# Performance Testing of Yardney MCMB-$LiNiCoAlO_2$ Lithium-Ion Cells Possessing Electrolytes with Improved Safety Characteristics

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45th Power Sources Conference
Las Vegas, Nevada
June 13, 2012

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- Background
- Approach and Methodology
- MCMB-$LiNiCoO_2$ Experimental 3-Electrode Cell Results
- MCMB-$LiNiCoAlO_2$ Prototype 7 Ah Cells (Yardney Cells)
  - First Generation TPP Electrolytes (i.e., 5% TPP)
  - 100% DOD Cycle Life Performance
  - Discharge Rate Performance vs. Temperature
  - Charge Rate Characteristics
- Graphite-$LiNiCoAlO_2$ Prototype 7 Ah Cells (Yardney Cells)
  - Second Generation TPP Electrolytes (i.e., 10-15% TPP)
  - 100% DOD Cycle Life Performance
  - Discharge Rate Performance vs. Temperature
  - Impedance Characteristics
  - Partial DOD Cycle Life Performance (30% DOD)
- 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
    - 1 mS cm-1 from –60 to 40°C
  - Wide liquid range (low melting point)
    - -60 to 75°C
  - Good electrochemical stability
    - Stability over wide voltage window (0 to 4.5V)
    - Minimal oxidative degradation of solvents/salts
  - Good chemical stability
  - Good compatibility with chosen electrode couple
    - Good SEI characteristics on electrode
    - Facile lithium intercalation/de-intercalation kinetics
  - Good thermal stability
  - Good low temperature performance throughout life of cell
    - Good resilience to high temperature exposure
    - Minimal impedance build-up with cycling and/or storage

- 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]

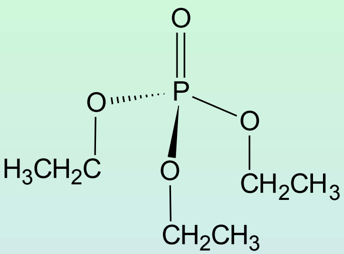

1) K. Xu, S. Zhang, J. L. Allen, T. R. Jow *J. Electrochem. Soc.*, **2002**, *149*, A1079

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).

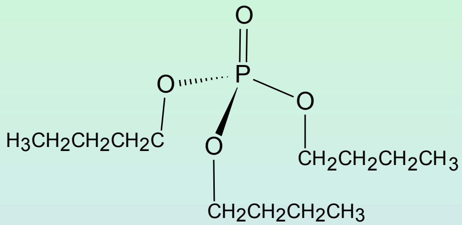
3) J. K. Feng, X. P. Ai, Y. L. Cao, and H. X. Yang, J. Power Sources, 177, 194-198 (2008).

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

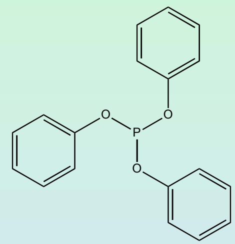
# Development of Electrolytes Containing Flame Retardant Additives



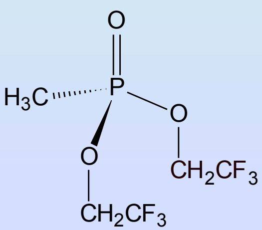

**Triethyl phosphate (TEP)**



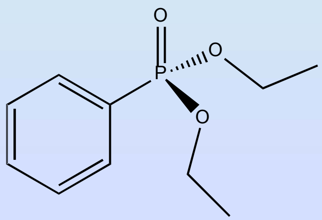

**Tributyl phosphate (TBP)**



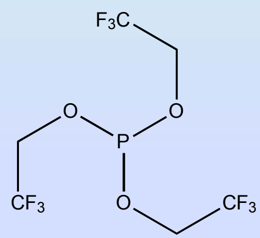
**Triphenyl phosphite (TPPi)**



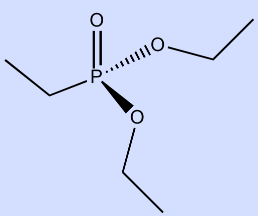

**Bis-(2,2,2-trifluoroethyl)methyl phosphonate (BTFEMP)**



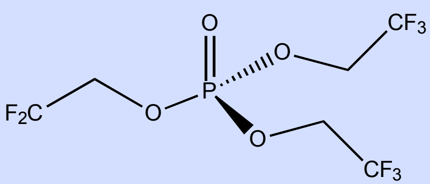

**Diethyl phenylphosphonate (DPP)**




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

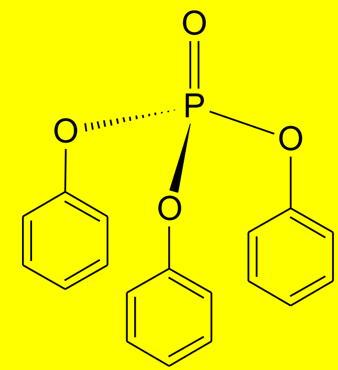



**Diethyl ethylphosphonate (DEP)**




**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

# Electrolytes Selected for Evaluation in Experimental Cells

Fluorinated esters were also coupled with FRAs to lower flammability →

- 1.0 M $LiPF_6$ in EC/EMB/TFEB/TPP (20:55:20:5 v/v%)
- 1.0 M $LiPF_6$ in EC/EMB/TFEB/TBP (20:55:20:5 v/v%)
- 1.0 M $LiPF_6$ in EC/EMB/TFEB/TEP (20:55:20:5 v/v%)
- 1.0 M $LiPF_6$ in EC/EMB/TFEB/ BTFEMP (20:55:20:5 v/v%)

1.0 M $LiPF_6$ in EC+EMC+TFPa (20:75:5 v/v %)
1.0 M $LiPF_6$ in EC+EMC+TFPi (20:75:5 v/v %)
1.0 M $LiPF_6$ in EC+EMC+TPPi (20:75:5 v/v %)
1.0 M $LiPF_6$ in EC+EMC+DEP (20:75:5 v/v %)
1.0 M $LiPF_6$ in EC+EMC+DPP (20:75:5 v/v %)
1.0 M $LiPF_6$ in EC+EMC (20:80 v/v %) (Baseline Solution)
1.0 M $LiPF_6$ in EC+EMC+TPP (20:75:5 v/v %)
1.0 M $LiPF_6$ in EC+EMC (20:80 v/v %) + 1.5 % VC
1.0 M $LiPF_6$ in EC+EMC+TPP (20:75:5 v/v %) + 1.5% VC

- **Where: TPP** = triphenyl phosphate, **TBP** = tributyl phosphate, **TEP** = triethyl phosphate, **BTFEMP =** bis-(2,2,2-trifluoroethyl)methyl phosphonate, **TFEB =** trifluoroethyl butyrate, **TFPa** = Tris(2,2,2-trifluoroethyl) phosphate, **TFPi =** Tris(2,2,2-trifluoroethyl) phosphite, **TPPi =** Triphenyl phosphite, **DEP =** Diethyl ethylphosphonate, **DPP =** Diethyl phenylphosphonate.

- Electrolytes were assessed in MCMB Carbon-$LiNiCoO_2$ glass wound (cylindrical) cells of 400-450 mAh size with Li metal reference electrodes.
- Performed assessment of performance (charge-discharge) at different rates and temperatures, high temperature resilience and detailed individual electrochemical kinetic measurements.
- **Early studies led to the identification of TPP as providing the best overall performance (i.e., cycle life, rate capability, and the ability to be coupled with high voltage systems).**

# Performance Testing of Aerospace Quality Prototype Li-Ion Cells

## *Performance of Advanced Electrolytes in 7Ah Cells*

- Obtained a 7 Ah cells (NCP 7) fabricated by Yardney Technical Products containing JPL developed electrolytes:

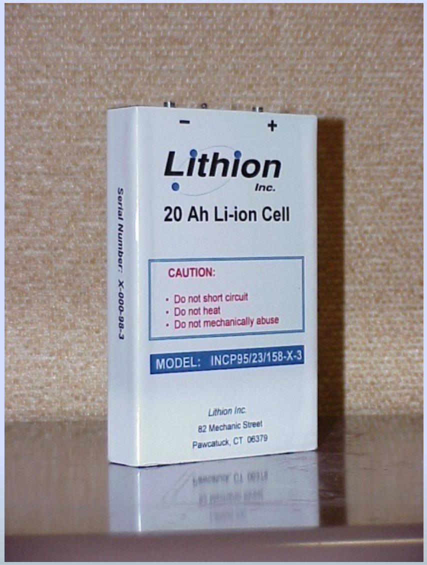
FRA Containing Electrolyte

1.0 M $LiPF_6$ EC+EMC+TPP+VC (20:74:5:1.5 v/v %) (TPP = triphenyl phosphate)
1.0 M $LiPF_6$ EC+EMC+TFEB (20:60:20 v/v %) (TFEB=2,2,2-trifluoroethyl butyrate)

1.0 M $LiPF_6$ EC+EMC (20:80 v/v %)
1.0 M $LiPF_6$ EC+DEC+DMC+EMC (1:1:1:3 v/v %)
1.0 M $LiPF_6$ EC+DEC+DMC (1:1:1 v/ %) (Baseline – 2003 MER Rover Electrolyte)

# Test Plan

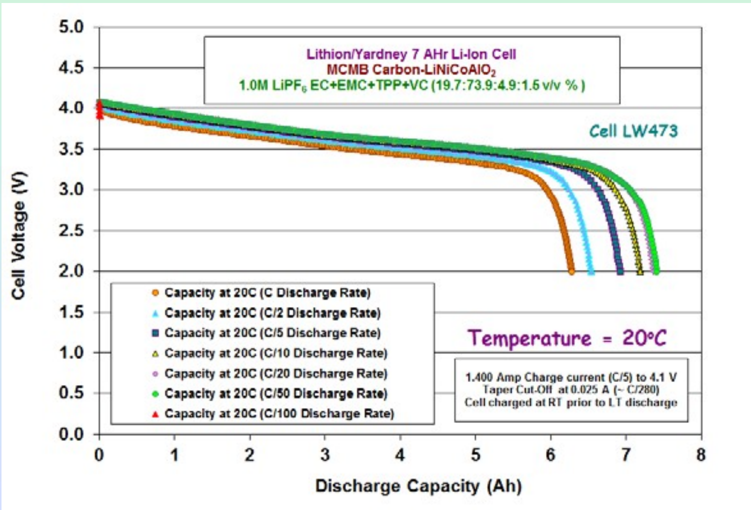
- Performed a number of performance evaluation tests
  - *Conditioning cycling performed at $20^o$, $0^o$, and $-20^oC$ (with impedance)*
  - *Discharge Rate Characterization at Various Temperatures*
    - *Wide temperature range (-80 to $20^oC$)*
    - *Wide range of discharge rates (C rate to C/400 rate)*
    - *Comparison of electrolyte types*
  - *Pulse Discharge Characterization at Various Temperatures*
  - *Current-Interrupt Impedance Measurements*

