Electrolytes for Use in High Energy Lithium-Ion Batteries with Wide Operating Temperature Range

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DOE-ABR/BATT Annual Meeting Review

Arlington, Virginia

May 14, 2013

Project ID = ES026

Overview

Timeline

- Start Date = October 2009
- End Date = October 2014
- Percent complete = ~ 70%

Budget

- Total project funding
  - 875K total (~ 175K/year)
  - Contractor share = 0K
- Funding received

FY'10 = 175K

FY'11 = 175K

FY'12 = 170K

FY'13 = 170K

Barriers

- Barriers addressed
  - Enhance low temperature performance
  - Define performance limitations that limit life
  - Develop long life systems stable at high voltage

Partners

- **Univ. Rhode Island (Brett Lucht)**
  (Analysis of harvested electrodes, on-going collaborator)
- **Argonne Nat. Lab (Khalil Amine)**
  (Source of electrodes, on-going collaborator)
- **LBNL (John Kerr, Li Yang)**
  (Evaluation of novel salts)
- **Loker Hydrocarbon Institute, USC (Prof. Surya Prakash)**
  (Fluorinated Solvents and novel salts)
- **North Carolina State Univ, NCSC (Prof. Wesley Henderson)**
  (novel salts and electrolytes)
- **A123 Systems, Inc.**
  (Electrolyte development, on-going collaborator)
- **Quallion, LCC**.
  (Electrolyte development, on-going collaborator)
- **Yardney Technical Products**
  (Electrolyte development, on-going collaborator)
- **Saft America, Inc.**
  (Collaborator, industrial partner under NASA program)
- **NREL (Smith/Pesaran)**
  (Supporting NREL in model development by supplying data)
- **Hunter College/CUNY (Prof. Steve Greenbaum)**
  (Analysis of harvested electrodes)
- **Sandia National Lab (Orendorff/Nagasubramanian)**

Objectives

- **Develop advanced Li-ion electrolytes that enable cell operation over a wide temperature range (i.e., -30 to +60°C).**
- **Improve the high temperature stability and lifetime characteristics of wide operating temperature electrolytes.**
- **Improve the high voltage stability of these candidate electrolytes systems to enable operation up to 5V with high specific energy cathode materials.**
- **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.**

Milestones

Month/Year	Milestone or Go/No-Go Decision
Sept. 2013	Milestone: Prepare and characterize experimental laboratory cells containing advanced electrolytes, designed to operate over a wide temperature range in high-voltage systems (i.e., $LiNiMnCoO_2$), and identify performance-limiting characteristics. (Sept. 13)
Sept. 2013	Milestone: Demonstrate improved performance of experimental and prototype cells with next generation electrolytes over a wide temperature range (-30° to +60°C) compared with baseline electrolytes. (Sept. 13)

Technical Approach

- **Electrolyte Development Approach:**
  - Optimization of carbonate solvent blends
  - Use of low viscosity, low melting ester-based co-solvents
  - Use of fluorinated esters and fluorinated carbonates as co-solvents
  - Use of "SEI promoting" and thermal stabilizing additives
  - Use of novel, alternative lithium based salts (with USC, LBNL)
- **Electrolyte Characterization Approach:**
  - Ionic conductivity and cyclic voltammetry measurements
  - Performance characteristics in 300-400 mAh three electrode cells
    - MCMB/$LiNi_{0.8}Co_{0.2}O_2$, MCMB/$LiNi_{0.8}Co_{0.2}AlO_2$, Graphite/$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$, and Graphite/LLC-$LiNiCoMnO_2$
    - Use of high specific energy electrode materials (from in-house NASA program and DOE)
    - Electrochemical Impedance Spectroscopy (EIS) Measurements as function of temperature, high temperature storage, and cycle life
    - DC Tafel and linear (micro) polarization measurements on electrodes
    - Ex-situ analysis of harvested electrodes (URI and Hunter College)
  - Performance characteristics in coin cells
    - Evaluation of electrolytes in conjunction with high voltage cathodes
- **Performance evaluation in prototype cells**
  - Yardney, A123, Saft, and/or Quallion Cells (0.300 mAh to 12 Ah size prototype cells)
  - Cells will be procured and/or obtained through on-going collaborations

Summary of Technical Accomplishments

1) **Demonstrated improved low temperature performance with methyl propionate-based electrolytes (i.e., methyl propionate) in Quallion 12 Ah prototype cells.**
   - Demonstrated wide operating temperature performance in large capacity (12 Ah) cells containing methyl propionate-based electrolytes (with and without FEC as additive).
   - Excellent performance was observed down to temperatures as low as -50°C, with over 75% of the room temperature capacity being delivered up to 2C rates with both formulations.
   - Completed 200 cycles (equivalent to 200 sols of surface operation) with 12 Ah Quallion NCA cells, with periodically characterizing the cells for capacity, low temperature capability (down to -50°C), and impedance.
   - The addition of FEC is observed to improve the preservation of low temperature capability throughout life.

2) **Demonstrated improved wide operating temperature range performance of Quallion prototype 0.25Ah cells using methyl propionate-based electrolytes:**
   - Performed a number of characterization tests on Quallion prototype 0.25Ah cells with methyl propionate-based electrolyte possessing varying FEC content and LiBOB as an additive.
   - All electrolytes are observed to provide improved performance at high rates at very low temperatures compared with the baseline electrolytes, with the cells containing LiBOB as an additive outperforming all formulations.
   - At a 20C discharge rate at -20°C, the cell containing the MP-based electrolyte delivered over 11 times greater discharge energy compared with the baseline (i.e., 62.2 Wh/kg vs. 5.5 Wh/kg).

Summary of Technical Accomplishments

2) Prototype 0.25Ah cells using methyl propionate-based electrolytes (Continued) :

- Thus far, the cells containing the MP-based wide operating temperature range electrolytes provide good life at 20^{o}C (100% DOD), with somewhat lower capacity displayed initially.
- At ambient temperatures, no degradation was observed when FEC was added to the electrolyte in high proportion (10 or 20%), even if present as the only cyclic carbonate.
- The cell containing LiPF6 in FEC+EMC+MP was observed to deliver > 99.5% of the initial capacity after completing 1,600 cycles (100% DOD).
- When the cells containing the MP-based wide operating temperature range electrolytes were cycled at 50^{o}C, the electrolyte with FEC added in high proportion (20%), provided the best performance.

3) Performance demonstration of $LiFePO_4$-based cells (A123) using JPL developed methyl butyrate-based electrolytes:

- Cells containing 1.2M $LiPF_6$ EC+EMC+MB (20:20:60) with the addition of 4% FEC or 2% VC demonstrated to have wide operating temperature range (i.e., -60^{o}C to +60^{o}C).
- The cells were observed to support > 11C rates at -40^{o}C (>90% of RT capacity).
- Impressive life characteristics are observed at 23^{o}C, with ~ 8,000 cycles being demonstrated (100 % DOD cycling). The methyl butyrate-based electrolytes delivers comparable performance to the baseline electrolyte (> 81% of the initial capacity after 8,000 cycles).
- Cells containing the JPL developed electrolytes demonstrate good preservation of the low temperature capability after being subjected to high temperature (i.e., +50^{o}C).

Summary of Technical Accomplishments

4) **Evaluated a number of methyl butyrate-based electrolytes in Conoco A12 Graphite/Toda HE5050LiNiCoMnO_2 three electrode cells (Argonne materials):**

- The MB-based formulations containing LiBOB delivered the best rate capability at low temperature, which is attributed to improved cathode kinetics. Whereas, the use of lithium oxalate as an additive lead to the highest reversible capacity and lower irreversible losses.
- At lower temperature and higher rates, the advantages of utilizing the high voltage system diminishes when compared a standard NCA material, again attributed to the relative cathode kinetics.
- When EIS measurements were performed each electrode (using 3-electode cells), both the NCA and NMC electrodes dominated the cell impedance. The LLC-NMC electrodes displayed much slower lithium de-intercalation kinetics compared to the NCA electrodes (attributed to poor charge transfer resistance of the electrodes).

5) **Other Activities/Accomplishments:**

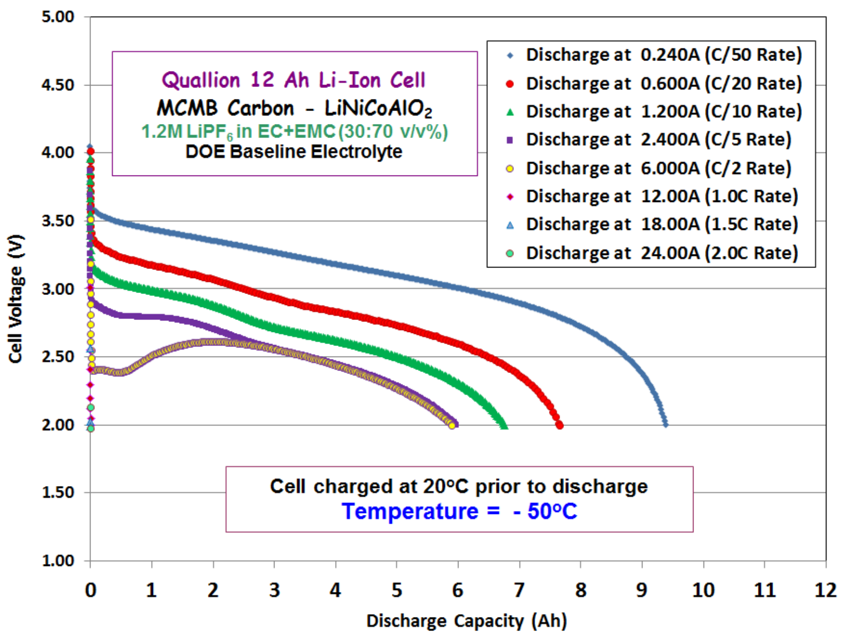
- Evaluated a number of Conoco Graphite/$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ cells containing electrolytes with low flammability that were developed under a NASA-funded program in collaboration with Sandia National Labs (Orendorff and Nagasubramanian).
- Collaborated with NREL (Kandler Smith) by providing long-term A123 test data generated at JPL of commercial of the shelf (COTS) cells subjected to partial DOD cycling.
- Collaborated with Prof. Steve Greenbaum of Hunter College, who performed multi-nuclear NMR studies on electrodes harvested from cells containing MB-based electrolytes.
- Collaborated with Prof. Lucht of Univ. of Rhode Island, who performed ex-situ analysis on electrodes harvested from cells containing MB-based electrolytes.
- Supported Prof. Wesley Henderson’s group in the evaluation of concentrated high voltage electrolytes. Initiated a separate study involving the evaluation of alternate lithium-based electrolytes salts.

