The Use of Triphenyl Phosphate as a Flame Retardant Additive in Lithium-Ion Battery Electrolytes Designed for High Voltage Systems

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Outline

- Introduction
- Objective and Approach
- Background
- Experimental
- Approach and Methodology

- Results in MCMB-$LiNiCoO_2$ Experimental Cells
  - Discharge Characteristics
  - Tafel Polarization Characteristics
- Results in 7 Ah MCMB-$LiNiCoO_2$ Prototype Cells
- Graphite-Toda $LiNiCoMnO_2$ Experimental Coin Cell Results
- Graphite-Toda $LiNiCoMnO_2$ Experimental 3-Electrode Cell Results
  - Discharge Characteristics
  - Tafel Polarization Characteristics
  - EIS Polarization Characteristics

- Conclusions

Introduction

- NASA is actively pursuing the development of advanced electrochemical energy storage and conversion devices for future lunar and Mars missions.

- The Exploration Technology Development Program, Energy Storage Project is sponsoring the development of ***advanced Li-ion batteries*** and PEM fuel cell and regenerative fuel cell systems for the Altair Lunar Lander, Extravehicular Activities (EVA), and rovers and as the primary energy storage system for Lunar Surface Systems.

- At JPL, in collaboration with NASA-GRC, NASA-JSC and industry, we are actively developing advanced Li-ion batteries with improved specific energy, energy density and safety. One effort is focused upon developing Li-ion battery electrolyte with enhanced safety characteristics (i.e., low flammability).

- A number of commercial applications also require Li-ion batteries with enhanced safety, especially for automotive applications.

Exploration Technology Development Program
Energy Storage Project

Exploration Technology Development Program

Multiple focused projects to develop enabling technologies addressing high priority needs for Lunar exploration. Matures technologies to the level of demonstration in a relevant environment – TRL 6

Energy Storage Project –

Developing electrochemical systems to address Constellation energy storage needs

Altair - Lunar Lander

- **Primary fuel cells – descent stage**
- **Secondary batteries – ascent stage**

EVA

- **Secondary batteries for the Portable Life Support System (PLSS)**

Lunar Surface Systems (LSS)

- **Regenerative fuel cell systems for surface systems**
- **Secondary batteries for mobility systems**

- These applications will require high energy density Li-ion batteries with improved safety characteristics.

Desired Properties of Lithium-Ion Electrolytes

- ***Electrolyte Selection Criteria***

➢ High conductivity over a wide range of temperatures
  - o 1 mS cm-1 from –60 to 40^{o}C

➢ Wide liquid range (low melting point)
  - o -60 to 75^{o}C

➢ Good electrochemical stability
  - o Stability over wide voltage window (0 to 4.5V)
  - o Minimal oxidative degradation of solvents/salts

➢ Good chemical stability

➢ Good compatibility with chosen electrode couple
  - o Good SEI characteristics on electrode
  - o Facile lithium intercalation/de-intercalation kinetics

➢ Good thermal stability

➢ Good low temperature performance throughout life of cell
  - o Good resilience to high temperature exposure
  - o Minimal impedance build-up with cycling and/or storage

➢ ***In addition to meeting these criteria, the electrolyte solutions should be ideally have low flammability and be non-toxic !!***

Flame Retardant Additives in Li-ion Cells for Improved Safety Characteristics

- Modification of electrolyte is one of the least invasive and cost effective ways to improve the safety characteristics of Li-ion cells. Common approaches include:
  - Use of Redox shuttles (to improve safety on overcharge)
  - Ionic liquids (have inherently low flammability, due to low vapor pressure)
  - Lithium salt modification
  - Flame retardant additives
  - Use of non-flammable solvents (i.e., halogenated solvents)
- Of these approaches, the use of flame retardant additives has been observed to possess the least impact upon cell performance.

Previous Work on Flame Retardant Additives in Li-ion Batteries

- Most flame retardant additives utilized contain phosphorus
  - Aromatic and alkyl phosphates most common
    - Tradeoff exists between flame retarding capabilities and electrochemical stability
  - Halogenated phosphate compounds
    - Tris (2,2,2-trifluoroethyl) phosphate reported to be one of the most promising FRAs examined to date - excellent performance characteristics[1]
  - Other potential FRAs include:
    - Phosphites[1]- P(III) oxidation state may lead to improve stability and act as Lewis acid scavenger
    - Phosphonates[3]
    - Phosphoramides
    - Phosphazenes[4]

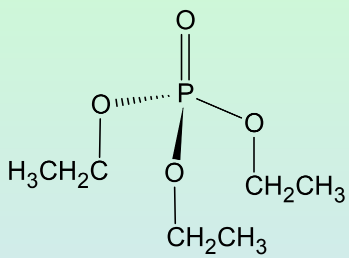
1) K. Xu, S. Zhang, J. L. Allen, T. R. Jow *J. Electrochem. Soc.*, **2002**, *149*, A1079

2) (a) S. S. Zhang, K. Xu, and T. R. Jow, *Journal of Power Sources* 113 (1), 166-172 (2003), (b) Nam, T.-H., Shim, E.-G., Kim, J.-G., Kim, H.-S., Moon, S.-I., *Journal of Power Sources* 180 (1), 561-567 (2008).

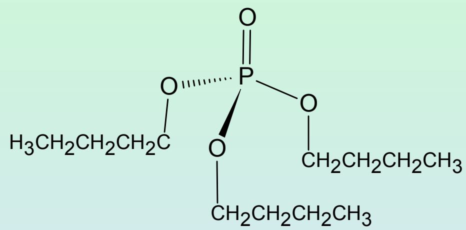
3) J. K. Feng, X. P. Ai, Y. L. Cao, and H. X. Yang, J. Power Sources, 177, 194-198 (2008).

4) T. Tsujikawa, K Yabuta, T. Matsushita, T. Matsushima, K. Hayashi, M. Arakawa, J. Power Sources, 189 (1) 429-434 (2009).

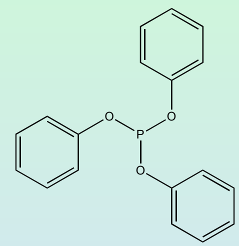
Development of Electrolytes Containing Flame Retardant Additives



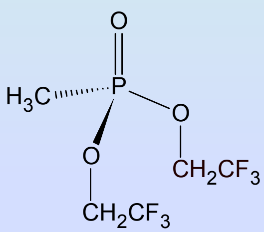
Triethyl phosphate (TEP)



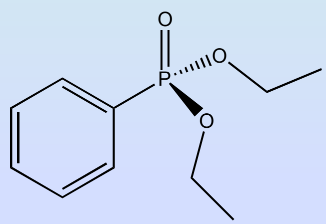
Tributyl phosphate (TBP)



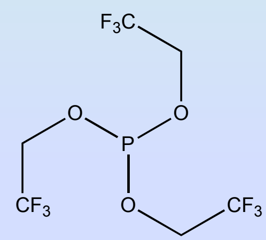
Triphenyl phosphite (TPPi)



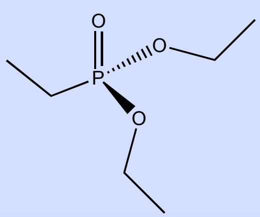
Bis-(2,2,2-trifluoroethyl)methyl phosphonate (BTFEMP)



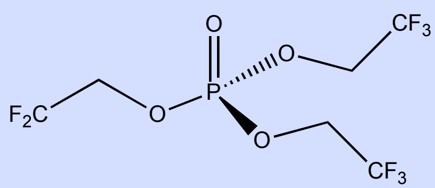
Diethyl phenylphosphonate (DPP)



Tris(2,2,2-trifluoroethyl) phosphite (TFPi)

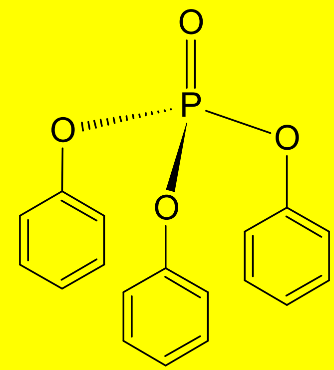


Diethyl ethylphosphonate (DEP)



Tris(2,2,2-trifluoroethyl) phosphate (TFPa)

TPP identified as being the most robust flame retardant additive



Triphenyl phosphate (TPP)

Electrolytes with the various additives were incorporated into three electrolyte cells with $LiNi_xCo_{1-x}O_2$ cathodes, MCMB anodes, and Li metal reference electrodes

1) Y. E. Hyung, D. R. Vissers, K. Amine
J. Power Sources, **2003**, *119-121*, 383

2) K. Xu, M. S. Ding, S. Zhang, J. L. Allen, T. R. Jow
J. Electrochem. Soc. **2002**, *149*, A622

Development of Electrolytes Containing Flame Retardant Additives

➢ Electrolytes and approaches investigated in NCA and NCO systems:

- 1.0M $LiPF_6$ EC+EMC+TPP (20:75:5 vol %)
- 1.0M $LiPF_6$ EC+EMC+TPP (20:70:10 vol %)
- 1.0M $LiPF_6$ EC+EMC+TPP (20:65:15 vol %)

← Varying Concentration of TPP

- 1.0M $LiPF_6$ EC+EMC+DTFEC+TPP (20:50:20:10 vol %)
- 1.0M $LiPF_6$ EC+EMC+DTFEC+TPP (20:30:40:10 vol %)
- 1.0M $LiPF_6$ EC+EMC+TFEMC+TPP (20:50:20:10 vol %)

← Use of Fluorinated Linear Carbonates

- 1.0M $LiPF_6$ FEC+EMC+TPP (20:70:10 vol %)
- 1.0M $LiPF_6$ FEC+EMC+TPP (20:65:15 vol %)
- 1.0M $LiPF_6$ FEC+EMC+TFEMC+TPP (20:50:20:10 vol %)

← Use of Fluorinated Ethylene Carbonate

- 1.0M $LiPF_6$ FEC+EMC+TFEMC+TPP (20:50:20:10 vol %) + 1.5% VC
- 1.0M $LiPF_6$ EC+EMC+TPP (20:75:5 vol %) + 1.5% VC
- 1.0M $LiPF_6$ EC+EMC+TPP (20:65:15 vol %) + 1.5% VC
- 1.0M $LiPF_6$ FEC+EMC+TPP (20:65:15 vol %) + 1.5% VC

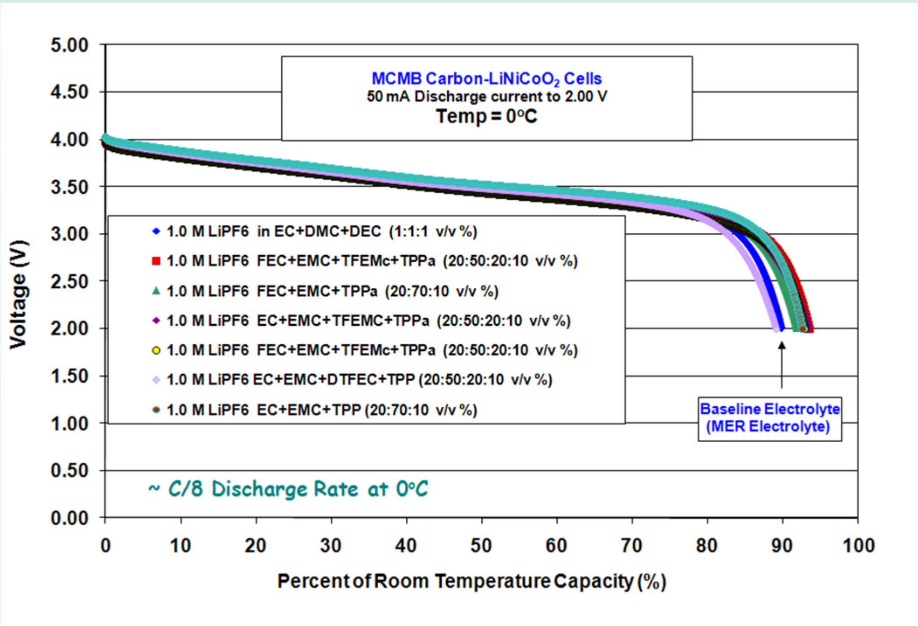
← Use of Additives (Vinylene Carbonate)

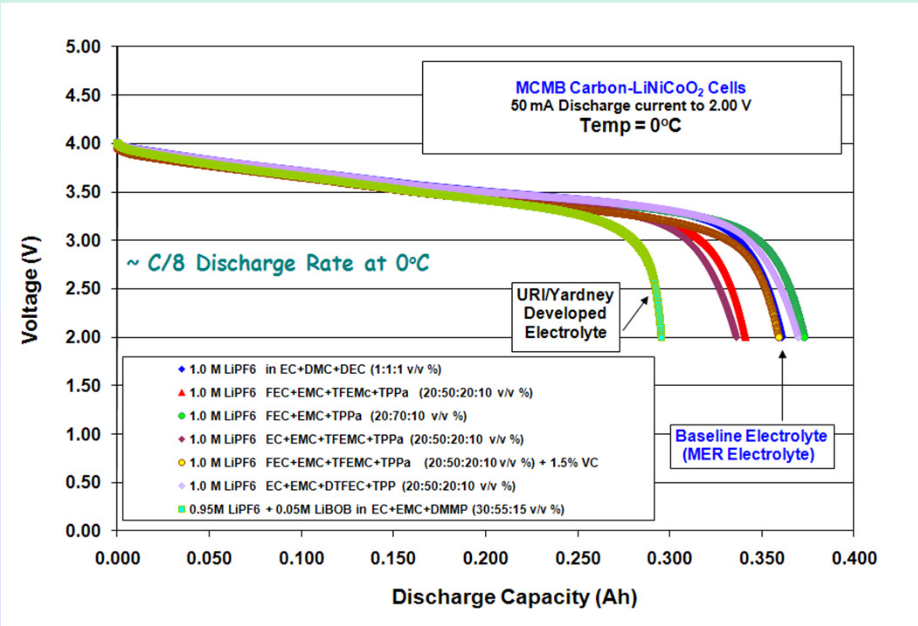
Where DTFEC = di-2,2,2-trifluoroethyl carbonate
TFEMC = 2,2,2-trifluoroethyl methyl carbonate
FEC = mono-fluoroethylene carbonate
TPP = triphenyl phosphate

