Lithium-Ion Cells with Safe and Low-Flammability Electrolytes

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High Energy Li-Ion Cells for Future Space Missions

- Current and Future missions
  - Astronaut's Extra Vehicular Activities
  - Human Landers
  - Planetary Habitat
- High energy batteries for applications with long cycle / calendar life)
    - Safe, reliable Li-ion cell with > 200 Wh/kg and good cycle life (> 1000 Cycles)
    - High voltage and high capacity cathodes (Li-rich, manganese rich layered layered composite oxides.
    - Safe (Low flammability) electrolytes
- Ultra-high energy batteries with Moderate Lifetime
    - Safe and reliable Li-Ion cells with > 250 Wh/kg and cycle life > 200 cycles
    - Combination of high energy cathode, safe electrolyte, with a high-capacity lithium alloy anode (Li-Si)

Portable Life Support System

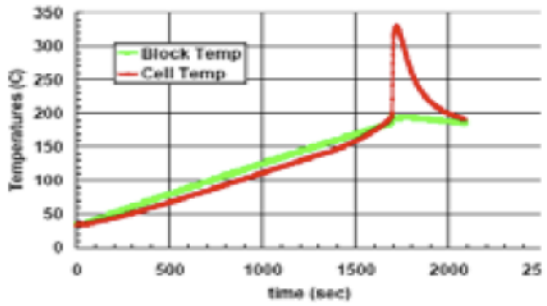
Lander

Thermal Runaway Assessment through ARC Studies

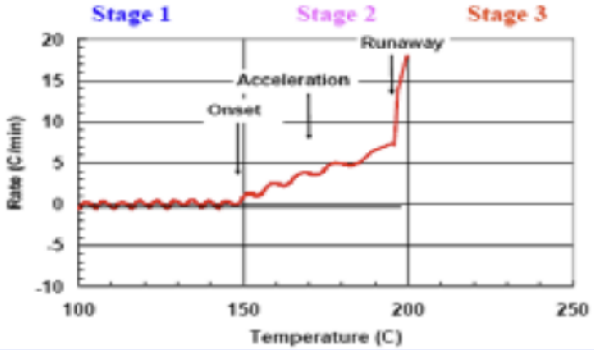
Thermal Ramp Response (100% SOC)

- **Stage 1: Room Temperature to 150°C – Onset of thermal runaway**
- **Stage 2: 150°C - 180°C – Venting and accelerated heating (smoke)**
- **Stage 3: 180°C and above – Explosive decomposition (flame)**

Ramp Temperatures



Differential Temperature Rate



- Stage 1 (RT-150°C):
  - Reaction and breakdown of SEI passivation layer on anode results in exothermic reduction of electrolyte by lithiated carbon
- Stage 2 (150°C - 180°C):
  - Continued electrolyte reaction at anode
  - *Onset of oxidation of electrolyte at cathode surface*
- Stage 3 (180°C and above):
  - *Cathode decomposition releasing oxygen which exothermically reacts at high rate with electrolyte*
  - Final breakdown of anode passivation layers and subsequent reaction
  - Exothermic decomposition of free electrolyte

- Failure propagated through the electrolyte.
- Low (or No) Flammability electrolyte is expected to enhance the safety of Li-ion cell

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]

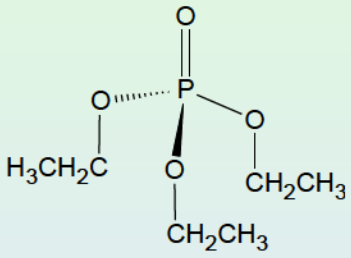
1) K. Xu, S. Zhang, J. L. Allen, T. R. Jow *J. Electrochem. Soc.*, **2002**, *149*, A1079

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).

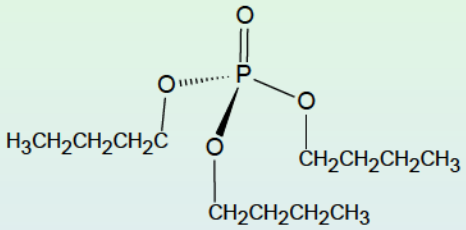
3) J. K. Feng, X. P. Ai, Y. L. Cao, and H. X. Yang, J. Power Sources, 177, 194-198 (2008).

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

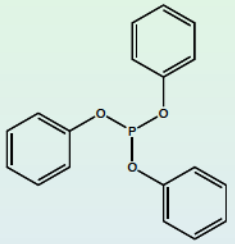
Flame Retardant Electrolyte Additives



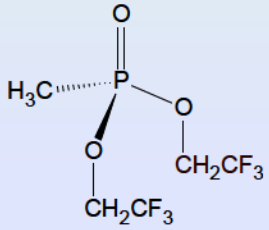
Triethyl phosphate (TEP)



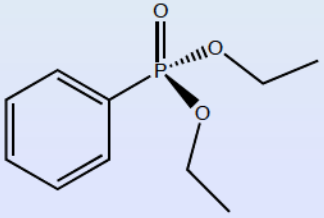
Tributyl phosphate (TBP)



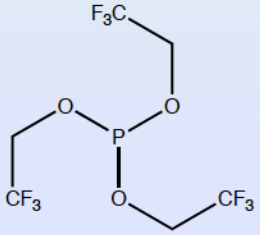
Triphenyl phosphite (TPPi)



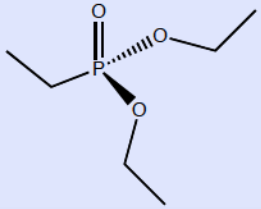
Bis-(2,2,2-trifluoroethyl)methyl phosphonate (BTFEMP)



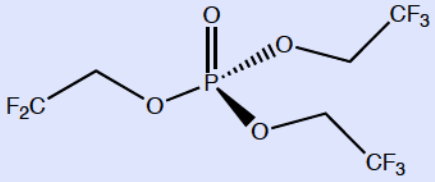
Diethyl phenylphosphonate (DPP)



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

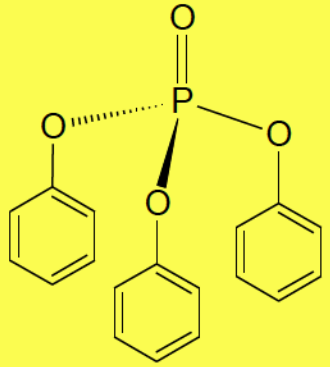


Diethyl ethylphosphonate (DEP)



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 with 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**

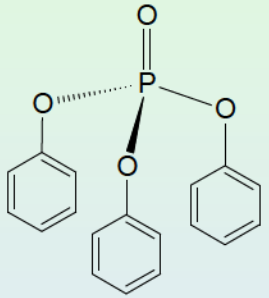
← Use of Additives (Vinylene Carbonate)

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

Laboratory Cells through Prototype Li-Ion Cells

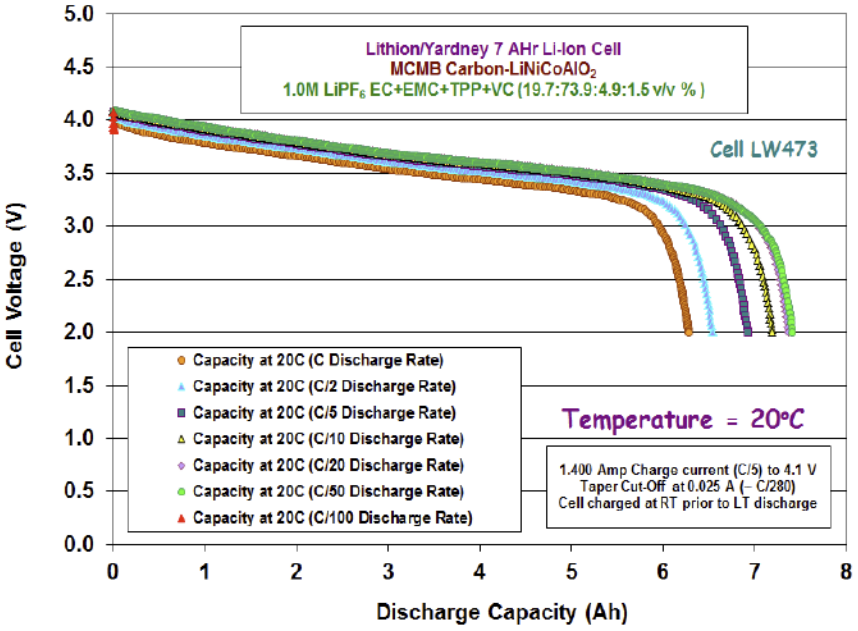
- Electrolytes were assessed in MCMB Carbon-$LiNiCoO_2$ glass wound (cylindrical) cells of 400-450 mAh size with Li metal reference electrodes.
- Performed assessment of performance (charge-discharge) at different rates and temperatures, high temperature resilience and detailed individual electrochemical 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).
- Prismatic 7 Ah cells (NCP 7) with MCMB anode and LiNi0.8Co0.2)2 Cathode fabricated by Yardney Technical Products.
- Electrolytes with Flame Retardant additives or Co-solvents
    - 1.0 M $LiPF_6$ EC+EMC+TPP+VC (20:74:5:1.5 v/v %)
    - 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)

