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

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# Overview

## Timeline

- Start Date = October 2009
- End Date = October 2014
- Percent complete = 25%

## Budget

- Total project funding
  - 875K total (~ 175K/year)
  - Contractor share = 0K
- Funding received
  - FY'09 = 0 K
  - FY'10 = 175K
  - FY'11 = 175K

## 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)
- **LBL (John Kerr, Li Yang)**  
(Evaluation of novel salts)
- **Loker Hydrocarbon Institute, USC (Prof. Surya Prakash)**  
(Fluorinated Solvents and novel salts)
- **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)



# 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. 2011	Milestone: Prepare and characterize experimental laboratory cells containing Gen-2 electrolytes and identify performance limiting characteristics at different temperatures.
Sept. 2011	Milestone: Demonstrate improved performance of first generation electrolyte over a wide temperature range compared with the baseline electrolyte (i.e., 1 M LiPF <sub>6</sub> in EC:DEC 1:2), especially at -30°C, in experimental and prototype cells



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# 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 novel “SEI promoting” and thermal stabilizing additives
  - Use of novel lithium based salts (with Materials Methods, LBNL)
- **Electrolyte Characterization Approach:**
  - Ionic conductivity and cyclic voltammetry measurements
  - Performance characteristics in ~ 400 mAh three electrode cells
    - MCMB /LiNi<sub>0.8</sub>Co<sub>0.2</sub>O<sub>2</sub> cells, MCMB /LiNi<sub>0.8</sub>Co<sub>0.2</sub>AlO<sub>2</sub> cells , Graphite /LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> cells
    - Use of high specific energy electrode materials (from in-house NASA program)
    - 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 LBNL)
  - 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 7 Ah size prototype cells)
  - Cells will be procured and/or obtained through on-going collaborations



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# Summary of Technical Accomplishments

## 1) Demonstrated improved performance with wide operating temperature electrolytes containing ester co-solvents (i.e., methyl propionate and ethyl butyrate) in Quallion prototype cells.

- At -40°C, the JPL developed MP-based electrolyte was demonstrated to deliver over 60% of the room temperature capacity using a 5C rate.
- Methyl propionate containing electrolytes have displayed dramatically improved rate capability compared to the baseline DOE formulation (i.e., 1.2M LiPF<sub>6</sub> in EC+EMC (30:70)).
- JPL developed electrolytes display wide operating temperature range (-40 to +70°C), with reasonable cycle life performance at 50°C.

## 2) Investigated a number of electrolyte additives to improve the performance of methyl propionate and methyl butyrate-based blends in MCMB-LiNiCoO<sub>2</sub> cells, MCMB-LiNiCoAl O<sub>2</sub> , and MCMB- LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> cells

- Formulations possessing mono-fluoroethylene carbonate (FEC), LiBOB, lithium oxalate, and vinylene carbonate have shown promise in experimental cells.
- Performed extensive electrochemical characterization to determine the degradation modes when subjected to extreme temperatures.
- The degradation of the anode kinetics was slowed most dramatically by the incorporation of VC and lithium oxalate into the electrolytes
- The greatest retention in the cathode kinetics was observed in the cell containing the electrolyte with FEC added.



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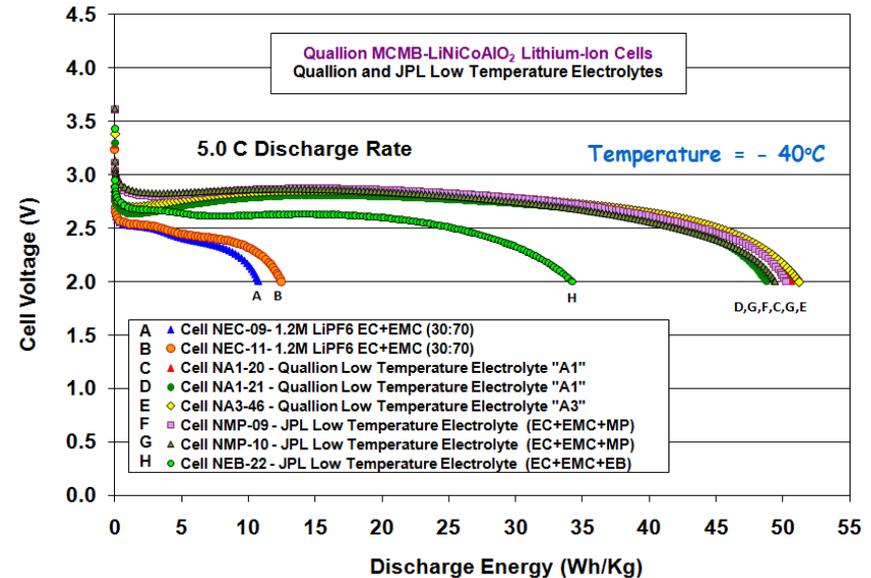
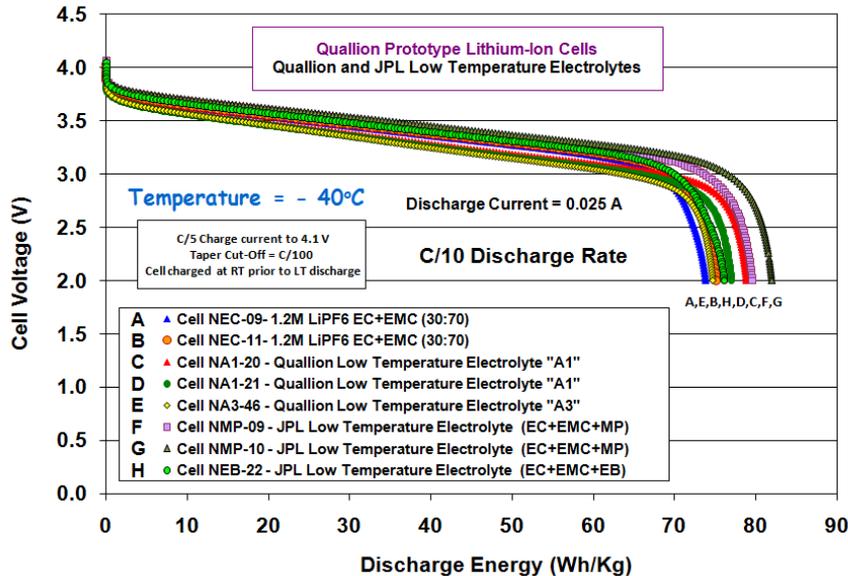
## Summary of Technical Accomplishments

- 3) **Investigated the use of methyl propionate-based and methyl butyrate-based electrolyte containing additives in conjunction with high voltage systems, including  $\text{Li}(\text{Li}_{0.17}\text{Ni}_{0.25}\text{Mn}_{0.58})\text{O}_2$  and Toda  $\text{LiNiCoMnO}_2$  cathode materials in experimental cells.**
  - Cells with an electrolyte containing methyl propionate and mono-fluoroethylene carbonate perform well with a high voltage cathode, delivering improved rated capability at lower temperatures.
- 4) **Demonstrated good cycle life and improved low temperature of A123 Systems  $\text{LiFePO}_4$ -based cells using methyl butyrate-based electrolytes:**
  - **1.2M  $\text{LiPF}_6$  EC+EMC+MB (20:20:60) + 4% FEC**
  - **1.2M  $\text{LiPF}_6$  EC+EMC+MB (20:20:60) + 4% VC**
  - **Systems are capable of supporting >11C discharge rates at -30°C, with over 90% of the room temperature capacity being delivered.**
  - **The cells were observed to perform well down to -60°C, with 80% of the room temperature capacity being delivered using a C/10 rate.**
- 5) **Investigated the use of lithium hexafluoroisopropoxide and the use of lithium malonate borate-based salts (in collaboration with Li Yang, John Kerr and Brett Lucht)**



# Technical Accomplishments

## 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<sub>6</sub> in EC+EMC (30:70)).

*Quallion developed electrolytes also display impressive improvements at low temperatures.*

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

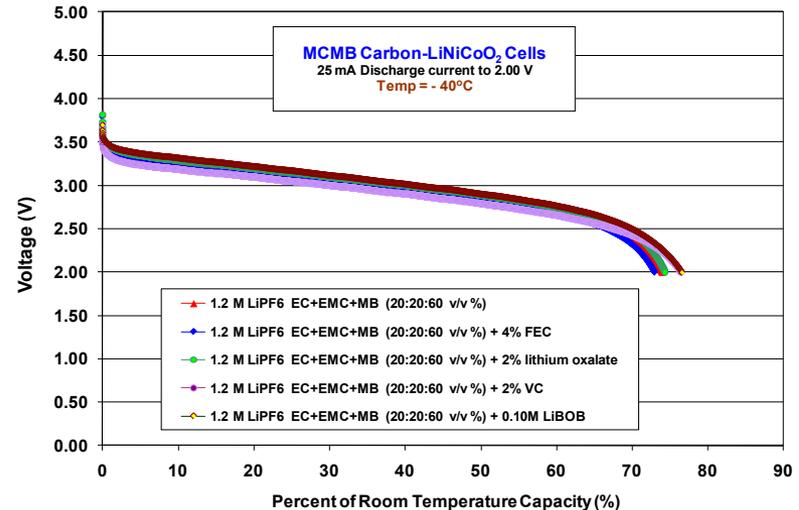
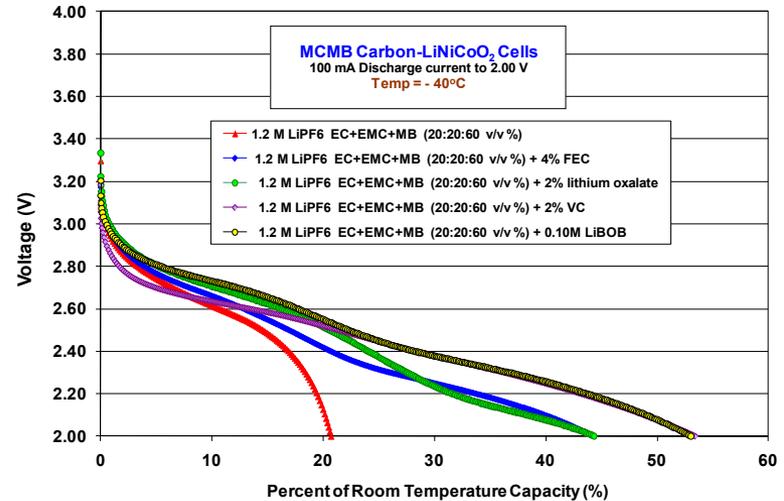


# Technical Accomplishments

Experimental lithium-ion cells (MCMB-LiNiCoO<sub>2</sub>) fabricated with methyl butyrate-based electrolytes containing various additives.