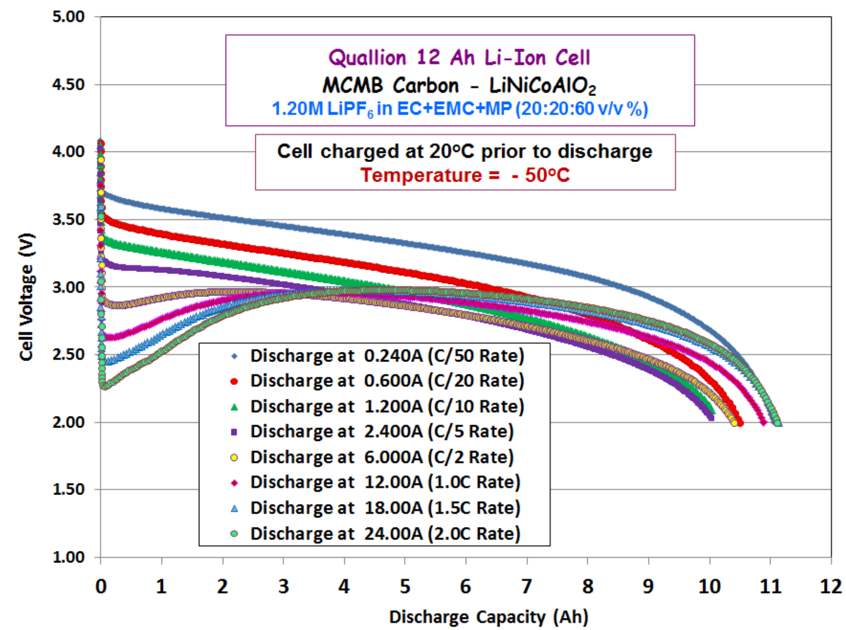
Technical Accomplishments

Quallion Prototype 12 Ah Li-Ion Cells

Wide Operating Temperature Electrolytes

Discharge Characterization at Various Temperatures





- **Performance of methyl propionate based electrolytes demonstrated in large capacity 12 Ah cells.**
- **Improved power capability demonstrated with methyl propionate-based electrolytes over a wide temperature range (able to support 2C rates down to -60°C), outperforming the baseline electrolyte under these conditions.**
- **Currently performing life tests (~ 50% DOD) in which the capacity, impedance, and rate capability at low temperature is measured periodically (every 100 days).**

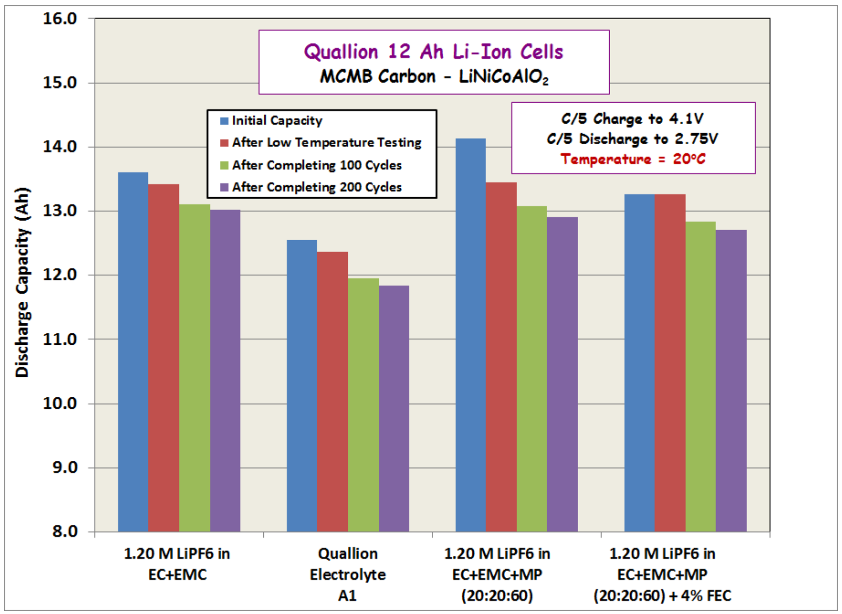
➢ *Quallion collaboration supported by NASA SBIR Program.*
(H. Tsakamoto, M. Tomcsi, M. Nagata, and V. Visco)

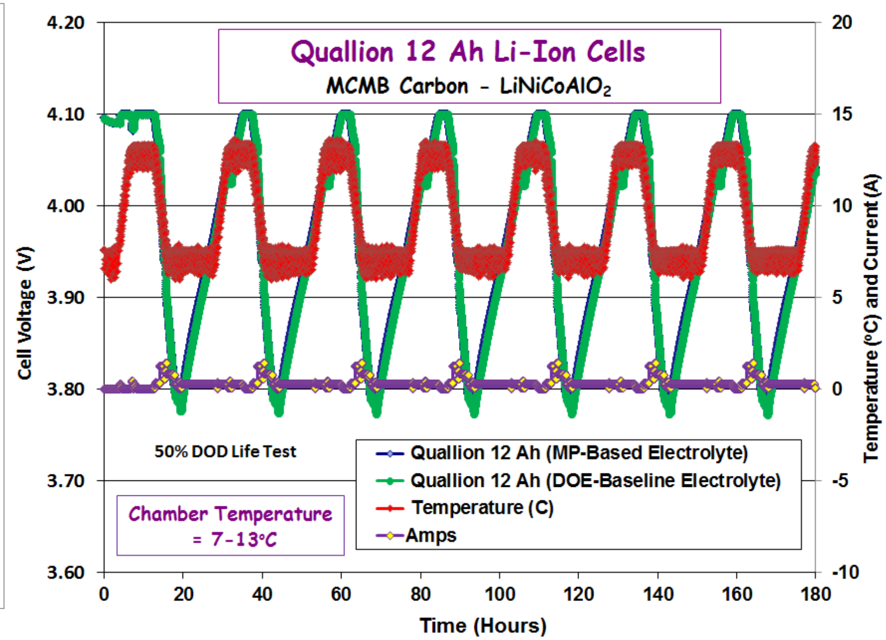
Technical Accomplishments

Quallion Prototype 12 Ah Li-Ion Cells

Wide Operating Temperature Electrolytes

Discharge Characterization at Various Temperatures





- Partial DOD cycling (~ 50% DOD) is being performed on four 12 Ah Quallion Cells.
- Cells have completed 200 cycles (200 days of operation) and have been recently characterized down to -50°C
- Periodically measuring the capacity, impedance, and rate capability at low temperature (every 100 days) to demonstrate the performance throughout the life of the cell.
- The addition of FEC improves the capacity retention as a result of cycling.

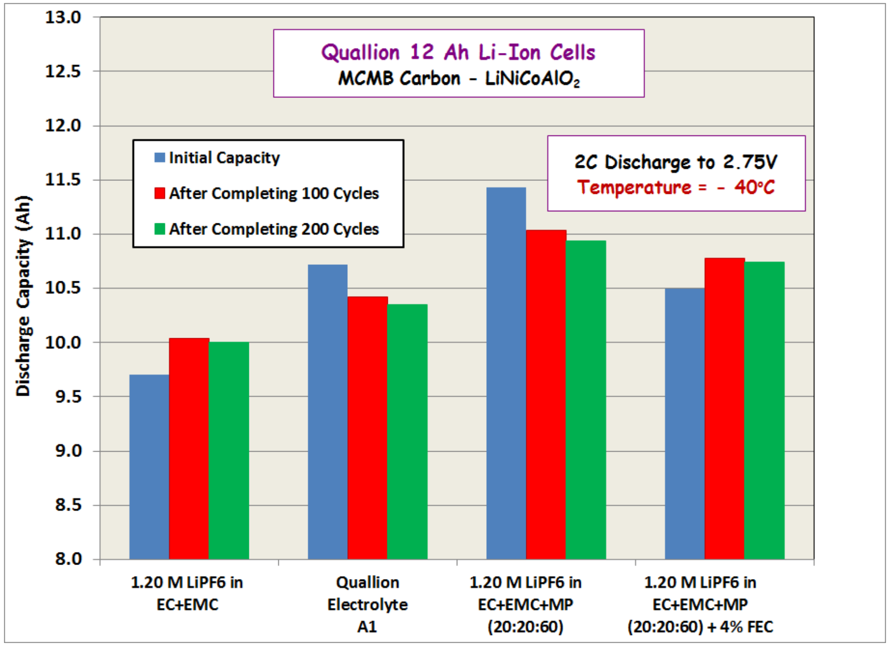
➢ *Quallion collaboration supported by NASA SBIR Program.*
(H. Tsakamoto, M. Tomcsi, M. Nagata, and V. Visco)