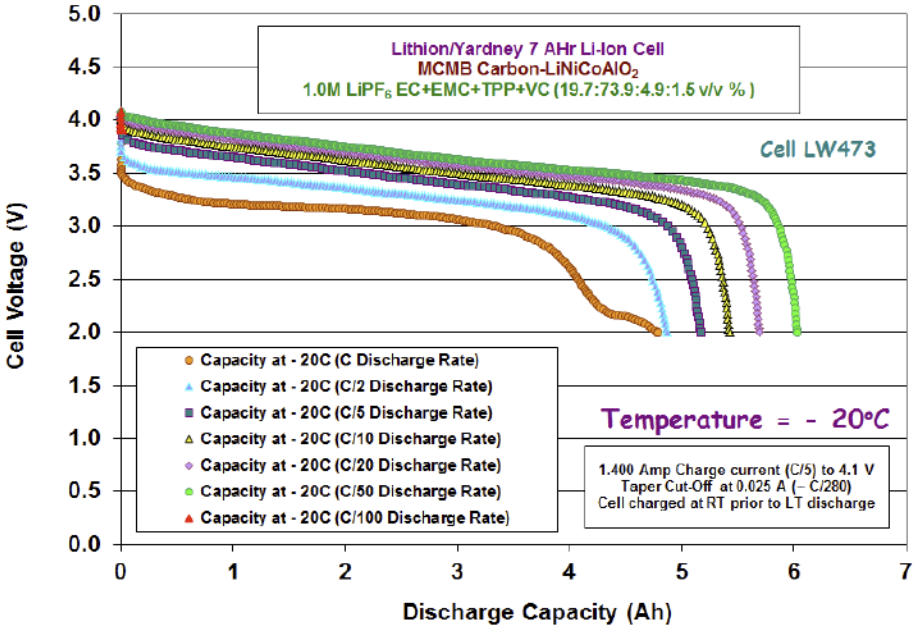


Triphenyl phosphate (TPP)

Yardney 7 Ah Li-Ion Cells with Gen-1 LF (Low Flammability) Electrolyte

Discharge Performance at 20°C and -20°C

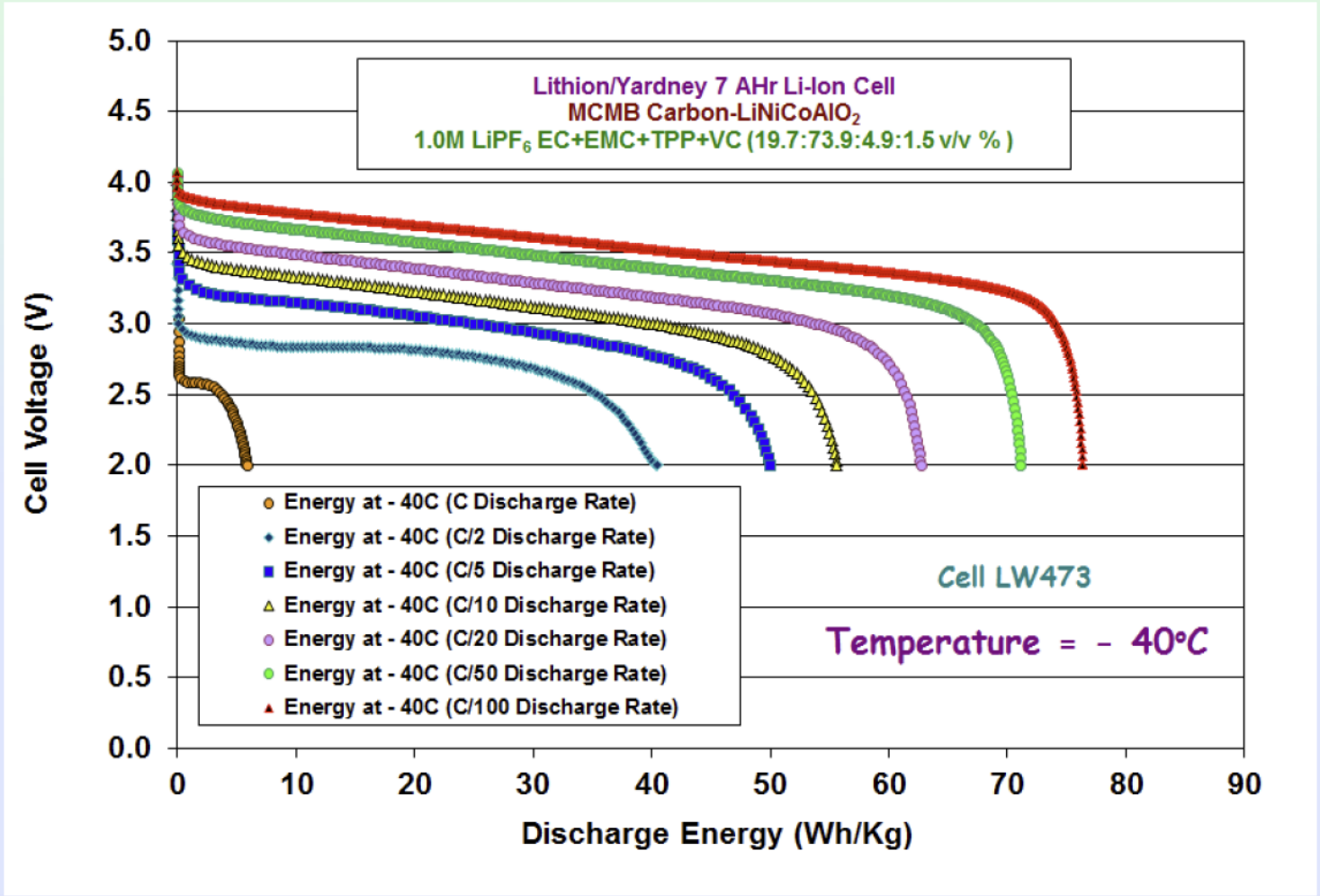




- Cells containing an electrolyte with a flame retardant additive (i.e., *1.0 M $LiPF_6$ in EC+EMC+TPP+VC*) are observed to display good performance over a range of temperatures.