Electrolyte Type		1.2 M LiPF <sub>6</sub> EC+EMC+MB (20:20:60 v/v %)		1.2 M LiPF <sub>6</sub> EC+EMC+MB (20:20:60 v/v %) + 4% FEC		1.2 M LiPF <sub>6</sub> EC+EMC+MB (20:20:60 v/v %) + 2% lithium oxalate		1.2 M LiPF <sub>6</sub> EC+EMC+MB (20:20:60 v/v %) + 2% VC		1.2 M LiPF <sub>6</sub> EC+EMC+MB (20:20:60 v/v %) + 0.10M LiBOB	
Temperature	Current (mA)	Capacity (Ahr)	Percent (%)	Capacity (Ahr)	Percent (%)	Capacity (Ahr)	Percent (%)	Capacity (Ahr)	Percent (%)	Capacity (Ahr)	Percent (%)
23°C	25 mA	0.3973	100.00	0.3825	100.00	0.3850	100.00	0.3868	100.00	0.3969	102.62
	50 mA	0.3484	87.70	0.3300	86.29	0.3384	87.90	0.3534	91.37	0.3503	88.26
	100 mA	0.3376	84.99	0.3177	83.06	0.3269	84.91	0.3432	88.72	0.3409	85.87
	150 mA	0.3269	82.27	0.3048	79.70	0.3178	82.55	0.3329	86.06	0.3296	83.03
0°C	25 mA	0.3514	88.46	0.3355	87.71	0.3431	89.12	0.3558	91.98	0.3549	89.40
	50 mA	0.3484	87.70	0.3300	86.29	0.3384	87.90	0.3534	91.37	0.3503	88.26
	100 mA	0.3376	84.99	0.3177	83.06	0.3269	84.91	0.3432	88.72	0.3409	85.87
	150 mA	0.3269	82.27	0.3048	79.70	0.3178	82.55	0.3329	86.06	0.3296	83.03
-20°C	25 mA	0.3438	86.53	0.3236	84.60	0.3299	85.70	0.3484	90.06	0.3502	88.23
	50 mA	0.3226	81.19	0.3022	79.01	0.3104	80.64	0.3285	84.92	0.3268	82.32
	100 mA	0.3051	76.79	0.2842	74.30	0.2967	77.05	0.3140	81.19	0.3149	79.32
	150 mA	0.2906	73.14	0.2714	70.96	0.2863	74.36	0.3011	77.84	0.3016	75.97
-30°C	25 mA	0.3179	80.01	0.3001	78.46	0.3030	78.71	0.3230	83.51	0.3289	82.86
	50 mA	0.2990	75.27	0.2808	73.43	0.2930	76.11	0.3090	79.88	0.3113	78.44
	100 mA	0.2704	68.07	0.2535	66.28	0.2730	70.91	0.2873	74.29	0.2879	72.52
	150 mA	0.2233	56.20	0.2095	54.78	0.2502	65.00	0.2642	68.31	0.2604	65.60
-40°C	25 mA	0.2938	73.95	0.2792	73.00	0.2861	74.32	0.2956	76.43	0.3038	76.53
	50 mA	0.2348	59.10	0.2355	61.57	0.2530	65.71	0.2634	68.09	0.2660	67.01
	100 mA	0.0823	20.71	0.1690	44.18	0.1709	44.39	0.2068	53.48	0.2106	53.04
	150 mA	0.0501	12.60	0.0388	10.14	0.0606	15.74	0.1104	28.54	0.0705	17.76
-50°C	25 mA	0.0709	17.83	0.0497	12.99	0.0939	24.40	0.1031	26.66	0.1694	42.69
	50 mA	0.0463	11.64	0.0310	8.11	0.0532	13.83	0.0450	11.63	0.0396	9.97
	100 mA	0.0203	5.12	0.0104	2.72	0.0285	7.41	0.0107	2.76	0.0167	4.21

- LiBOB was observed to improve the low temperature performance.
- The benefit of LiBOB was determined to be due to improved kinetics at the cathode.





# Technical Accomplishments

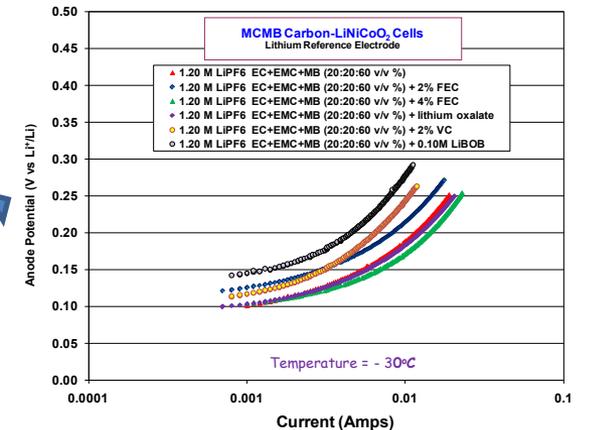
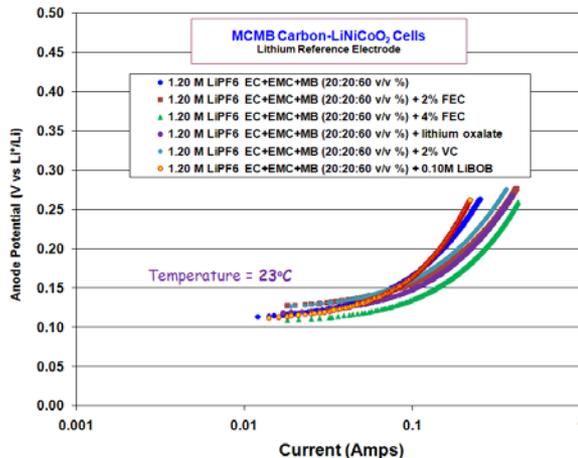
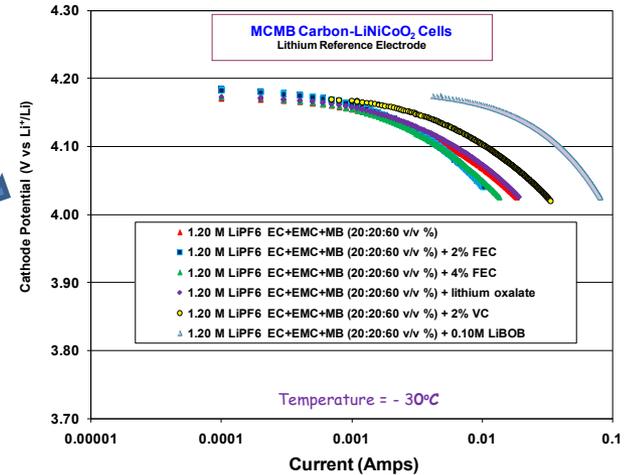
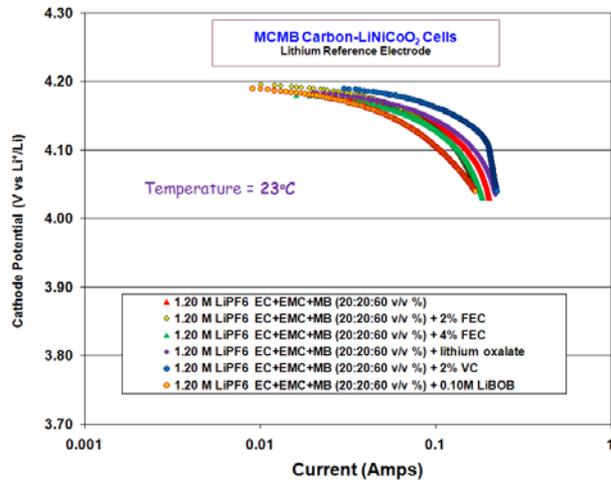
Experimental lithium-ion cells (MCMB-LiNiCoO<sub>2</sub>) fabricated with **methyl butyrate**-based electrolytes containing various additives.

At -30°C, electrolytes with LiBOB and VC resulted in the high limiting current densities at the cathode.

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

Some additives have the beneficial effect of improving the lithium kinetics through the formation of desirable SEI layers on both electrodes.

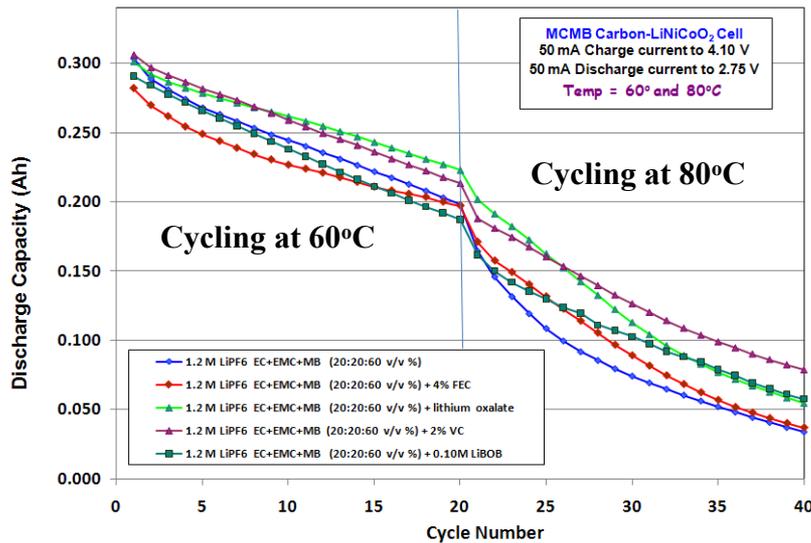
At -30°C, electrolytes with FEC and lithium oxalate resulted in the high limiting current densities at the cathode.





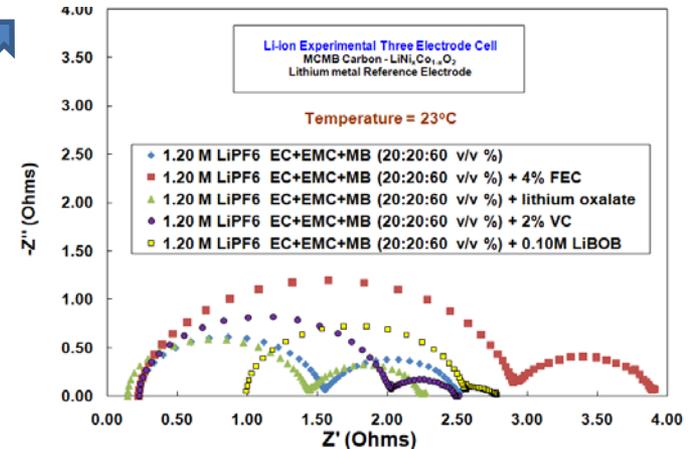
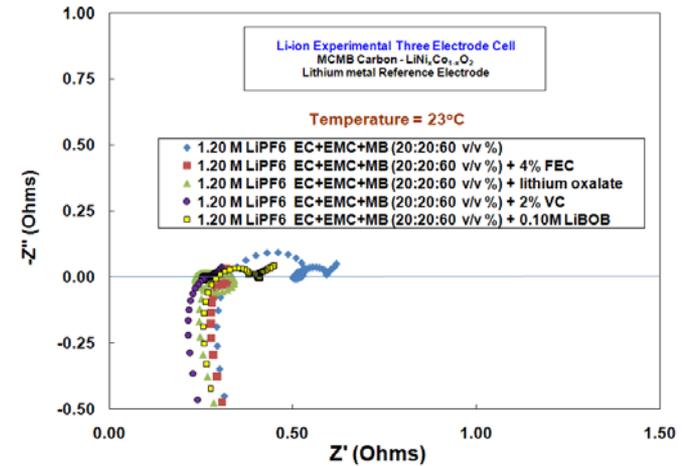
# Experimental lithium-ion cells (MCMB-LiNiCoO<sub>2</sub>) fabricated with methyl butyrate-based electrolytes containing various additives: Results of High Temperature Cycling

➤ Main objective of adding electrolyte additives is to improve system stability when exposed to high temperature cycling or storage.