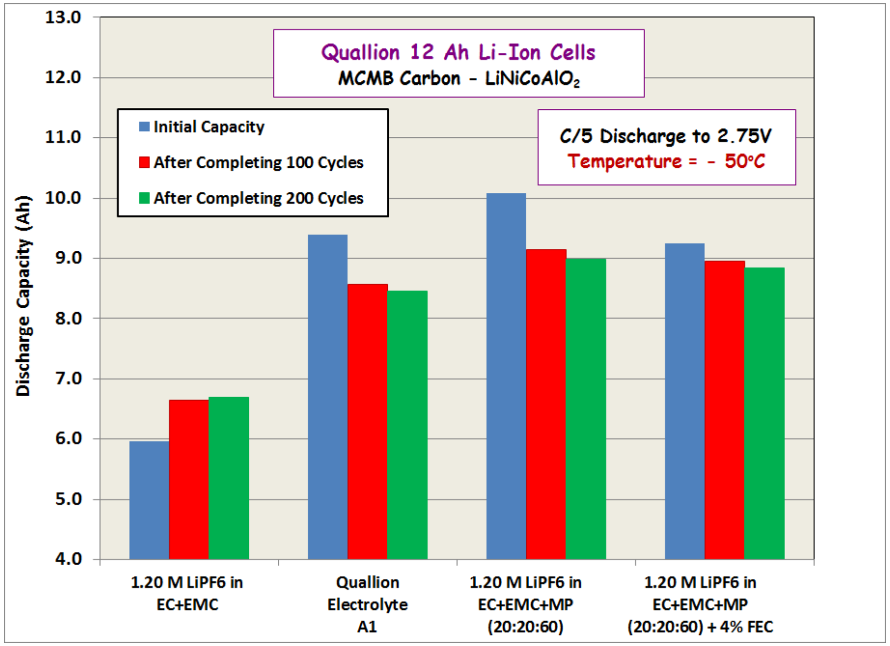
Technical Accomplishments

Quallion Prototype 12 Ah Li-Ion Cells

Wide Operating Temperature Electrolytes

Discharge Characterization at Various Temperatures





- **When the cells were characterized at low temperature after cycling, the methyl propionate-based electrolytes were observed to deliver the highest capacities.**
- **The addition of FEC observed to improve the preservation of low temperature capability throughout life.**
- **Higher capacity seen in some cases compared to initially, which is attributed to internal cell heating on discharge associated with cell impedance increase.**
- **Based on data obtained on smaller prototype cells (0.25Ah size), the larger cells are anticipated to support much higher discharge rates at low temperature (discharge currents evaluated limited by channel capability of 25A).**

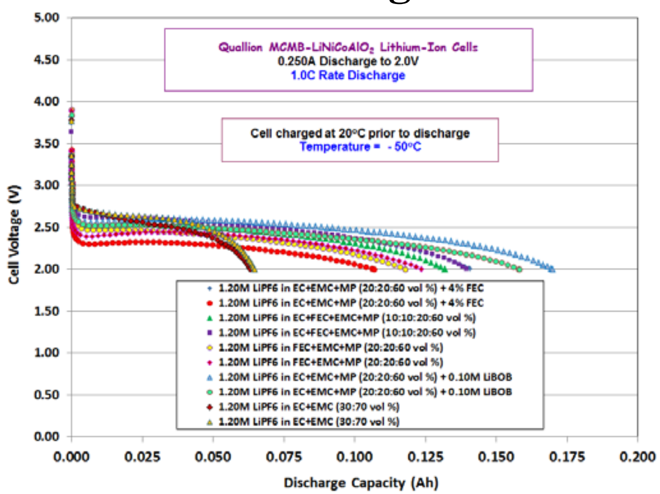
Technical Accomplishments

Quallion Prototype 0.25 Ah Li-Ion Cells

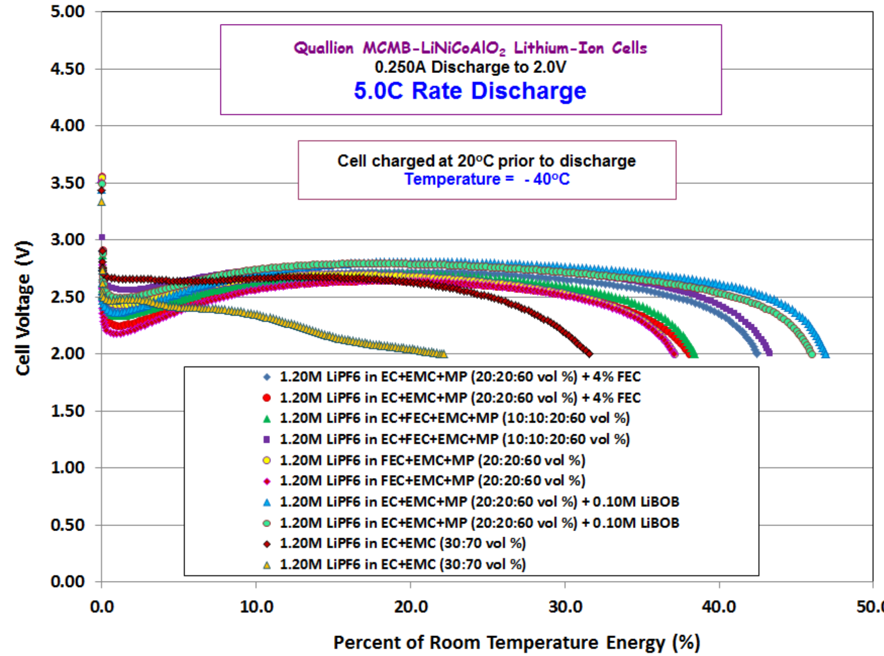
Discharge Characterization at Low Temperatures

- We are currently evaluating a number of 0.30 Ah Quallion cells with the following JPL electrolytes:
- **1.2M LiPF6 in EC+EMC+MP (20:20:60) + 4% FEC**
- **1.2M LiPF6 in EC+FEC+EMC+MP (10:10:20:60)**
- **1.2M LiPF6 in FEC+EMC+MP (20:20:60)**
- **1.2M LiPF6 in EC+EMC+MP (20:20:60) + 0.10M LiBOB**

1C Rate Discharge at -50°C



5C Rate Discharge at -40°C



- **Electrolytes selected for evaluation include methyl propionate-based electrolytes with increasing FEC content and the use of LiBOB as an additive.**
- **All electrolytes are observed to provide improved performance at high rates at very low temperatures compared with the baseline electrolytes, with the LiBOB outperforming all formulations.**
- **The incorporation of LiBOB has been attributed to increase cathode kinetics at low temperatures, as determined by Tafel Polarization measurements performed on 3-electrode cells.**