Yardney 7 Ah Prismatic Li-Ion Cells with Gen 1 LF Electrolyte

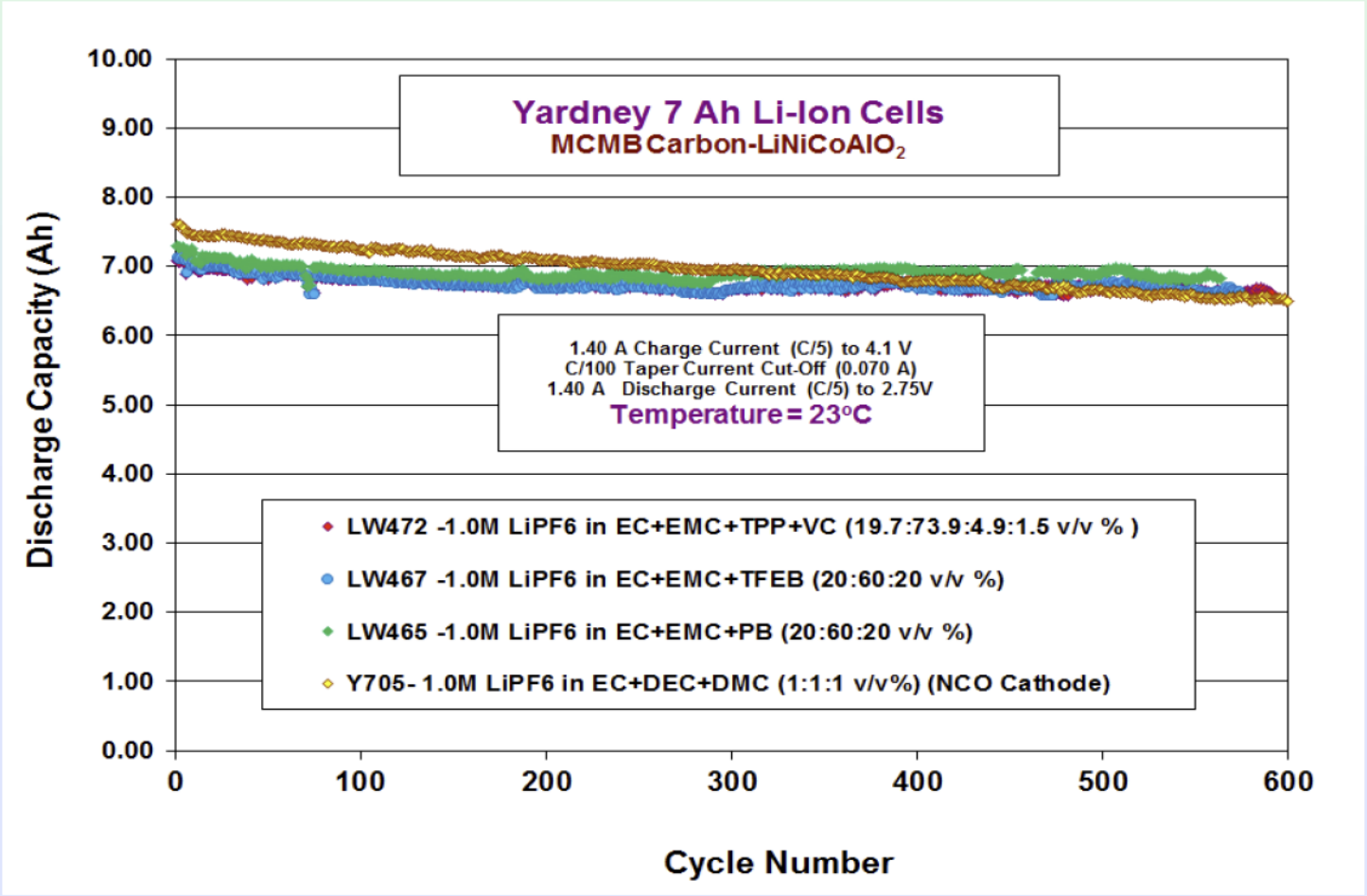
Discharge Performance at - 40°C



- 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 with Gen 1 LF Electrolyte

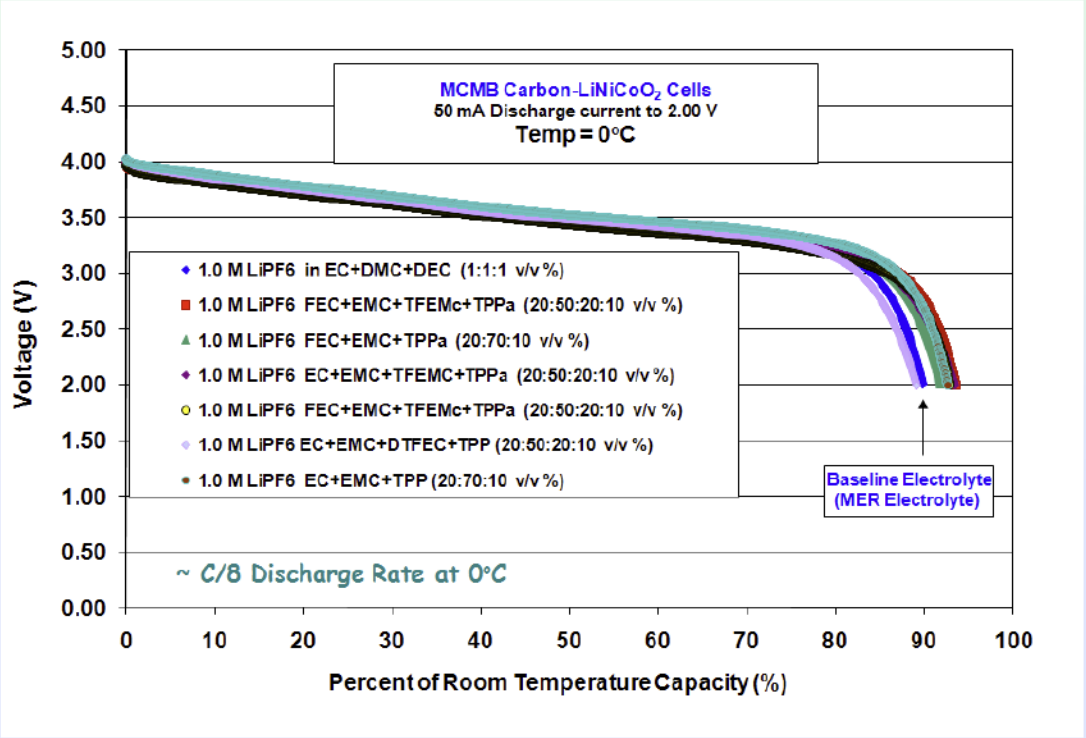
100 % DOD Cycle Life Testing at Room Temperature



- 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.

Gen 2 LF Electrolyte for Yardney Li-Ion cells

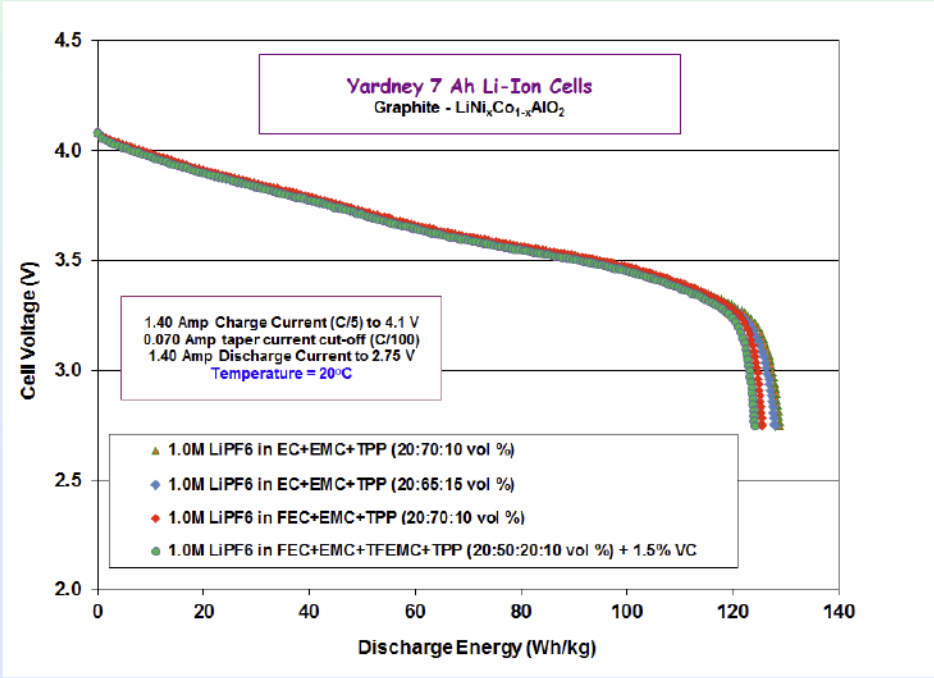
Discharge Characteristics of Three Electrode MCMB-$LiNi_xCo_{1-x}O_2$ Cells

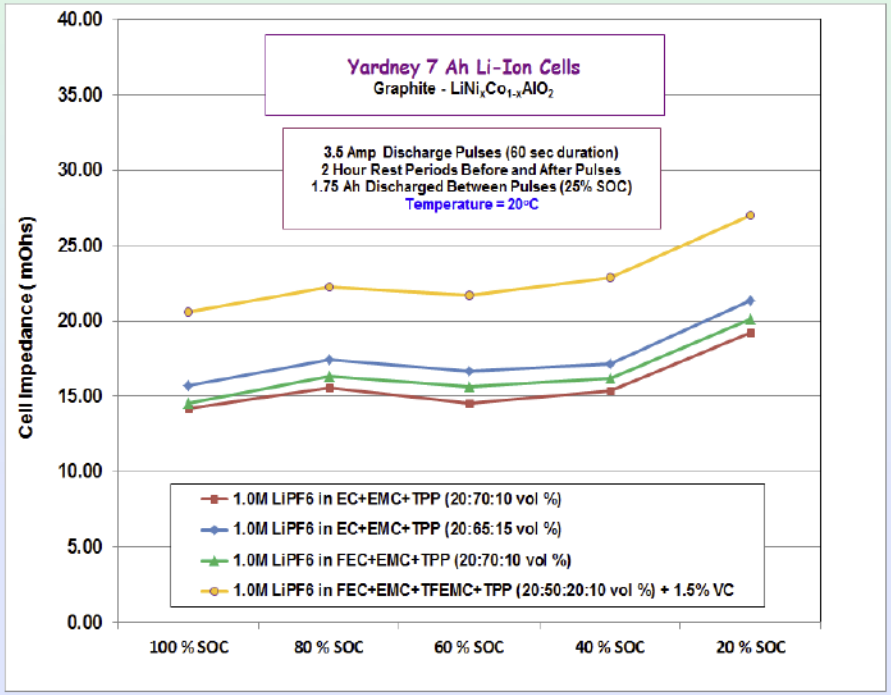


1)1.0 M $LiPF_6$ in EC+EMC+TPP (20:70:10 vol %)
2)1.0 M $LiPF_6$ in EC+EMC+TPP (20:65:15 vol %)
3)1.0 M $LiPF_6$ in FEC+EMC+TPP (20:70:10 vol %)
4)1.0 M $LiPF_6$ in FEC+EMC+TFEMC+TPP (20:50:20:10 vol %) + 1.5% VC