➤ A number of electrolyte additives were observed to improve the stability of the methyl butyrate system when exposed to high temperature cycling (60°C).

## Results of EIS Measurements: After Cycling at 60°C





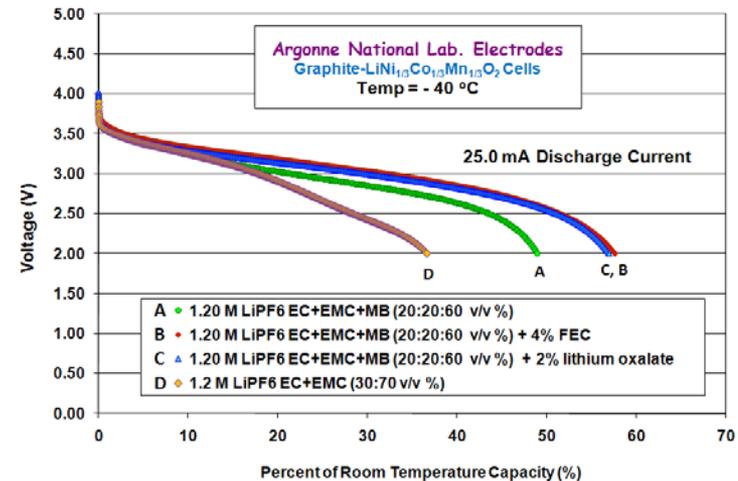
# Experimental Graphite-LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> Cells

## Argonne National Lab. Electrodes (K.Amine)

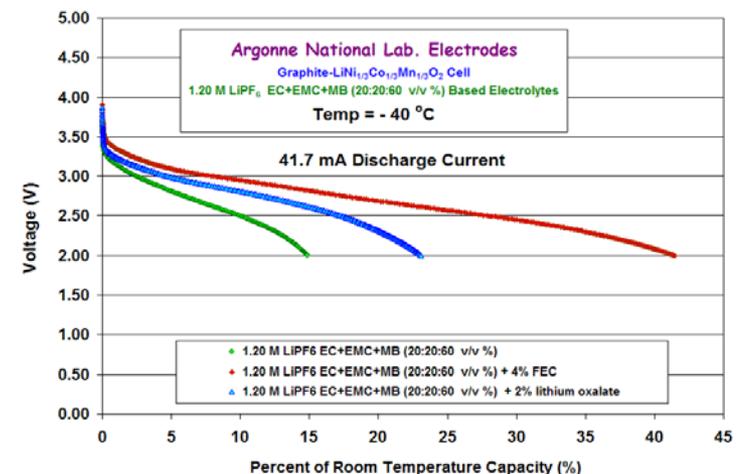
### Formation Characteristics

Electrolyte Type	Charge Capacity (mAh) 1st Cycle	Discharge Capacity (mAh) 1st Cycle	Irreversible Capacity (1st Cycle) (mAh)	Coulombic Efficiency (1st Cycle)	Charge Capacity (mAh) 5th Cycle	Reversible Capacity (mAh) 5th Cycle	Cummulative Irreversible Capacity (1st-5th Cycle) (mAh)	Coulombic Efficiency (5th Cycle)
1.0 M LiPF <sub>6</sub> EC+EMC (20:80 v/v %)	164.86	134.08	30.78	81.33	139.18	136.82	40.71	97.59
1.2 M LiPF <sub>6</sub> EC+EMC (20:80 v/v %)	168.51	140.58	27.93	83.43	141.96	139.11	35.26	98.00
1.2 M LiPF <sub>6</sub> EC+EMC (30:70 v/v %)	156.01	127.94	28.07	82.01	129.12	126.52	39.69	97.99
1.0 M LiPF <sub>6</sub> EC+EMC+MB (20:20:60 v/v %)	144.92	116.16	28.75	80.16	109.94	106.55	47.94	96.92
1.0 M LiPF <sub>6</sub> EC+EMC+MB (20:20:60 v/v %) + 4% FEC	144.44	119.59	24.85	82.79	117.93	114.86	37.57	97.40
1.0 M LiPF <sub>6</sub> EC+EMC+MB (20:20:60 v/v %) + lithium oxalate	142.71	115.06	27.65	80.63	110.47	107.94	43.30	97.71

### Discharge Characteristics



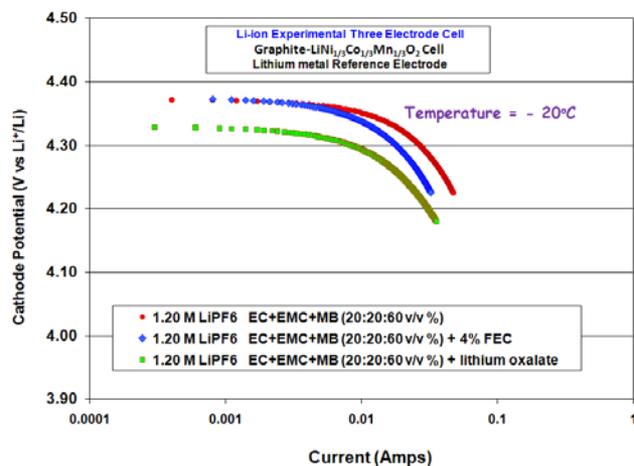
Temperature (°C)	Current (mA)	Rate	1.0 M LiPF <sub>6</sub> in EC+EMC (20:80 v/v %)		1.2 M LiPF <sub>6</sub> in EC+EMC (20:80 v/v %)		1.2 M LiPF <sub>6</sub> in EC+EMC (30:70 v/v %)		1.20 M LiPF <sub>6</sub> in EC+EMC+MB (20:20:60 v/v %)		1.20 M LiPF <sub>6</sub> in EC+EMC+MB (20:20:60 v/v %) + 4% FEC		1.20 M LiPF <sub>6</sub> in EC+EMC+MB (20:20:60 v/v %) + 2% lithium oxalate	
			Capacity (Ah)	Percent (%)	Capacity (Ah)	Percent (%)	Capacity (Ah)	Percent (%)	Capacity (Ah)	Percent (%)	Capacity (Ah)	Percent (%)	Capacity (Ah)	Percent (%)
23°C	25.00	C/5	0.13592	100.00	0.13911	100.00	0.12652	100.00	0.10655	100.00	0.11486	100.00	0.10794	100.00
-20°C	8.25	C/20	0.09695	71.38	0.08783	63.14	0.10658	84.24	0.07743	72.67	0.09486	82.59	0.09734	90.18
	8.33	C/15	0.08662	63.78	0.07829	56.28	0.10064	79.54	0.07191	67.49	0.09237	80.42	0.09607	89.00
	12.50	C/10	0.08758	64.48	0.08050	57.87	0.09376	74.11	0.06533	61.31	0.08757	76.24	0.09084	84.16
	25.00	C/5	0.08209	60.44	0.07604	54.67	0.08947	70.71	0.06143	57.65	0.08334	72.56	0.08515	78.89
	41.67	C/3	0.07936	58.43	0.07380	53.05	0.08616	68.10	0.05703	53.53	0.07851	68.35	0.07858	72.80
	62.50	C	0.07601	55.97	0.07047	50.66	0.08332	65.85	0.04341	40.74	0.07153	62.28	0.07216	66.85
-40°C	8.25	C/20	0.08337	61.38	0.08163	58.68	0.08181	64.66	0.07796	73.17	0.08384	73.00	0.08243	76.37
	8.33	C/15	0.08172	60.17	0.08193	58.89	0.07946	62.80	0.05455	51.19	0.07379	64.24	0.06930	64.21
	12.50	C/10	0.07891	58.10	0.08029	57.72	0.07365	58.21	0.05985	56.17	0.07287	63.44	0.07160	66.33
	25.00	C/5	0.07089	52.19	0.07503	53.94	0.04636	36.64	0.05212	48.92	0.06611	57.56	0.06146	56.94
	41.67	C/3	0.03462	25.49	0.03609	25.94	0.01732	13.69	0.01584	14.87	0.04761	41.45	0.02495	23.12
	62.50	C	0.01394	10.26	0.01618	11.63	0.01110	8.77	0.00854	8.02	0.02444	21.28	0.01410	13.06
-50°C	8.25	C/20	0.05091	37.48	0.05421	38.97	0.04468	35.31	0.03944	37.01	0.06311	54.95	0.04852	44.95
	8.33	C/15	0.03605	26.54	0.04065	29.22	0.03216	25.42	0.03098	29.07	0.06107	53.17	0.04824	44.69
	12.50	C/10	0.02613	19.24	0.03546	25.49	0.01651	13.05	0.02135	20.04	0.05437	47.33	0.04157	38.51
	25.00	C/5	0.01188	8.74	0.01325	9.53	0.00528	4.17	0.00766	7.19	0.03567	31.06	0.02348	21.75
	41.67	C/3	0.00479	3.52	0.00392	2.81	0.0012317	0.97	0.00312	2.93	0.00796	6.93	0.00555	5.14
-60°C	8.25	C/20	0.00606	4.46	0.00778	5.59	0.00353	2.79	0.00827	7.76	0.02632	22.91	0.01275	11.81
	8.33	C/15							0.00399	3.74	0.00878	7.65	0.01411	13.07
	12.50	C/10							0.00162	1.52	0.00315	2.74	0.00792	7.33





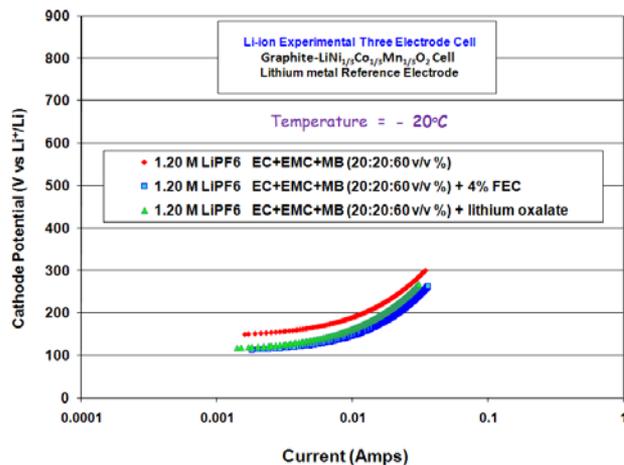
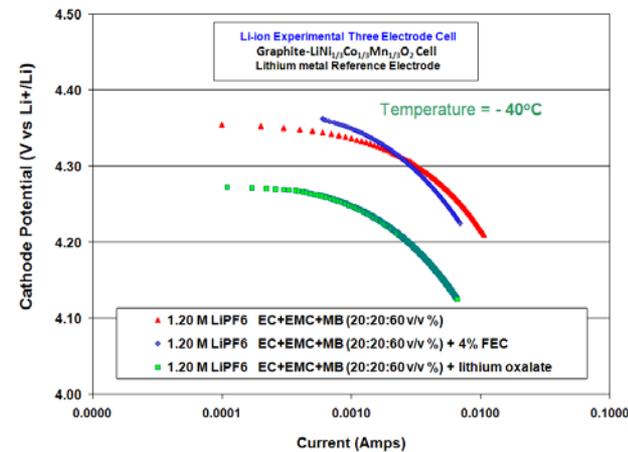
# Experimental Graphite-LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> Cells Tafel Polarization Measurements