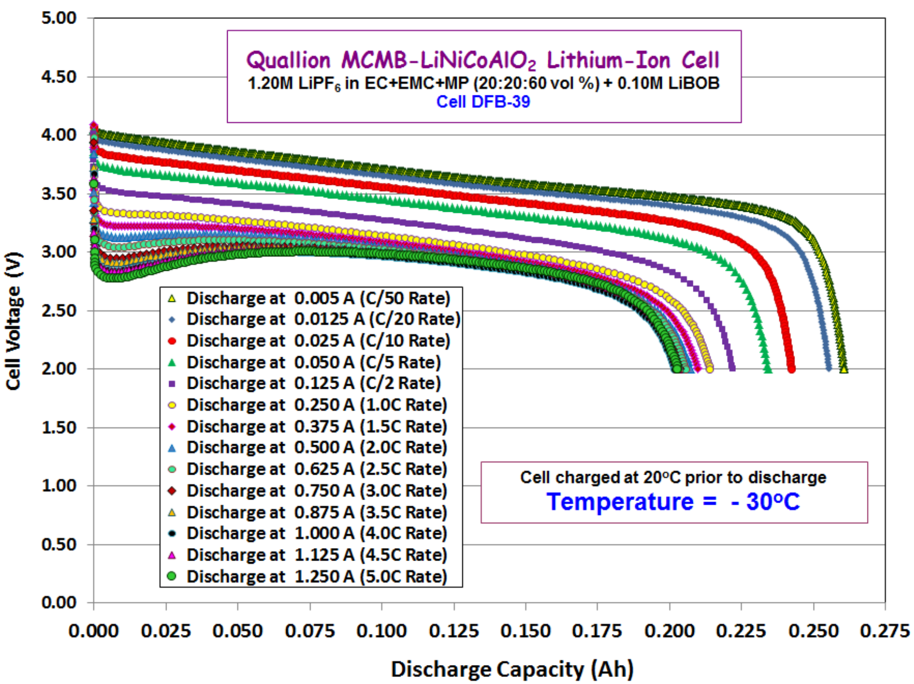
Technical Accomplishments

Quallion Prototype 0.25 Ah Li-Ion Cells

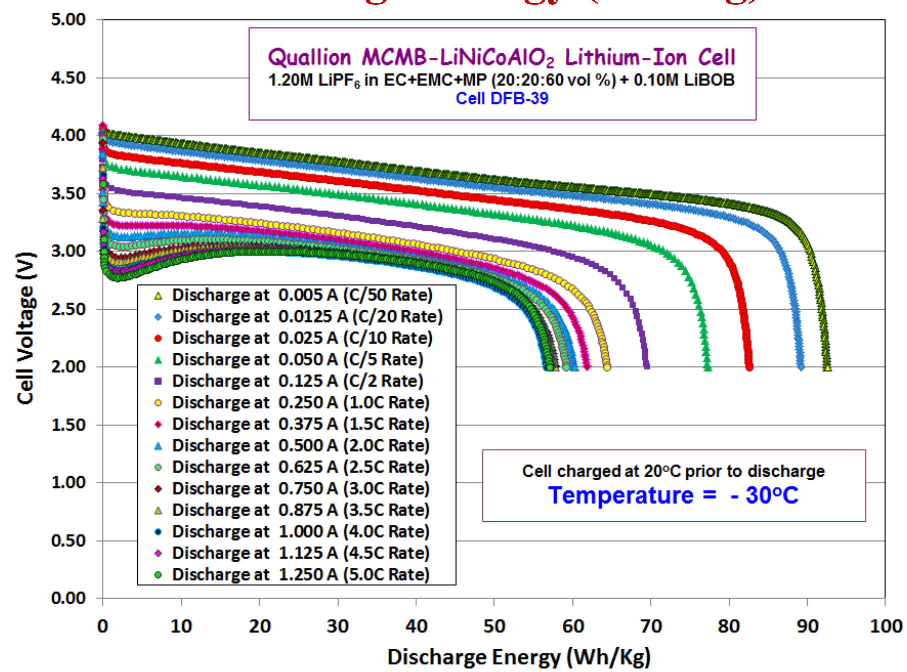
Discharge Performance at - 30°C

Electrolyte : 1.2M $LiPF_6$ + 0.10M LiBOB in EC+EMC+MP (20:20:60 v/v %)

Capacity (Ah)



Discharge Energy (Wh/Kg)



- **The cell containing the electrolyte with methyl propionate and LiBOB has displayed excellent power capability at -30°C.**
- **The incorporation of LiBOB has been attributed to increase cathode kinetics at low temperatures, as determined by Tafel Polarization measurements performed on 3-electrode cells.**

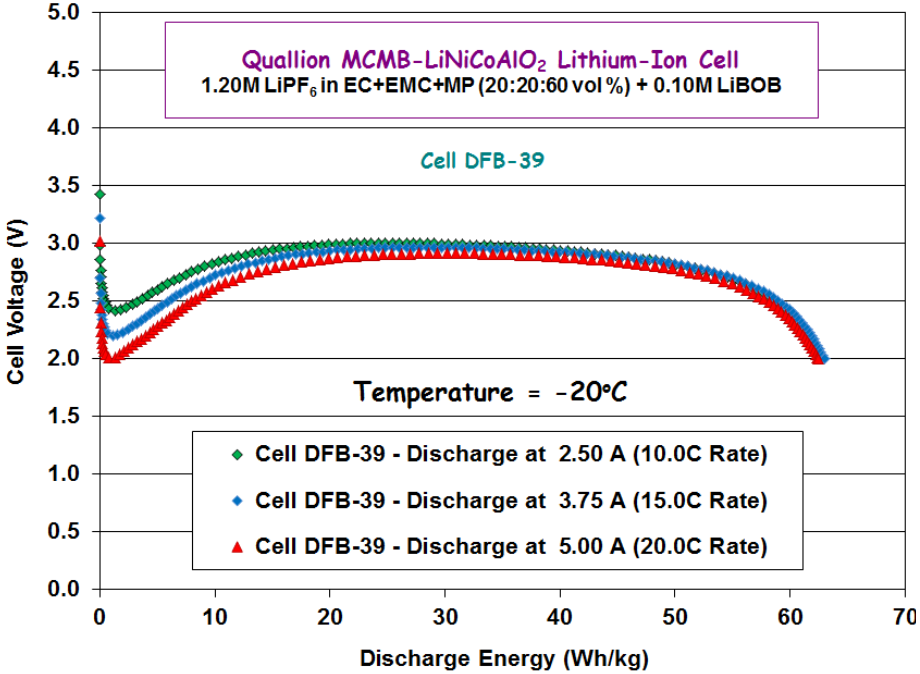
Technical Accomplishments

Quallion Prototype 0.25 Ah Li-Ion Cells

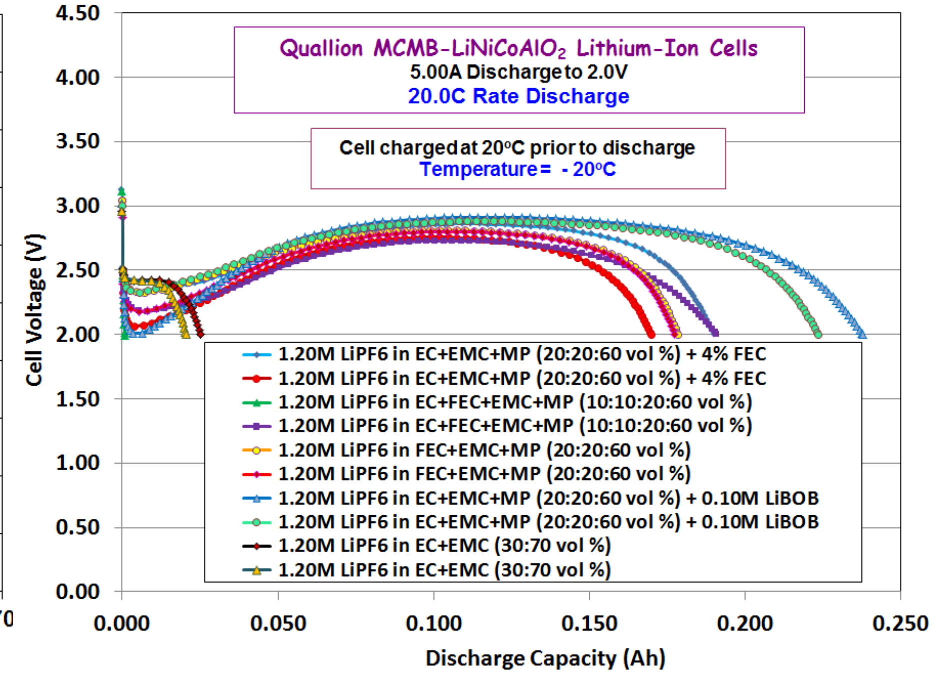
Discharge Performance at - 20°C

High Rate Discharge Performance at Low Temperature (up to 20C Rates)

MP + LiBOB Electrolyte



20C Discharge at -20°C



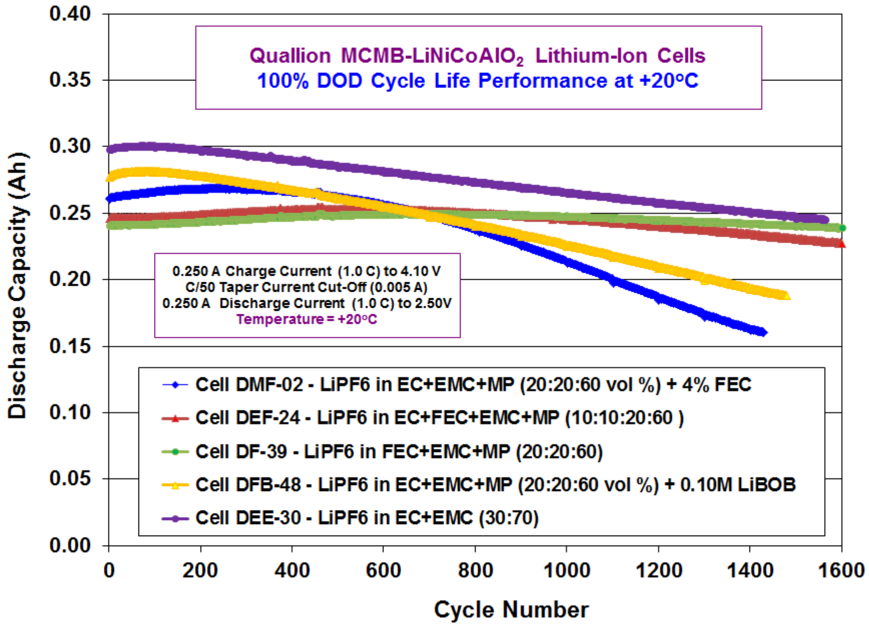
- The cell containing the electrolyte with methyl propionate and LiBOB has displayed very high power capability at -20°C, being able to provide over 60 Wh/kg at a 20C discharge rate.
  - All of the MP-based electrolytes displayed dramatically improved power capability.
- At a 20C discharge rate at -20°C, the cell containing the MP-based electrolyte delivered over 11 times greater discharge energy (i.e., 62.2 Wh/kg compared to only 5.5 Wh/kg for the baseline).