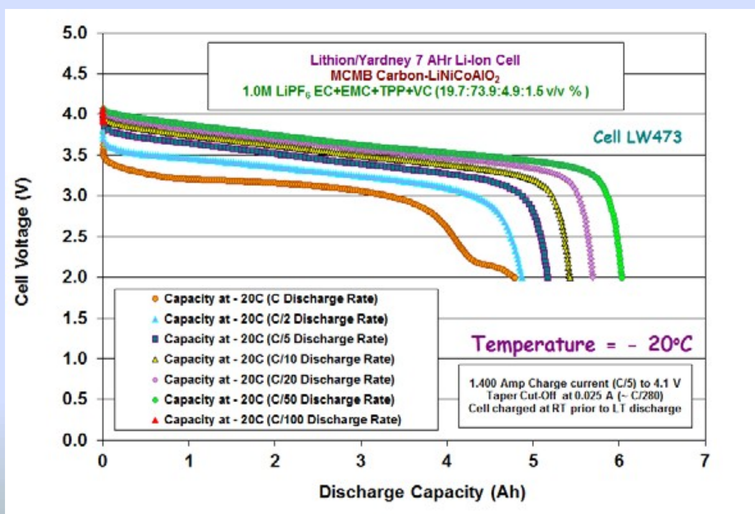


# Yardney 7 Ah Prismatic Li-Ion Cells

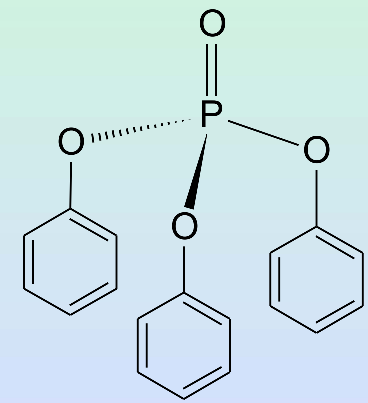
## Characterization of Cells Containing Electrolytes With FRAs

### Discharge Performance at 20°C and -20°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**

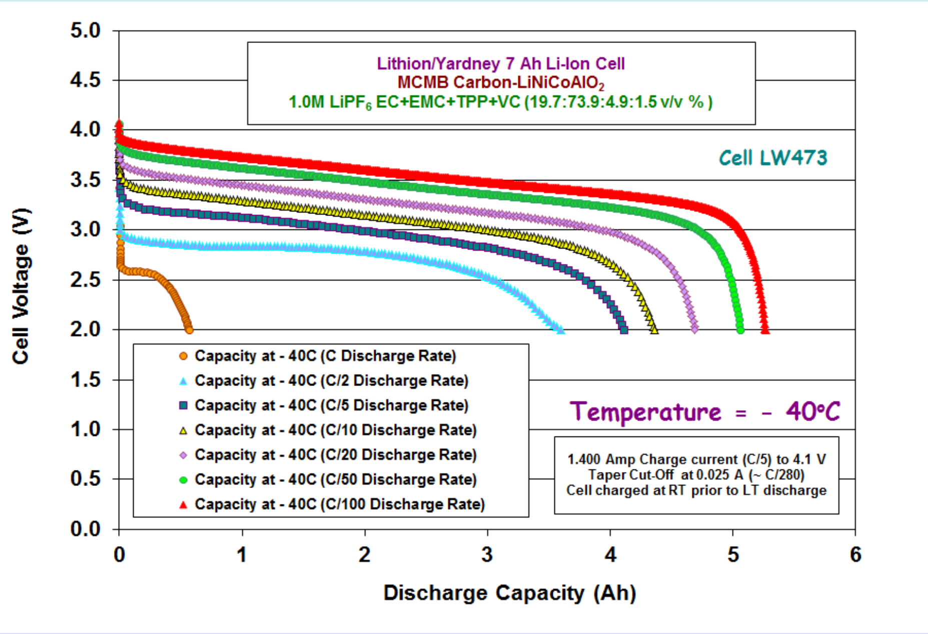
# Yardney 7 Ah Prismatic Li-Ion Cells

## Characterization of Cells Containing Advanced Electrolytes

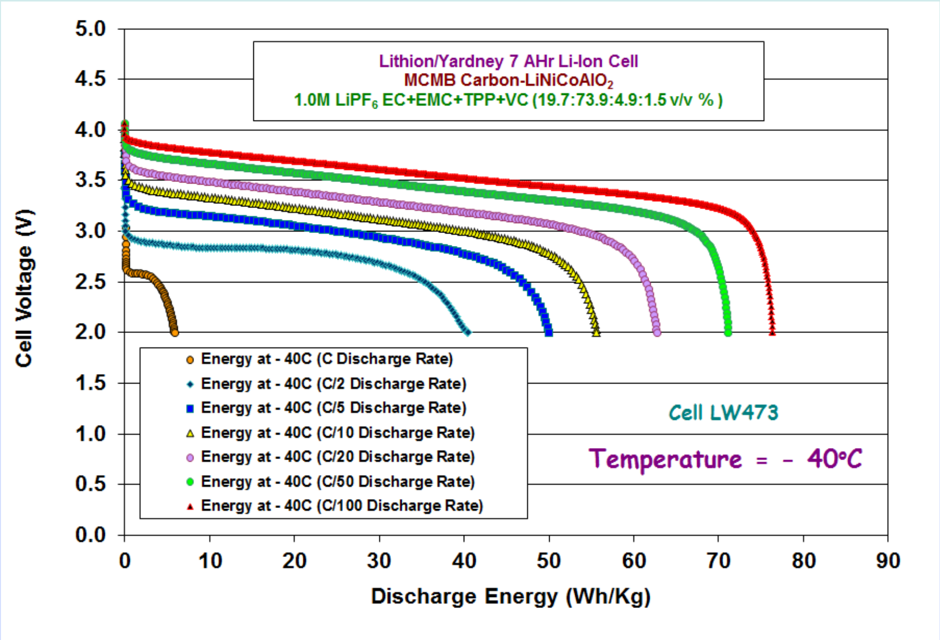
### Summary of Discharge Characterization Testing at Various Temperatures

### Discharge Performance at - 40°C

Discharge Capacity (Ah) at - 40°C




Discharge Energy (Wh/Kg) at - 40°C



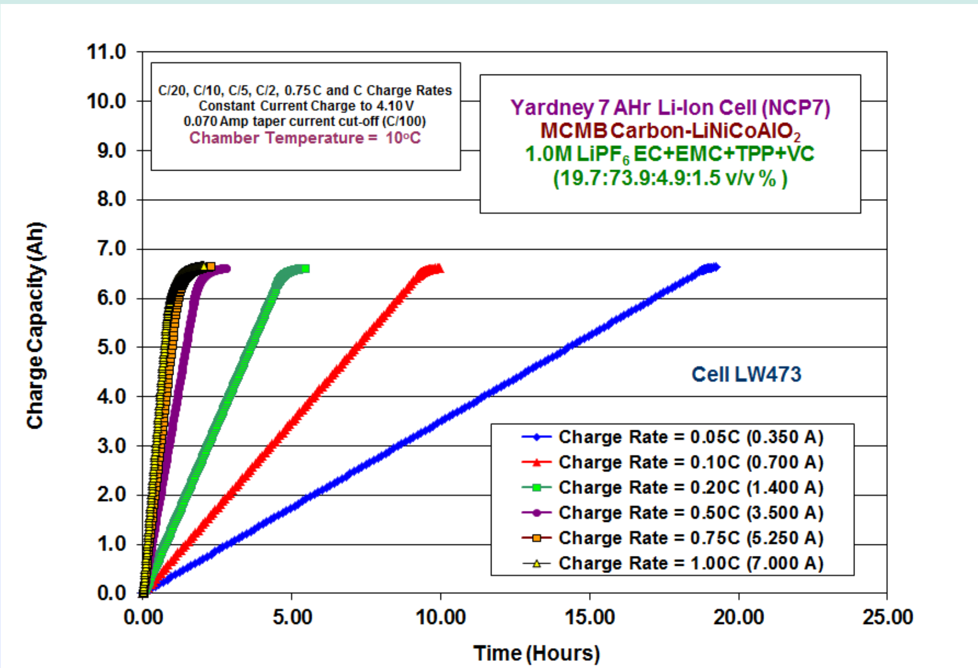

Cells containing an electrolyte with a flame retardant additive (i.e., *1.0 M $LiPF_6$ in EC+EMC+TPP+VC*) are observed to display good performance over a range of temperatures.