Temperature = - 20°C



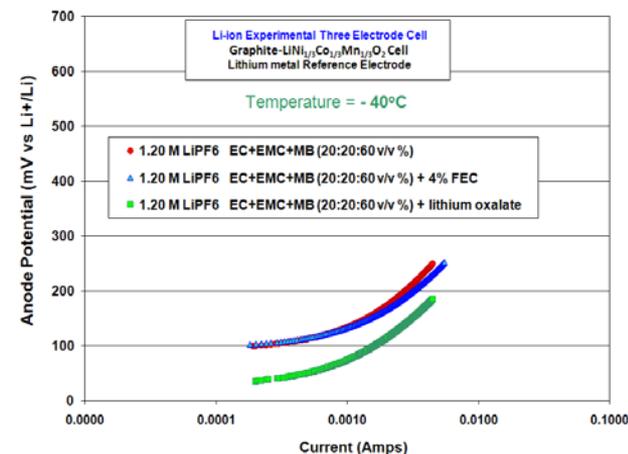
Initially, The cell with the **1.2 M LiPF<sub>6</sub> EC+EMC+MB (20:20:60)** electrolyte exhibited the highest limiting current densities on **GRAPHITE** electrodes at - 20°C.

The cell with the **1.0 M LiPF<sub>6</sub> EC+EMC+MB (20:20:60) + 4% FEC** electrolyte exhibited the highest limiting current densities on **LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub>** electrodes at - 20°C.



Initially, The cell with the **1.2 M LiPF<sub>6</sub> EC+EMC+MB (20:20:60)** electrolyte exhibited the highest limiting current densities on **GRAPHITE** electrodes at - 40°C.

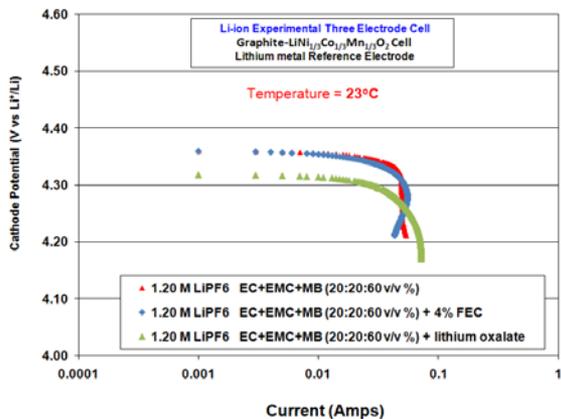
The cell with the **1.0 M LiPF<sub>6</sub> EC+EMC+MB (20:20:60) + 4% FEC** electrolyte exhibited the highest limiting current densities on **LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub>** electrodes at - 40°C. However all electrolyte displayed somewhat comparable performance.





# Experimental Graphite-LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> Cells Tafel Polarization Measurements

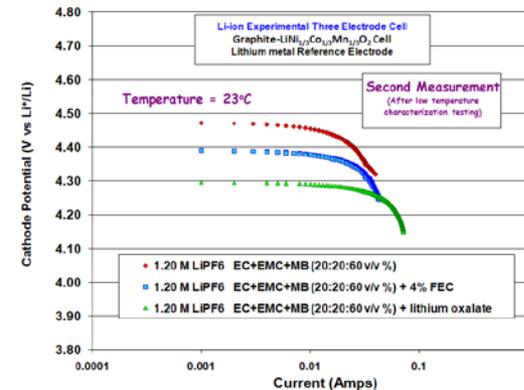
Temperature = 23°C



Initially, The cell with the **1.2 M LiPF<sub>6</sub> EC+EMC+MB (20:20:60)** electrolyte exhibited the highest limiting current densities on **GRAPHITE** electrodes at 23°C.

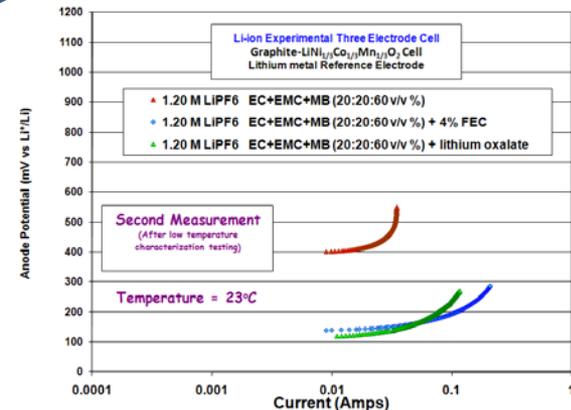
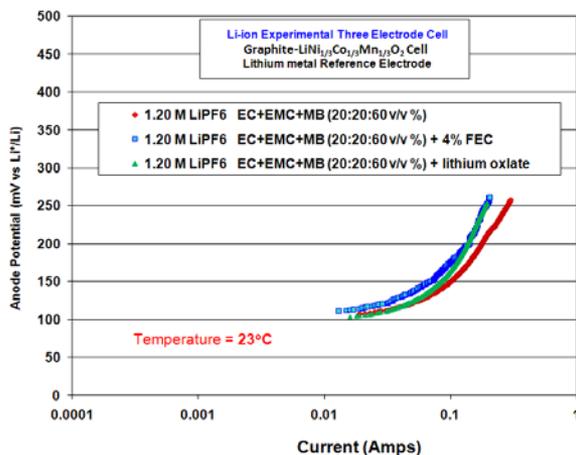
The cell with the **1.0 M LiPF<sub>6</sub> EC+EMC+MB (20:20:60) + lithium oxalate** electrolyte exhibited the highest limiting current densities on **LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub>** electrodes at 23°C.

Temperature = 23°C  
After Characterization/Cycling



After characterization, The cell with the **1.2M LiPF<sub>6</sub> EC+EMC+MB (20:20:60)** electrolyte displayed much lower limiting current densities on **GRAPHITE** electrodes, with the addition of FEC greatly stabilizing the system.

The cell with the **1.0 M LiPF<sub>6</sub> EC+EMC+MB (20:20:60) + lithium oxalate** electrolyte exhibited the highest limiting current densities on **LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub>** electrodes after low temperature cycling characterization.

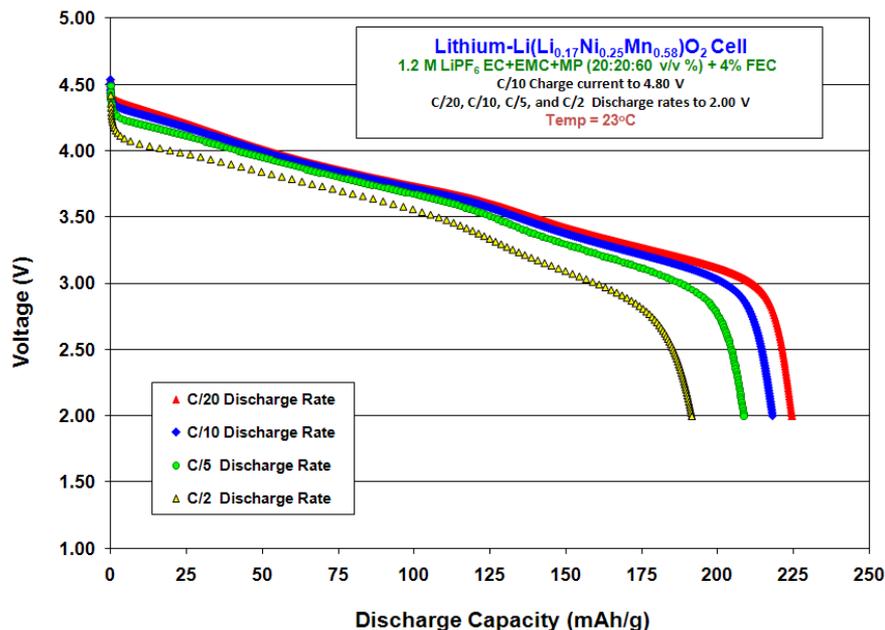




# Technical Accomplishments

## Electrolytes With Operating Temperature Performance and High Voltage Stability

### Formation Characteristics in $\text{Li-Li}(\text{Li}_{0.17}\text{Ni}_{0.25}\text{Mn}_{0.58})\text{O}_2$ cells



		1.0 M LiPF <sub>6</sub> EC+DEC+ DMC (1:1:1 v/v %)						1.2 M LiPF <sub>6</sub> EC+EMC+MP (20:20:60 v/v %) + 4% FEC					
		Cell JZ35			JZ36			Cell JZ37			JZ38		
Temp (°C)	Discharge Rate	mAh	mAh/g	% of C20 Capacity (mAh/g)	mAh	mAh/g	% of C20 Capacity (mAh/g)	mAh	mAh/g	% of C20 Capacity (mAh/g)	mAh	mAh/g	% of C20 Capacity (mAh/g)
23°C	C/20	2.721	226.77	100	2.709	227.28	100	2.678	224.67	100	2.556	223.45	100
	C/10	2.636	219.64	96.86	2.626	220.34	96.94	2.602	218.26	97.15	2.487	217.40	97.29
	C/5	2.510	209.18	92.25	2.500	209.72	92.27	2.488	208.70	92.89	2.381	208.13	93.14
	C/2	2.283	190.28	83.91	2.122	178.00	78.32	2.283	191.49	85.23	2.183	190.80	85.39
0°C	C/20	2.147	178.92	78.90	2.102	176.34	77.59	2.118	177.66	79.08	2.043	178.62	79.9378
	C/10	2.051	170.94	75.38	1.993	167.17	73.55	2.017	169.20	75.31	1.948	170.26	76.19
	C/5	1.881	156.73	69.11	1.678	140.80	61.95	1.845	154.75	68.88	1.780	155.57	69.62
	C/2	1.416	118.04	52.05	0.877	73.55	32.36	1.535	128.77	57.32	1.494	130.57	58.43
-10°C	C/20	1.947	162.25	71.55	1.876	157.41	69.26	1.925	161.46	71.86	1.865	163.02	72.95
	C/10	1.744	145.30	64.08	1.651	138.51	60.94	1.717	144.05	64.12	1.666	145.63	65.17
	C/5	1.410	117.47	51.80	1.065	89.31	39.29	1.475	123.71	55.06	1.435	125.40	56.12
	C/2	0.658	54.84	24.18	0.651	54.59	24.02	0.889	74.59	33.20	1.057	92.37	41.34

- A promising wide operating temperature range electrolyte formation (EC+EMC+MP+ FEC) was evaluated with high voltage, high specific energy cathode materials.
  - Formation characteristics very comparable to all carbonate baseline electrolytes.
- Current efforts are focused upon investigating electrolytes compatible with carbon-NMC system and ABR developed high voltage systems (i.e., LTO-LMNO).