Technical Accomplishments

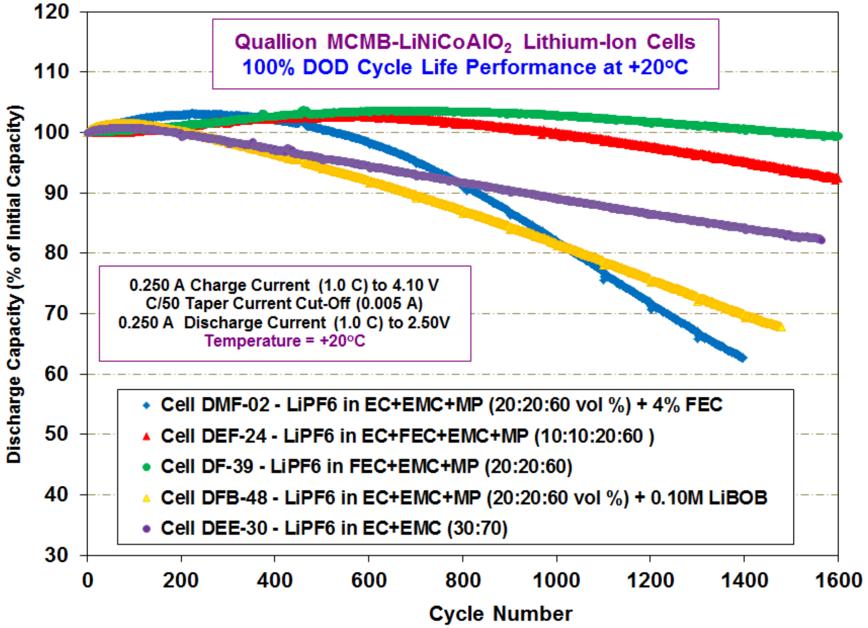
Quallion Prototype 0.25 Ah Li-Ion Cells

100% DOD Cycle Life at +20°C

Capacity (Ah)



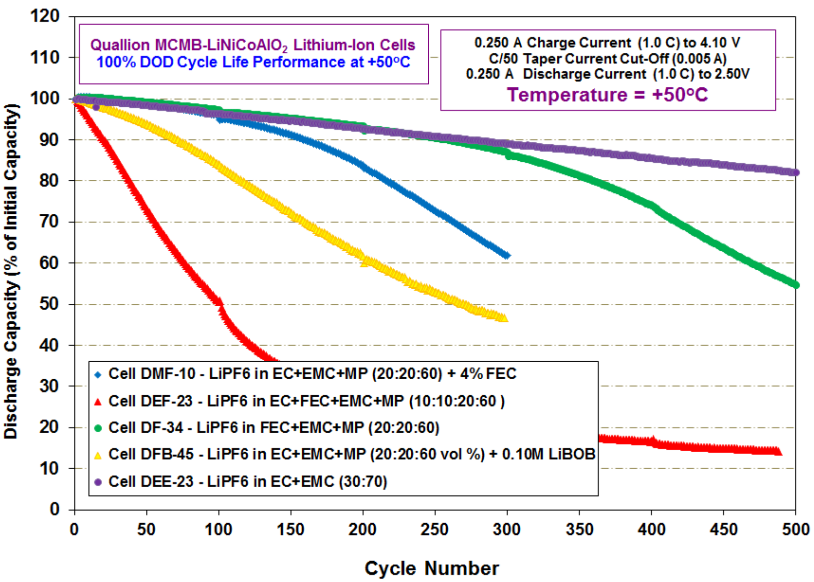
Percent of Initial Capacity (Ah)



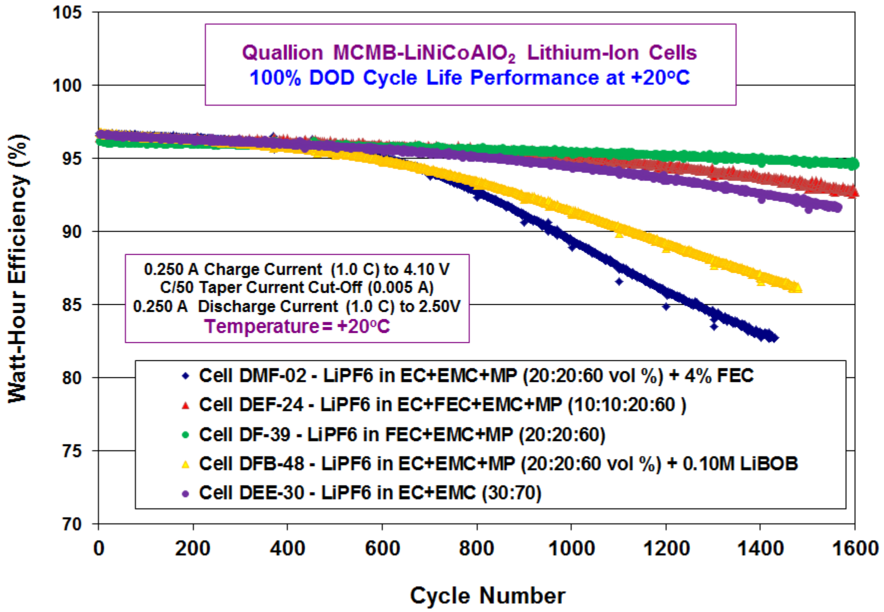
- Thus far, the cells containing the MP-based wide operating temperature range electrolytes provide good life at 20°C, with somewhat lower capacity displayed initially.
- Unlike initial testing at high temperature (i.e. 50°C) , no degradation was observed when FEC was added to the electrolyte in high proportion (10 or 20%), even if present as the only cyclic carbonate.
  - The cell containing $LiPF_6$ in FEC+EMC+MP was observed to deliver > 99.5% of the initial capacity after completing 1,600 cycles (100% DOD).

Technical Accomplishments
Quallion Prototype 0.25 Ah Li-Ion Cells

100% DOD Cycle Life at +50°C
Percent of Initial Capacity (Ah)



100% DOD Cycle Life at +20°C
Watt-Hour Efficiency (%)

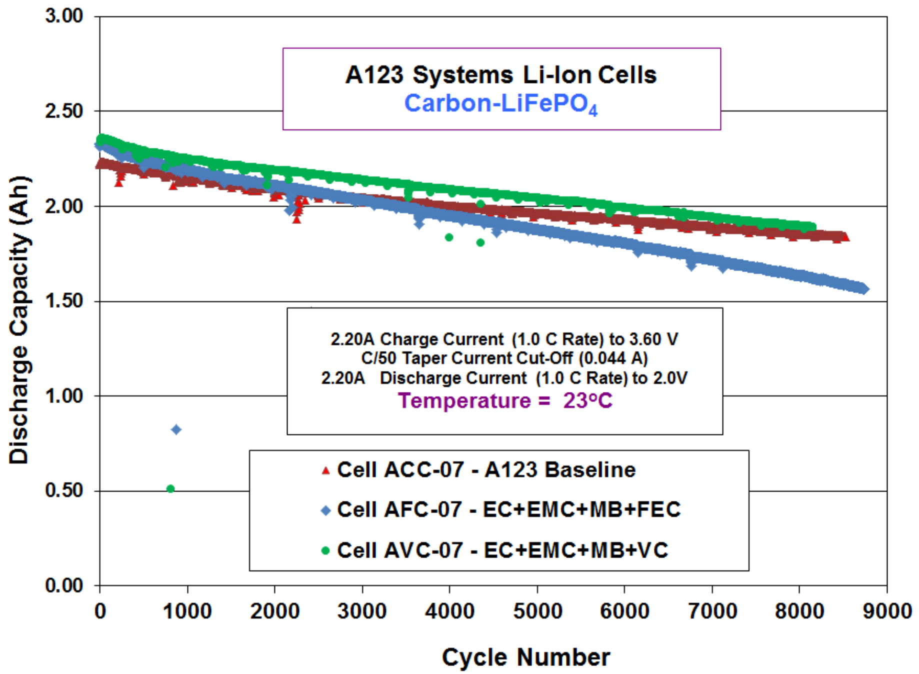


- Excellent retention of the watt-hour efficiency was observed with the cell containing $LiPF_6$ in FEC+EMC+MP when subjected to cycling at +20oC, suggesting minimal impedance growth.
- When the cells containing the MP-based wide operating temperature range electrolytes were cycled at 50°C, the electrolyte with FEC added in high proportion (20%), provided the best performance.
- Future efforts will be devoted to coupling additives targeted at improving the high temperature resilience with the FEC-rich methyl propionate blends.