# Yardney 7 Ah Prismatic Li-Ion Cells

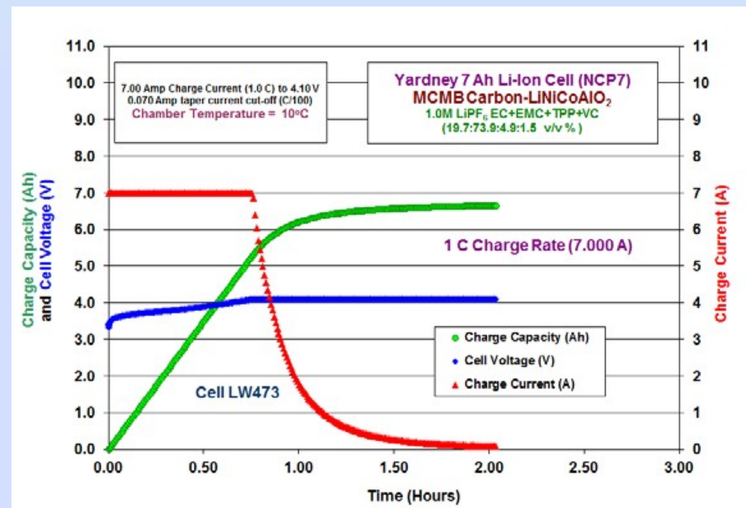
## Characterization of Cells Containing Advanced Electrolytes

### Charge Characteristics at 10°C

**Charge Capacity (Ah)**




| Charge Rate | Charge Current (A) | Charge Capacity (Ah) | Charge Time (Hours) | Percent C/10 Capacity | Percent C/10 Capacity at 20°C |
|---|---|---|---|---|---|
| C/20 | 0.350 | 6.6347 | 19.2328 | 100.00 | 94.42 |
| C/10 | 0.700 | 6.6185 | 9.9440 | 99.76 | 94.19 |
| C/5 | 1.400 | 6.6230 | 5.4156 | 99.82 | 94.25 |
| C/2 | 3.500 | 6.6205 | 2.7775 | 99.79 | 94.21 |
| 0.75 C | 5.250 | 6.6541 | 2.2816 | 100.29 | 94.69 |
| 1.00 C | 7.000 | 6.6553 | 2.0344 | 100.31 | 94.71 |



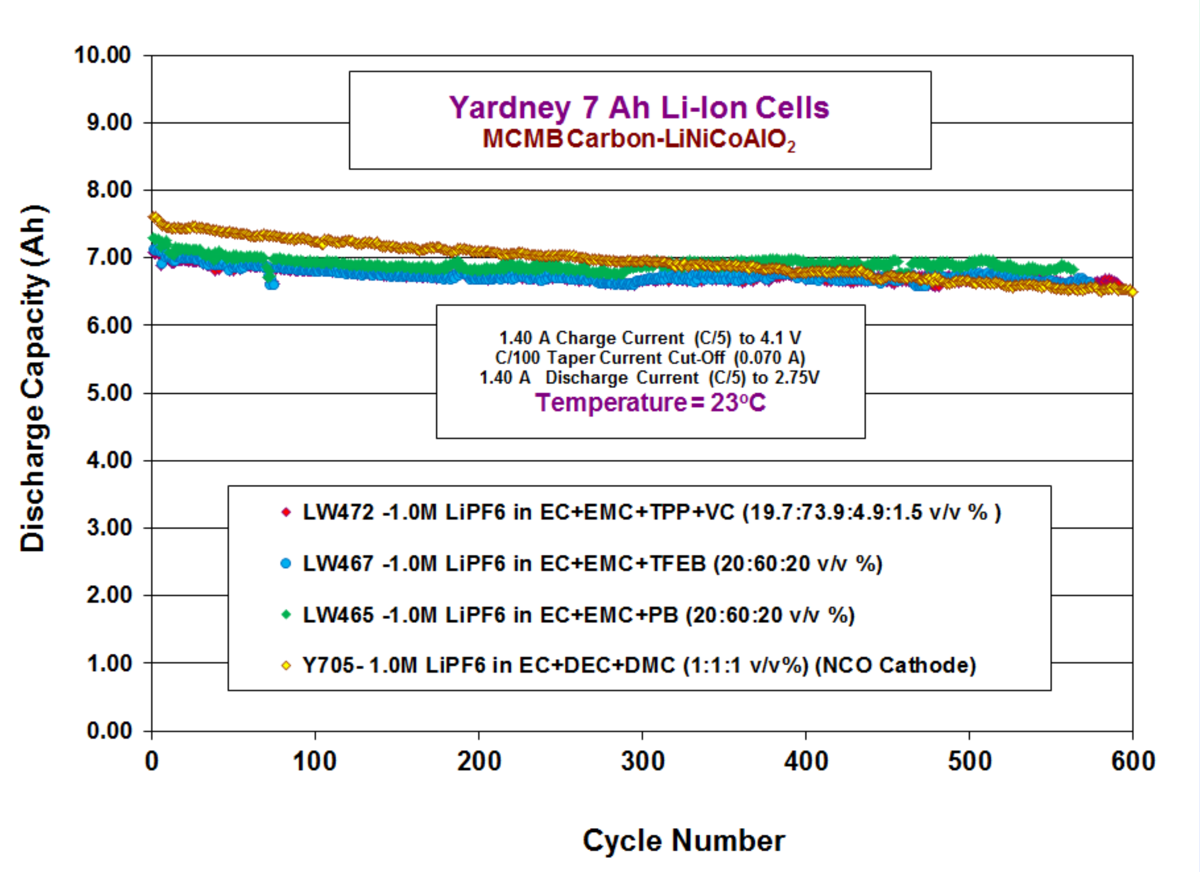

Cells were subjected to C/20, C/10, C/5, C/2 and C charge rates.
Charge rate characterization was performed at various temperatures.

# Yardney 7 Ah Prismatic Li-Ion Cells

## Characterization of Cells Containing Advanced Electrolytes

### 100 % DOD Cycle Life Testing at Room Temperature

Discharge Capacity (Ah)




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.

# 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

# Advanced Low Temperature, Non-flammable Electrolytes

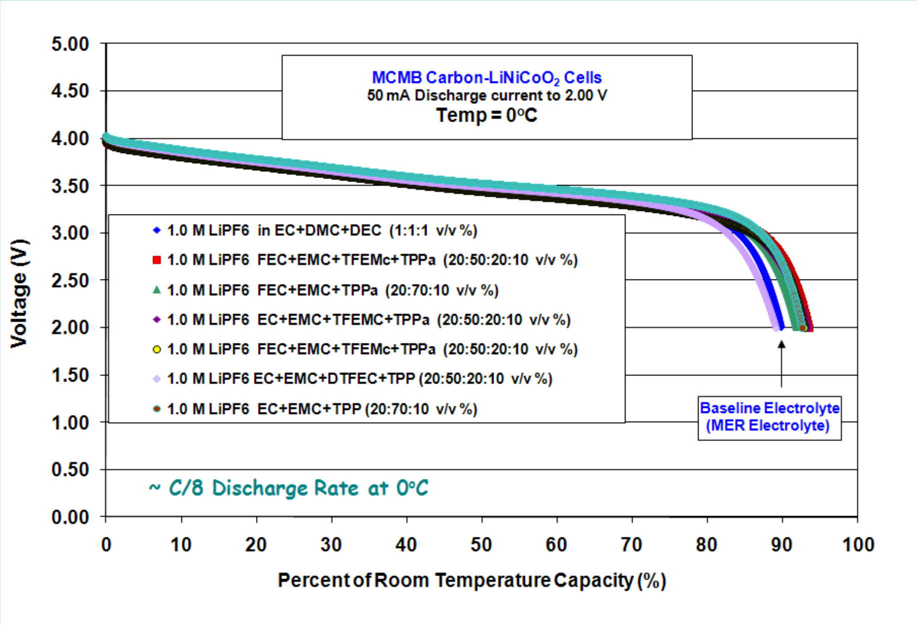
## Summary Discharge Characteristics at Low Temperatures

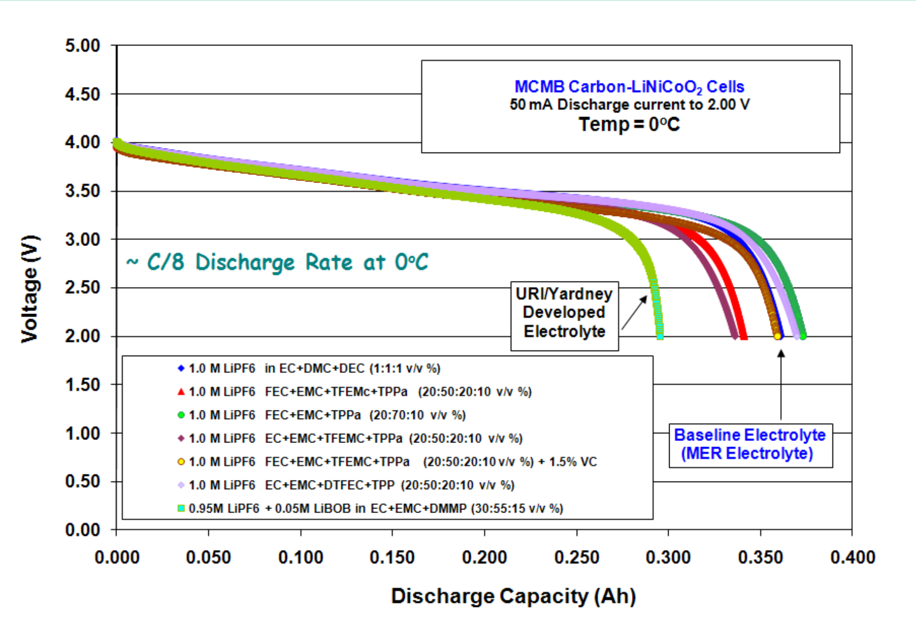
| Electrolyte Type → | | 1.0 M $LiPF_6$ EC+DEC+DMC (1:1:1 v/v %) | | 1.0 M $LiPF_6$ FEC+EMC+TFEMC+TPPa (20:50:20:10 v/v %) | | 1.0 M $LiPF_6$ FEC+EMC+TPP (20:70:10 v/v %) | | 1.0 M $LiPF_6$ EC+EMC+TFEMC+TPP (20:30:40:10 v/v %) | | 1.0 M $LiPF_6$ FEC+EMC+TFEMC+TPPa (20:50:20:10 v/v %) + 1.5% VC | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Temp. | Current (mA) | Capacity (Ah) | Percent (%) | Capacity (Ah) | Percent (%) | Capacity (Ah) | Percent (%) | Capacity (Ah) | Percent (%) | Capacity (Ah) | Percent (%) |
| 23°C | 25 mA | 0.4022 | 100.00 | 0.3646 | 100.00 | 0.4063 | 100.00 | 0.3596 | 100.00 | 0.3867 | 100.00 |
| 0°C | 25 mA | 0.3633 | 90.31 | 0.3497 | 95.92 | 0.3805 | 93.63 | 0.3410 | 94.81 | 0.3621 | 93.64 |
| | 50 mA | 0.3609 | 89.73 | 0.3409 | 93.48 | 0.3731 | 91.82 | 0.3362 | 93.47 | 0.3591 | 92.88 |
| | 100 mA | 0.3199 | 79.55 | 0.3037 | 83.30 | 0.3374 | 83.04 | 0.2945 | 81.89 | 0.3207 | 82.93 |
| | 150 mA | 0.2950 | 73.35 | 0.2539 | 69.62 | 0.3053 | 75.14 | 0.2298 | 63.89 | 0.2914 | 75.35 |
| - 10°C | 25 mA | 0.3202 | 79.60 | 0.3148 | 86.33 | 0.3544 | 87.23 | 0.3158 | 87.82 | 0.3238 | 83.74 |
| | 50 mA | 0.2974 | 73.95 | 0.2926 | 80.26 | 0.3216 | 79.15 | 0.3013 | 83.79 | 0.3071 | 79.41 |
| | 100 mA | 0.2607 | 64.82 | 0.2026 | 55.57 | 0.2324 | 57.20 | 0.2144 | 59.60 | 0.2593 | 67.07 |
| | 150 mA | 0.2182 | 54.25 | 0.0802 | 22.01 | 0.1793 | 44.14 | 0.1174 | 32.65 | 0.2219 | 57.38 |
| - 20°C | 25 mA | 0.2723 | 67.70 | 0.2982 | 81.79 | 0.3388 | 83.39 | 0.3010 | 83.68 | 0.3127 | 80.88 |
| | 50 mA | 0.2313 | 57.51 | 0.2458 | 67.40 | 0.2876 | 70.79 | 0.2544 | 70.73 | 0.2728 | 70.54 |
| | 100 mA | 0.0661 | 16.43 | 0.0772 | 21.18 | 0.1670 | 41.10 | 0.0778 | 21.62 | 0.1694 | 43.81 |
| | 150 mA | 0.0312 | 7.77 | 0.0287 | 7.88 | 0.0411 | 10.12 | 0.0272 | 7.57 | 0.0493 | 12.76 |
| - 30°C | 25 mA | 0.0288 | 7.16 | 0.2467 | 67.67 | 0.2844 | 69.99 | 0.2654 | 73.79 | 0.2664 | 68.90 |
| | 50 mA | 0.0198 | 4.93 | 0.1069 | 29.31 | 0.1979 | 48.71 | 0.1178 | 32.74 | 0.2050 | 53.03 |
| - 40°C | 25 mA | 0.0203 | 5.06 | 0.0759 | 20.82 | 0.1611 | 39.64 | 0.0511 | 14.21 | 0.1673 | 43.27 |
| - 50°C | 25 mA | 0.0059 | 1.46 | 0.0000 | 0.01 | 0.0377 | 9.27 | 0.0135 | 3.75 | 0.0234 | 6.04 |