# A123 2.20 Ah High Power Lithium-Ion Cells

## Discharge Rate Characterization Testing

Temperature Range 20 to 0°C;  
Cells Discharged to 0.50V

Temperature Range 20°C to -50°C;  
Cells Discharged to 0.50V

Temperature (°C)	Rate	Current (A)	ACC-05				AVC-05				AFC-05			
			BASELINE Electrolyte				1.2M LiPF6 in EC+EMC+MB (20:20:60 v/v %) + 2% VC				1.2M LiPF6 in EC+EMC+MB (20:20:60 v/v %) + 4% FEC			
			Capacity (Ah)	Watt-Hours (Wh)	Energy (Wh/Kg)	% of Room Temp	Capacity (Ah)	Watt-Hours (Wh)	Energy (Wh/Kg)	% of Room Temp	Capacity (Ah)	Watt-Hours (Wh)	Energy (Wh/Kg)	% of Room Temp
20°C (Initial)	C/5	0.400	2.2422	7.284	102.69	100	2.380	7.712	108.31	100.00	2.3167	7.506	105.70	100
20°C	11.40C	25.0	2.1811	5.9123	83.272	97.27	2.1385	5.4224	76.158	89.85	2.0836	5.0039	70.48	89.94
	10.20C	22.5	2.1948	6.0378	85.039	97.89	2.1604	5.6371	79.172	90.77	2.1086	5.4457	76.70	91.02
	9.1C	20.0	2.1956	6.1263	86.286	97.92	2.1752	5.8164	81.690	91.39	2.1207	5.6697	79.85	91.64
	8.0C	17.5	2.1962	6.2213	87.623	97.95	2.1891	5.9898	84.126	91.98	2.1310	5.8654	82.47	91.98
	6.8C	15.0	2.1977	6.3238	89.068	98.02	2.2035	6.1641	86.676	92.58	2.1421	6.0288	84.91	92.46
	5.7C	12.5	2.1902	6.4061	90.227	97.68	2.2128	6.3233	88.810	92.97	2.1479	6.1816	87.06	92.71
	4.8C	10.0	2.2034	6.5599	92.393	98.27	2.2377	6.5336	91.763	94.02	2.1697	6.3826	89.89	93.66
	3.4C	7.5	2.2085	6.6973	94.328	98.60	2.2683	6.7383	94.639	94.88	2.1865	6.5713	92.55	94.38
	2.3C	5.0	2.2197	6.8724	96.794	99.00	2.2837	6.9768	97.976	96.95	2.2062	6.7792	96.48	96.23
10°C	11.40C	25.0	2.2067	5.7553	81.060	98.42	2.1747	5.3529	75.181	91.37	2.1258	4.9557	69.80	91.75
	10.20C	22.5	2.2001	5.8103	81.835	98.12	2.1889	5.5275	77.634	91.88	2.1391	5.3777	75.74	92.33
	9.1C	20.0	2.2090	5.9039	83.153	98.52	2.2205	5.7405	80.625	93.30	2.1563	5.6074	78.98	93.08
	8.0C	17.5	2.2064	5.9843	84.286	98.40	2.2154	5.8659	82.386	93.08	2.1615	5.7813	81.43	93.30
	6.8C	15.0	2.2094	6.0850	85.704	98.54	2.2079	5.9799	83.988	92.77	2.1743	5.9635	83.99	93.85
	5.7C	12.5	2.1985	6.1525	86.655	98.05	2.2396	6.2021	87.109	94.10	2.1763	6.1076	86.02	93.94
	4.8C	10.0	2.2133	6.3130	88.916	98.71	2.2638	6.4125	90.063	95.11	2.1991	6.3143	88.93	94.92
	3.4C	7.5	2.2171	6.4547	90.911	98.88	2.2833	6.6130	92.879	95.93	2.2150	6.4989	91.53	95.61
	2.3C	5.0	2.2265	6.6691	93.930	99.30	2.3053	6.8613	96.367	96.86	2.2313	6.7150	94.58	96.32
0°C	11.40C	25.0	2.1900	5.4308	76.491	97.67	2.1736	5.0944	71.551	91.33	2.1472	4.8055	67.58	92.69
	10.20C	22.5	2.1969	5.5119	77.633	97.98	2.1992	5.3234	74.767	92.40	2.1674	5.2519	73.97	93.56
	9.1C	20.0	2.2025	5.5865	78.683	98.23	2.2168	5.4961	77.193	93.14	2.1802	5.4610	76.91	94.11
	8.0C	17.5	2.2051	5.6569	79.675	98.34	2.2320	5.6552	79.427	93.78	2.1898	5.6328	79.34	94.52
	6.8C	15.0	2.2082	5.7362	80.792	98.48	2.2500	5.8231	81.785	94.54	2.2017	5.8062	81.78	95.04
	5.7C	12.5	2.2022	5.7940	81.606	98.21	2.2582	5.9622	83.738	94.88	2.2055	5.9476	83.77	95.20
	4.8C	10.0	2.2067	5.9064	83.176	98.42	2.2756	6.1488	86.369	96.61	2.2202	6.1324	86.37	96.83
	3.4C	7.5	2.2079	6.0400	85.070	98.47	2.2928	6.3616	89.208	96.33	2.2346	6.3237	89.07	96.46
	2.3C	5.0	2.2208	6.2900	88.692	99.06	2.3103	6.5973	92.669	97.07	2.2473	6.6382	92.09	97.00

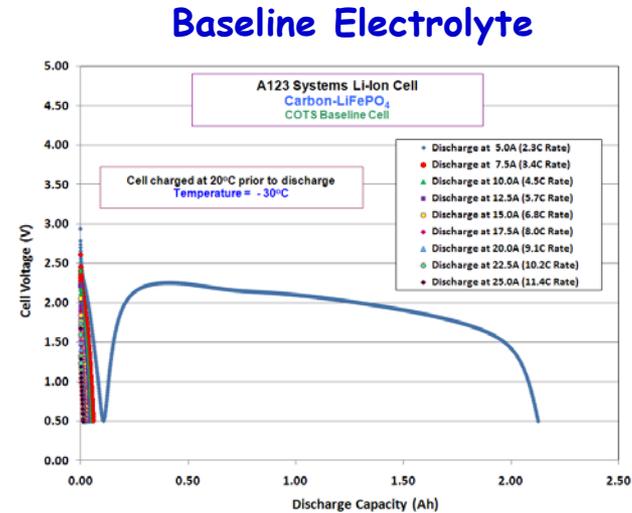
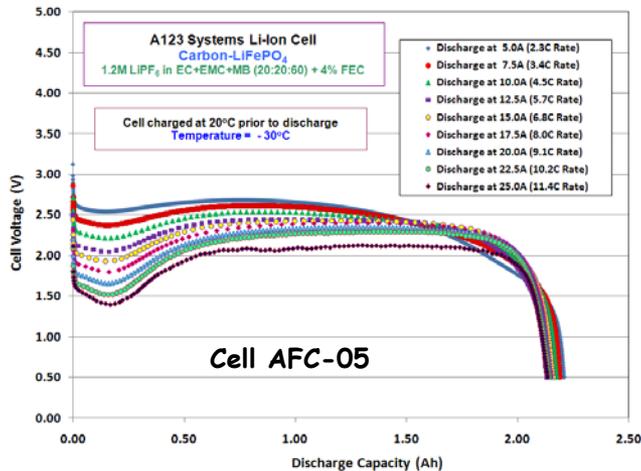
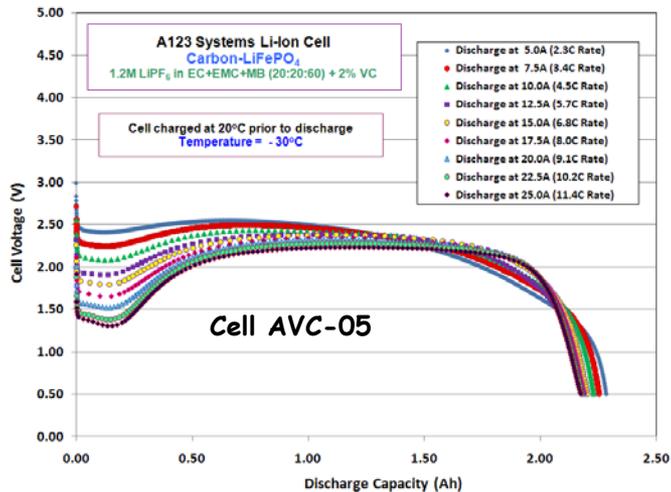
Temperature (°C)	Rate	Current (A)	ACC-05				AVC-05				AFC-05			
			BASELINE Electrolyte				1.2M LiPF6 in EC+EMC+MB (20:20:60 v/v %) + 2% VC				1.2M LiPF6 in EC+EMC+MB (20:20:60 v/v %) + 4% FEC			
			Capacity (Ah)	Watt-Hours (Wh)	Energy (Wh/Kg)	% of Room Temp	Capacity (Ah)	Watt-Hours (Wh)	Energy (Wh/Kg)	% of Room Temp	Capacity (Ah)	Watt-Hours (Wh)	Energy (Wh/Kg)	% of Room Temp
20°C (Initial)	C/5	0.400	2.2422	7.284	102.59	100	2.380	7.712	108.31	100.00	2.3167	7.506	105.70	100
-20°C	11.40C	25.0	0.0561	0.0792	1.116	2.50	2.1834	4.5665	64.136	91.74	2.1342	4.2968	60.52	92.12
	10.20C	22.5	0.0626	0.0921	1.297	2.79	2.1889	4.7069	66.108	91.97	2.1406	4.6829	65.96	92.40
	9.1C	20.0	0.0717	0.1101	1.550	3.20	2.1977	4.8495	68.111	92.34	2.1470	4.8679	68.56	92.67
	8.0C	17.5	0.0836	0.1335	1.880	3.73	2.2072	4.9812	69.961	92.74	2.1528	5.0226	70.74	92.93
	6.8C	15.0	0.0954	0.1562	2.201	4.26	2.2182	5.0652	71.140	93.20	2.1644	5.1671	72.78	93.42
	5.7C	12.5	2.1367	4.7826	67.360	95.30	2.2356	5.1980	73.006	93.93	2.1729	5.2893	74.50	93.79
-30°C	11.40C	25.0	0.0133	0.012	0.169	0.59	2.1742	4.2765	60.063	91.35	2.1335	4.1116	57.91	92.09
	10.20C	22.5	0.0134	0.012	0.175	0.60	2.1781	4.3645	61.299	91.52	2.1416	4.4236	62.30	92.44
	9.1C	20.0	0.0169	0.017	0.240	0.75	2.1842	4.4827	62.959	91.77	2.1476	4.5831	64.55	92.70
	8.0C	17.5	0.0209	0.023	0.326	0.93	2.1899	4.5847	64.392	92.01	2.1518	4.7165	66.43	92.88
	6.8C	15.0	0.0258	0.031	0.440	1.15	2.2029	4.6949	65.940	92.56	2.1592	4.8436	68.22	93.20
	5.7C	12.5	0.0326	0.043	0.609	1.45	2.1857	4.6835	66.780	91.84	2.1313	4.8215	67.91	92.00
	4.8C	10.0	0.0422	0.062	0.868	1.88	2.2301	4.8821	68.569	93.70	2.1745	5.0710	71.42	93.86
	3.4C	7.5	0.0575	0.092	1.295	2.56	2.2530	4.9692	69.793	94.66	2.1892	5.1815	72.98	94.49
	2.3C	5.0	2.1277	4.044	56.957	94.89	2.2823	5.0549	70.996	95.89	2.2066	5.2904	74.51	95.25
-40°C	11.40C	25.0	0.0000	0.000	0.000	0.00	0.0971	0.0623	0.875	4.08	2.1463	4.0134	56.53	92.65
	10.20C	22.5	0.0000	0.000	0.000	0.00	2.1838	4.0748	57.231	91.76	2.1637	4.1968	59.11	92.96
	9.1C	20.0	0.0000	0.000	0.000	0.00	2.1846	4.1430	58.188	91.79	2.1507	4.2987	60.55	92.84
	8.0C	17.5	0.0000	0.000	0.000	0.00	2.1842	4.2071	59.089	91.77	2.1494	4.3991	61.96	92.78
	6.8C	15.0	0.0000	0.000	0.000	0.00	2.1916	4.2578	59.800	92.08	2.1634	4.4934	63.29	92.95
	5.7C	12.5	0.0016	0.0011	0.016	0.07	2.1912	4.2981	60.366	92.07	2.1365	4.5392	63.93	92.22
	4.8C	10.0	0.0060	0.0051	0.072	0.27	2.1763	4.2646	59.996	91.44	2.1600	4.6114	64.95	92.80
-50°C	11.40C	25.0	0.0000	0.000	0.000	0.00	0.0002	0.0001	0.002	0.01	0.0009	0.0006	0.01	0.04
	10.20C	22.5	0.0000	0.000	0.000	0.00	0.0003	0.0002	0.003	0.01	0.0016	0.0011	0.02	0.07
	9.1C	20.0	0.0001	0.000	0.000	0.01	0.0007	0.0005	0.007	0.03	0.0029	0.0020	0.03	0.13
	8.0C	17.5	0.0000	0.000	0.000	0.00	0.0016	0.0011	0.015	0.07	0.0053	0.0036	0.04	0.25
	6.8C	15.0	0.0000	0.000	0.000	0.00	0.0033	0.0023	0.032	0.14	0.0098	0.00630	0.09	3.88
	5.7C	12.5	0.0000	0.000	0.000	0.00	0.0070	0.00675	0.949	4.07	2.1362	4.1794	58.86	92.21
	4.8C	10.0	0.0000	0.000	0.000	0.00	2.1843	3.8318	53.818	91.77	2.1596	4.2429	59.76	93.22
	3.4C	7.5	0.0000	0.000	0.000	0.00	2.1651	3.6314	51.003	90.55	2.1456	4.1495	58.44	92.61
	2.3C	5.0	0.0000	0.000	0.000	0.00	2.1350	3.4121	47.923	89.70	2.1602	4.1228	58.07	93.25