Flammability tests have been performed on select samples by Prof. Lucht at Univ. Rhode Island

Electrolytes With Improved Safety and Good High Voltage Stability

Discharge Characteristics of Three Electrode MCMB-$LiNi_xCo_{1-x}O_2$ Cells



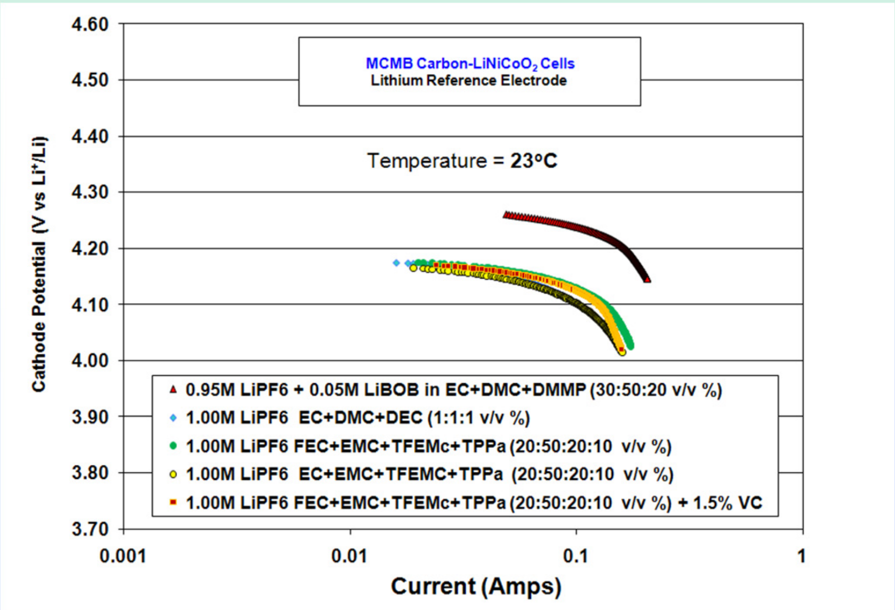


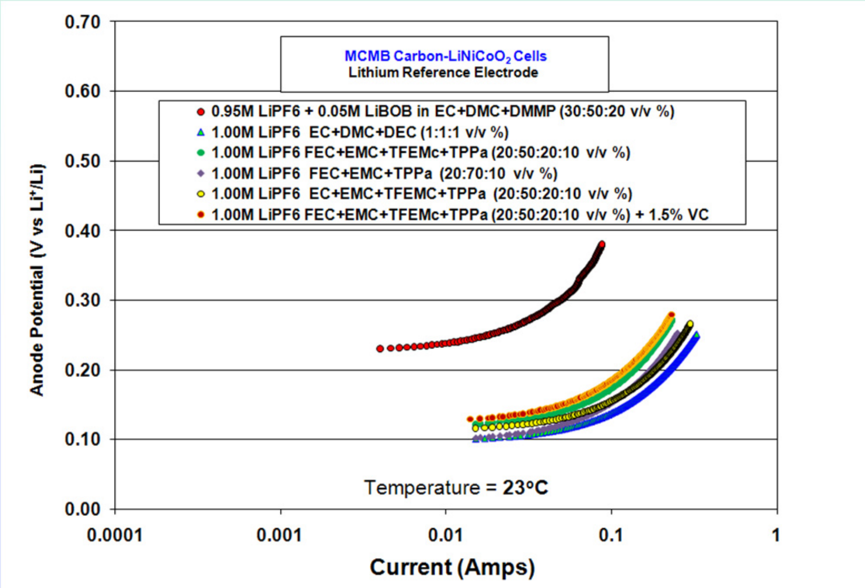
When the electrolytes were evaluated in MCMB-$LiNiCoO_2$ cells, generally good performance was observed with the electrolytes studied. Good performance was even observed when the EC was replaced completely with FEC and TFEMC was added as well at a ~ **C/4 rate at 0°C.**

For details regarding the URI/Yardney electrolyte see:
S. Dalavi, M. Xu, B. Ravdel, L. Zhou, and B. L. Lucht, *J. Electrochem. Soc.*, **157**, A1113 (2010).

Electrolytes With Improved Safety and Good High Voltage Stability

Tafel Characteristics of Three Electrode MCMB-$LiNi_xCo_{1-x}O_2$ Cells



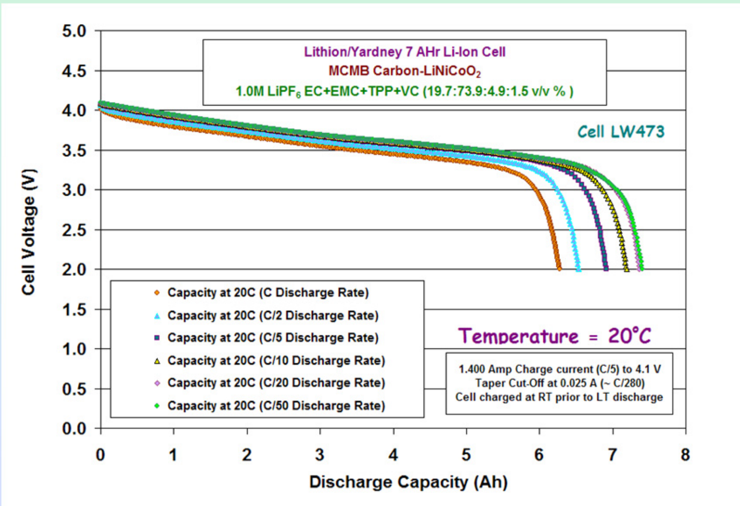


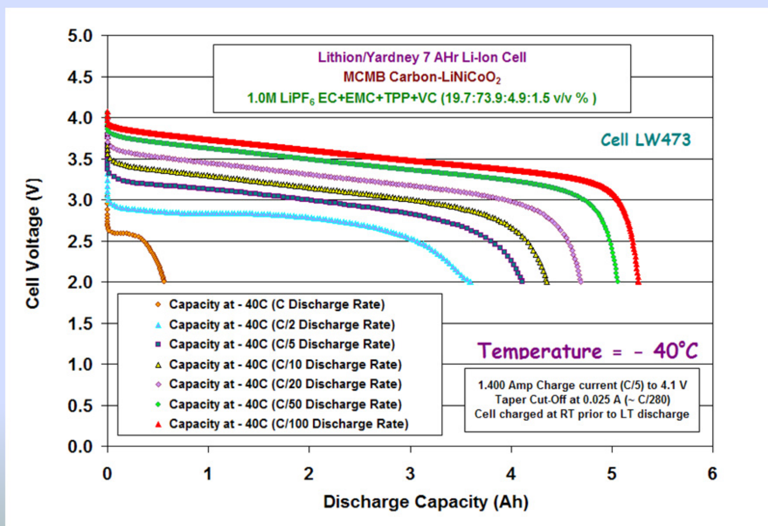
- **Performance of Yardney/URI electrolyte compared with baseline solution.**
- **Although lithium kinetics are observed to be facile at the cathode with the cell containing the Yardney/URI electrolyte, the lithium kinetics at the anode are dramatically lower compared with the baseline system.**

Yardney 7 Ah Prismatic Li-Ion Cells

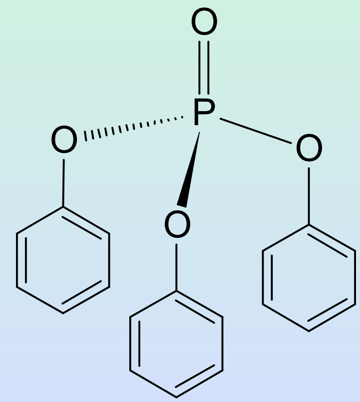
Characterization of Cells Containing Electrolytes With FRAs

Discharge Performance at 20°C and -40°C





Triphenyl phosphate (TPP)



Cells containing an electrolyte with a flame retardant additive (i.e., *1.0 M* $LiPF_6$ *in EC+EMC+TPP+VC*) are observed to display good performance over a range of temperatures.

Cell contains 5% TPP Content

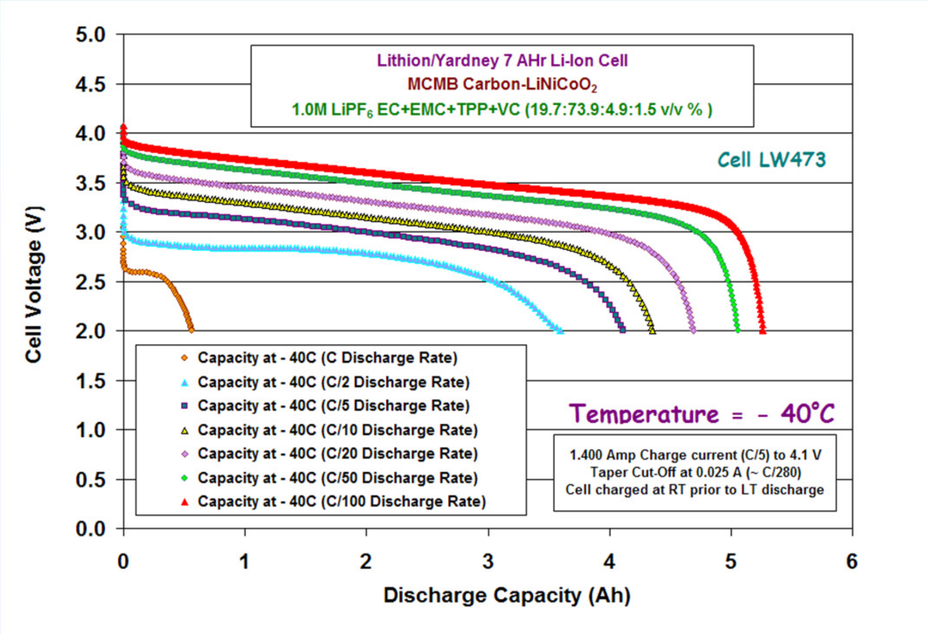
Yardney 7 Ah Prismatic Li-Ion Cells

Characterization of Cells Containing Advanced Electrolytes

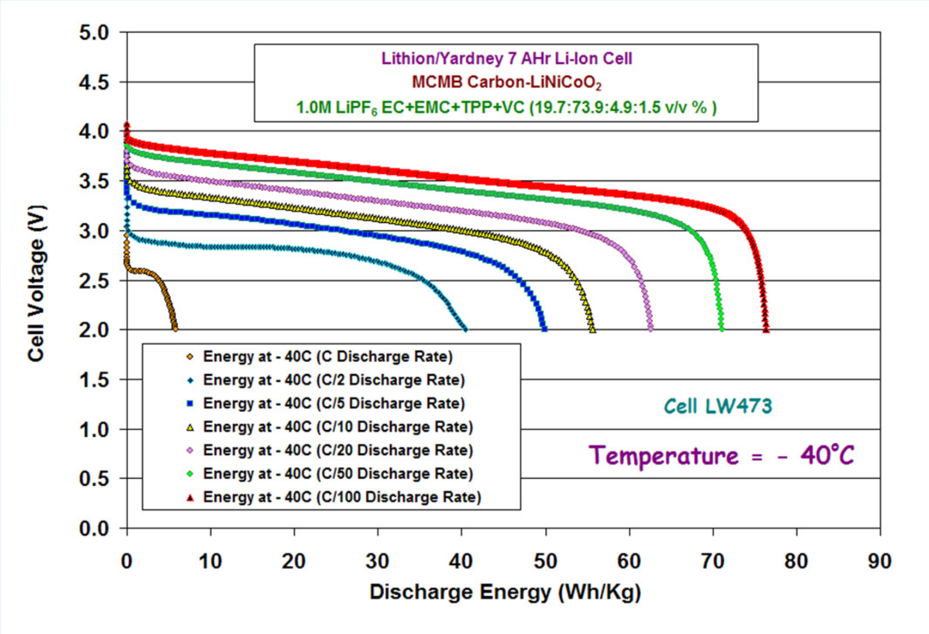
Summary of Discharge Characterization Testing at Various Temperatures