***Some formulations investigated have up to 40% of a partially fluorinated solvent and 10% flame retardant additive***

# Electrolytes With Improved Safety and Good High Voltage Stability

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



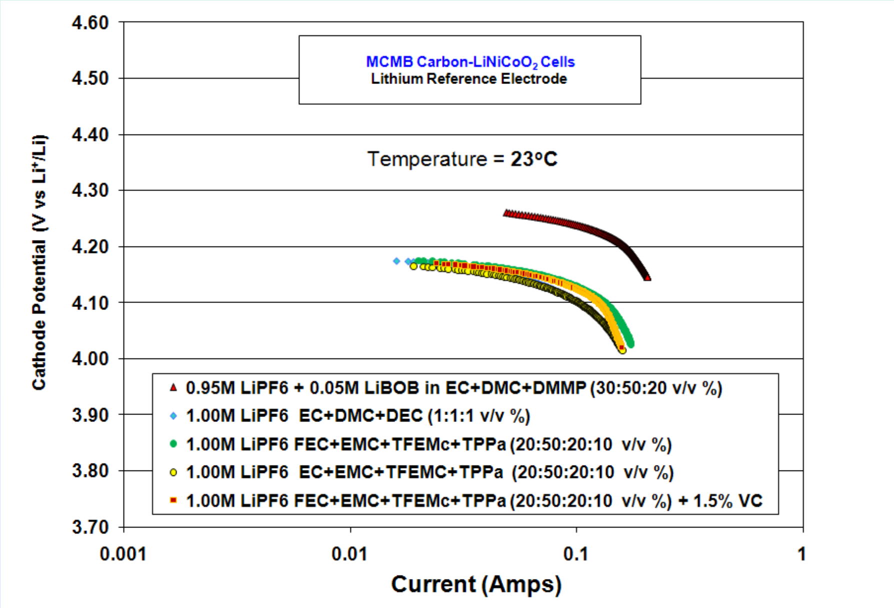



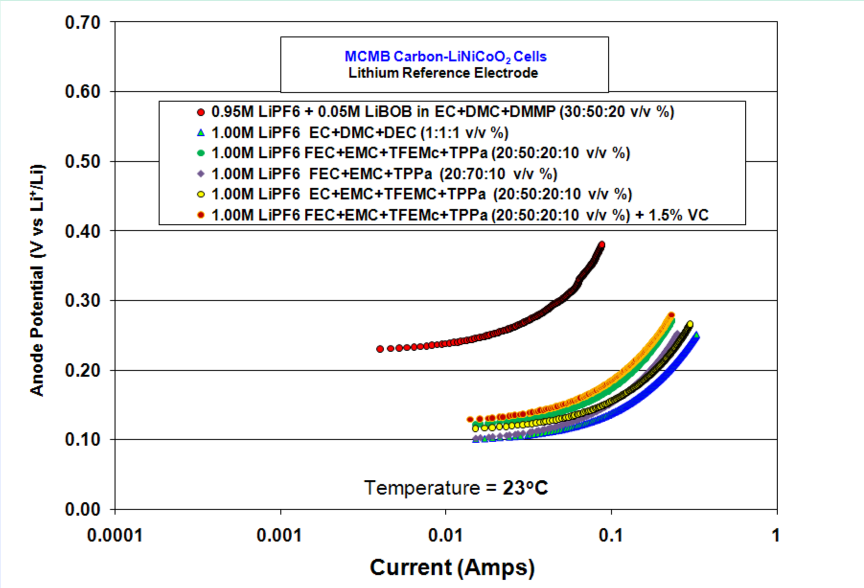

When the electrolytes were evaluated in MCMB-LiNiCo$O_2$ cells, generally good performance was observed with the electrolytes studied. Good performance was even observed when the EC was replaced completely with FEC and TFEMC was added as well at a ~ **C/4 rate at 0°C.**

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.

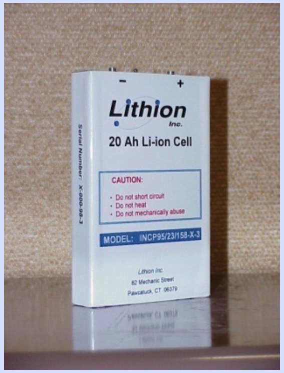
## Performance in Prototype Graphite / $LiNiCoAlO_2$ 7 Ah Cells

### Overview of Study

- The testing of graphite / $LiNiCoAlO_2$ 7 Ah Yardney cells containing advanced electrolytes with flame retardant additives is on-going. The cells contain the following:

**1) 1.0 M $LiPF_6$ in EC+EMC+TPP (20:70:10 vol %)**
**2) 1.0 M $LiPF_6$ in EC+EMC+TPP (20:65:15 vol %)**
**3) 1.0 M $LiPF_6$ in FEC+EMC+TPP (20:70:10 vol %)**
**4) 1.0 M $LiPF_6$ in FEC+EMC+TFEMC+TPP (20:50:20:10 vol %) + 1.5% VC**

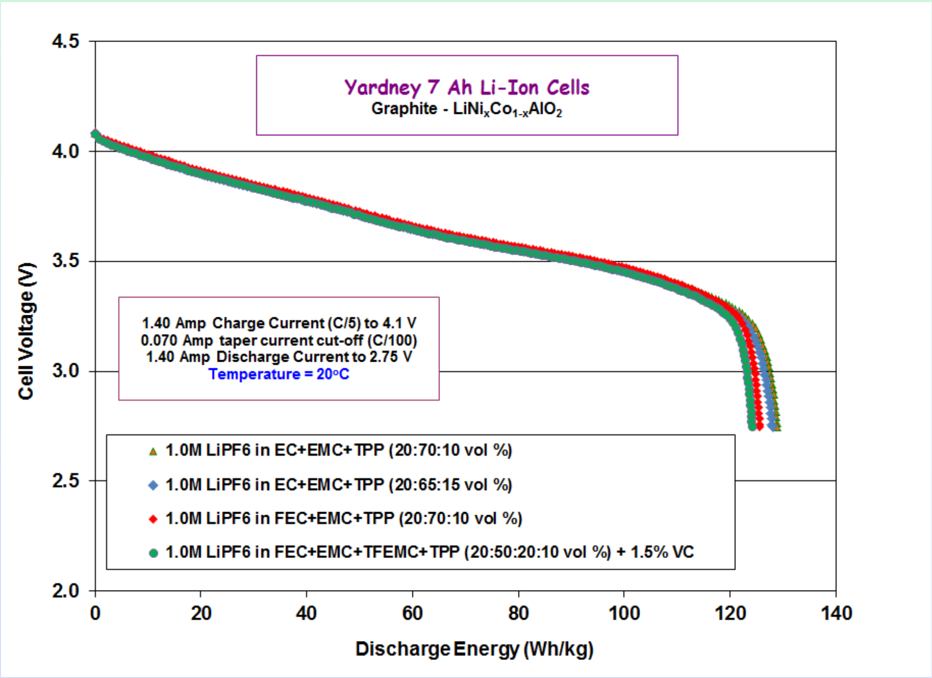
- Performed characterization cycling at various temperatures (20, 0, and -20$^{o}$C).
- Tests include capacity and impedance determination
- Performed discharge characterization over a wide temperature range (cells charged at room temperature prior to discharge)
- Currently performing 100% DOD and 30% DOD cycle life testing

