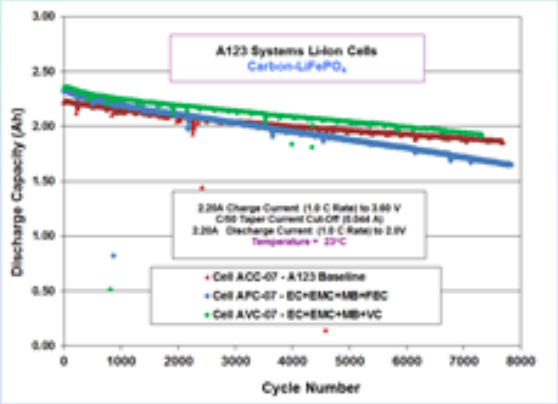
ELECTROCHEMICAL TECHNOLOGIES GROUP

A123 2.20 Ah High Power Lithium-Ion Cells

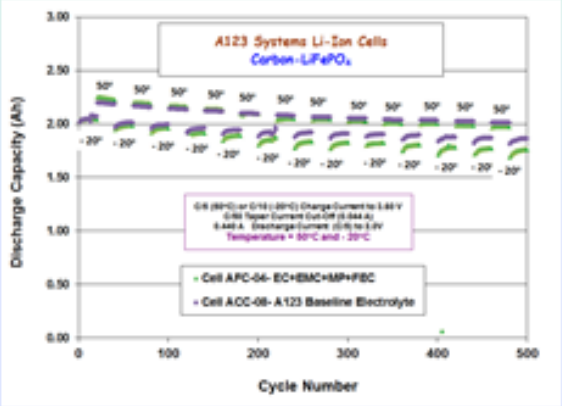
100% DOD Cycle Life Characterization Testing

Test Articles (Three Different Electrolyte Variations)

Cycle Life Performance at 23°C



Variable Temperature Performance



- Although modestly higher capacity fade rates were observed with the MB-based electrolytes compared with the baseline, generally good cycle life characteristics were observed (i.e., over 90% of the initial capacity after 7,000 cycles).
- Observed trend (in increasing capacity fade rate): Baseline < MB+VC < MB+FEC

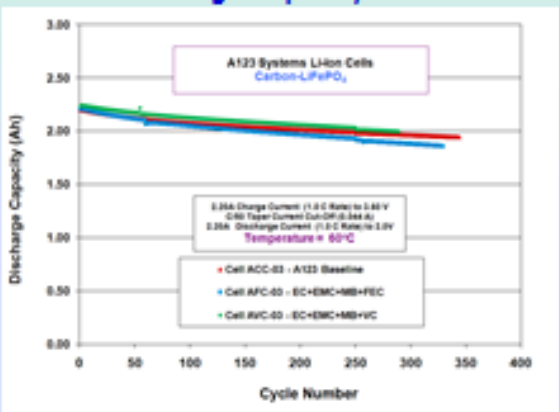
ELECTROCHEMICAL TECHNOLOGIES GROUP

A123 2.20 Ah High Power Lithium-Ion Cells

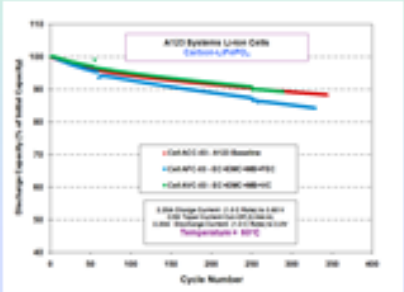
100% DOD Cycle Life Characterization Testing at 60°C

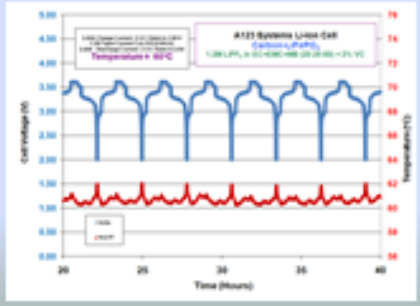
Test Articles (Three Different Electrolyte Variations)

Discharge Capacity at 60°C



Percent of Initial Capacity at 60°C





- Good performance has been demonstrated thus far when cycling continuously at +60°C
- SOA aerospace cells do not operate well at such temperatures without rapid capacity fade with the possibility of venting.

SUMMARY and CONCLUSIONS

- *Wide Operating Temperature Electrolytes Demonstrated in Various Prototype Cells*
  - *A number of ester containing electrolytes have been evaluated in various chemistries (i.e., NCO, NCA, NCM, LFP)*
  - *The lower molecular weight esters provide higher electrolyte conductivity and low temperature capability, however, there is some diminished high temperature resilience.*
  - *Higher proportions of ester co-solvent result in greater low temperature capability.*
  - *A number of additives, including FEC, VC, and LiBOB were observed to improved the electrode kinetics at low temperature and lead to improved high temperature resilience.*
- *Performance of A123 Cells Containing Low Temperature Electrolytes*
  - *Excellent performance demonstrated down to -60°C.*
  - *While charging at -30oC, cells were demonstrated to be able to support 5C discharge rates.*
  - *Best low temperature performance generally exhibited by electrolyte solution containing a low proportion of EC and high proportion of MB, however, this chemistry was observed to degrade when exposed to high temperatures.*
  - *The MB-based solutions containing higher EC-content displayed improved low temperature performance, while still providing reasonable life characteristics.*
  - *The all carbonate-based solutions displayed reasonable performance enhancement at low temperature, while providing the best resilience to high temperature.*

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