Discharge Performance at - 40^{o}C

Discharge Capacity (Ah) at - 40^{o}C



Discharge Energy (Wh/Kg) at - 40^{o}C



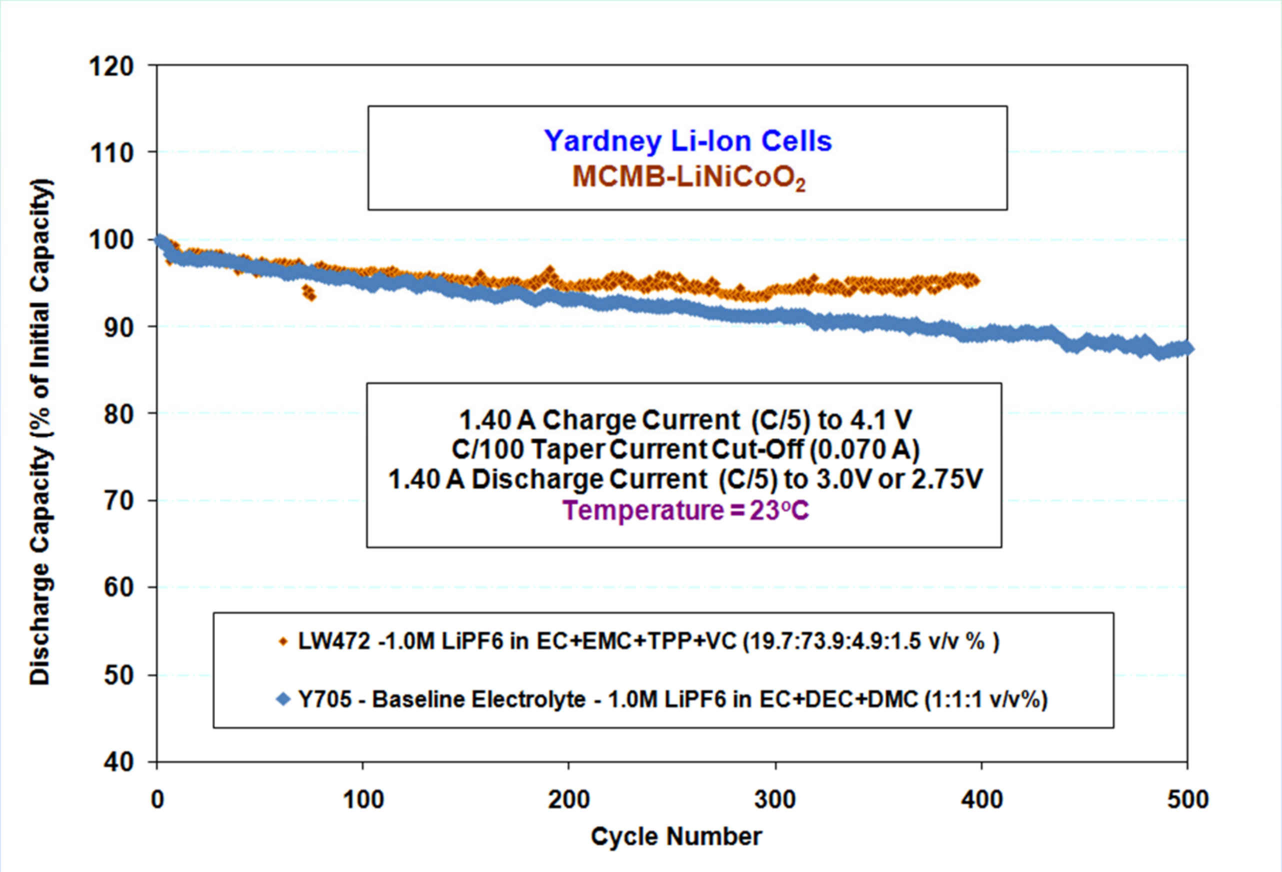
Cells containing an electrolyte with a flame retardant additive (i.e., *1.0 M $LiPF_6$ in EC+EMC+TPP+VC*) are observed to display good performance over a range of temperatures.

Yardney 7 Ah Prismatic Li-Ion Cells

Characterization of Cells Containing Advanced Electrolytes

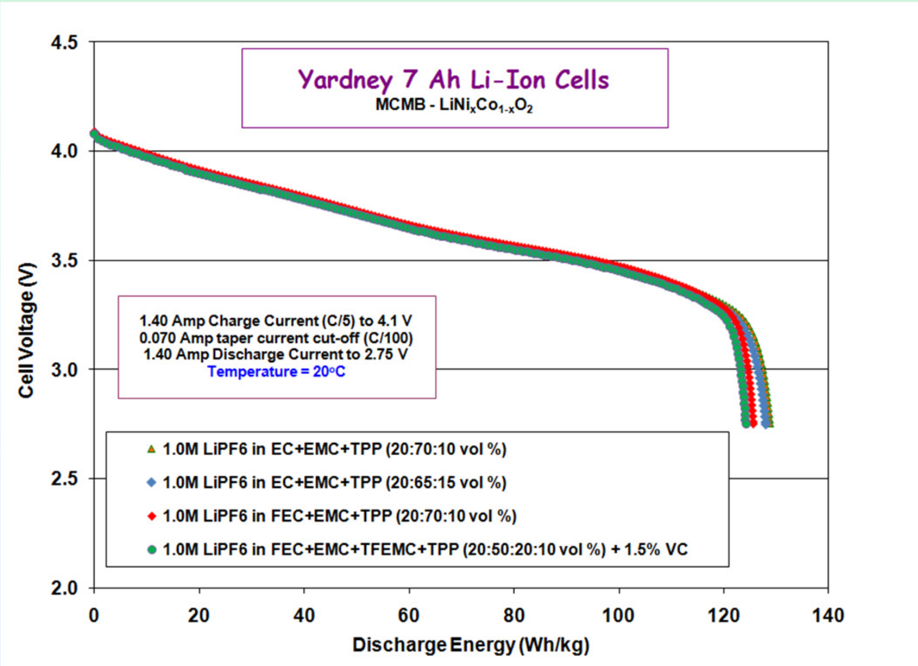
100 % DOD Cycle Life Testing at Room Temperature

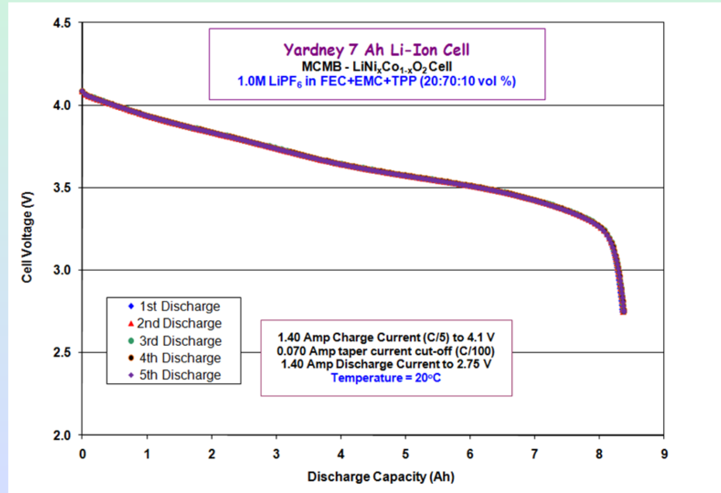
Percentage of Initial Capacity (%)

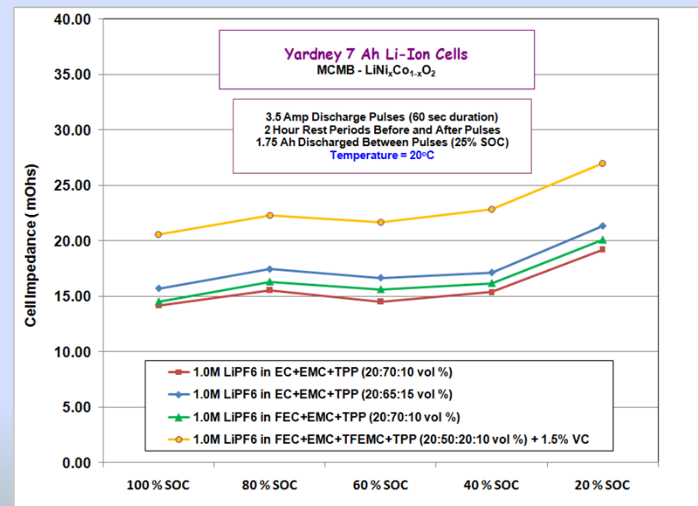


Cells containing an electrolyte with a flame retardant additive (i.e., *1.0 M $LiPF_6$ in EC+EMC+TPP+VC*) are observed to display good cycle life compared to the baseline formulation.

Discharge Characteristics MCMB / $LiNiCoO_2$ 7 Ah Cells
Conditioning at 20°C
Comparison of Electrolyte Types





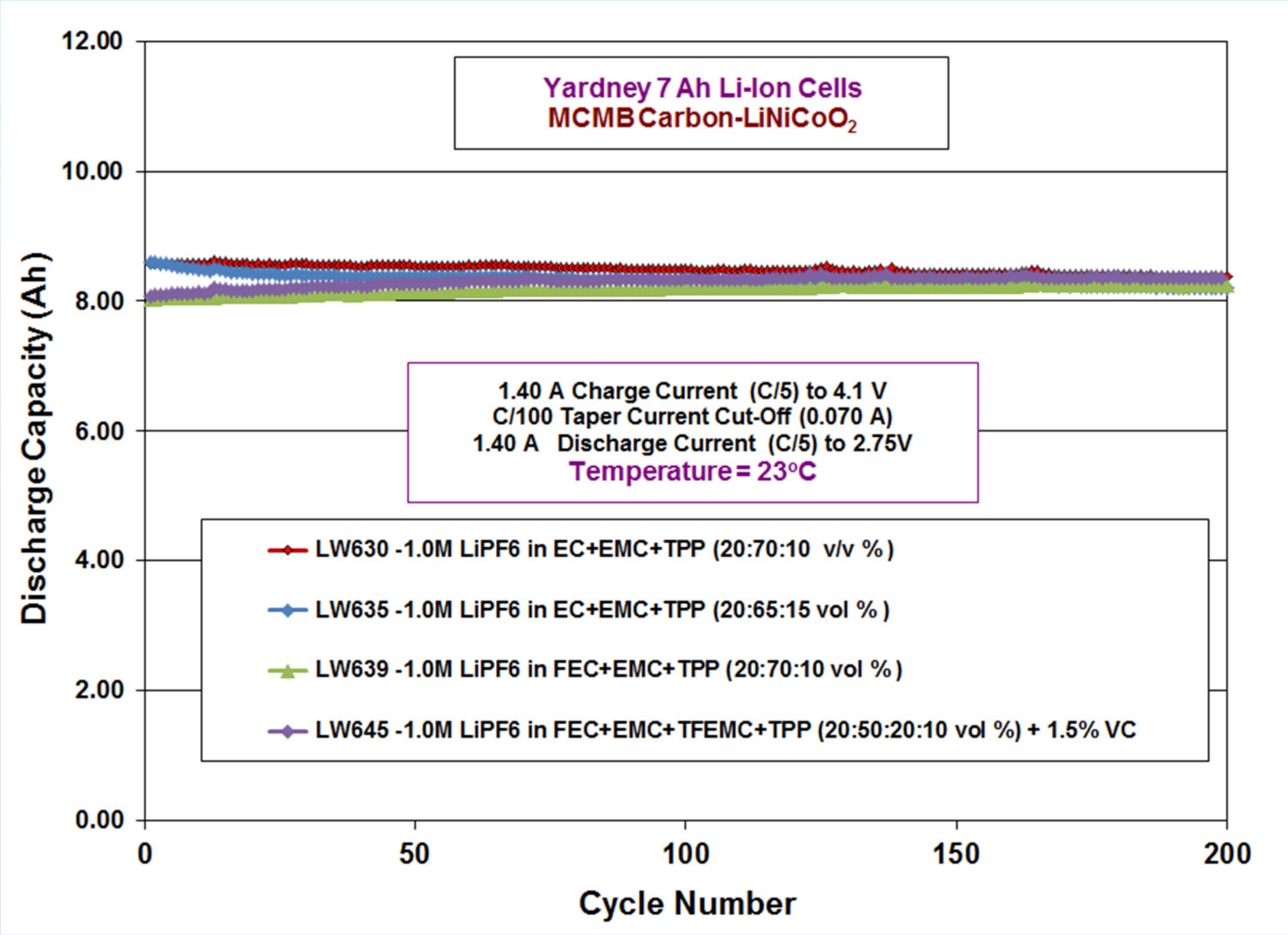


- We are currently evaluating a number of cells which possess electrolytes with
  (a) higher TPP content (up to 15%),
  (b) the use of FEC in lieu of EC, and
  (c) the addition of 2,2,2-trifluoroethyl methyl carbonate (TFEMC).

Initial results are very promising, suggesting good compatibility with the system.