- Increasing TPP content (5% to 15%)
- The incorporation of FEC into electrolytes
- The use of fluorinated carbonates (i.e., trifluoroethyl methyl carbonate)

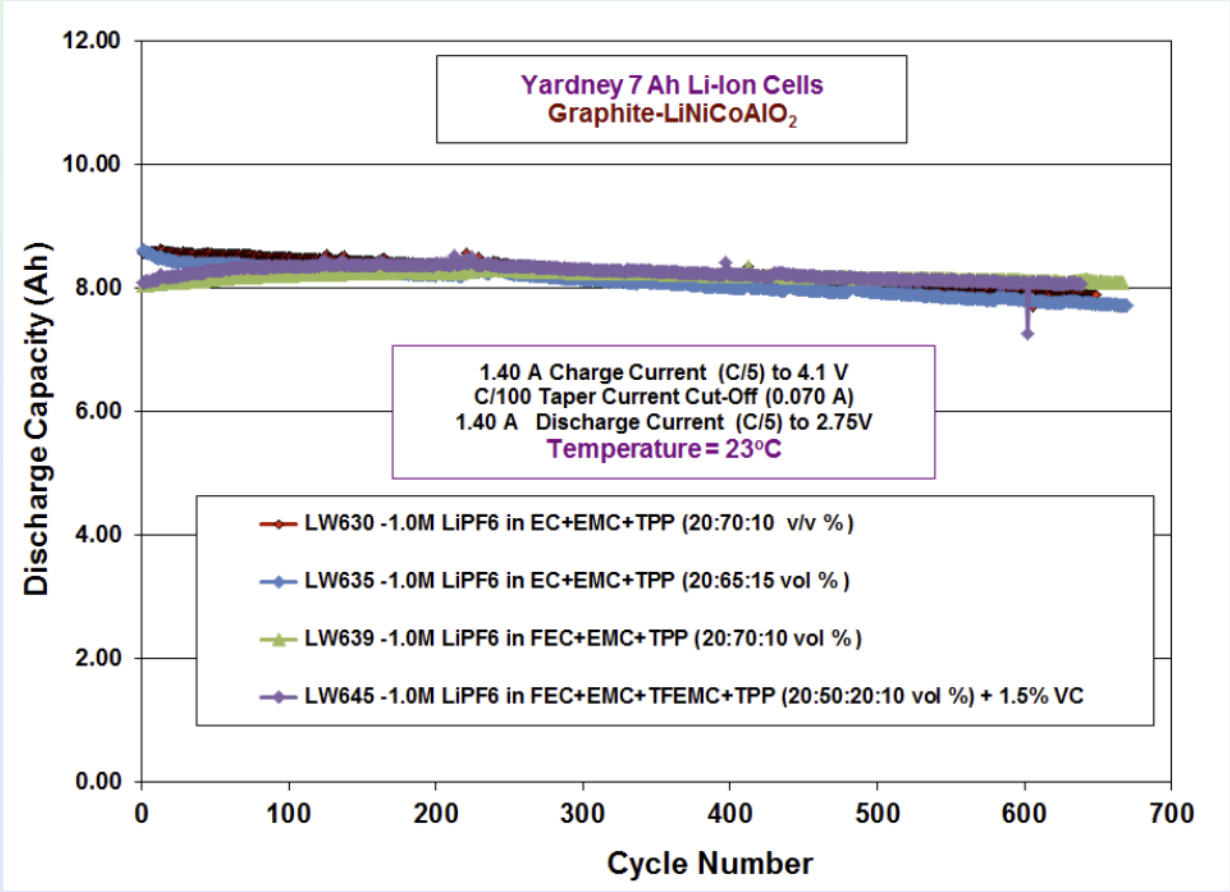
Discharge Characteristics Graphite / $LiNiCoAlO_2$ 7 Ah Cells
Conditioning at 20°C - Comparison of Electrolyte Types





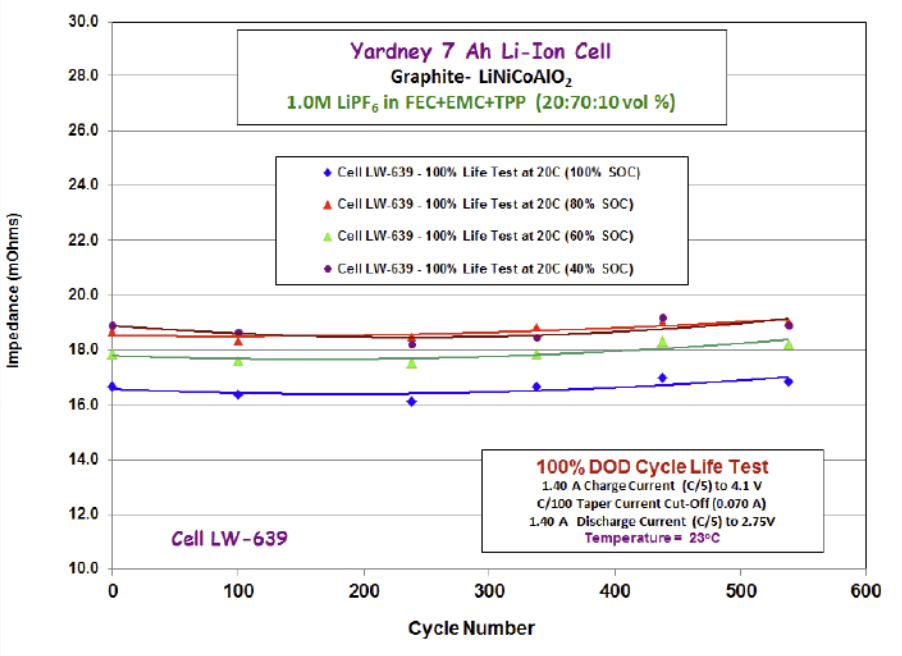
• **Upon being subjected to initial capacity and impedance characterization at 20°C, all cells displayed comparable performance.**

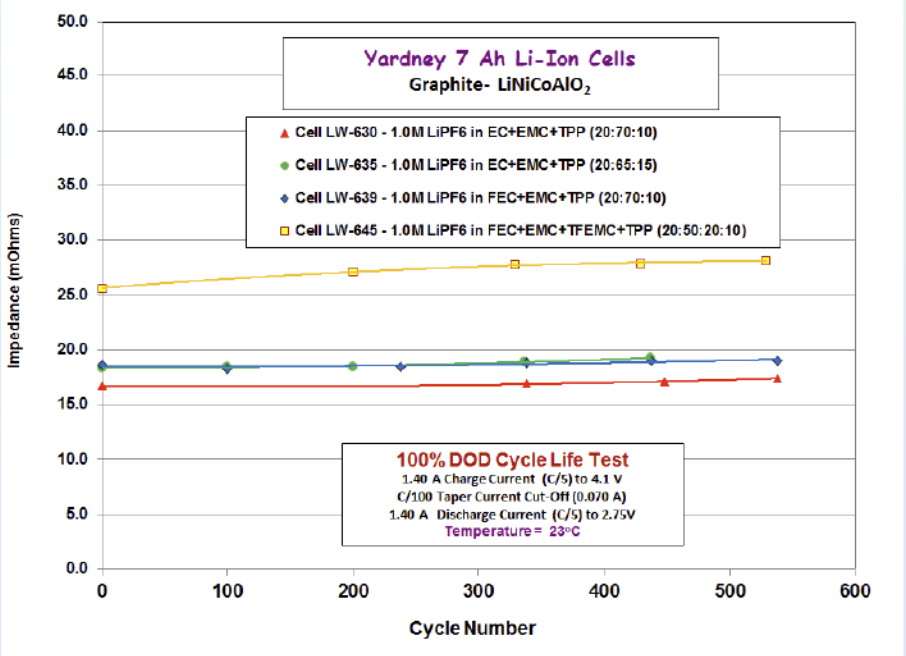
Cycle Life Testing of Graphite / $LiNiCoAlO_2$ 7 Ah Cells
100 % DOD Cycle Life Performance



- 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.