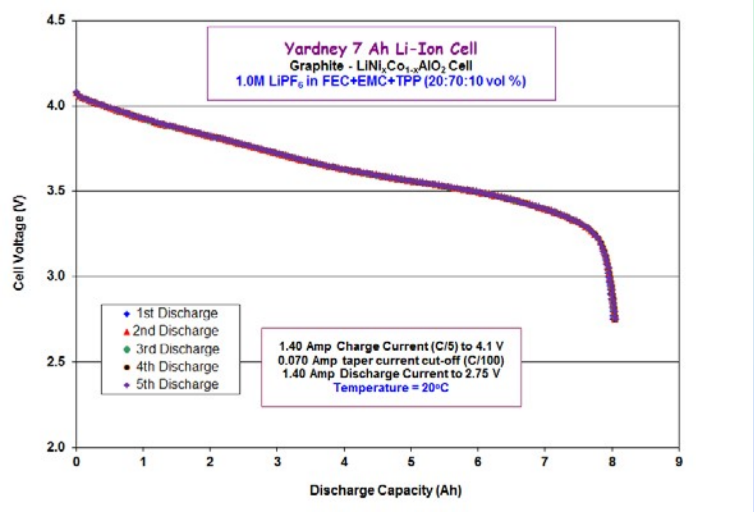



➢ **Study addresses the following variables in electrolyte design:**
- **Increasing TPP content (5% to 15%)**
- **The incorporation of FEC into electrolytes**
- **The use of fluorinated carbonates (i.e., trifluoroethyl methyl carbonate)**

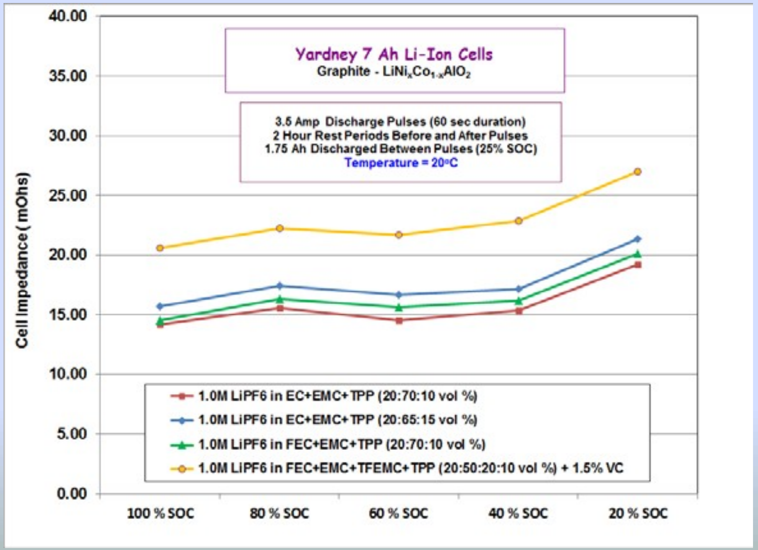
# Discharge Characteristics Graphite / $LiNiCoAlO_2$ 7 Ah Cells Conditioning at 20°C

## Comparison of Electrolyte Types



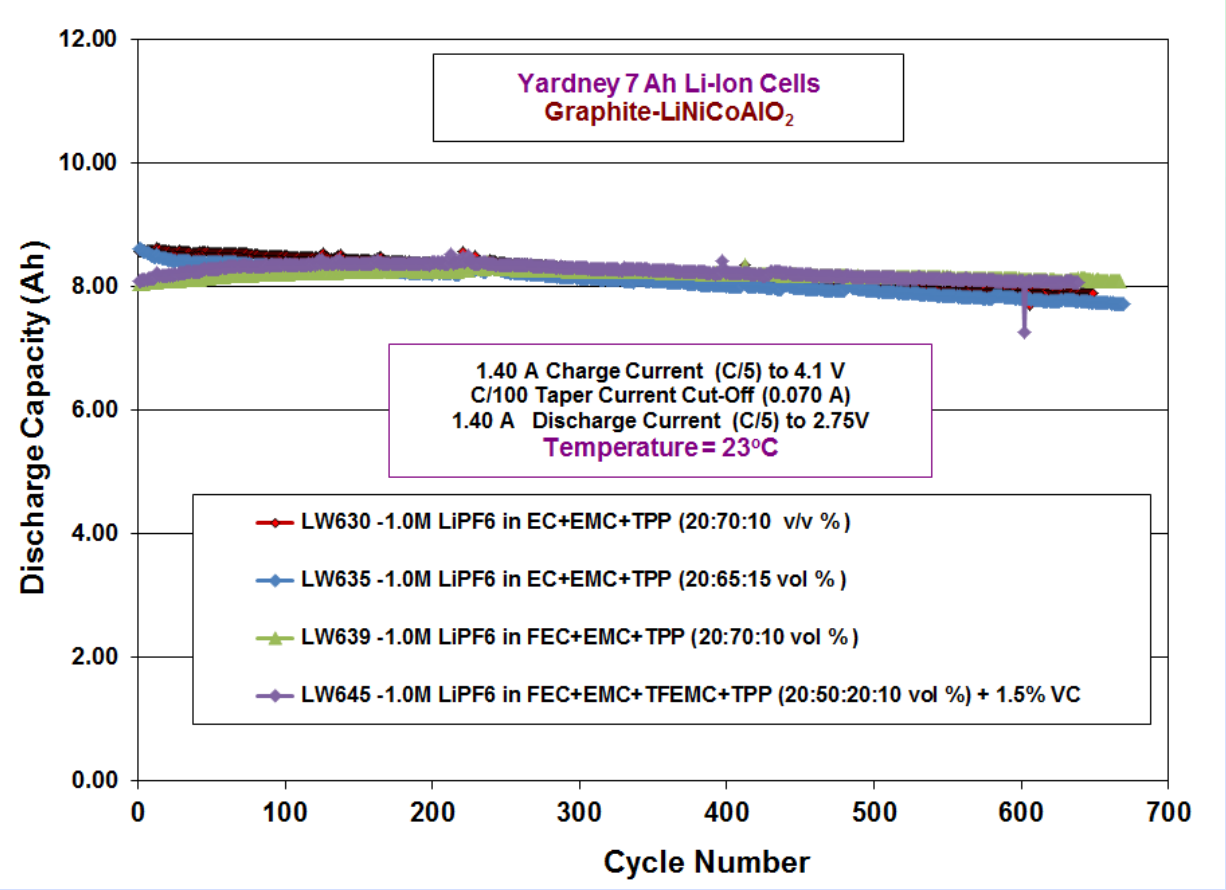




• Upon being subjected to initial capacity and impedance characterization at 20°C, all cells displayed comparable performance.



# Cycle Life Testing of Graphite / $LiNiCoAlO_2$ 7 Ah Cells

## 100 % DOD Cycle Life Performance

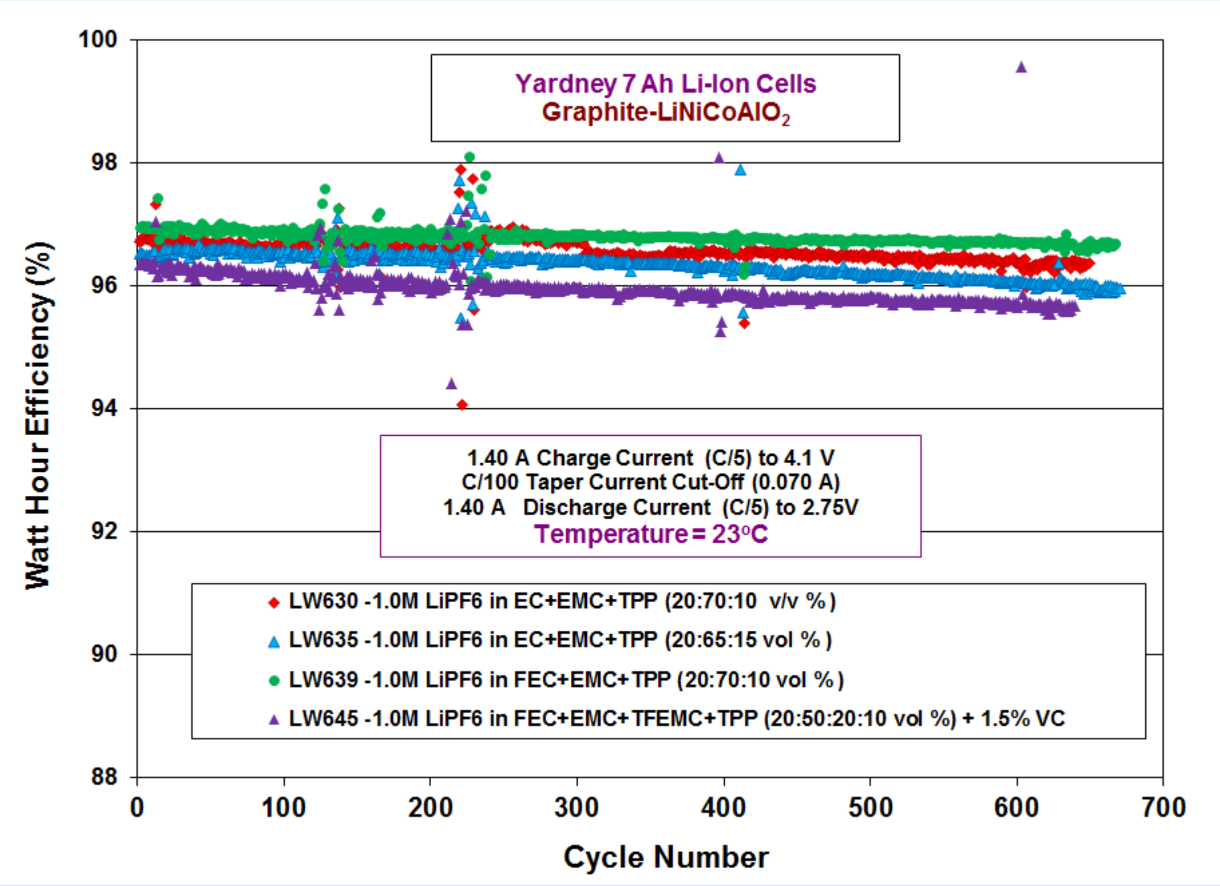



- Initial results are very promising, suggesting good compatibility with the system.
- Excellent cycle life has been obtained thus far (> 600 full depth of discharge cycles).
- Cells containing up to 15% FRA display good life.
- The use of fluorinated co-solvents does not have a negative impact on life.