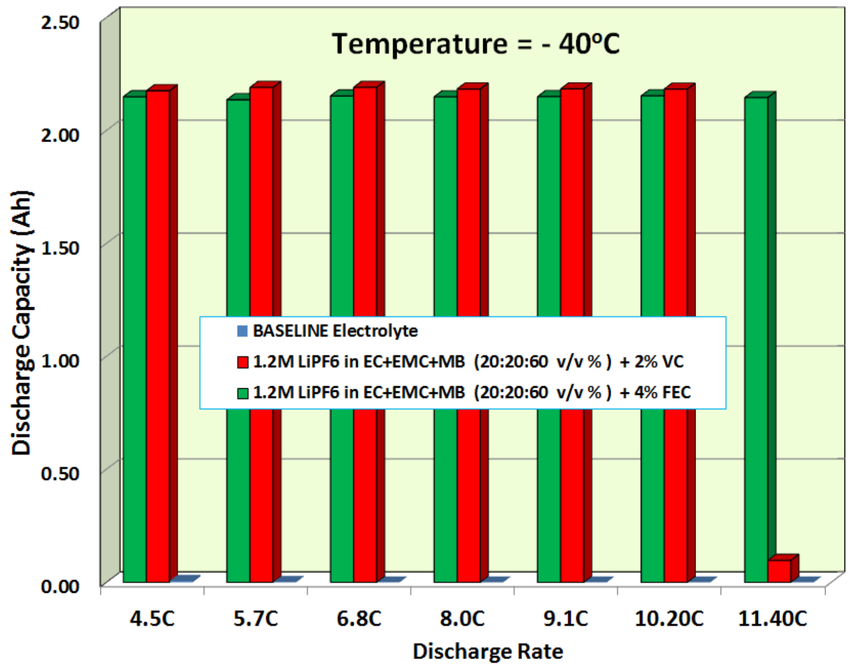
Technical Accomplishments

A123 2.20 Ah High Power Lithium-Ion Cells

100 % DOD Cycle Life at 23°C



Discharge Rate Capability at -40°C



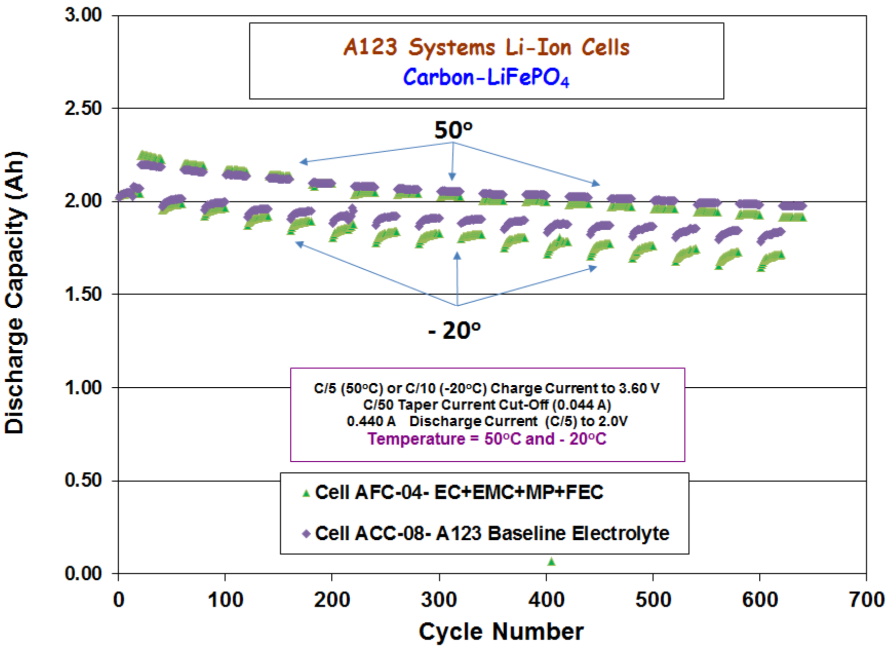
- **Cells were previously demonstrated to support >11C discharge rates at -40°C, with over 90% of the room temperature capacity being delivered.**
- **Impressive life characteristics are observed at 23°C, with ~ 8,000 cycles being demonstrated (100 % DOD cycling). The methyl butyrate-based electrolytes delivers comparable performance to the baseline electrolyte (> 81% of the initial capacity after completing 8,000 cycles).**

Technical Accomplishments

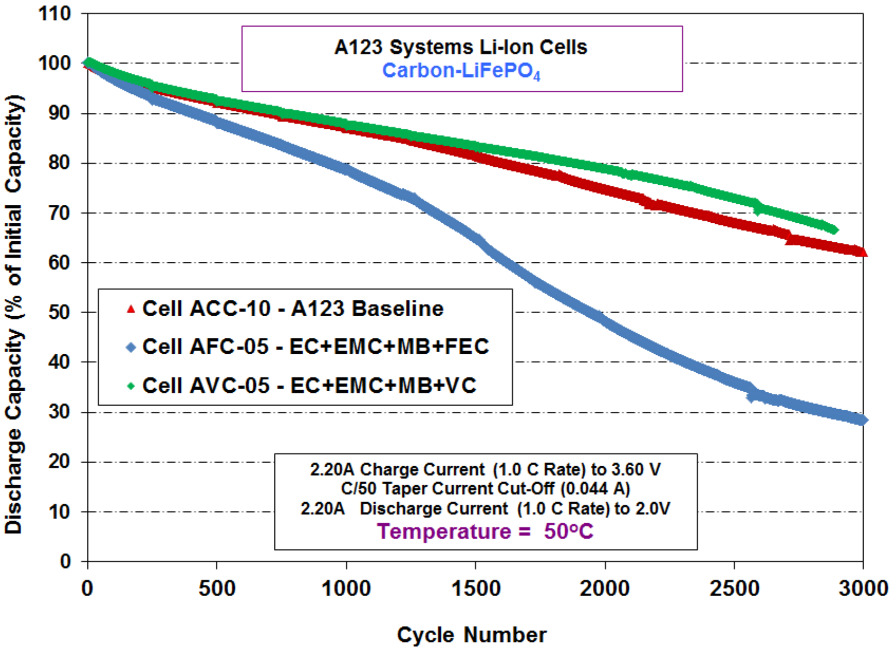
A123 2.20 Ah High Power Lithium-Ion Cells

High Temperature Cycling Performance

Varible Temperature Cycling (-20 to +50°C)



100 % DOD Cycle Life at +50°C



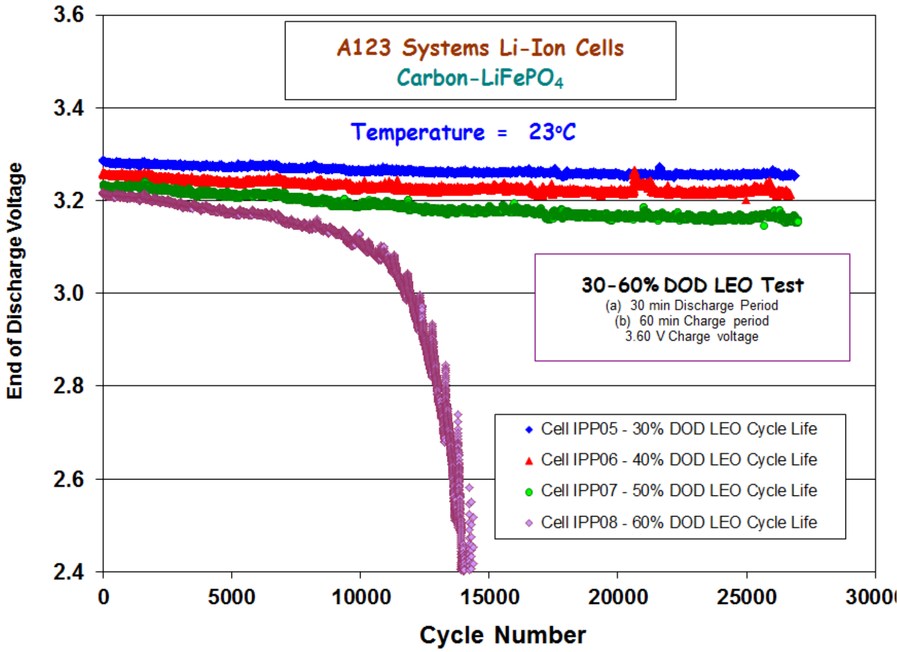
- Good life characteristics were observed at up to 50°C with the EC+EMC+MB+VC system, outperforming the baseline electrolyte with >2,800 cycles being demonstrated.
- Cells containing the JPL developed electrolytes demonstrate good preservation of the low temperature capability after being subjected to high temperature (i.e., +50°C).

Technical Accomplishments

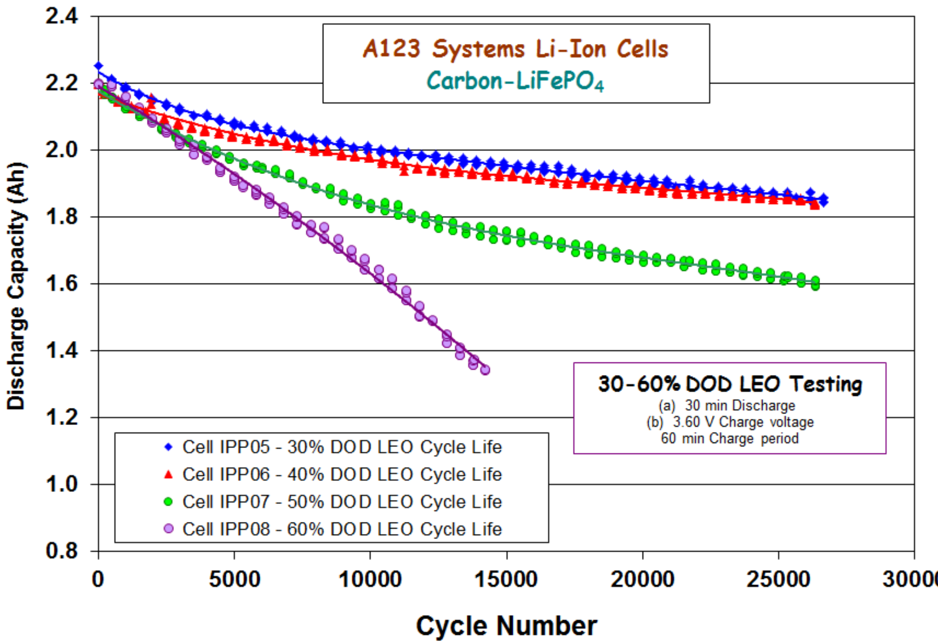
A123 2.20 Ah High Power Lithium-Ion Cells