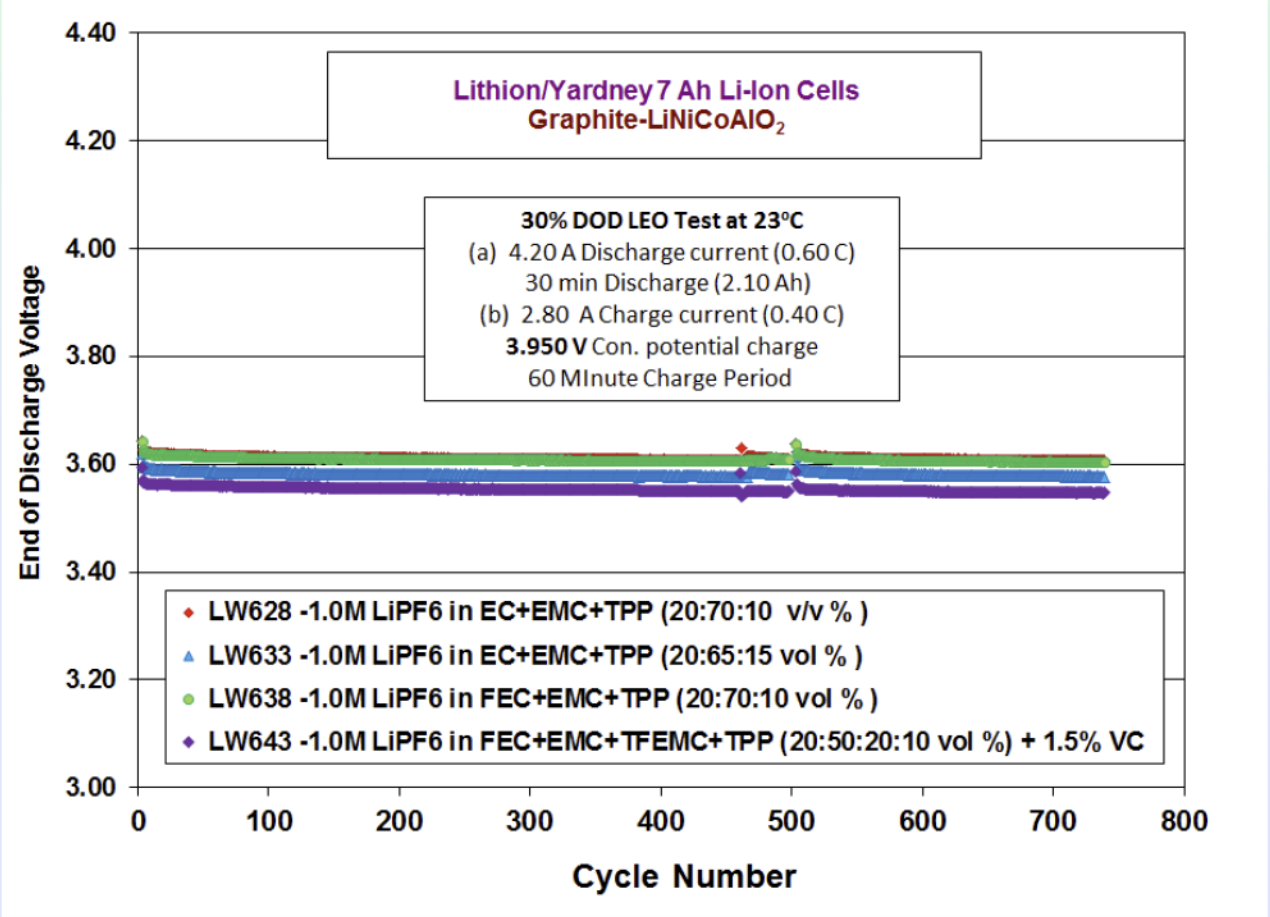
Cycle Life Testing of MCMB-1028 / $LiNiCoO_2$ 7 Ah Cells
100 % DOD Cycle Life Performance: Impedance Growth





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

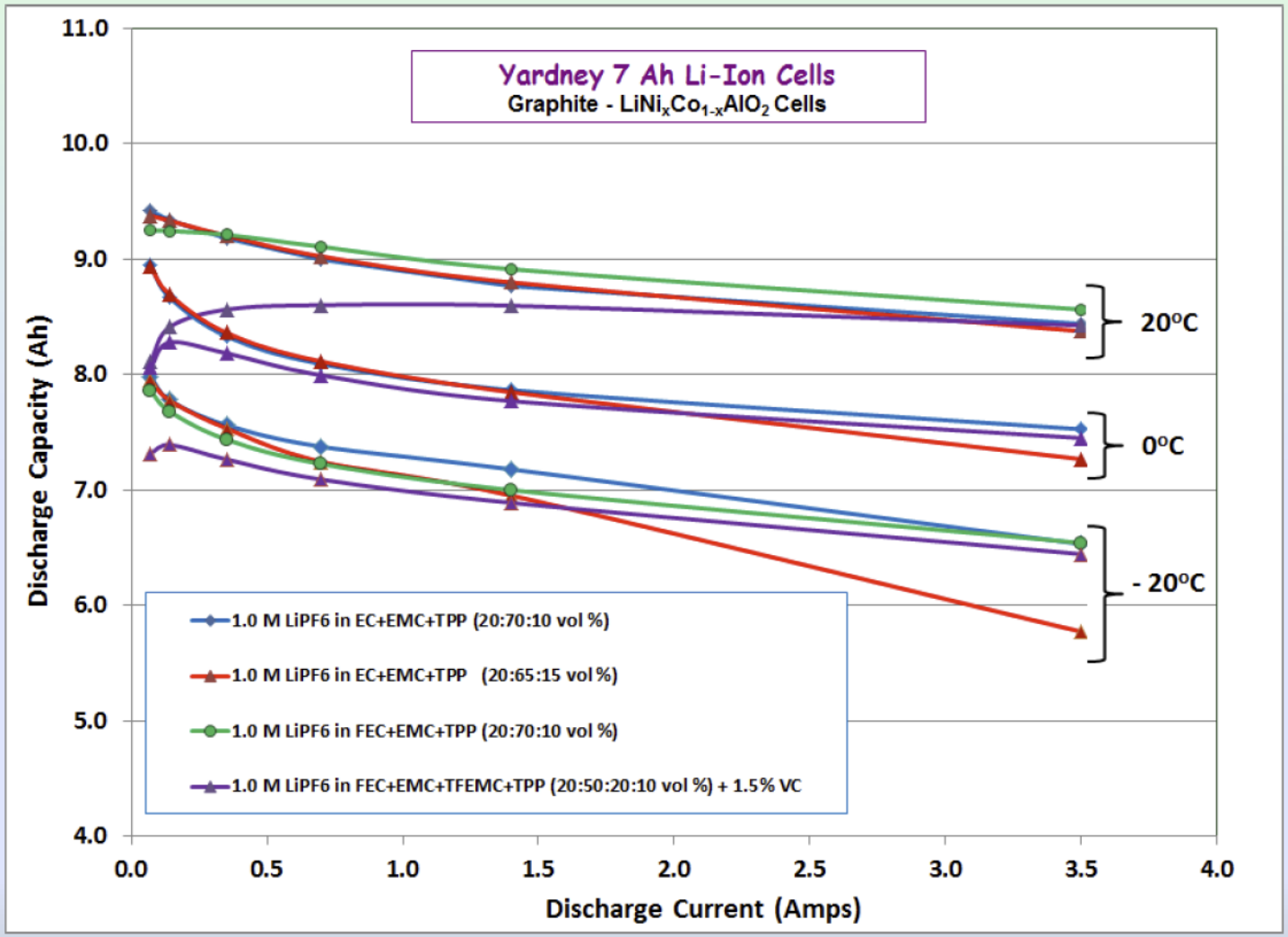
Cycle Life Testing of Graphite / $LiNiCoAlO_2$ 7 Ah Cells
30 % DOD Cycle Life Performance