# Cycle Life Testing of Graphite / $LiNiCoAlO_2$ 7 Ah Cells

## 100 % DOD Cycle Life Performance

### Watt Hour Efficiency (%)




- Initial results are very promising, suggesting good compatibility with the system.
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- Cells containing up to 15% FRA display good life.
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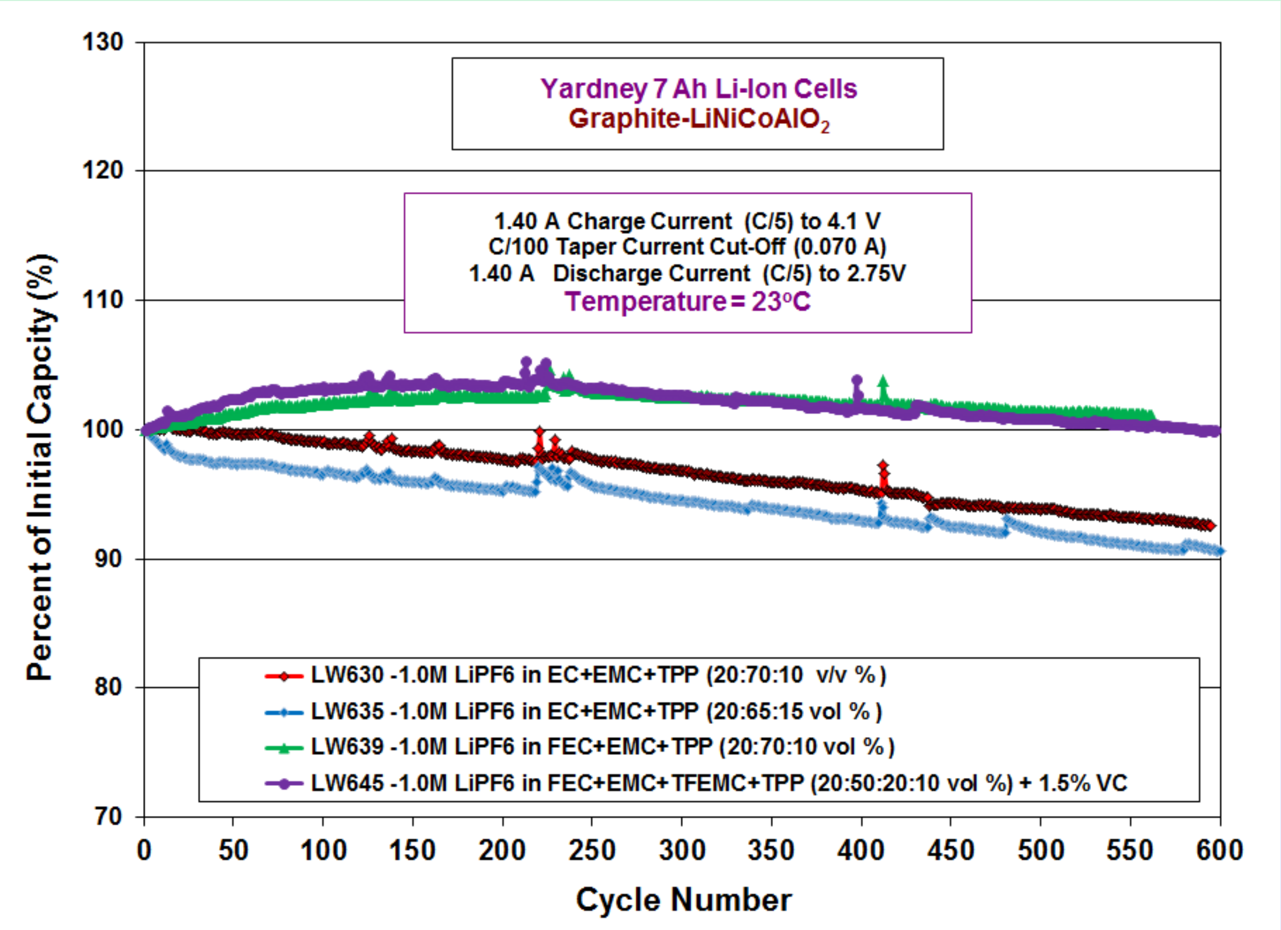
# Cycle Life Testing of MCMB-1028 / $LiNiCoO_2$ 7 Ah Cells

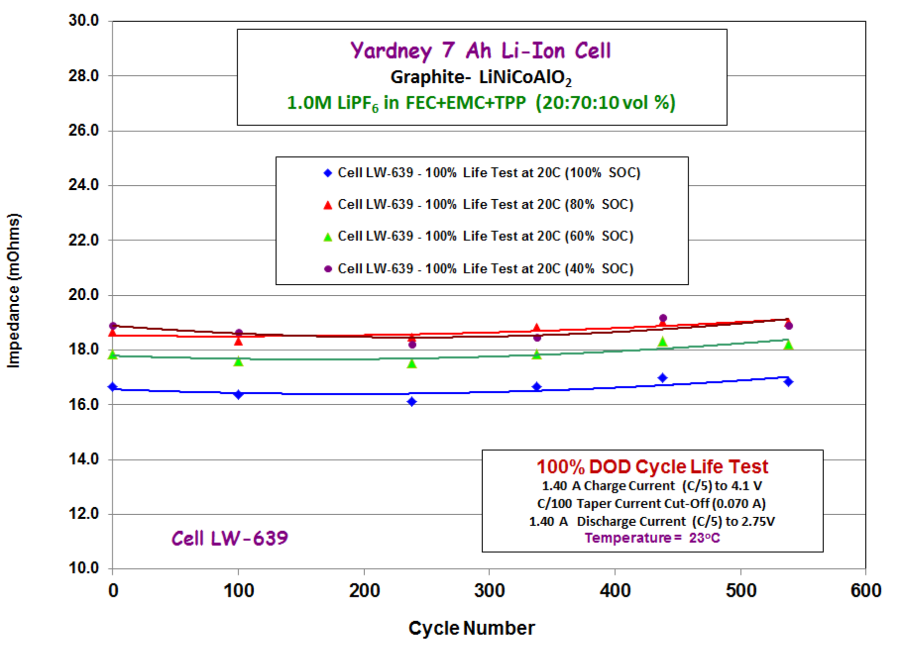
## 100 % DOD Cycle Life Performance

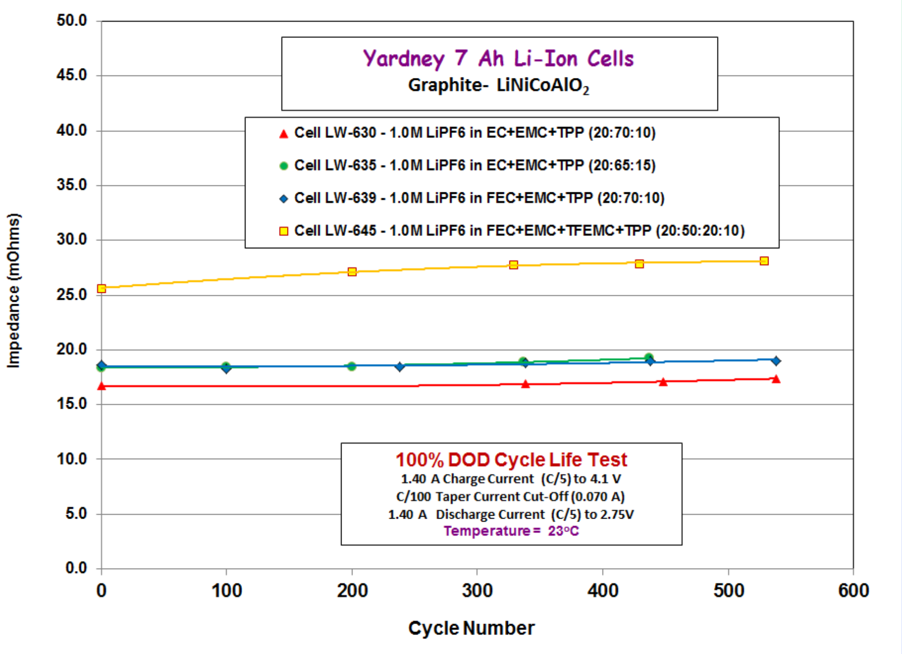



- A gradual capacity rise have been observed with the cells containing the fluorinated co-solvents, with no capacity loss over 500 cycles.