# A123 2.20 Ah High Power Lithium-Ion Cells

## Discharge Rate Characterization Testing

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



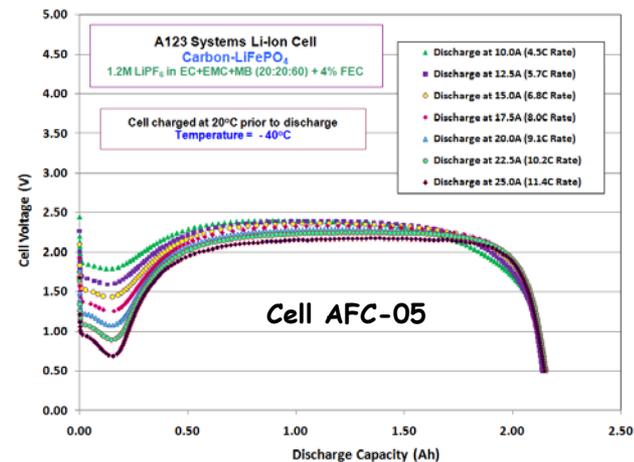
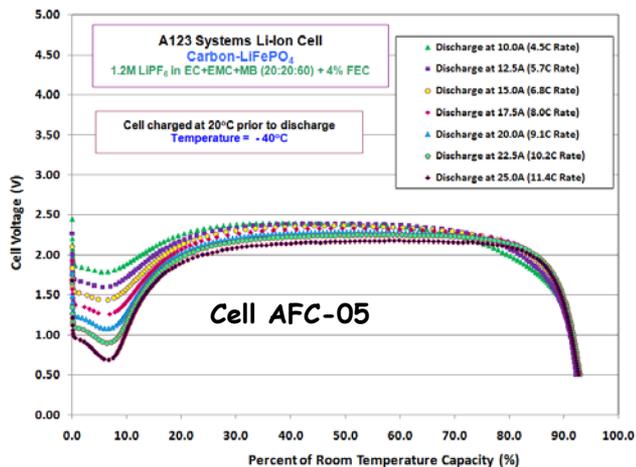
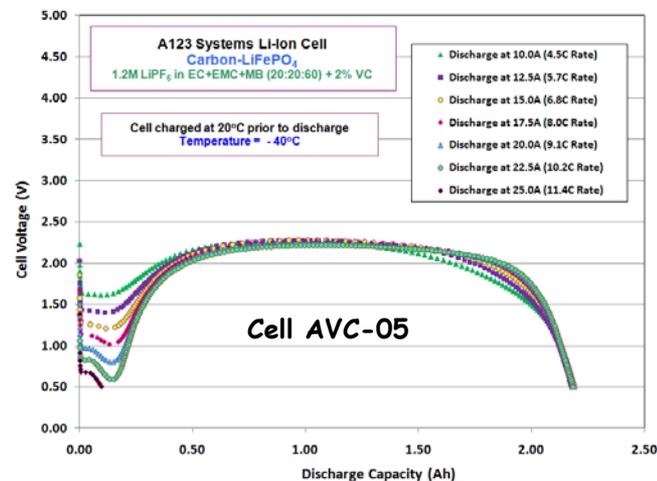
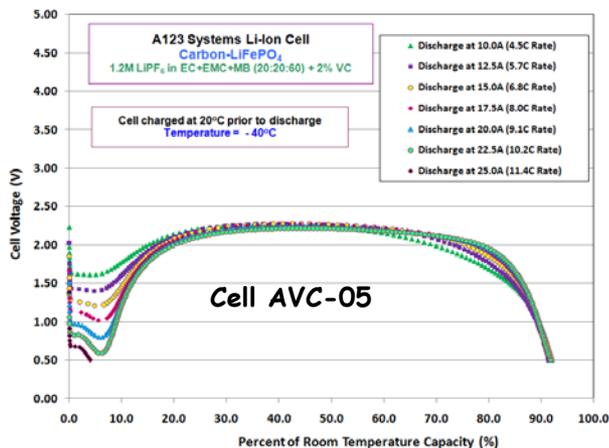
- The MB-based systems are capable of supporting greater than 11C discharge rates at -30°C, with over 90% of the room temperature capacity being delivered.
- Whereas, negligible capacity delivered with the baseline system under similar conditions.



# A123 2.20 Ah High Power Lithium-Ion Cells

## Discharge Rate Characterization Testing

Temperature = -40°C; Cells Discharged to 0.50V



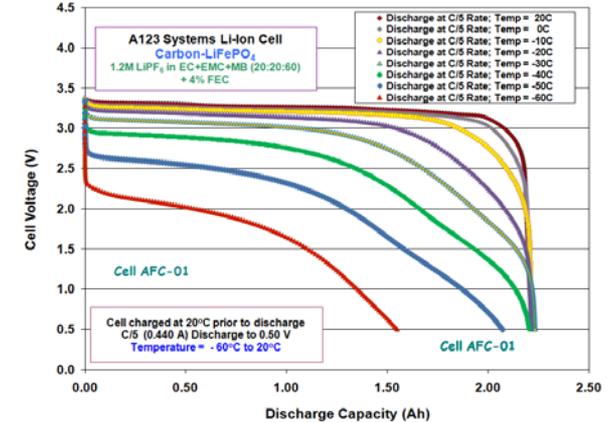


# A123 2.20 Ah High Power Lithium-Ion Cells

## Discharge Rate Characterization Testing : Cell Discharged to 0.50V

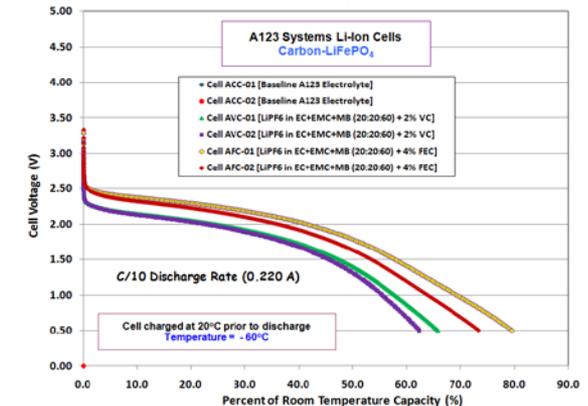
			ACC-01				ACC-02				AVC-01			
			BASELINE Electrolyte				BASELINE Electrolyte				1.2M LiPF <sub>6</sub> in EC+EMC+MB (20:20:60 v/v %) + 2% VC			
Temperature (oC)	Rate	Current (A)	Capacity (Ah)	Watt-Hours (Wh)	Energy (Wh/Kg)	% of Room Temp	Capacity (Ah)	Watt-Hours (Wh)	Energy (Wh/Kg)	% of Room Temp	Capacity (Ah)	Watt-Hours (Wh)	Energy (Wh/Kg)	% of Room Temp
20°C (Initial)	C/5	0.400	2.1845	7.079	99.7	100	2.1287	6.882	96.9299	100	2.367	7.666	107.67	100.00
-50°C	2.0C	4.4	0.0003	0.000	0.003	0.02	0.0009	0.001	0.009	0.04	2.1920	3.6872	51.787	92.59
	1.0C	2.200	0.0071	0.007	0.098	0.32	0.0065	0.006	0.089	0.31	2.0991	3.3378	46.879	88.67
	C/2	1.100	0.0206	0.028	0.396	0.95	0.0200	0.027	0.377	0.94	1.9076	3.2225	45.259	80.58
	C/5	0.440	0.0529	0.091	1.282	2.42	0.0528	0.091	1.276	2.48	1.9441	3.6606	51.412	82.12
	C/10	0.220	0.1101	0.211	2.968	5.04	0.2543	0.344	4.846	11.95	2.0913	4.3253	60.749	88.34
-60°C	C/20	0.110	0.1978	0.406	5.714	9.06	0.8887	1.202	16.930	41.75	2.2267	4.9607	69.673	94.06
	2.0C	4.400	0.0000	0.000	0.000	0.00	0.0000	0.000	0.000	0.00	0.0776	0.0523	0.735	3.28
	1.0C	2.200	0.0000	0.000	0.000	0.00	0.0000	0.000	0.000	0.00	1.7678	2.1979	30.870	74.67
	C/2	1.100	0.0000	0.000	0.000	0.00	0.0000	0.000	0.000	0.00	1.1856	1.7511	24.594	50.08
	C/5	0.440	0.0000	0.000	0.000	0.00	0.0000	0.000	0.000	0.00	1.2975	2.0892	29.343	54.81
C/10	0.220	0.0000	0.000	0.000	0.00	0.0000	0.000	0.000	0.00	1.5576	2.6671	37.459	65.79	
C/20	0.110	0.0000	0.000	0.000	0.00	0.0000	0.000	0.000	0.00	1.6461	3.0460	42.781	69.53	

### Discharge Capacity vs. Temperature (C/5 Discharge Rate)



➤ The MB-based containing FEC was observed to deliver good performance down to -60°C, being able to support high discharge rates.