Cycling Life Testing of Baseline COTS Cells

LEO Cycle Life of COTS Cells at 23°C
EODV



LEO Cycle Life at of COTS Cells at 23°C
100% DOD Capacity Check



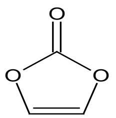
- We have supported NREL's Li-ion battery modeling activities by providing long-term A123 test data.
- DOE encourages collaborations across institutions.
- Collaboration has resulted in an up-coming publication:
- M. Jun, K. Smith, E. Wood, and M. C. Smart, "Battery Capacity Estimation of Low-Earth Orbit Satellite Application", International Journal of Prognostics and Health Management

Technical Accomplishments

Characterization of Three Electrode Conoco Graphite/Toda HE5050 $LiNiCoMnO_2$ Cells

Electrolyte Type	Charge Capacity (mAh/g) 1st Cycle	Discharge Capacity (mAh/g) 1st Cycle	Irreversible Capacity (mAh/g) (1st Cycle)	Couloumbic Efficiency (1st Cyle)	Reversible Capacity (mAh/g) 5th Cycle	Cummulative Irreversible Capacity (mAh/g) (1st-5th Cycle)	Cathode Type
1.0M LiPF6 + 0.10M LiBOB EC+EMC+MB (20:20:60 vol%)	323.57	246.10	77.47	76.06	243.87	138.98	Argonne NMC (Toda HE 5050)
1.0M LiPF6 EC+EMC+MB (20:20:60 vol%) + 1.5% VC	325.89	233.46	92.43	71.64	224.33	211.93	Argonne NMC (Toda HE 5050)
1.0M LiPF6 EC+EMC+MB (20:20:60) + lithium oxalate	337.29	261.84	75.45	77.63	257.10	125.28	Argonne NMC (Toda HE 5050)
1.0M LiPF6 + 0.10M LiBOB EC+EMC+MB (20:20:60 vol%)	182.62	161.05	21.57	88.19	153.90	91.64	Argonne NCA ($LiNiCoAlO_2$)

- A number of methyl butyrate-based electrolytes have been evaluated in a high voltage system (i.e., LLC-NMC received from Argonne) and compared the NCA system.
- The MB-based formulations containing LiBOB delivered the best rate capability at low temperature, which is attributed to improved cathode kinetics. Whereas, the use of lithium oxalate as an additive lead to the highest reversible capacity and lower irreversible losses.
- At lower temperature and higher rates, the advantages of utilizing the high voltage system diminishes, again attributed to the relative cathode kinetics.



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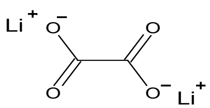

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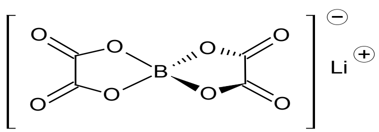

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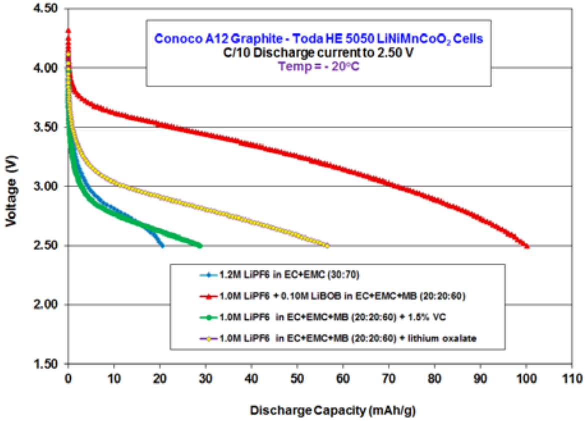
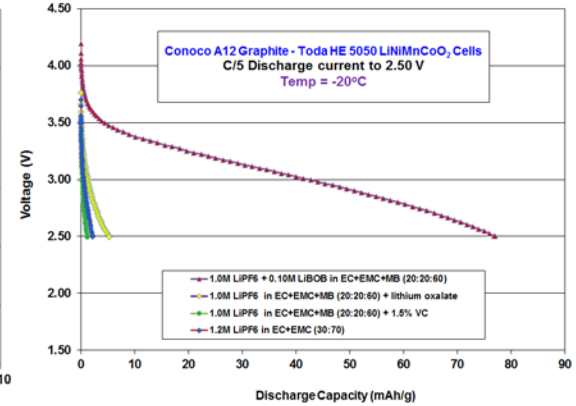
- Of the electrolytes evaluated, the MB-based system with LiBOB consistently displayed the best low temperature performance, which is attributed to (i) to improved kinetics at the cathode and to a lesser extent (ii) improved ionic conductivity of the electrolyte at low temperature.

C/10 Discharge at - 20°C



C/5 Discharge at - 20°C

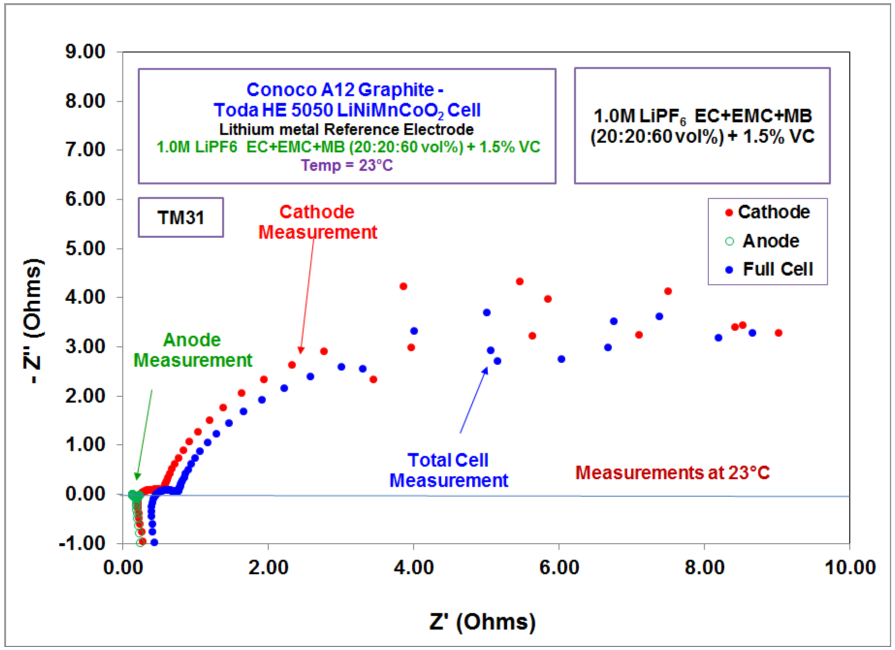


Technical Accomplishments

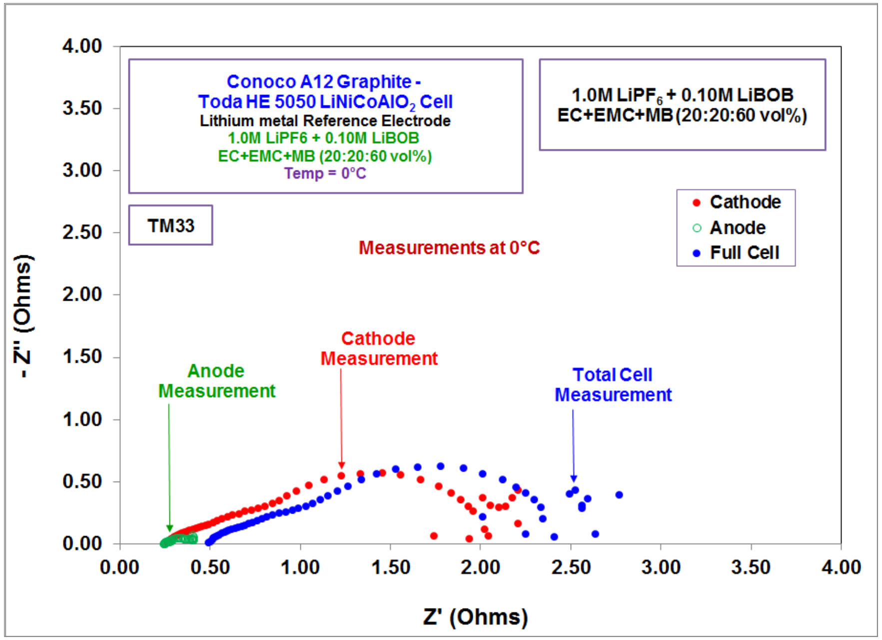
Characterization of Three Electrode Conoco Graphite/Toda HE5050 $LiNiCoMnO_2$ Cells

EIS Measurements at 23 and 0°C

NCM-Based Cell



NCA-Based Cell



- ➢ **When EIS measurements were performed each electrode (using 3-electode cells), both the NCA and NMC electrodes dominated the cell impedance.**
- ➢ **Of the different cathodes, the LLC-NMC electrodes (received from Argonne) displayed a more dramatic charge transfer resistance, which is exacerbated at lower temperatures.**

Technical Accomplishments

Characterization of Three Electrode Conoco Graphite/Toda HE5050 $LiNiCoMnO_2$ Cells