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

## 100 % DOD Cycle Life Performance: Impedance Growth

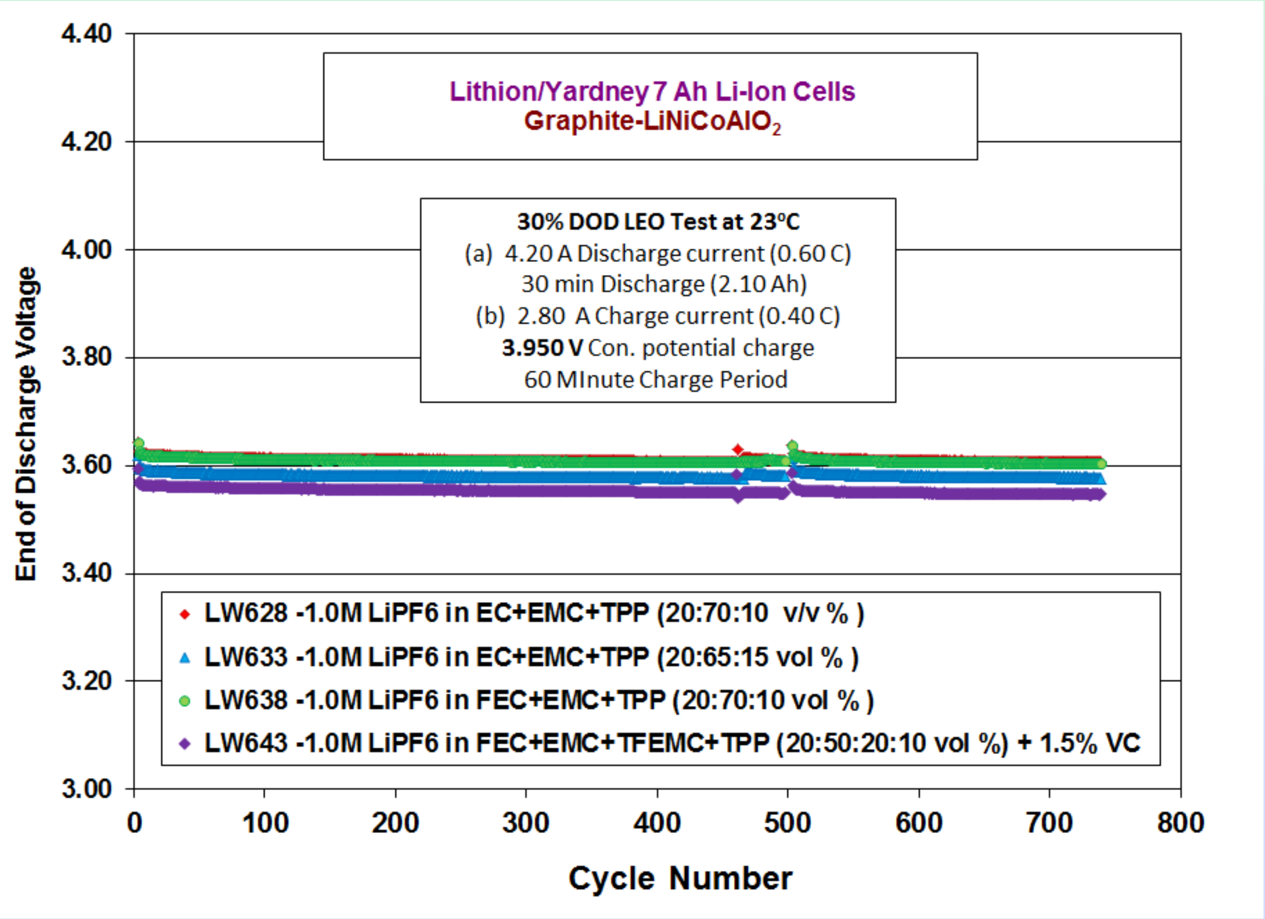



- The incorporation of TPP does not result in significant impedance growth during cycling.
- The use of FEC and TPP increases the cell impedance modestly.
- The use of TFEMC results in increased cell impedance and accelerated impedance growth during cycling.

# Cycle Life Testing of Graphite / $LiNiCoAlO_2$ 7 Ah Cells

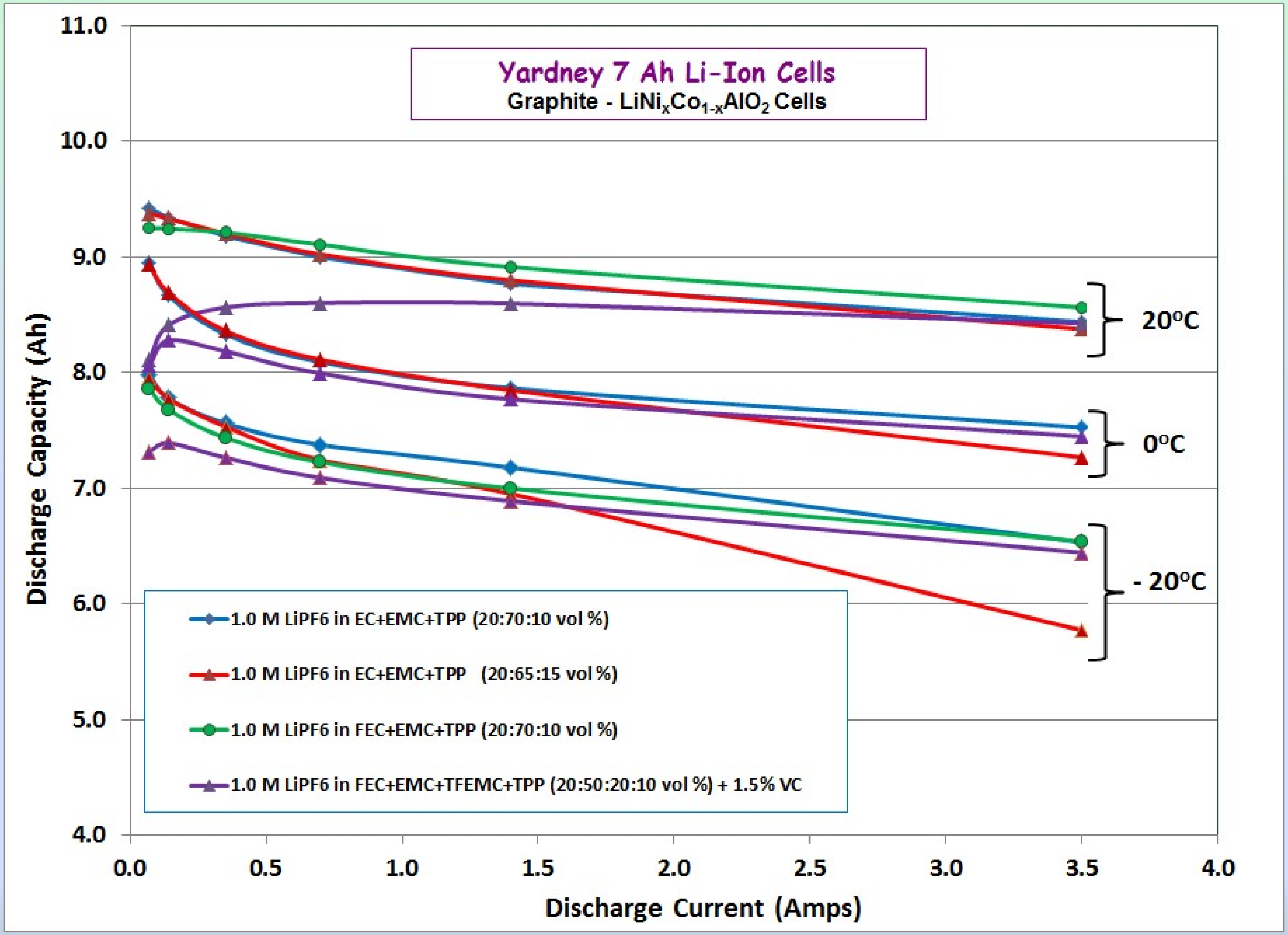
## 30 % DOD Cycle Life Performance




• 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.

# Discharge Characteristics Graphite / $LiNiCoAlO_2$ 7 Ah Cells

## Discharge Characterization Testing at 20°, 0°, and -20°C

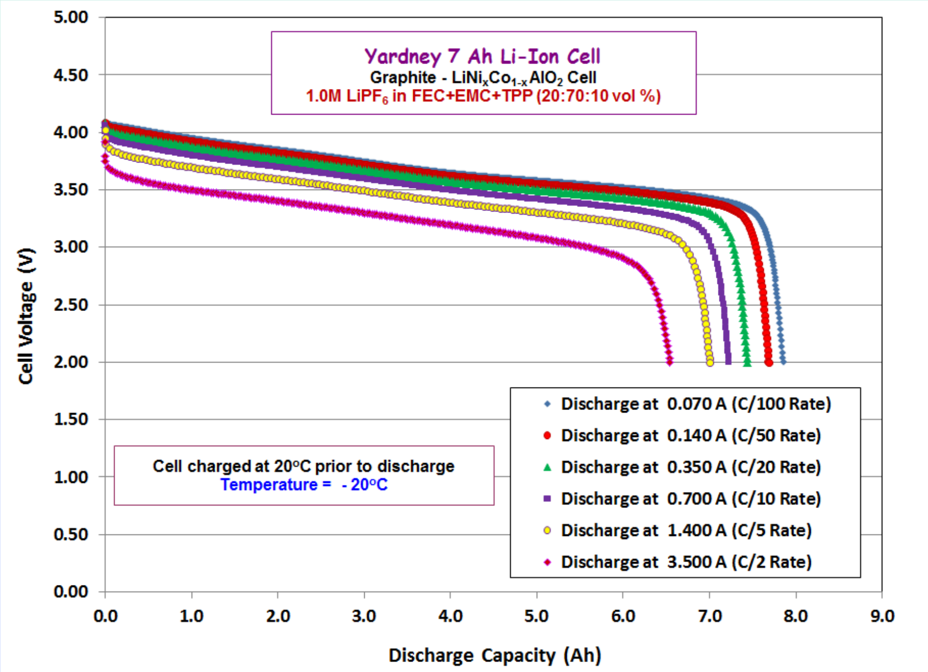



Cells charged at room temperature and discharged at the respective temperature.

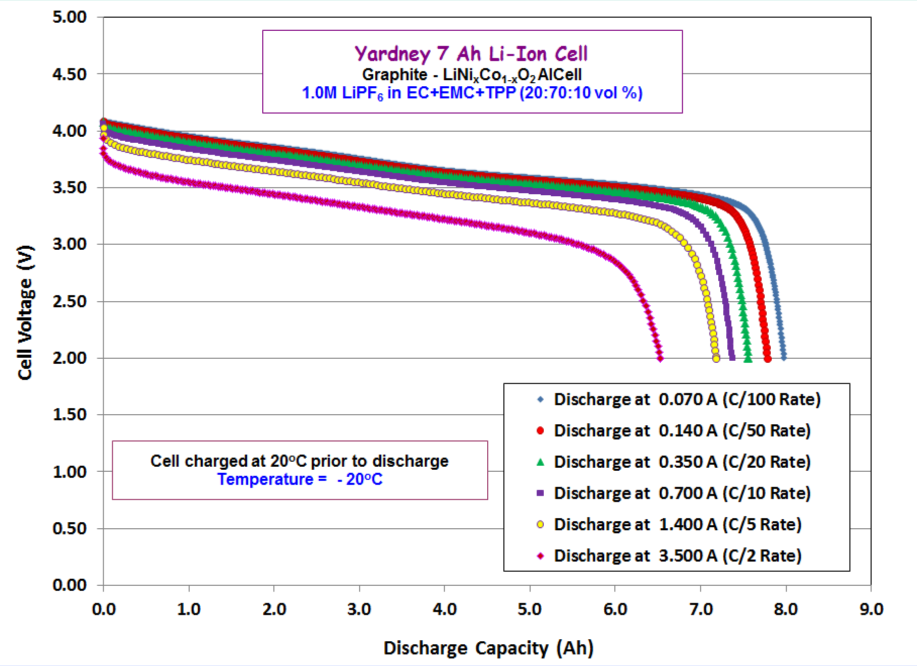
# Discharge Characteristics Graphite / $LiNiCoAlO_2$ 7 Ah Cells