- 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

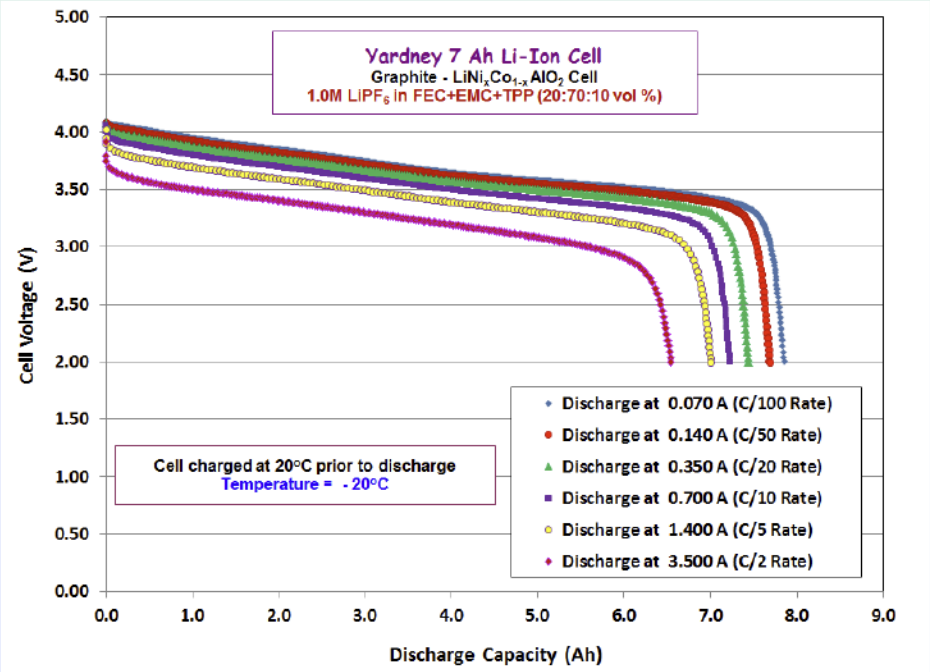


- Cells charged at room temperature and discharged at the respective temperature.

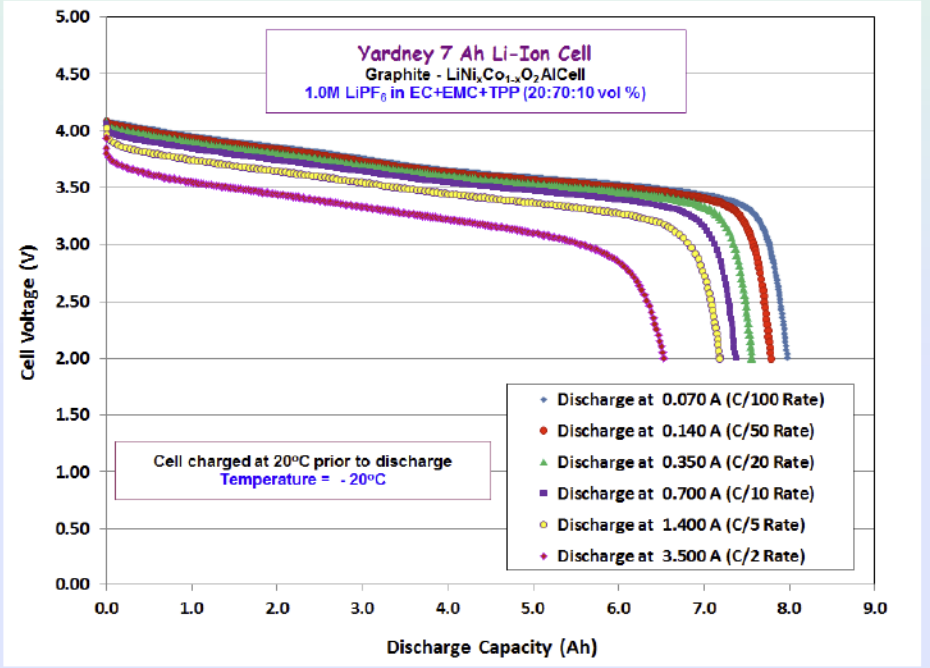
Discharge Characteristics Graphite / $LiNiCoAlO_2$ 7 Ah Cells

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

FEC-Based Electrolyte



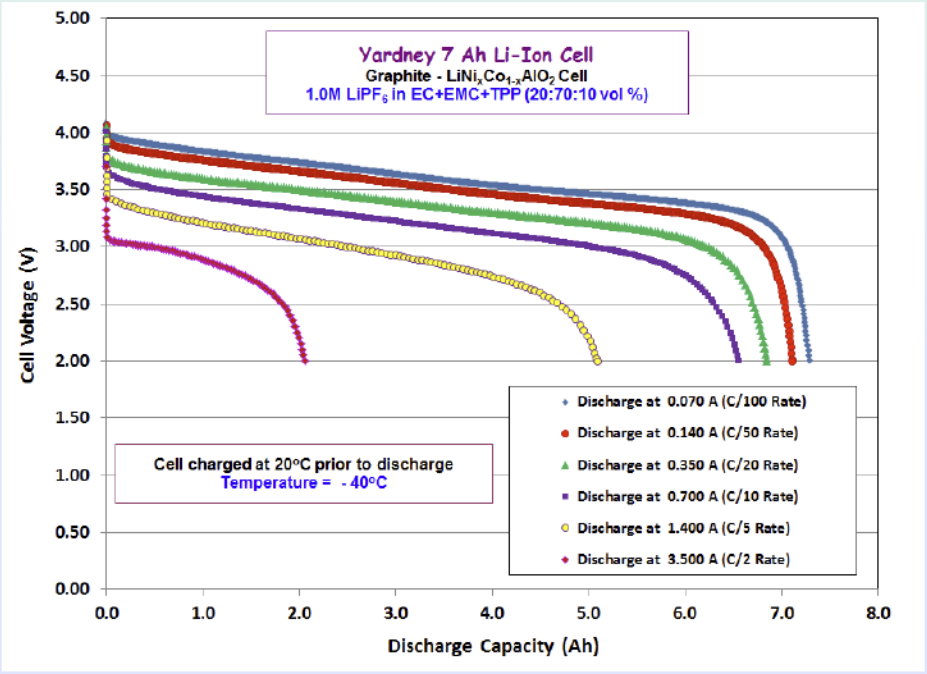
EC-Based Electrolyte



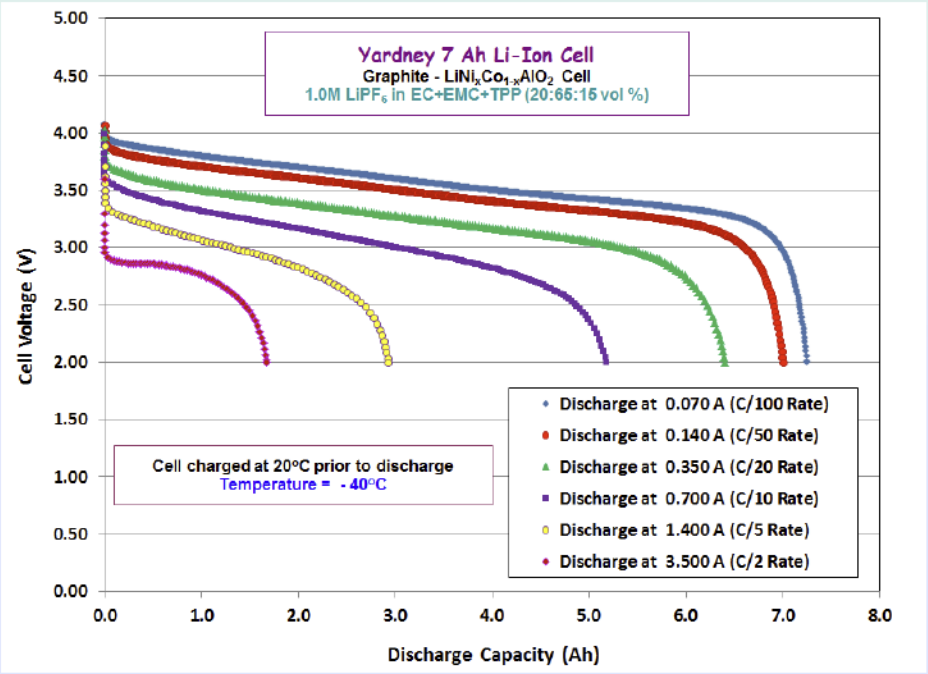
- **Cells containing electrolytes with 10% TPP (with and without FEC) displayed good performance at -20°C.**