Cycle Life Testing of MCMB-1028 / $LiNiCoO_2$ 7 Ah Cells

100 % DOD Cycle Life Performance



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Discharge Characteristics MCMB-1028 / $LiNiCoO_2$ 7 Ah Cells

Discharge Characterization Testing at -50°, -40°, -30°C, -20°C, and -10°C

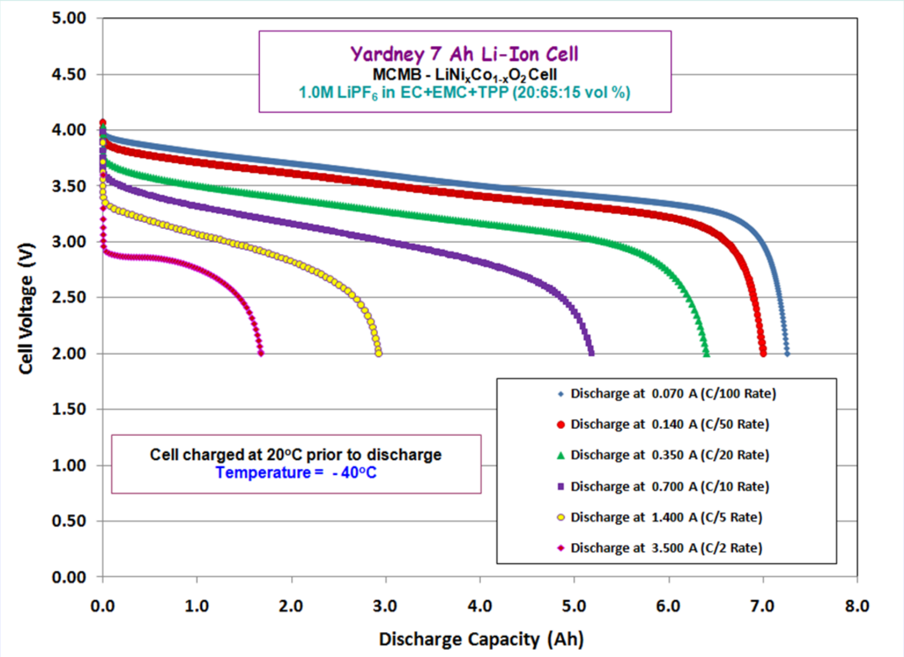
			LW-628				LW-633				LW-638				LW-643			
			1.0 M $LiPF_6$ in EC+EMC+TPP (20:70:10 vol %)				1.0 M $LiPF_6$ in EC+EMC+TPP (20:65:15 vol %)				1.0 M $LiPF_6$ in FEC+EMC+TPP (20:70:10 vol %)				1.0 M $LiPF_6$ in FEC+EMC+TFEMC+TPP (20:50:20:10 vol %) + 1.5% VC			
Temperature (°C)	Rate	Current (A)	Capacity (mAh)	Watt-Hours (Wh)	Energy (Wh/Kg)	% of Room Temp	Capacity (mAh)	Watt-Hours (Wh)	Energy (Wh/Kg)	% of Room Temp	Capacity (mAh)	Watt-Hours (Wh)	Energy (Wh/Kg)	% of Room Temp	Capacity (mAh)	Watt-Hours (Wh)	Energy (Wh/Kg)	% of Room Temp
20°C (Initial)	C/5	1.800	8.6346	31.321	128.89	100	8.5956	31.107	128.01	100	8.382	30.531	125.64	100.00	8.3124	30.174	124.17	100
- 10°C	C/2	3.500	7.1174	24.460	100.66	82.43	6.5625	22.133	91.08	76.35	6.9941	23.920	98.44	83.44	6.9972	22.784	93.76	84.18
	C/5	1.400	7.5053	26.773	110.18	86.92	7.3849	26.115	107.47	85.91	7.3809	26.221	107.90	88.05	7.3069	24.997	102.87	87.90
	C/10	0.700	7.7070	27.872	114.70	89.26	7.6991	27.705	114.01	89.57	7.6109	27.488	113.12	90.80	7.5202	26.387	108.59	90.47
	C/20	0.350	7.9092	28.788	118.47	91.60	7.9258	28.772	118.40	92.21	7.8318	28.530	117.41	93.43	7.6915	27.458	113.00	92.53
	C/50	0.140	8.1849	29.851	122.84	94.79	8.2043	29.890	123.00	95.45	8.1050	29.633	121.95	96.69	7.8163	28.255	116.27	94.03
	C/100	0.070	8.4388	30.735	126.48	97.73	8.4300	30.683	126.27	98.07	8.3203	30.400	125.10	99.26	7.7262	28.034	115.37	92.95
- 20°C	C/2	3.500	6.5310	21.316	87.72	75.64	5.7709	17.433	71.74	67.14	6.5404	21.218	87.32	78.03	6.4434	19.445	80.02	77.51
	C/5	1.400	7.1777	24.922	102.56	83.13	6.9503	23.710	97.57	80.86	6.9982	24.023	98.86	83.49	6.8884	22.347	91.96	82.87
	C/10	0.700	7.3738	26.278	108.14	85.40	7.2425	25.556	105.17	84.26	7.2248	25.504	104.95	86.19	7.0896	23.883	98.29	85.29
	C/20	0.350	7.5605	27.358	112.59	87.56	7.5326	27.098	111.51	87.63	7.4358	26.773	110.18	88.71	7.2637	25.196	103.69	87.38
	C/50	0.140	7.7772	28.375	116.77	90.07	7.7752	28.290	116.42	90.46	7.6800	28.004	115.24	91.62	7.3899	26.260	108.07	88.90
	C/100	0.070	7.9828	29.168	120.03	92.45	7.9560	29.019	119.42	92.56	7.8585	28.754	118.33	93.75	7.3156	26.289	108.19	88.01
- 30°C	C/2	3.500	5.6841	16.159	66.50	65.83	2.5714	7.780	32.01	29.92	5.9703	17.408	71.64	71.23	4.1560	11.647	47.93	50.00
	C/5	1.400	6.7463	22.124	91.05	78.13	5.9217	18.776	77.27	68.89	6.5635	21.175	87.14	78.30	6.3906	18.895	77.76	76.88
	C/10	0.700	7.0301	24.080	99.10	81.42	6.6754	22.383	92.11	77.66	6.8208	22.945	94.42	81.37	6.6289	20.768	85.46	79.75
	C/20	0.350	7.2345	25.554	105.16	83.79	7.1297	24.863	102.31	82.95	7.0587	24.553	101.04	84.21	6.8484	22.472	92.48	82.39
	C/50	0.140	7.4587	26.942	110.87	86.38	7.4493	26.731	110.00	86.66	7.3159	26.172	107.71	87.28	7.0290	24.010	98.81	84.56
	C/100	0.070	7.6480	27.868	114.68	88.57	7.6288	27.692	113.96	88.75	7.5199	27.269	112.22	89.71	6.9617	24.332	100.13	83.75
- 40°C	C/2	3.500	2.0564	5.779	23.78	23.82	1.6729	4.556	18.75	19.46	3.0160	8.200	33.75	35.98	2.2447	5.607	23.07	27.00
	C/5	1.400	5.0890	15.036	61.88	58.94	2.9252	8.546	35.17	34.03	5.9081	16.856	69.37	70.48	4.4335	11.475	47.22	53.34
	C/10	0.700	6.5585	20.698	85.18	75.96	5.1821	15.730	64.73	60.29	6.3322	19.490	80.21	75.54	5.9530	16.289	67.03	71.62
	C/20	0.350	6.8429	22.764	93.68	79.25	6.4030	20.652	84.99	74.49	6.5969	21.377	87.97	78.70	6.2793	18.494	76.11	75.54
	C/50	0.140	7.1078	24.810	102.10	82.32	7.0010	24.067	99.04	81.45	6.9084	23.589	97.07	82.42	6.5284	20.740	85.35	78.54
	C/100	0.070	7.2897	25.955	106.81	84.42	7.2567	25.570	105.23	84.42	7.1132	24.867	102.33	84.86	6.5356	21.444	88.25	78.62
- 50°C	C/2	3.500	1.5258	3.737	15.38	17.67	0.1515	0.320	1.32	1.76	1.7480	4.232	17.42	20.85	0.0007	0.001	0.01	0.01
	C/5	1.400	2.0512	5.467	22.50	23.76	1.6810	4.253	17.50	19.56	3.4992	8.902	36.63	41.75	1.9124	4.393	18.08	23.01
	C/10	0.700	3.4467	9.350	38.48	39.92	1.9536	5.131	21.11	22.73	5.2567	13.546	55.74	62.71	2.6355	6.1760	25.42	31.71
	C/20	0.350	5.5685	16.078	66.17	64.49	3.2507	9.023	37.13	37.82	5.8360	16.259	66.91	69.62	4.3607	10.669	43.90	52.46
	C/50	0.140	6.5550	20.993	86.39	75.92	5.4680	16.677	68.63	63.61	6.3063	19.472	80.13	75.23	5.7507	15.601	64.20	69.18
	C/100	0.070	6.8471	23.035	94.79	79.30	6.4017	20.973	86.31	74.48	6.5928	21.483	88.41	78.65	5.8984	17.303	71.21	70.96

Currently performing the discharge rate characterization testing at **0°, 10° and 20°C**

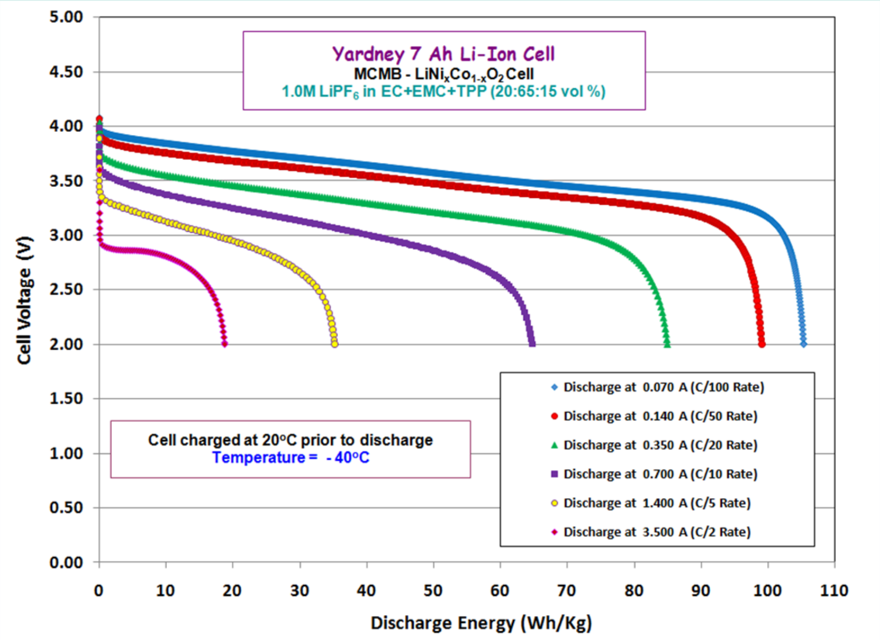
Discharge Characteristics MCMB-1028 / $LiNiCoO_2$ 7 Ah Cells

Discharge Characterization Testing at -40°C: Electrolyte with 15% TPP Content

Discharge Capacity (Ah)



Discharge Energy (Wh/kg)



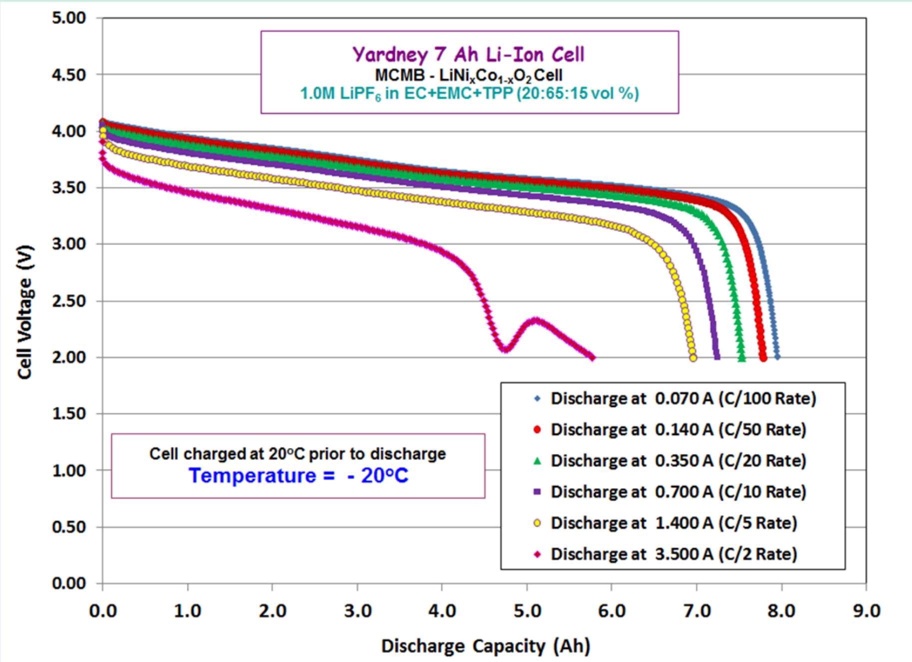
A cell containing an electrolyte with 15% TPP displayed good performance at -40°C, however, somewhat decreased rate capability at low temperature was observed compared to 10% TPP.