## Discharge Characterization Testing at -20°C: Electrolytes with 10% TPP Content

### FEC-Based Electrolyte




### EC-Based Electrolyte

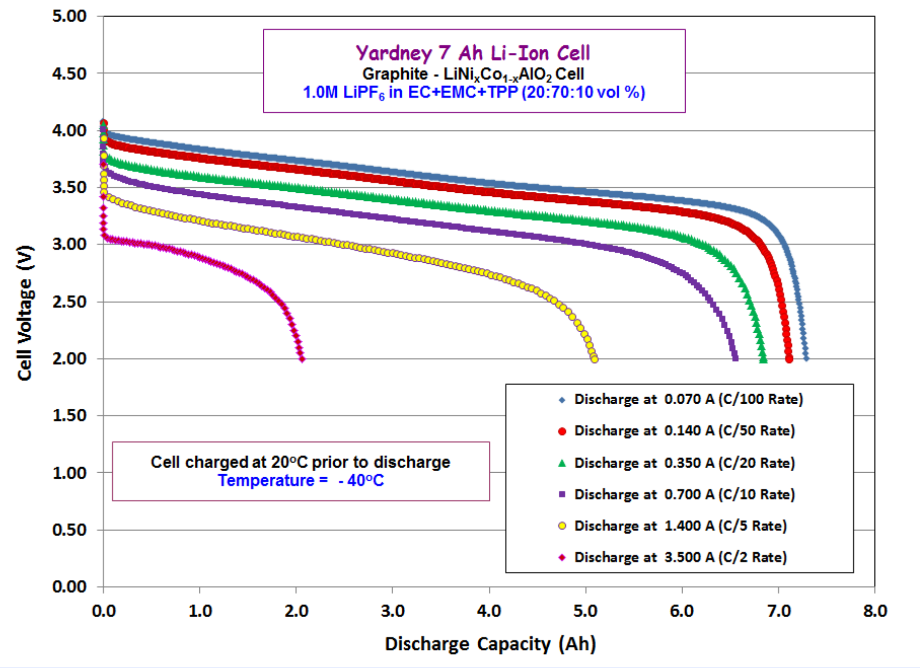



**Cells containing electrolytes with 10% TPP (with and without FEC) displayed good performance at -20°C.**

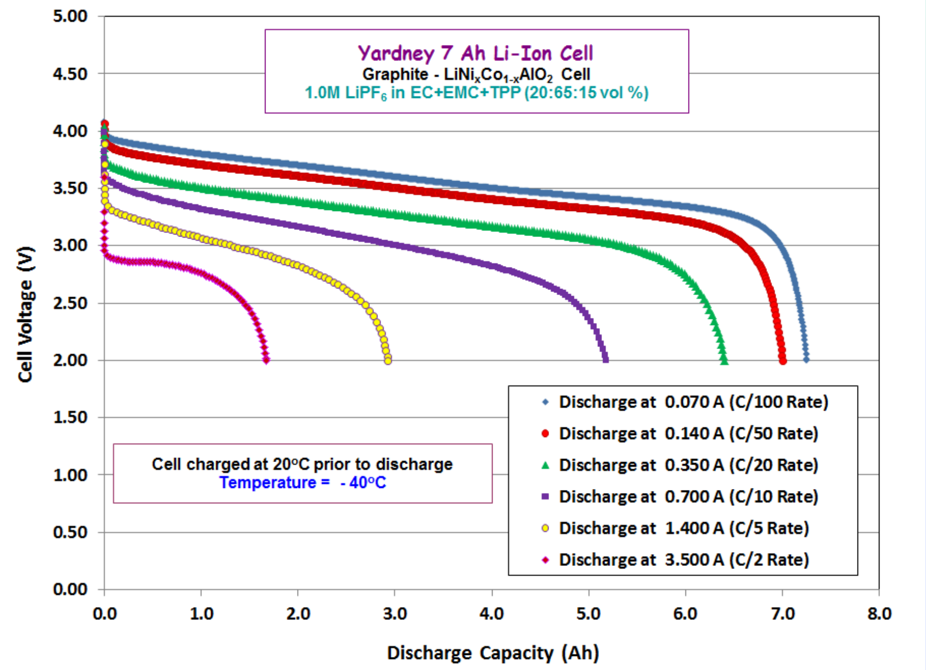
# Discharge Characteristics Graphite / $LiNiCoAlO_2$ 7 Ah Cells

## Discharge Characterization Testing at -40°C: Electrolyte with 10% TPP Content

### 10% TPP Content



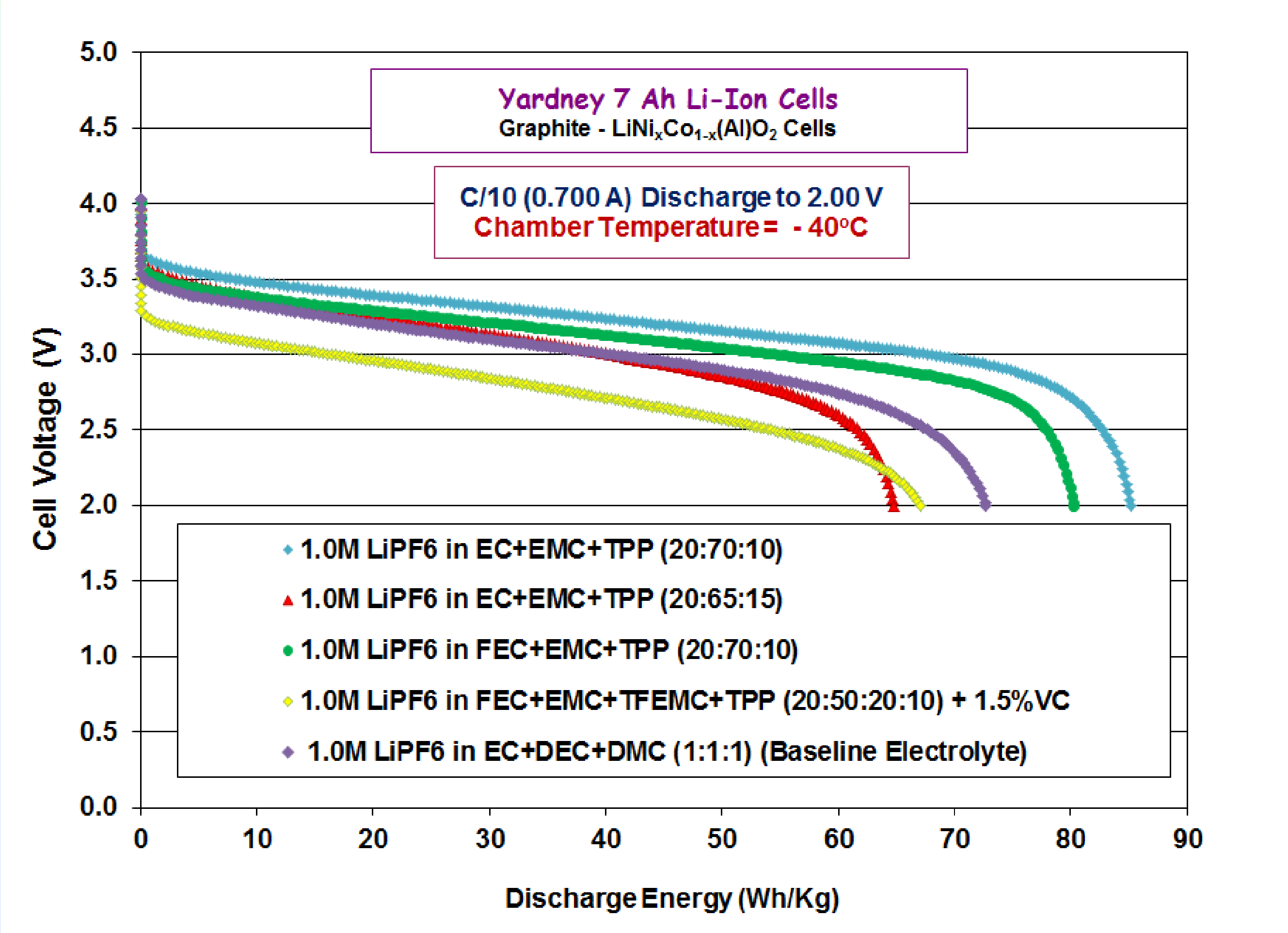

### 15% TPP Content




**Decreased discharge rate capability was observed with higher TPP content. However, reasonable performance was obtained at -40°C.**

# Discharge Characteristics Graphite / $LiNiCoAlO_2$ 7 Ah Cells

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




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

# SUMMARY and CONCLUSIONS

- ***Performance in experimental three electrode MCMB-LiNiCo$O_2$ Cells and Graphite-LiNiCoAl$O_2$ Cells***
  - *Many electrolytes containing flame retardant additives were observed to perform well in experimental MCMB-$LiNi_xCo_{1-x}O_2$ cells.*
  - *Using electrochemical characterization techniques, the anode kinetics were more dramatically affected by the presence of FRAs compared to the cathode.*
  - *Various approaches have been taken to improve the compatibility within the systems, including using VC, FEC, LiBOB and fluorinated carbonates.*
- ***Performance in large capacity prototype MCMB-LiNiCo$O_2$ Cells***
  - *An electrolyte formulation containing 5% TPP content and the use of VC has been demonstrated to provide good cycle life and rate capability in LCO-based cells.*
- ***Performance in large capacity prototype graphite-LiNiCoAl$O_2$ Cells***
  - *Electrolytes containing 10-15% TPP content (with and without the use of fluorinated solvents) have been demonstrated to provide excellent cycle life and good discharge rate capability over a wide temperature range in LCO-based cells.*
  - *The use of FEC (which is envisioned to improve the safety of the electrolyte) appears to have a beneficial effect upon life and does not negatively impact the low temperature capability.*
  - *Although cells containing up to 15% TPP content display good life characteristics, some negative impact upon the discharge rate capability was observed, largely due to the lower ionic conductivity (which is more dramatic at low temperature temperatures).*

**Future efforts will be devoted to (a) establishing the safety characteristics of these electrolytes in prototype cells in collaboration with Sandia National Lab., and (b) demonstrating permutations of these electrolytes with advanced systems (i.e., NMC cathodes and Si Anodes).**

# 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).