Tafel Polarization Measurements at 0°C

Electrolyte Type →		1.0M $LiPF_6$ + 0.10M LiBOB EC+EMC+MB (20:20:60 vol%)			1.0M $LiPF_6$ EC+EMC+MB (20:20:60 vol%) + 1.5% VC			1.0M $LiPF_6$ EC+EMC+MB (20:20:60) + lithium oxalate			1.2M $LiPF_6$ EC+EMC (30:70 vol%)		
Temperature	Current (mA)	Capacity (Ahr)	Capacity (mAh/g)	Percent (%)	Capacity (Ahr)	Capacity (mAh/g)	Percent (%)	Capacity (Ahr)	Capacity (mAh/g)	Percent (%)	Capacity (Ahr)	Capacity (mAh/g)	Percent (%)
23°C	C/20	0.1100	243.87	100.00	0.1018	224.33	100.00	0.1168	257.10	100.00	0.1211	266.57	100.00
	C/10	0.1059	234.95	96.34	0.1001	220.53	98.31	0.1130	248.60	96.69	0.1108	243.84	91.47
	C/5	0.0973	215.91	88.54	0.0947	208.66	93.01	0.1039	228.57	88.90	0.1029	226.42	84.94
	C/2	0.0843	186.92	76.65	0.0840	185.03	82.48	0.0900	197.97	77.00	0.0896	197.16	73.96
10°C	C/20	0.0972	215.59	88.40	0.0829	182.73	81.45	0.0974	214.33	83.37	0.1037	228.15	85.58
	C/10	0.0911	201.99	82.82	0.0798	175.82	78.37	0.0894	196.81	76.55	0.0858	188.84	70.84
	C/5	0.0798	177.06	72.60	0.0717	158.05	70.46	0.0798	175.55	68.28	0.0599	131.77	49.43
	C/2	0.0636	141.14	57.88	0.0526	116.01	51.71	0.0585	128.72	50.07	0.0335	73.81	27.69
	C/2	0.0642	142.39	58.39	0.0500	110.25	49.15	0.0567	124.85	48.56	0.0360	79.11	29.68
0°C	C/20	0.0848	187.98	77.08	0.0668	147.14	65.59	0.0808	177.86	69.18	0.0748	164.70	61.78
	C/10	0.0745	165.15	67.72	0.0559	123.14	54.89	0.0670	147.33	57.30	0.0349	76.85	28.83
	C/5	0.0646	143.21	58.72	0.0467	102.91	45.88	0.0559	123.02	47.85	0.0250	55.12	20.68
	C/2	0.0491	108.92	44.66	0.0235	51.71	23.05	0.0334	73.53	28.60	0.0130	28.57	10.72

- A The MB-based formulations containing LiBOB delivered the best rate capability at low temperature, which is attributed to improved cathode kinetics. Whereas, the use of lithium oxalate as an additive lead to the highest reversible capacity and lower irreversible losses.
- At lower temperature and higher rates, the advantages of utilizing the high voltage system diminishes, again attributed to the relative cathode kinetics.

Summary

- **Met programmatic milestones for program.**
- **Demonstrated improved performance with methyl propionate-containing electrolytes in prototype cells (both large capacity 12 Ah cells and smaller 0.25Ah cells):**
  - Demonstrated the wide operating temperature range capability in large cells (12 Ah), successfully scaling up technology from 0.25 Ah size cells.
  - Demonstrated improved performance at low temperature and good cycle life at with methyl propionate-based electrolyte containing increasing FEC content and the use of LiBOB as an additive.
  - Demonstrated the ability to support 20C discharge rate at -20^{o}C, with the cell containing the MP-based electrolyte delivered over 11 times greater discharge energy compared with the baseline.
- **Demonstrated improved performance with wide operating temperature electrolytes containing ester co-solvents (i.e., methyl butyrate) containing electrolyte additives in A123 prototype cells:**
  - Previously demonstrated excellent low temperature performance, including 11C rates at -40^{o}C and the ability to perform well down to -60^{o}C.
  - Excellent cycle life at room temperature has been displayed, with over 8,000 cycles being demonstrated.
  - Good retention of the low temperature performance observed after cycling at +50^{o}C.
- **Utilized three-electrode cells to investigate the electrochemical characteristics of high voltage systems coupled with wide operating temperature range electrolytes:**
  - The MB-based formulations containing LiBOB delivered the best rate capability at low temperature, which is attributed to improved cathode kinetics.
  - When EIS measurements were performed each electrode (using 3-electode cells), both the NCA and NMC electrodes dominated the cell impedance. The LLC-NMC electrodes displayed much slower lithium de-intercalation kinetics compared to the NCA electrodes (attributed to poor charge transfer resistance of the electrodes).

Future Work

- ***Continue the investigation of the use of additives in conjunction with ester-based wide operating temperature range electrolytes.***
  - *Expand study to include other potential additives (i.e., mixed lithium salt solutions and additives).*
  - *Continue to study the cycle life behavior and high temperature resilience and identify performance limiting degradation modes.*
  - *Explore the use of fluorinated esters, especially with high voltage systems, including trifluoroethyl butyrate, ethyl trifluoroacetate, and trifluoroethyl acetate.*
  - *Continue studying the wide operating temperature range systems in conjunction with ABR developed electrodes, which were recently received from Argonne, focusing upon improving the low temperature capability of these systems.*
  - *Investigate the use of the ARL developed high voltage additives (Kang Xu) in conjunction with the wide operating temperature range electrolytes.*

- ***Continue the investigation of alternate lithium-based electrolyte salts***
  - *Continue investigating the use lithium hexafluoroisopropoxide (and other analogues), lithium malonate borate-based salts (in collaboration with Li Yang, John Kerr and Brett Lucht), as well as other LiBOB derivatives to determine their impact in high voltage systems (in collaboration with Wesley Henderson and his group).*
  - *Explore the utility of these salts in conjunction with alternate solvent mixtures and explore concentration effects.*
  - *Investigate the impact that these additives have upon the high temperature resilience of lithium ion cells.*

– ***Continue the assessment of candidate electrolytes in high capacity prototype cells.***

Collaborations

- Quallion, LCC: Provided prototype cells , on-going collaborator (NASA SBIR Phase II)
- A123 Systems, Inc. : Provided prototype cells with DOE developed electrolytes
- Argonne Nat. Lab (Khalil Amine): ANL provided electrodes for evaluation (on-going collaborator)
- Loker Hydrocarbon Institute, USC (Prof. Surya Prakash), (Fluorinated Solvents and novel salts)
- North Carolina State Univ, NCSC (Prof. Wesley Henderson), (novel salts)
- LBNL (Li Yang and John Kerr): LBNL provided novel lithium malonate-based salt
- Yardney Technical Products: Electrolyte development (on-going collaborator)
- Univ. Rhode Island (Brett Lucht): Analysis of harvested electrodes, (on-going collaborator)
- Saft America, Inc.: Collaborator, industrial partner under NASA program
- NREL (Smith/Pesaran): Supporting NREL in model development by supplying prototype cell data.
- Sandia Nat. Lab. (Orendorff/Nagasubramanian): Future safety testing of low flammability electrolyte/cells, electrode source

Publications and Presentations

- M. C. Smart, et. al., "Development of Low Temperature Electrolytes for Lithium-Ion Batteries", Advanced Automotive Batteries Conference, Pasadena, CA, February 5, 2013.
- M. C. Smart, C. Hwang, F. C. Krause, J. Soler, W. C. West, B. V. Ratnakumar, and K. Amine, "Wide Operating Temperature Range Electrolytes for High Voltage and High Specific Energy Li-Ion Cells", 2013 ECS Transactions (accepted.)
- M. Jun, K. Smith, E. Wood, and M. C. Smart, "Battery Capacity Estimation of Low-Earth Orbit Satellite Application", *International Journal of Prognostics and Health Management*, submitted.
- M. C. Smart, C. Hwang, F. C. Krause, J. Soler, W. C. West, B. V. Ratnakumar, and K. Amine, "Wide Operating Temperature Range Electrolytes for High Voltage and High Specific Energy Li-Ion Cells", 222nd Meeting of the Electrochemical Society, Honolulu, HI, October 7-12, 2012. (Abstract #1235).
- M. C. Smart, B. L. Lucht, S. Dalavi, F. C. Krause, and B. V. Ratnakumar, "The Effect of Additives upon the Performance of MCMB/$LiNiCoO_2$ Li-Ion Cells Containing Methyl Butyrate-Based Wide Operating Temperature Range Electrolytes", J. Electrochem. Soc., **159 (6)**, A739-A751 (2012).
- S. DeSilvan, V. Udinwe, P. Sideris, S. G. Greenbaum, M. C. Smart, F. C. Krause, K. A. Smith and C. Hwang, "Multinuclear NMR Studies of Electrolyte Breakdown Products in the SEI of Lithium-Ion Batteries", *ECS Trans.* ***41 (41),*** *207 (2012).*
- M. C. Smart, M. R. Tomcsi, C. Hwang, L. D. Whitcanack, B. V. Ratnakumar, M. Nagata, V. Visco, and H. Tsukamoto, "Improved Wide Operating Temperature Range of $LiNiCoAlO_2$-Based Li-ion Cells with Methyl Propionate-Based Electrolytes", 221st Meeting of the Electrochemical Society, Seattle, WA, May 6-10, 2012.

Acknowledgments

The work described here was carried out at the Jet Propulsion Laboratory, California Institute of Technology, under contract with the National Aeronautics and Space Administration (NASA).