Currently performing the discharge rate characterization testing at **0°, 10° and 20°C**

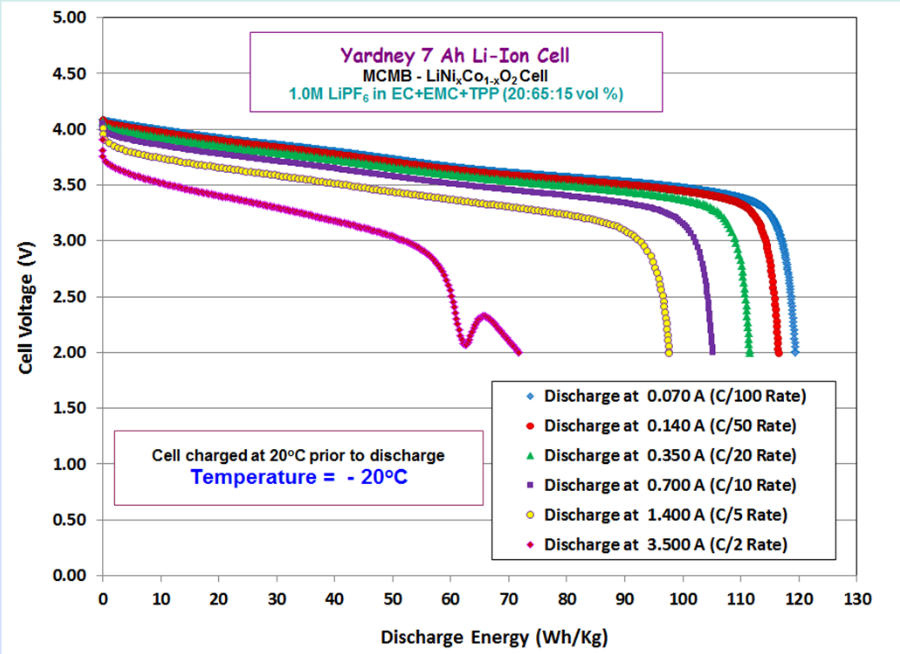
Discharge Characteristics MCMB-1028 / $LiNiCoO_2$ 7 Ah Cells

Discharge Characterization Testing at -20°C: Electrolyte with 15% TPP Content

Discharge Capacity (Ah)



Discharge Energy (Wh/kg)

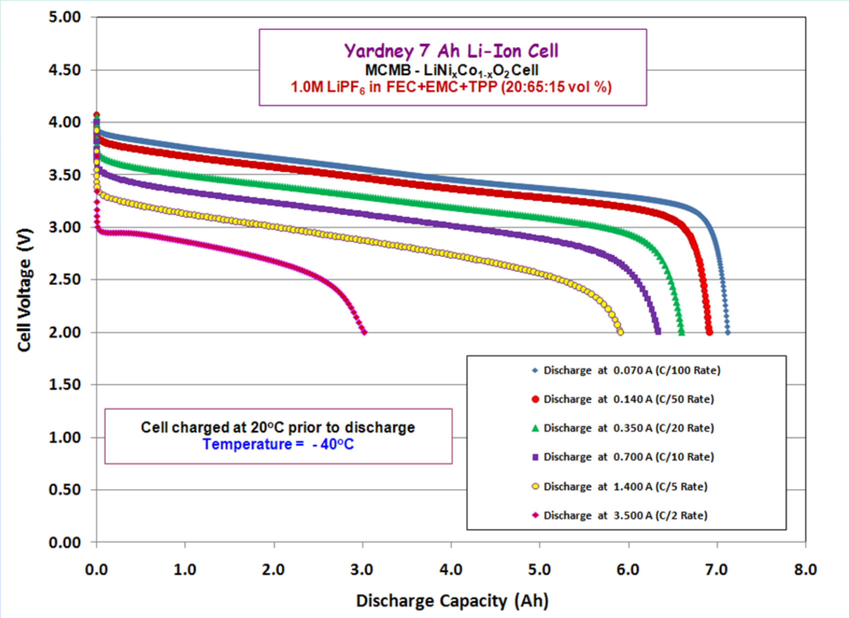


A cell containing an electrolyte with 15% TPP displayed good performance at -20°C, however, somewhat decreased rate capability at low temperature was observed compared to 10% TPP.

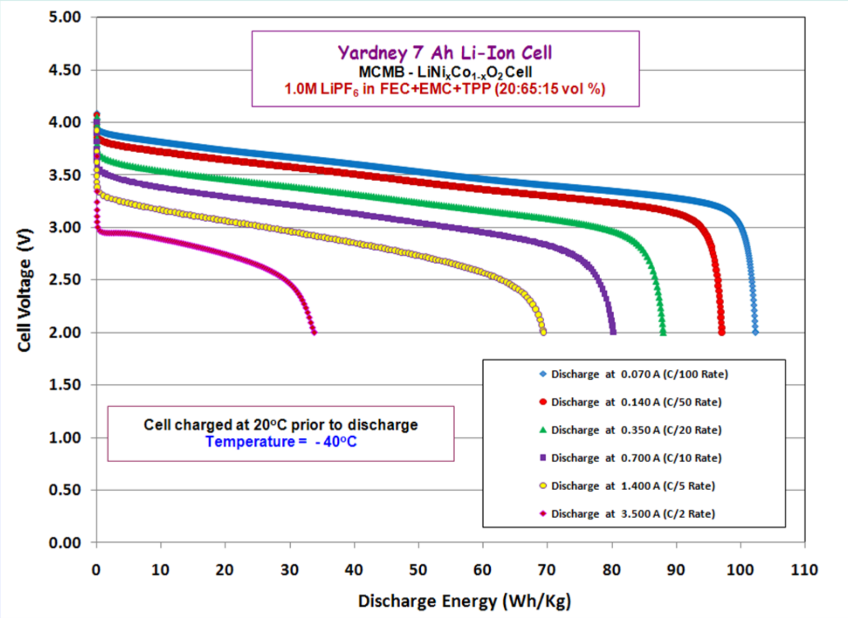
Discharge Characteristics MCMB-1028 / $LiNiCoO_2$ 7 Ah Cells

Discharge Characterization Testing at -40°C: Electrolyte with 15% TPP Content
Electrolyte possess FEC in place of EC

Discharge Capacity (Ah)



Discharge Energy (Wh/kg)

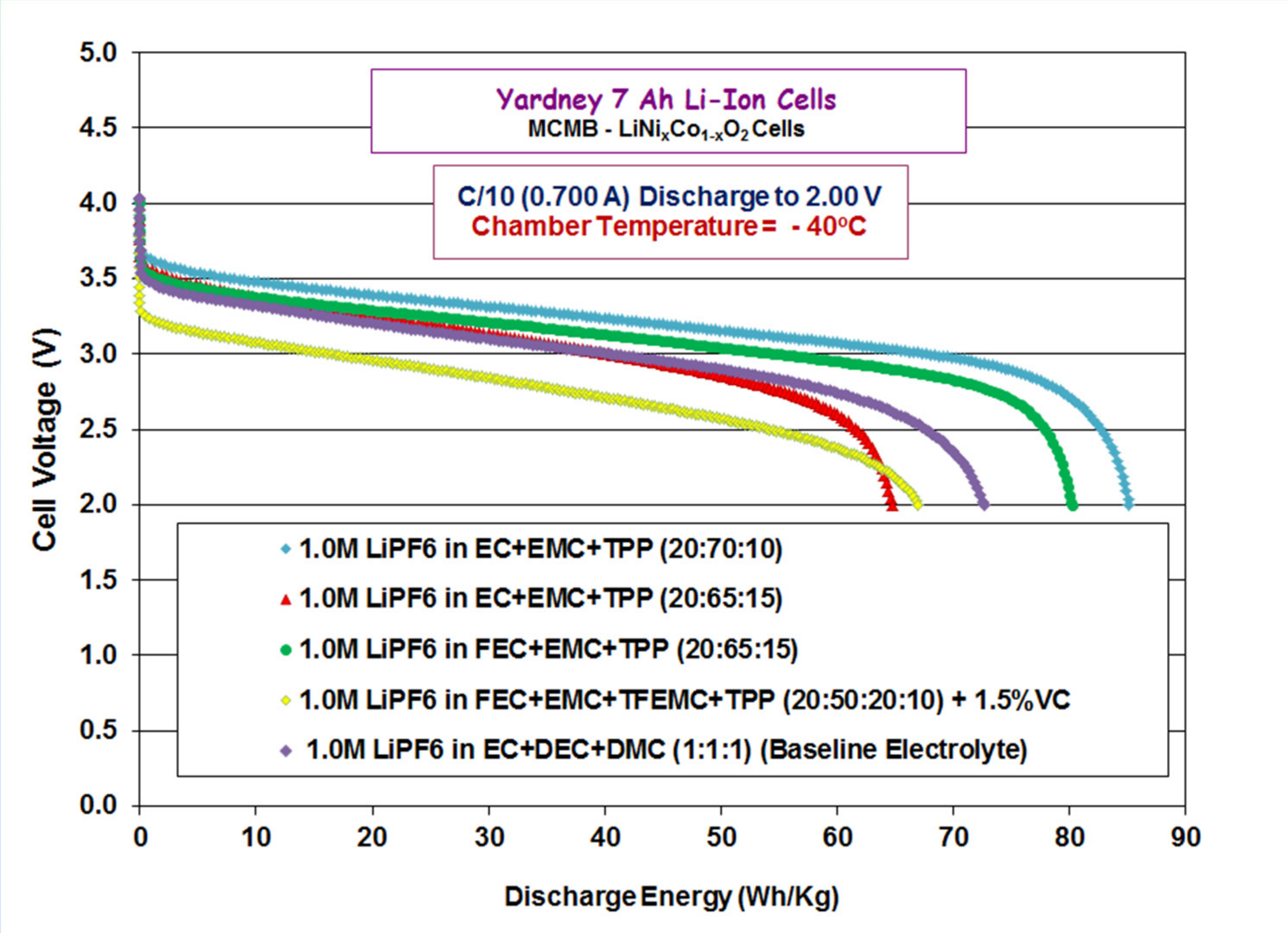


A cell containing an electrolyte with 15% TPP displayed good capability at -40°C, and the presence of FEC improved the low temperature performance compared with both 10% and 15% TPP solutions.

Currently performing the discharge rate characterization testing at **0°, 10° and 20°C**

Discharge Characteristics MCMB-1028 / $LiNiCoO_2$ 7 Ah Cells

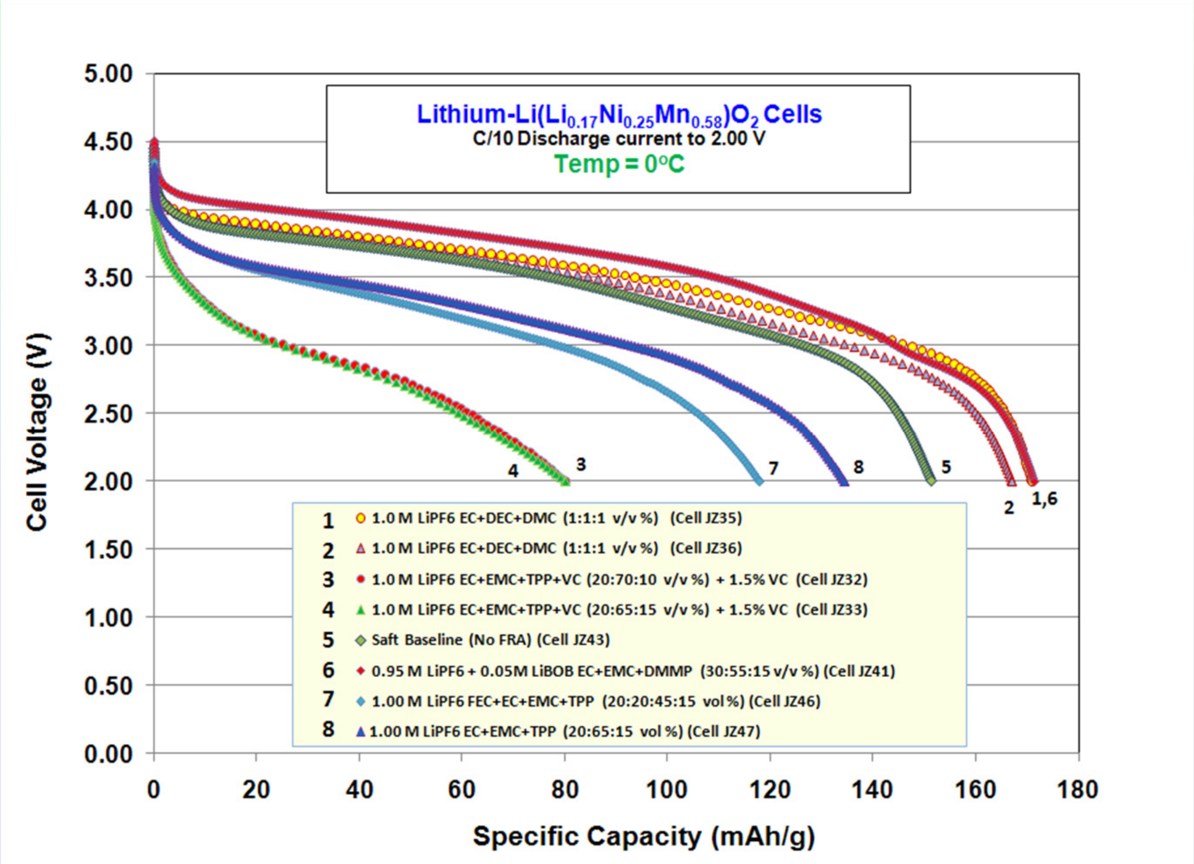
Discharge Characterization Testing at -40°C: Comparison of Electrolyte Types



Cells containing both 10% and 15%TPP have been observed to perform better than the baseline electrolyte at -40°C (C/10). Cell designs are comparable, however, some difference are present.,

Electrolytes With Improved Safety and High Voltage Stability

Li-Li($Li_{0.17}Ni_{0.25}Mn_{0.58}$)$O_2$ cells = Rate Capability at Low Temperature