			AVC-02				AFC-01				AFC-02			
			1.2M LiPF <sub>6</sub> in EC+EMC+MB (20:20:60 v/v %) + 2% VC				1.2M LiPF <sub>6</sub> in EC+EMC+MB (20:20:60 v/v %) + 4% FEC				1.2M LiPF <sub>6</sub> in EC+EMC+MB (20:20:60 v/v %) + 4% FEC			
Temperature (oC)	Rate	Current (A)	Capacity (Ah)	Watt-Hours (Wh)	Energy (Wh/Kg)	% of Room Temp	Capacity (Ah)	Watt-Hours (Wh)	Energy (Wh/Kg)	% of Room Temp	Capacity (Ah)	Watt-Hours (Wh)	Energy (Wh/Kg)	% of Room Temp
20°C (Initial)	C/5	0.400	2.361	7.645	107.37	100.00	2.3226	7.511	105.79	100	2.3115	7.490	105.50	100
-50°C	2.0C	4.4	2.2605	4.3563	61.184	95.76	2.1547	3.9919	56.22	92.77	2.0616	3.3731	47.51	89.19
	1.0C	2.200	2.2465	4.0824	57.337	95.17	2.1368	3.8107	53.67	92.00			0.00	0.00
	C/2	1.100	2.1434	3.8110	53.525	90.80	2.0841	3.8386	54.07	89.73	1.8740	3.3751	47.54	81.07
	C/5	0.440	2.0374	3.9063	54.863	86.31	2.0728	4.1971	59.11	89.25	2.0055	4.0077	56.45	86.76
	C/10	0.220	2.1145	4.4063	61.886	89.58	2.1403	4.7116	66.36	92.15	2.1213	4.6323	65.24	91.77
-60°C	C/20	0.110	2.2219	4.9761	69.890	94.13	2.2079	5.1914	73.12	95.06	2.2089	5.1795	72.95	95.56
	2.0C	4.400	2.2216	3.5010	49.172	94.11	0.6380	1.0049	14.15	27.47	1.8806	2.353	33.14	81.36
	1.0C	2.200	1.4061	1.5815	22.212	59.57	1.8368	2.6085	36.74	79.08	1.3663	1.6266	22.91	59.11
	C/2	1.100	0.9061	1.2827	18.015	38.39	1.6426	2.4223	34.12	70.72	0.9161	1.4289	20.13	39.63
	C/5	0.440	1.1637	1.8289	25.686	49.30	1.5480	2.6287	37.02	66.65	1.2838	2.1715	30.58	55.54
C/10	0.220	1.4723	2.5295	35.527	62.37	1.8468	3.3788	47.59	79.52	1.6963	3.0543	43.02	73.39	
C/20	0.110	1.5755	2.9099	40.870	66.75	1.9478	3.8672	54.47	83.86	1.8801	3.6737	51.74	81.34	



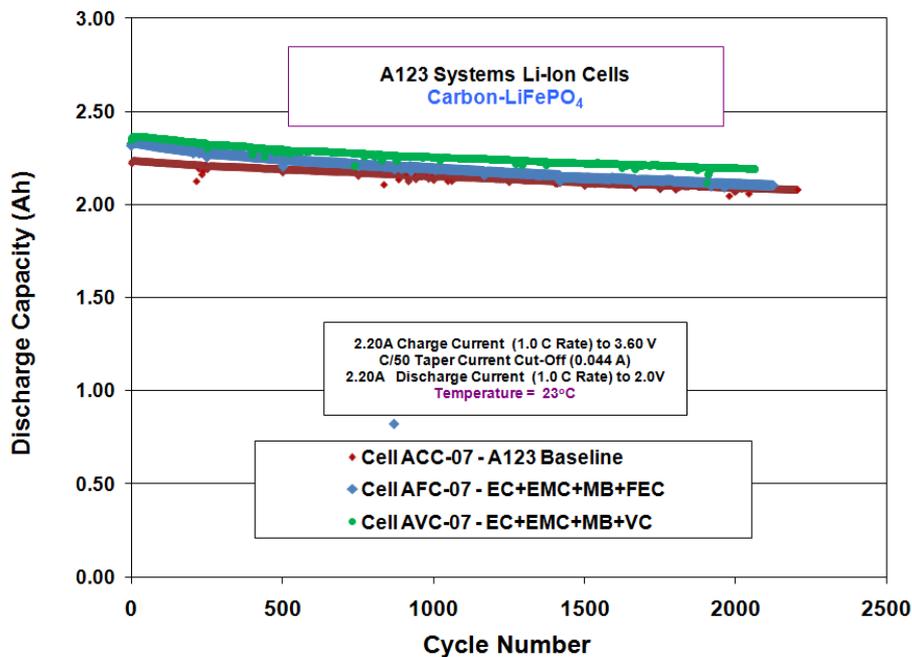


# A123 2.20 Ah High Power Lithium-Ion Cells

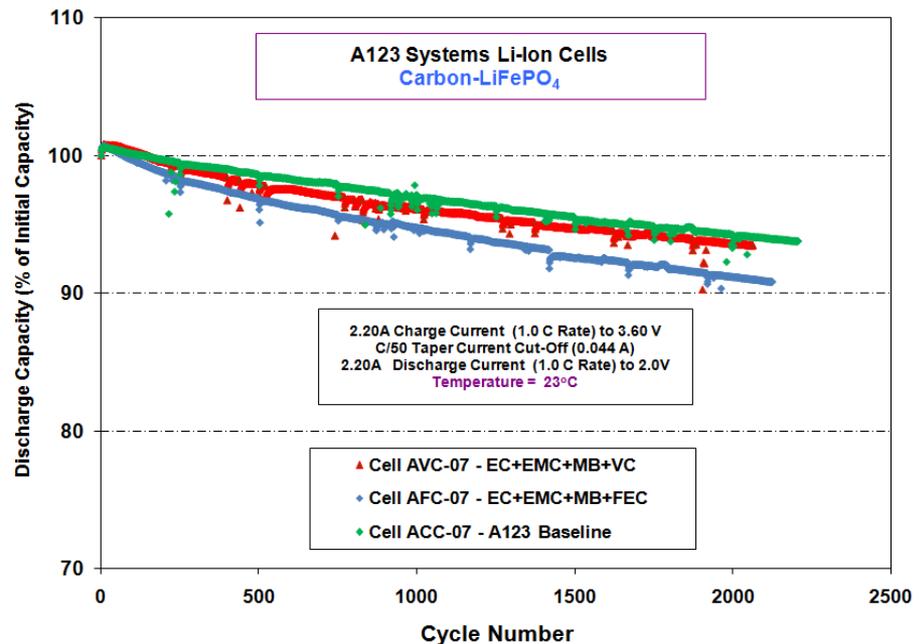
## 100% DOD Cycle Life Characterization Testing at 23°C

### Test Articles (Three Different Electrolyte Variations)

### Discharge Capacity (Ah)



### Percent of Initial Capacity (Ah)



- 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 2,000 cycles).
- Observed trend (in increasing capacity fade rate): Baseline < MB+VC < MB+FEC

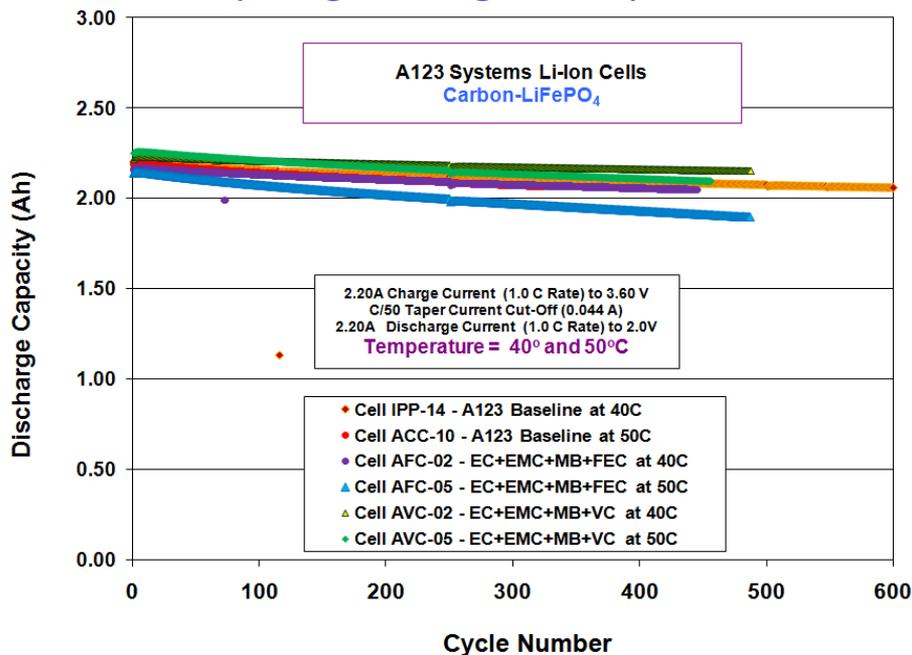


# A123 2.20 Ah High Power Lithium-Ion Cells

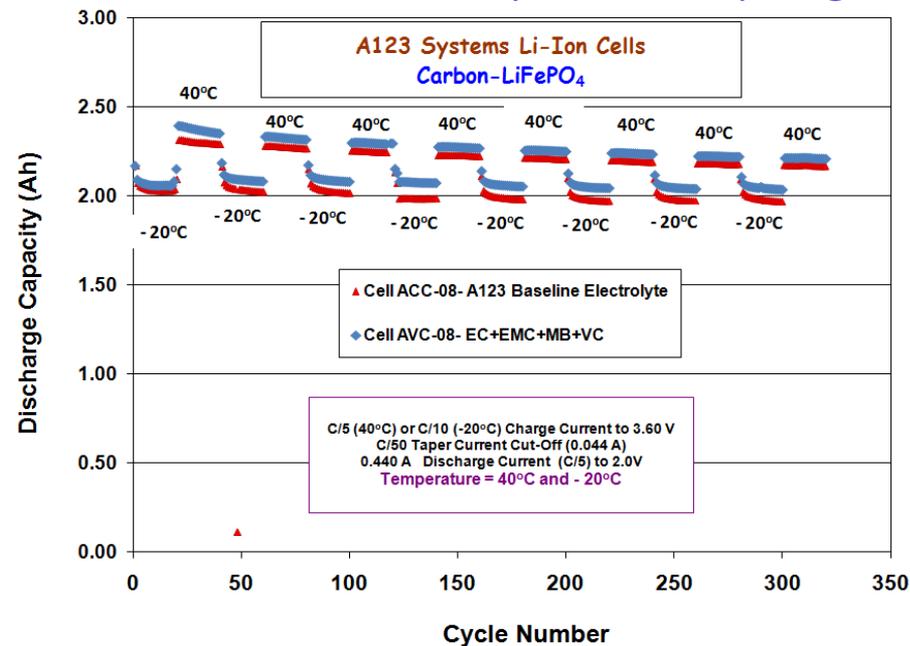
## 100% DOD Cycle Life Characterization Testing at 40 and 50°C

### Test Articles (Three Different Electrolyte Variations)

#### Cycling at High Temperature



#### Variable Temperature Cycling



- Generally good resilience to high temperature cycling observed with the MB+VC and MB+FEC systems.
- Good resilience to low temperature charging also observed (no apparent lithium plating).