Discharge Characteristics Graphite / $LiNiCoAlO_2$ 7 Ah Cells
Discharge at -40°C: Electrolyte with 10% TPP Content

10% TPP Content



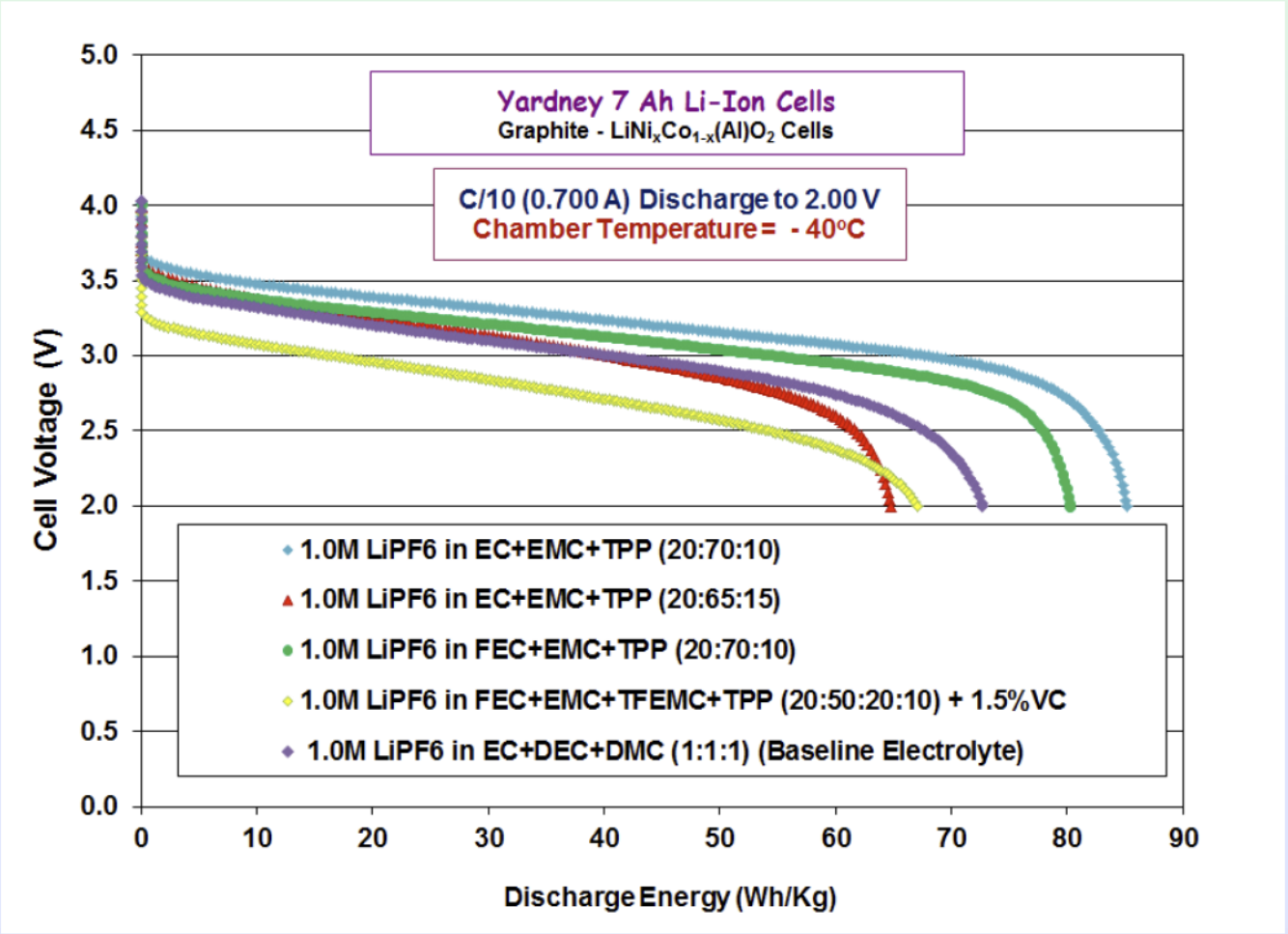
15% TPP Content



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

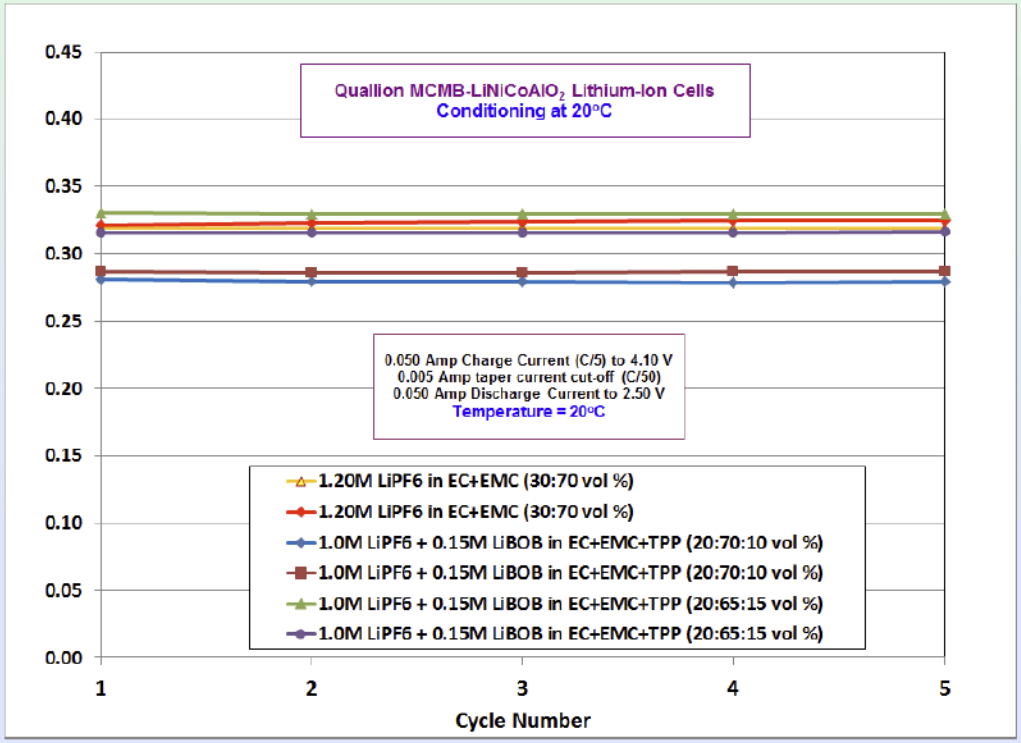
Discharge Characteristics Graphite / $LiNiCoAlO_2$ 7 Ah Cells

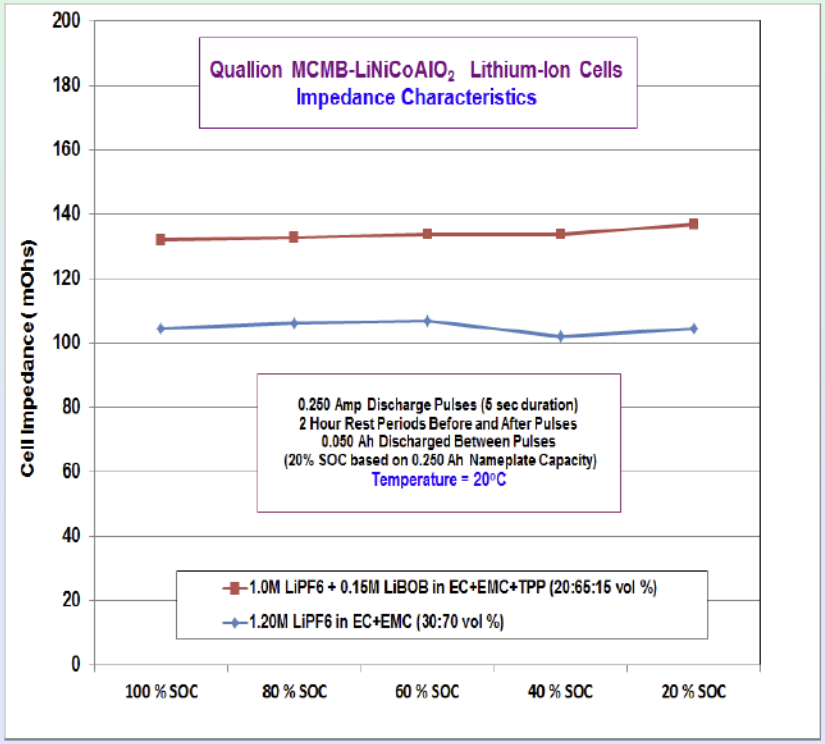
Discharge Characterization Testing at -40°C: Comparison of Electrolyte Types