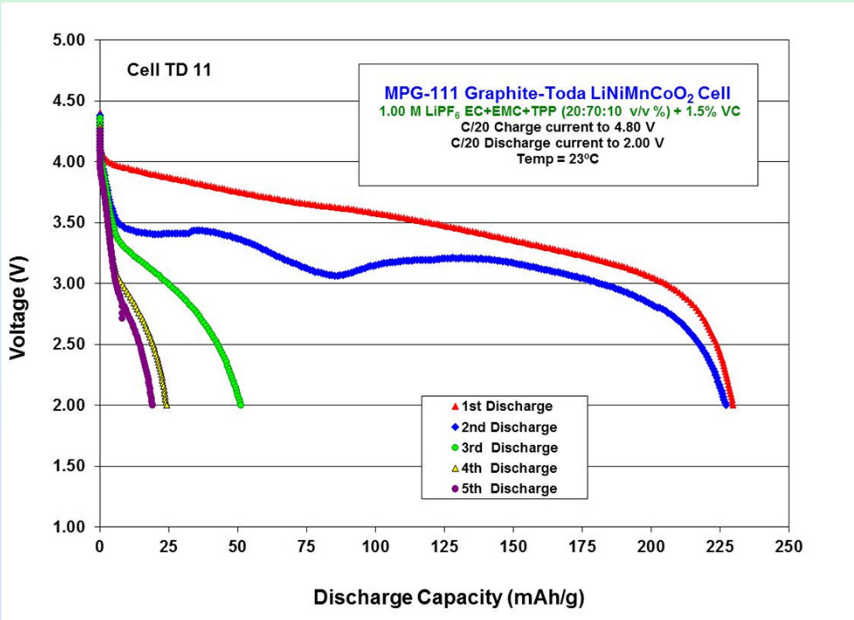


- **The URI/Yardney electrolyte performs very well with the NEI-D cathode, but much poorer when evaluated with carbon electrodes.**
- **High TPP content (with and without FEC and/or VC) appears to perform well in cells with carbonaceous anodes, but some performance decline observed when coupled with high voltage cathode (i.e., in Li/NEI-D cells).**
- ***However, when these electrolytes were evaluated in the MPG-111/Toda cathode system, the performance was very poor necessitating further development. This lead to further modifications to the electrolytes !!***

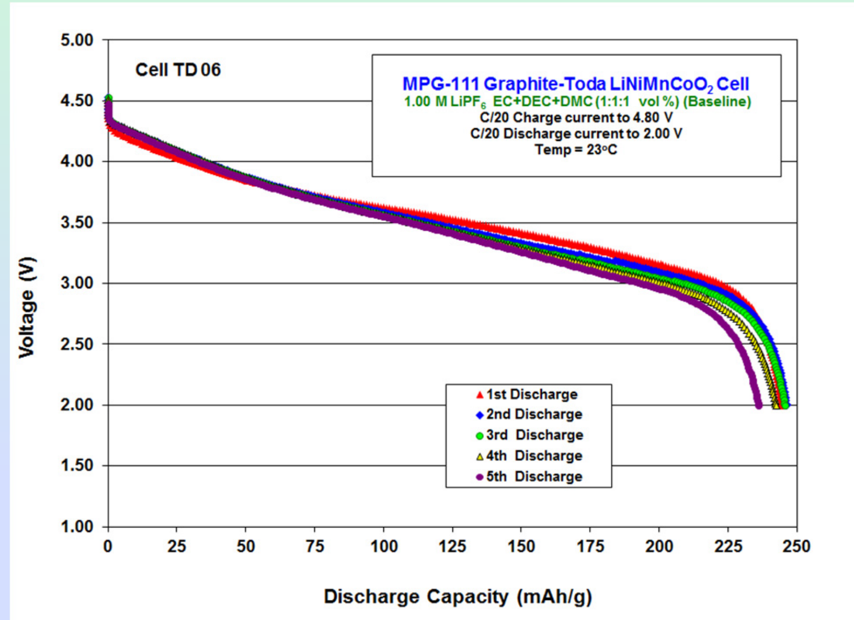
Results Electrolytes Evaluated with the MPG-111-$LiNiMnCoO_2$ System

Comparison of Electrolyte Types (Formation)

Early Generation TPP Electrolyte



Baseline Electrolyte



- *Rapid capacity fade of the TPP-containing electrolyte, presumably due to reactivity of the TPP at the cathode.*
- *Baseline all carbonate blend performed much better.*
- ***Observed performance necessitated further development to provide improved compatibility and led to the use of LiBOB to improve high voltage stability.***

(a) B. Yu,W. Qiu, F. Li, L. Cheng, J. Power Sources 166 (2007) 499.

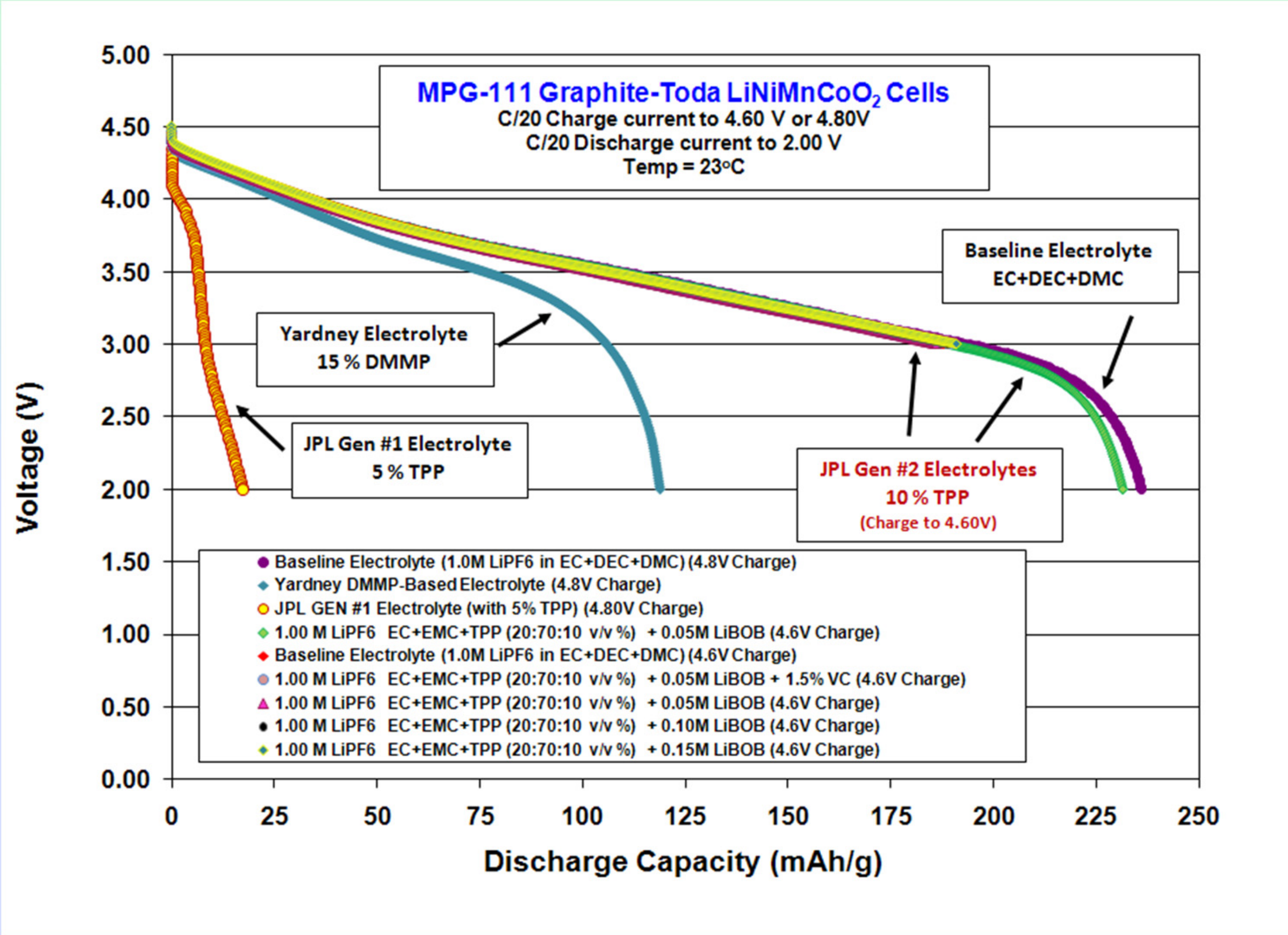
(a) J.C. Arrebola, A. Caballero, L. Hernan, J. Morales, Journal of Power Sources 183 (2008) 310–315.

(b) B. L. Lucht, 5th Lithium Mobile Power, Boston, MA (2009).

(b) S. Dalavi, M. Xu, B. Ravdel, L. Zhou, and B. L. Lucht, J. Electrochem. Soc., 157, A1113 (2010).

Results from Electrolytes Evaluated in the MPG-111-Toda System

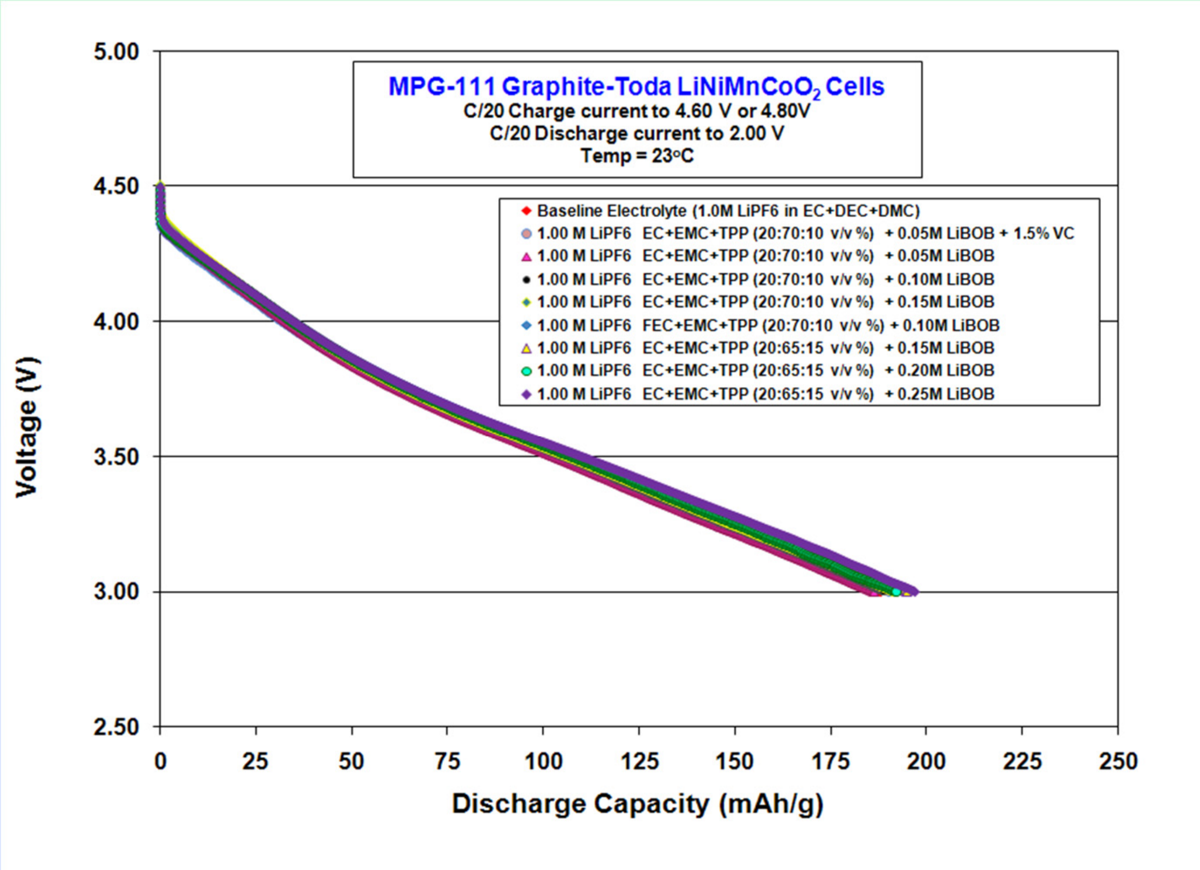
Comparison of Electrolyte Types (After Formation)



- *Comparable performance was obtained with the JPL Gen #2 electrolytes (containing LiBOB) compared with the baseline solution.*
- *There is no observed capacity (or voltage) benefit observed with charging to 4.80V*

Results of Electrolytes Evaluated in the MPG-111-Toda System

Comparison of Electrolyte Types (After Formation)