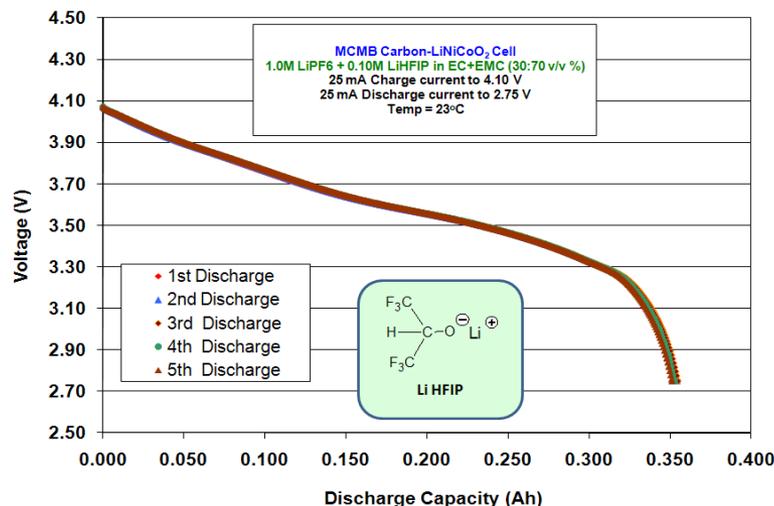
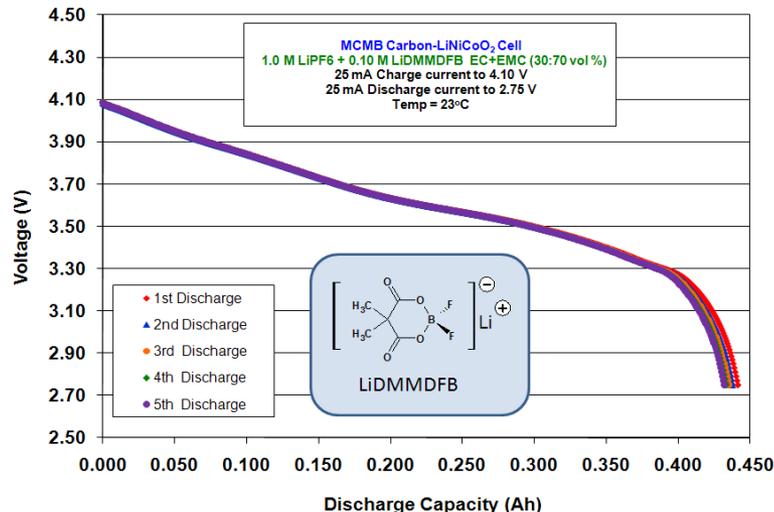
Testing involves alternating between performing 20 cycles at -20°C (using C/10 charge and C/5 discharge) and performing 20 cycles at 40°C (using C/5 charge and C/5 discharge).



# Technical Accomplishments

## Formation Characteristics of Three Electrode MCMB-LiNi<sub>x</sub>Co<sub>1-x</sub>O<sub>2</sub> Cells

Electrolyte Type	Charge Capacity (Ah) 1st Cycle	Discharge Capacity (Ah) 1st Cycle	Irreversible Capacity (1st Cycle)	Coulombic Efficiency (1st Cycle)	Charge Capacity (Ah) 5th Cycle	Reversible Capacity (Ah) 5th Cycle	Cummulative Irreversible Capacity (1st-5th Cycle)	Coulombic Efficiency (5th Cycle)
1.0 M LiPF <sub>6</sub> EC+EMC (30:70 vol %)	0.4504	0.3768	0.074	83.64	0.3799	0.3676	0.1356	96.75
1.0 M LiPF <sub>6</sub> EC+EMC (30:70 vol %) + 0.10M LiHFIP	0.4705	0.3978	0.073	84.55	0.3969	0.3819	0.1449	96.20
1.0 M LiPF <sub>6</sub> + 0.10 M LiBOB EC+EMC (30:70 vol %)	0.4657	0.3939	0.072	84.59	0.3895	0.3834	0.1057	98.42
1.0 M LiPF <sub>6</sub> + 0.10 M LiDMMDFB EC+EMC (30:70 vol %)	0.5005	0.4417	0.059	88.25	0.4337	0.4320	0.0776	99.60



➤ In collaboration with Dr. Li Yang, Dr. John Kerr (LBNL), and Prof. Brett Lucht, we have received a new malonate borate-based Li-salt that is anticipated to result in improved high temperature resilience.

➤ We are also evaluating lithium hexafluoro isopropoxide as a potential lithium electrolyte salt that can serve both as an additive and as an ionically conductive salt.



# Summary

- **Met programmatic milestones for program.**
- **Demonstrated improved performance with wide operating temperature electrolytes containing ester co-solvents (i.e., methyl butyrate) containing electrolyte additives in A123 prototype cells:**
  - **At -30°C, cells were demonstrated to deliver over 90% of the room temperature capacity using greater than 11C rates.**
  - **The cells were observed to perform well down to -60°C, with 80% of the room temperature capacity being delivered using a C/10 rate.**
  - **Good Cycle life performance was also observed up to 50°C, and displayed resilience to variable temperature cycling (which involves charging and discharging at low temperature as well as high).**
- **Developed a number of methyl propionate and methyl butyrate containing electrolyte that contain various additives intended to improve the high temperature resilience:**
  - **Demonstrated improved low temperature performance with many formulations.**
  - **Improved low temperature electrode kinetics observed with many additives.**
  - **Studied degradation modes when exposed to high temperature cycling.**
  - **Formulations possessing mono-fluoroethylene carbonate (FEC), LiBOB, lithium oxalate, and vinylene carbonate have shown promise in experimental cells.**
  - **Investigated with many chemistries (i.e.,  $\text{LiNiCoO}_2$ ,  $\text{LiNiCoAlO}_2$ ,  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ ,  $\text{Li}(\text{Li}_{0.17}\text{Ni}_{0.25}\text{Mn}_{0.58})$ )**
- **Initiated the investigation of a lithium malonate borate-based electrolyte additive/salt (with LBNL/URI). Preliminary investigation also started to evaluate the utility of using lithium isopropoxide as an electrolyte additive/salt.**



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# 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.*
  - *Study the cycle life behavior and high temperature resilience more thoroughly.*
  - *Correlate trends in electrochemical data with charge/discharge behavior*
  - *Identify performance limiting aspects at extreme temperatures*
  - *Explore the use of **fluorinated esters**, especially with high voltage systems, including trifluoroethyl butyrate, ethyl trifluoroacetate, and trifluoroethyl acetate.*
  - *Study wide operating temperature range systems in conjunction with ABR developed electrodes, which were recently received from Argonne.*
  
- **Continue the investigation of alternate lithium-based electrolyte salts**
  - *Continue the investigation of LiDNA as an electrolyte additive.*
  - *Investigate the use lithium hexafluoroisopropoxide (preliminary results are encouraging)*
  - *Investigate the use lithium malonate borate-based salts (in collaboration with Li Yang, John Kerr and Brett Lucht)*
  - *Explore the utility of these salts in conjunction with alternate solvent mixtures.*
  - *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, on-going collaborator
- Argonne Nat. Lab (Khalil Amine): ANL provided electrodes for evaluation (on-going collaborator)
- LBNL (Li Yang and John Kerr): Mat Methods provided novel lithium dinitrimide 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.

## Publications and Presentations

- 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, B. V. Ratnakumar, L. D. Whitcanack, K. A. Smith, S. Santee, F. J. Puglia, and R. Gitzendanner, "Performance Demonstration of MCMB-LiNi<sub>x</sub>Co<sub>1-x</sub>O<sub>2</sub> Cells Containing Electrolytes Designed for Wide Operating Temperature Range", *ECS Transactions*, **25** (36), 273 (2010).
- M. C. Smart, B. V. Ratnakumar, A. S. Gozdz, and S. Mani, "The Effect of Electrolyte Additives upon the Lithium Kinetics of Li-Ion Cells Containing MCMB and LiNi<sub>x</sub>Co<sub>1-x</sub>O<sub>2</sub> Electrodes and Exposed to High Temperatures", *ECS Transactions*, **25** (36), 37 (2010).
- N. Leifer, M. C. Smart, G. K. S. Prakash, L. Gonzalez, L. Sanchez, K. A. Smith, P. Bhall, C. P. Grey, and S. G. Greenbaum, "13C Solid State NMR Study of SEI Formation of Lithium Ion Battery Anodes Cycled in Isotopically Enriched Electrolytes Suggest Unusual Breakdown Products", *J. Electrochem.Soc.*, in press.
- M. C. Smart and B. V. Ratnakumar, " Effects of Electrolyte Composition on Lithium Plating in Lithium-ion Cells", *J. Electrochem. Soc.*, **158** (4), A379-A389 (2011).
- B. V. Ratnakumar, and M. C. Smart, "Lithium plating in a Li-ion cell – A correlation with Li intercalation kinetics into graphite", *ECS Trans.* **25** (36), 241 (2010)
- M. C. Smart, B. V. Ratnakumar, F. C. Krouse, W. C. West, and L. W. Whitcanack, "The Development of Li-Ion Electrolytes with Improved Operating Temperature Range and Safety Characteristics", 2010 Space Power Workshop, Manhattan Beach, CA, April 22, 2010.
- M. C. Smart, B. V. Ratnakumar, M. R. Tomcsi, M. Nagata, V. Visco, and H. Tsukamoto, "Performance of Wide Operating Temperature Range Electrolytes in Quallion Prototype Li-Ion Cells", 2010 Power Sources Conference, Las Vegas, NV, June 16, 2010.
- M. C. Smart, B. V. Ratankumar, and K. Amine, "Improved wide operating temperature range of MCMB-Li<sub>1+x</sub>(Co<sub>1/3</sub>Ni<sub>1/3</sub>Mn<sub>1/3</sub>)<sub>1-x</sub>O<sub>2</sub> cells with methyl butyrate-based electrolytes", 218<sup>th</sup> Meeting of the Electrochemical Society, Las Vegas, Nevada, Oct. 13, 2010.

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