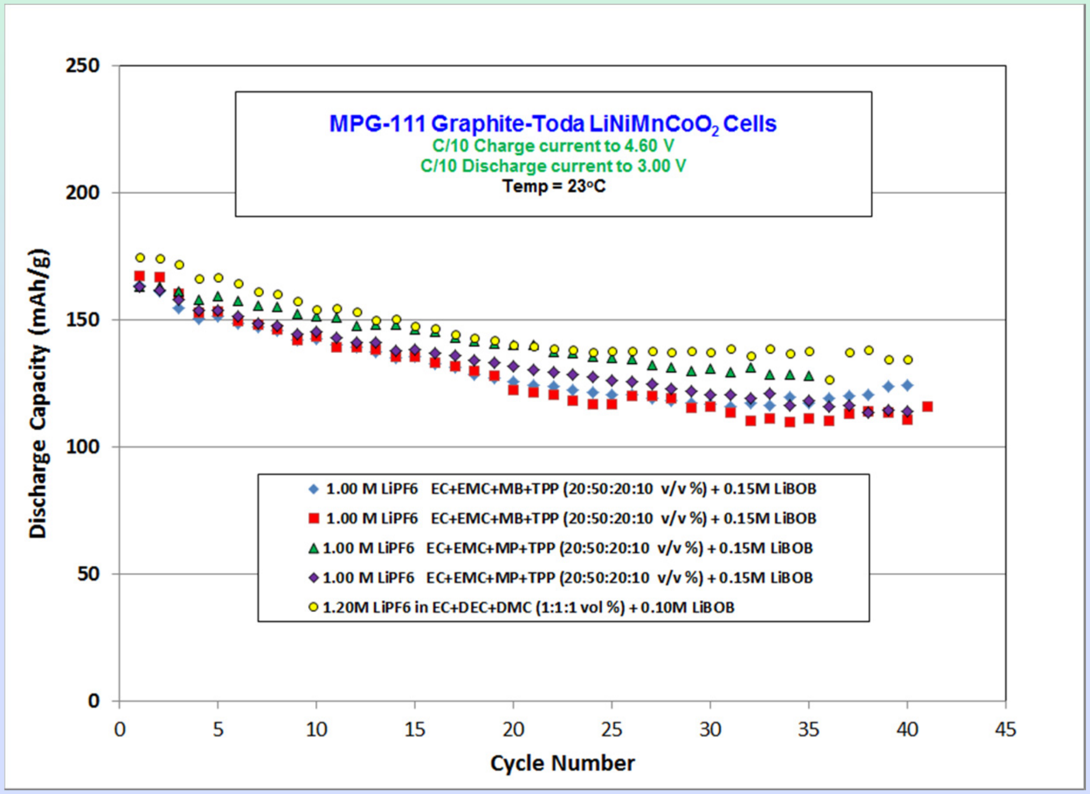
On-going work to identify further improvements (i.e., increasing TPP content and varying LiBOB concentrations)

- *A number of electrolytes displayed comparable performance with the the baseline solution, including the JPL Gen #2 electrolyte as well as newer iterations with increased TPP content (15%) and an FEC-containing blend.*
- *Cell cycled over the voltage range of 3.00 to 4.60V.*

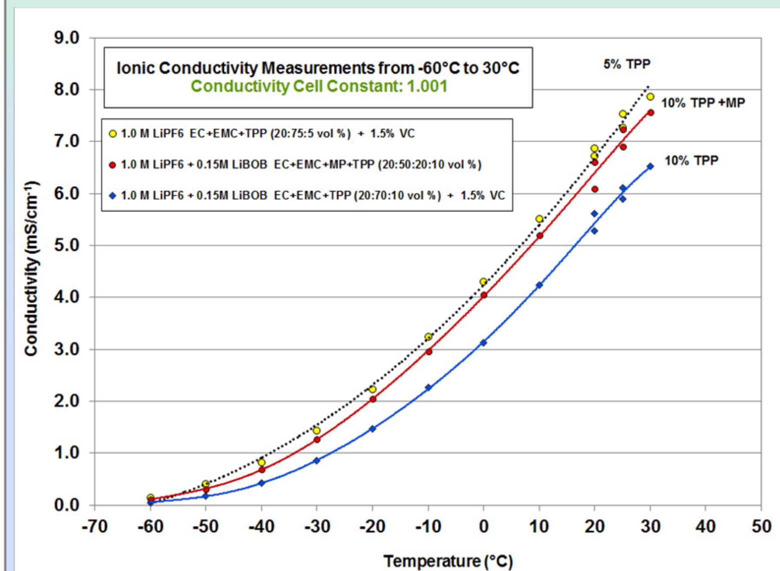
MPG-111-Toda System Coin Cells

The use of ester co-solvents to improve the conductivity of TPP electrolytes

Cycle Life at 23^{o}C



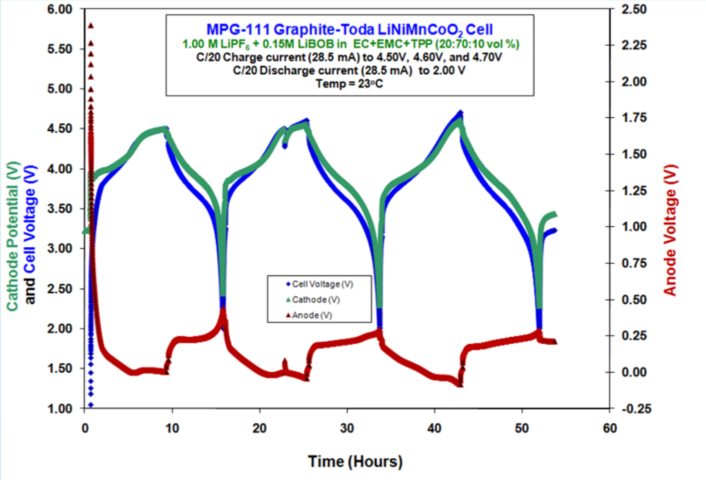
Ionic Conductivity

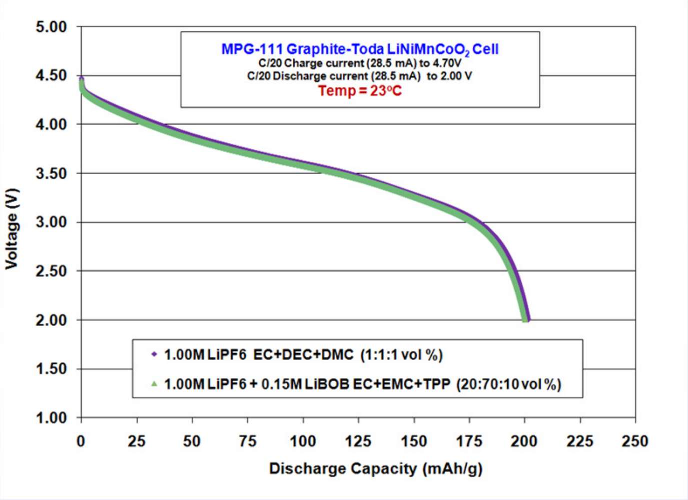


- The incorporation of TPP in conjunction with methyl butyrate or methyl propionate do not appear to dramatically impact the life characteristics of the cells.
- The use of ester co-solvents was employed to off-set the increase of viscosity associated with the addition of TPP

Formation Characteristics of MPG-111-Toda Experimental Cells

Discharge Capacity





- Nearly identical reversible capacity was obtained with both electrolyte types.
- The discharge voltage profiles are very similar also.

Cell TM01
Baseline Electrolyte

Cycle #	Charge (Ah)	Discharge Capacity (Ah)	Irreversible Capacity (Ah)	Efficiency (%)	Reversible Capacity (mAh/g)	Irreversible Capacity (mAh/g)
1	0.28674	0.20135	0.085	70.22	162.38	68.86
2	0.25745	0.23368	0.024	90.77	188.45	19.17
3	0.25257	0.24971	0.003	98.86	201.38	2.31

Cumulative Irreversible Capcity Loss = 0.1120 Ah
Cumulative Irreversible Capcity Loss = 90.34 mAh/g

Cell TM02
JPL Generation II Electrolyte

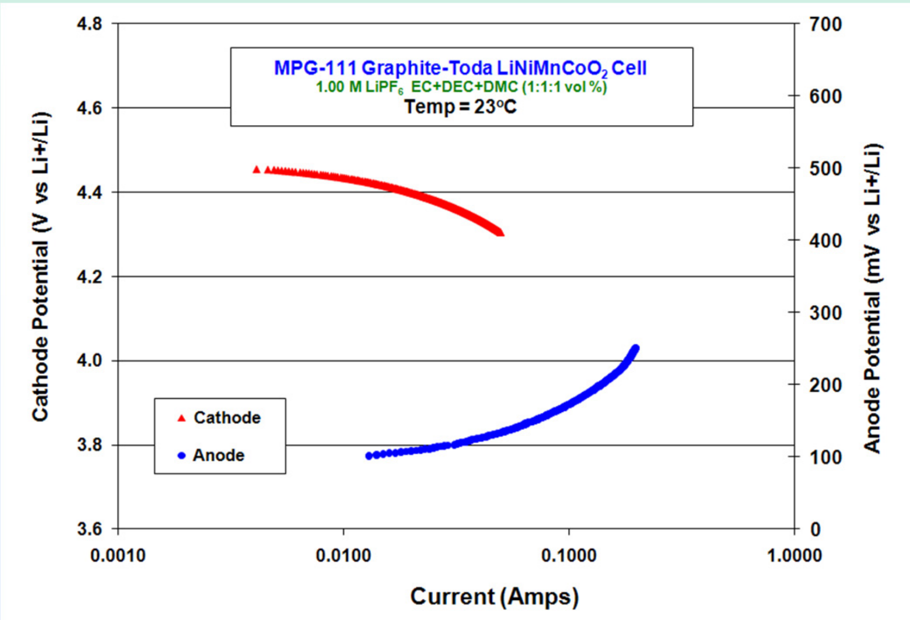
Cycle #	Charge (Ah)	Discharge Capacity (Ah)	Irreversible Capacity (Ah)	Efficiency (%)	Reversible Capacity (mAh/g)	Irreversible Capacity (mAh/g)
1	0.24729	0.17637	0.071	71.32	142.35	57.19
2	0.26617	0.22849	0.038	85.84	184.41	30.39
3	0.25655	0.24780	0.009	96.59	200.00	7.06

Cumulative Irreversible Capcity Loss = 0.11735 Ah
Cumulative Irreversible Capcity Loss = 94.64 mAh/g

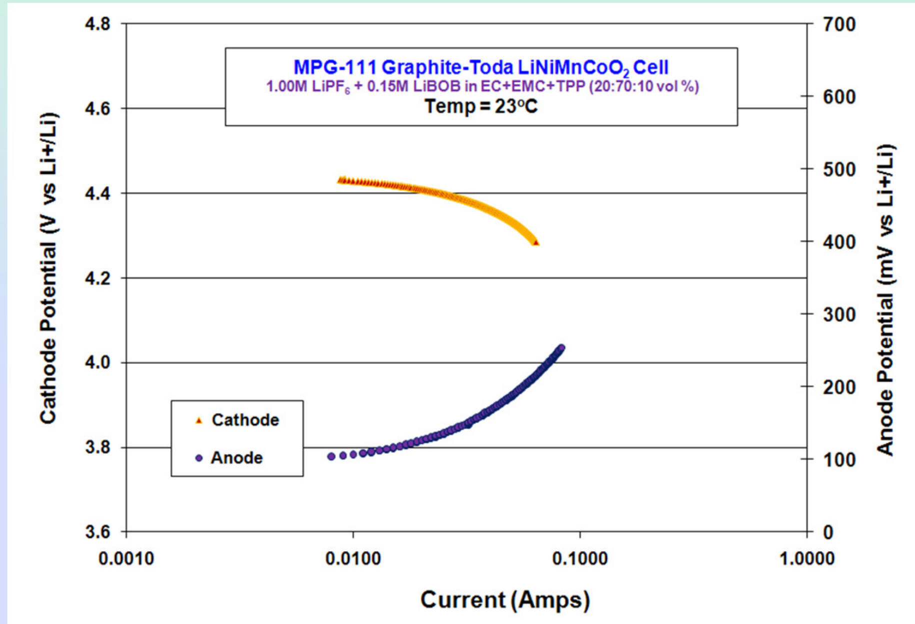
Electrochemical Characteristics of MPG-111-Toda Experimental Cells

Tafel Polarization Measurements

Cell TM01
Baseline Electrolyte



Cell TM02
JPL Generation II Electrolyte

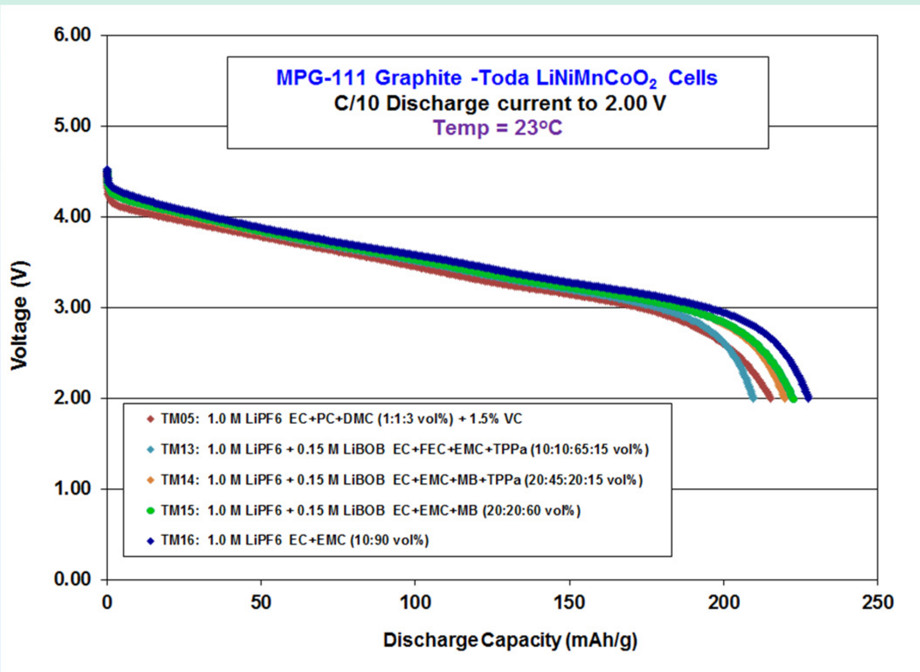


- In both cells, in terms of the lithium kinetics the cathode appears to be the limiting electrode as determined by Tafel polarization measurements.
- However, due to decreased kinetics at the anode of the cell containing the JPL Gen II electrolyte, the difference between the anode and cathode lithium kinetics is less dramatic.

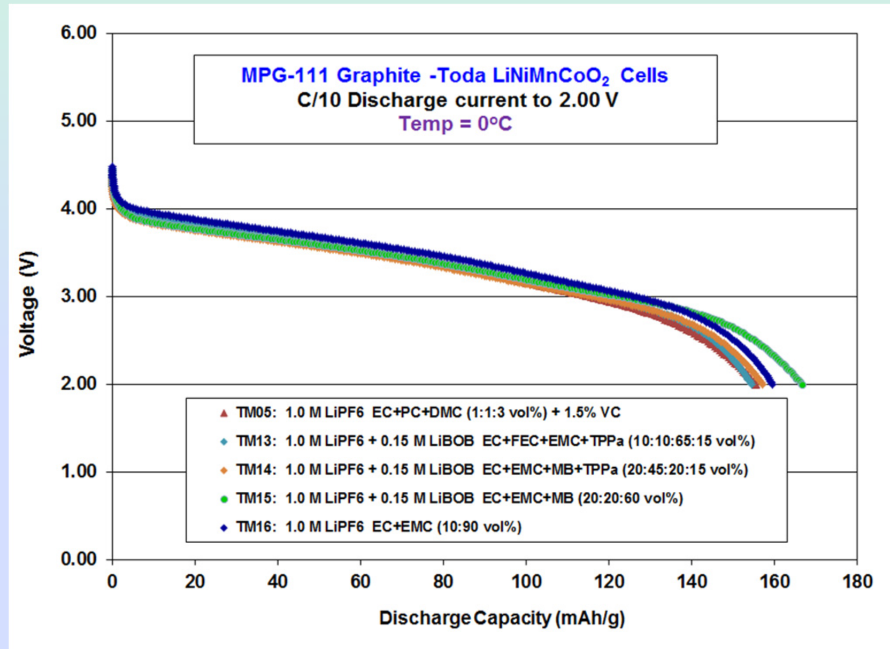
Electrochemical Characteristics of MPG-111-Toda Experimental Cells

Discharge Characteristics of High Voltage Systems with Electrolyte with Improved Safety

Temperature = 23°C



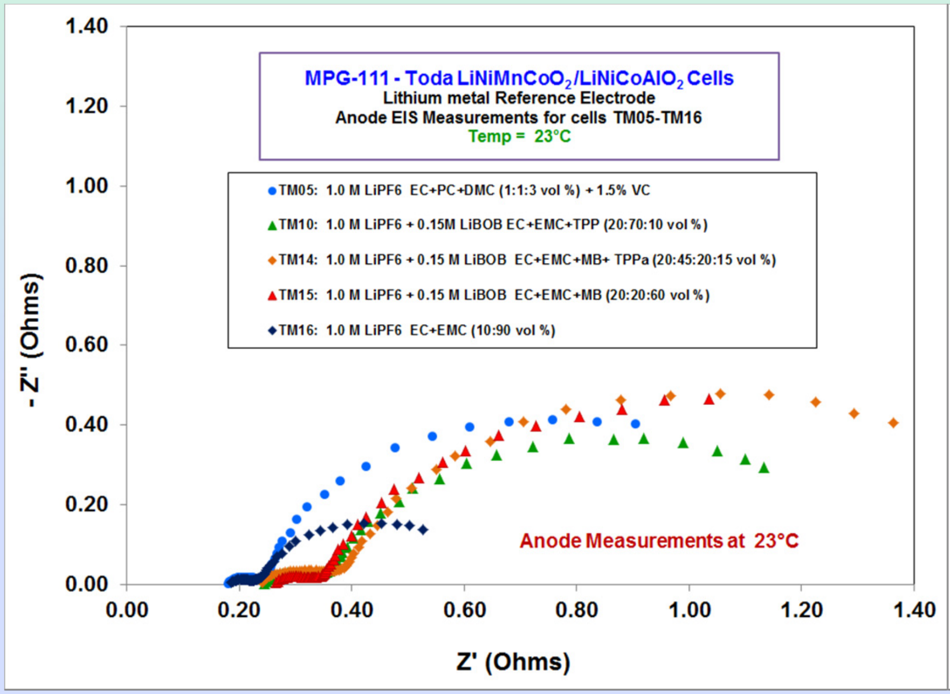
Temperature = 0°C



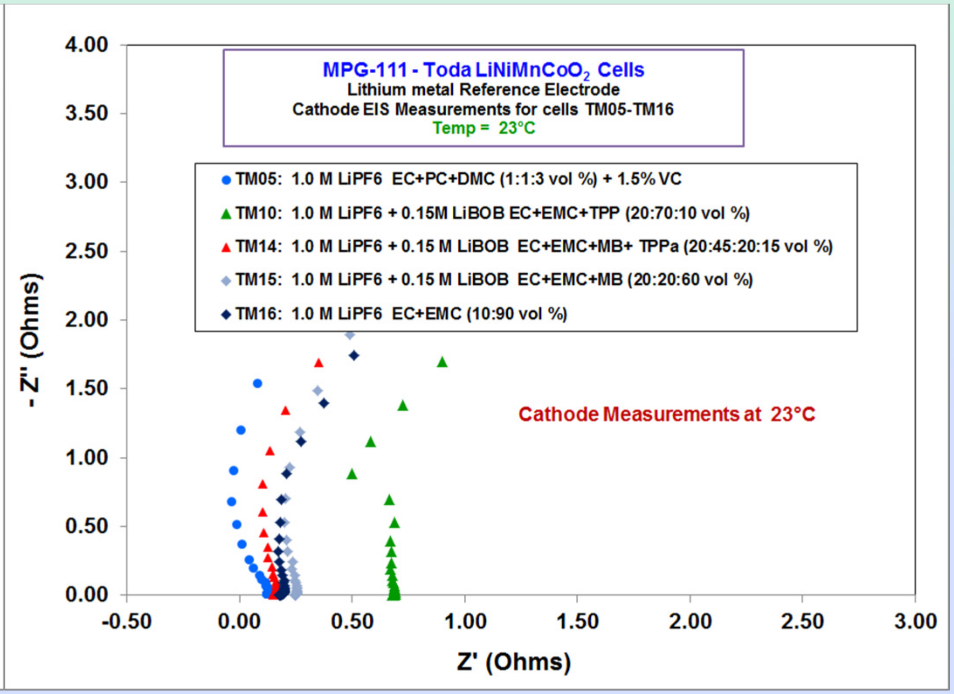
- A number of TPP-containing electrolytes (with high TPP content) display good discharge characteristics compared with baseline electrolytes, as well as some formulation intended to provide good wide operating temperature range performance.

Electrochemical Characteristics of MPG-111-Toda Experimental Cells
EIS Measurements

Anode Measurements



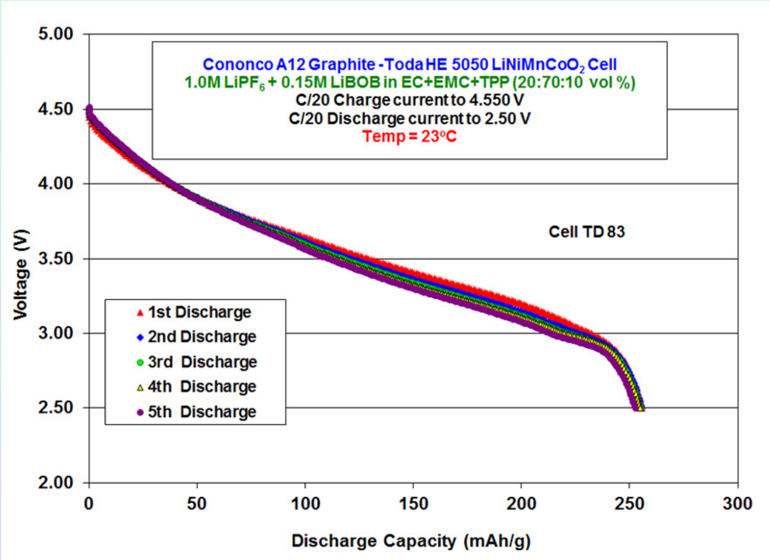
Cathode Measurements

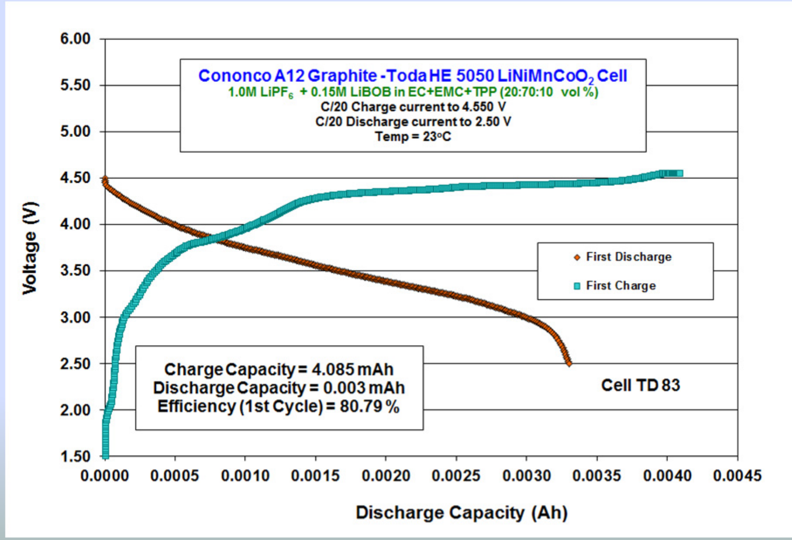


- The EIS measurements suggest that either the presence of TPP or LiBOB results in high film resistance at the anode. Based on previous studies, the LiBOB is likely to contribute more to the SEI build up.

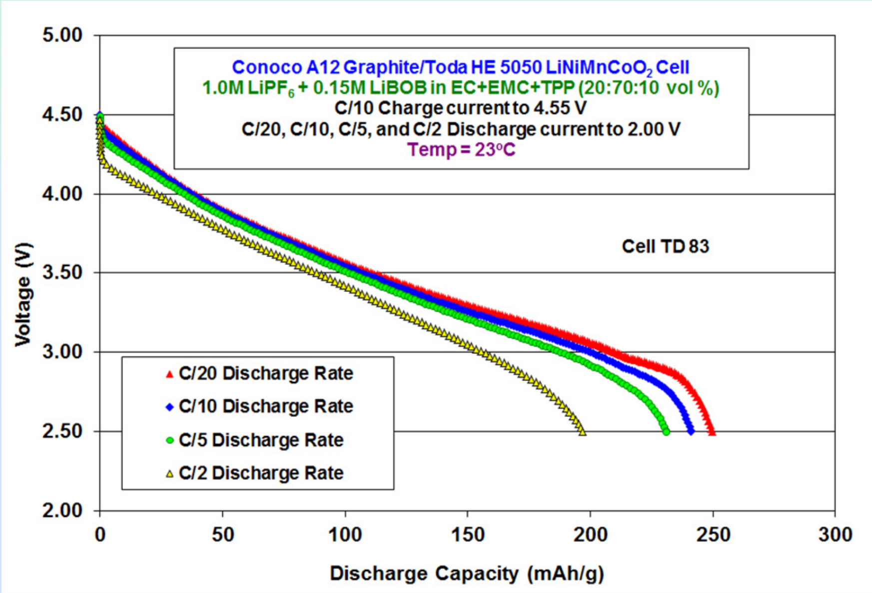
Argonne Cononco A12 Graphite-Toda HE 5050 $LiNiMnCoO_2$ Cells

Formation Characteristics





Rate Characteristics



- Electrolytes possessing TPP in conjunction with LiBOB have also displayed very promising behavior in LiNiCoMnO2-based systems developed at Argonne National Laboratory.
- Work is on-going to demonstrate the life characteristics.

SUMMARY and CONCLUSIONS

- **Performance in MCMB-$LiNiCoO_2$ Cells**
  - *Many electrolytes containing flame retardant additives were observed to perform well in prototype MCMB-$LiNi_xCo_{1-x}O_2$ cells.*
  - *Excellent cycle life is observed with cells containing electrolytes possessing high TPP content*
  - *Good rate capability is observed over a wide temperature range, with good performance at temperatures as low -40^{o}C.*
  - *A formulation possessing FEC (in lieu of EC) and high TPP content (15%) was demonstrated to have good low temperature performance, outperforming an all carbonate baseline.*
- **Performance in Graphite-Toda $LiNiCoMnO_2$ Coin Cells**
  - *Many electrolyte identified as promising based on conclusions made from lithium metal anode cells performed very poorly.*
  - *This necessitated the development of further improved electrolytes aimed at improving the compatibility of the TPP-based systems (i.e., incorporation of LiBOB).*
  - *A number of high TPP-content electrolytes have been demonstrated to perform well with high voltage layered metal oxide cathode systems.*
  - *These electrolytes have also been demonstrated to have good compatibility with carbonaceous anodes.*
- **Future Work**
  - *Future work will focus upon establishing the enhanced safety characteristics of these systems in prototype cells.*

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).