- 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.,

Quallion MCMC-$LiNiCoAlO_2$ Prototype Cells
Initial Characterization at 20°C



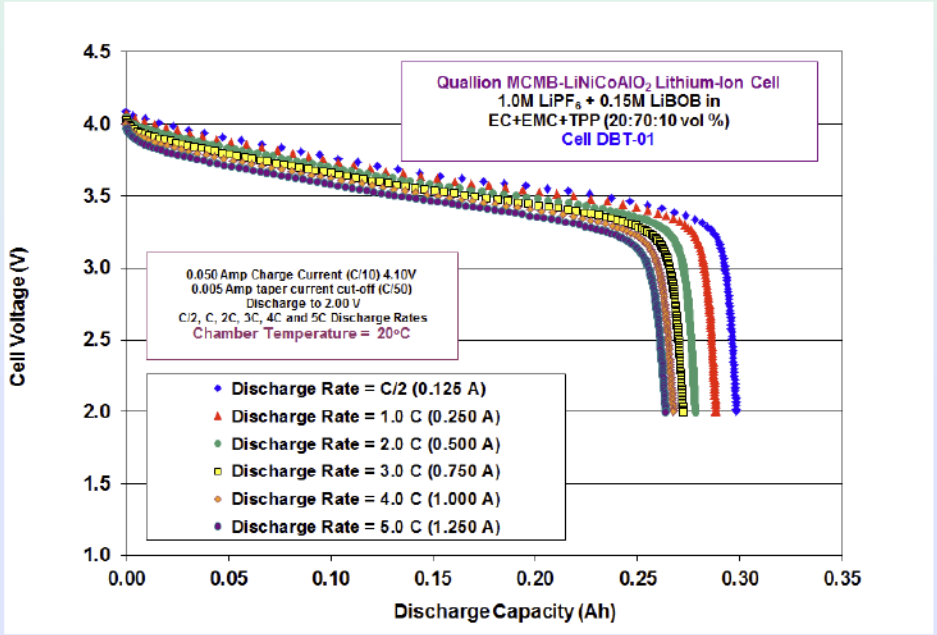


- Formulations containing TPP in conjunction with LiBOB were also evaluated in prototype cells containing MCMB and $LiNiCoAlO_2$.

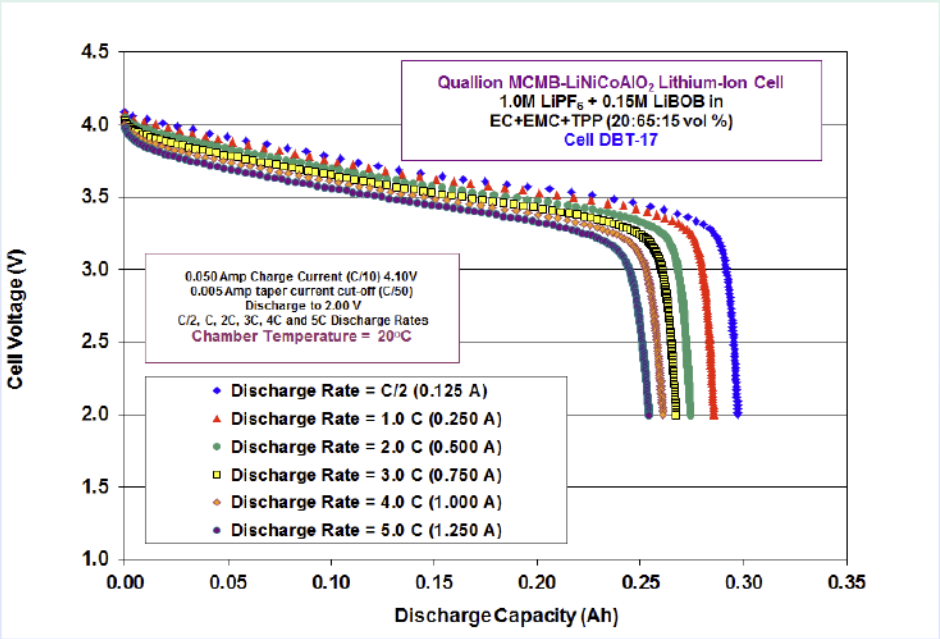
- Testing is aimed at demonstrating the rate capability, cycle life performance at various temperatures, and safety characteristics.

Quallion MCMC-$LiNiCoAlO_2$ Prototype Cells Rate Characterization at 20°C

10 % TPP

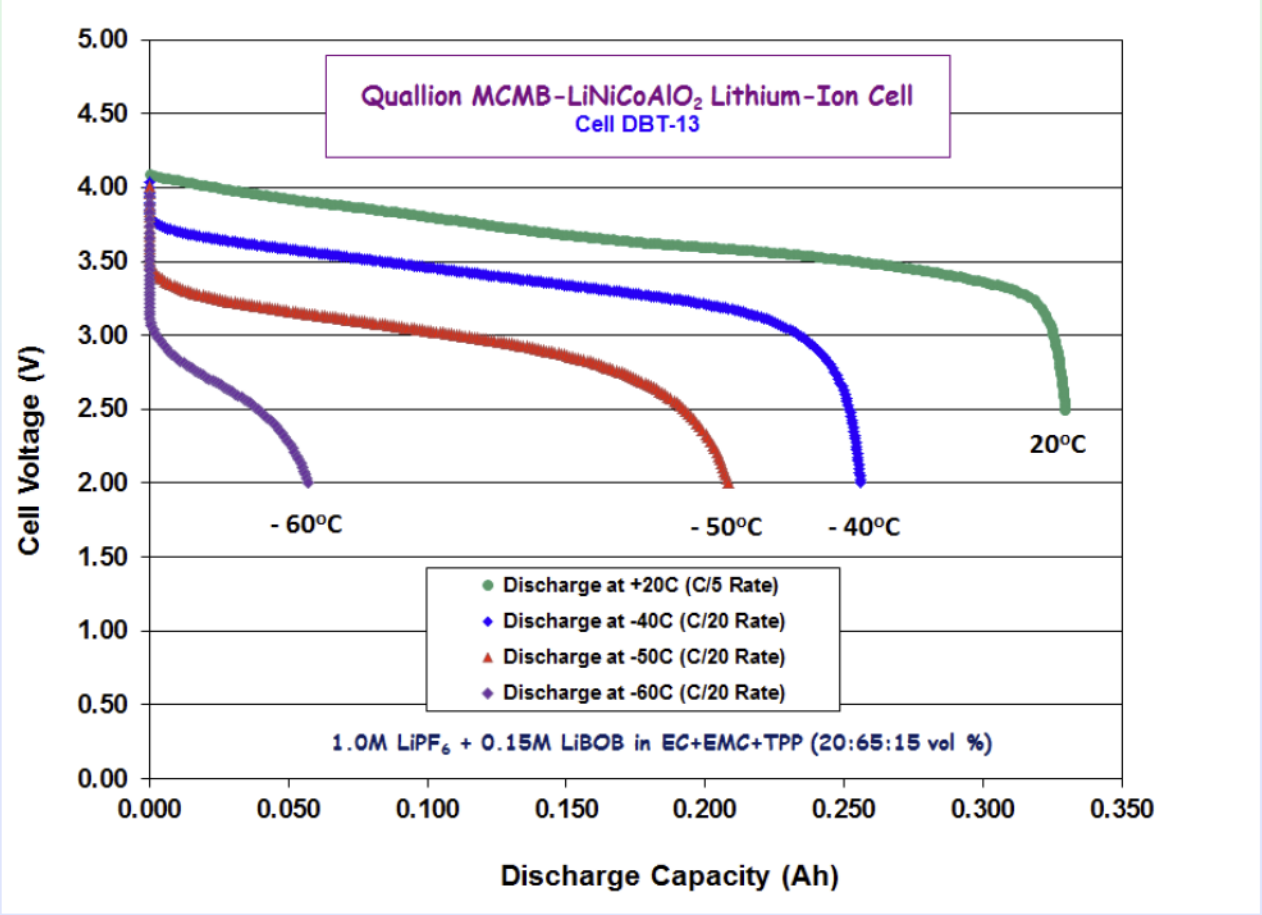


10 % TPP



- Good rate capability was observed (up to 5C rates) at 20°C in cells with TPP in the electrolyte.
- Modestly lower rate capability was observed with the solution with 15% TPP compared to 10%.

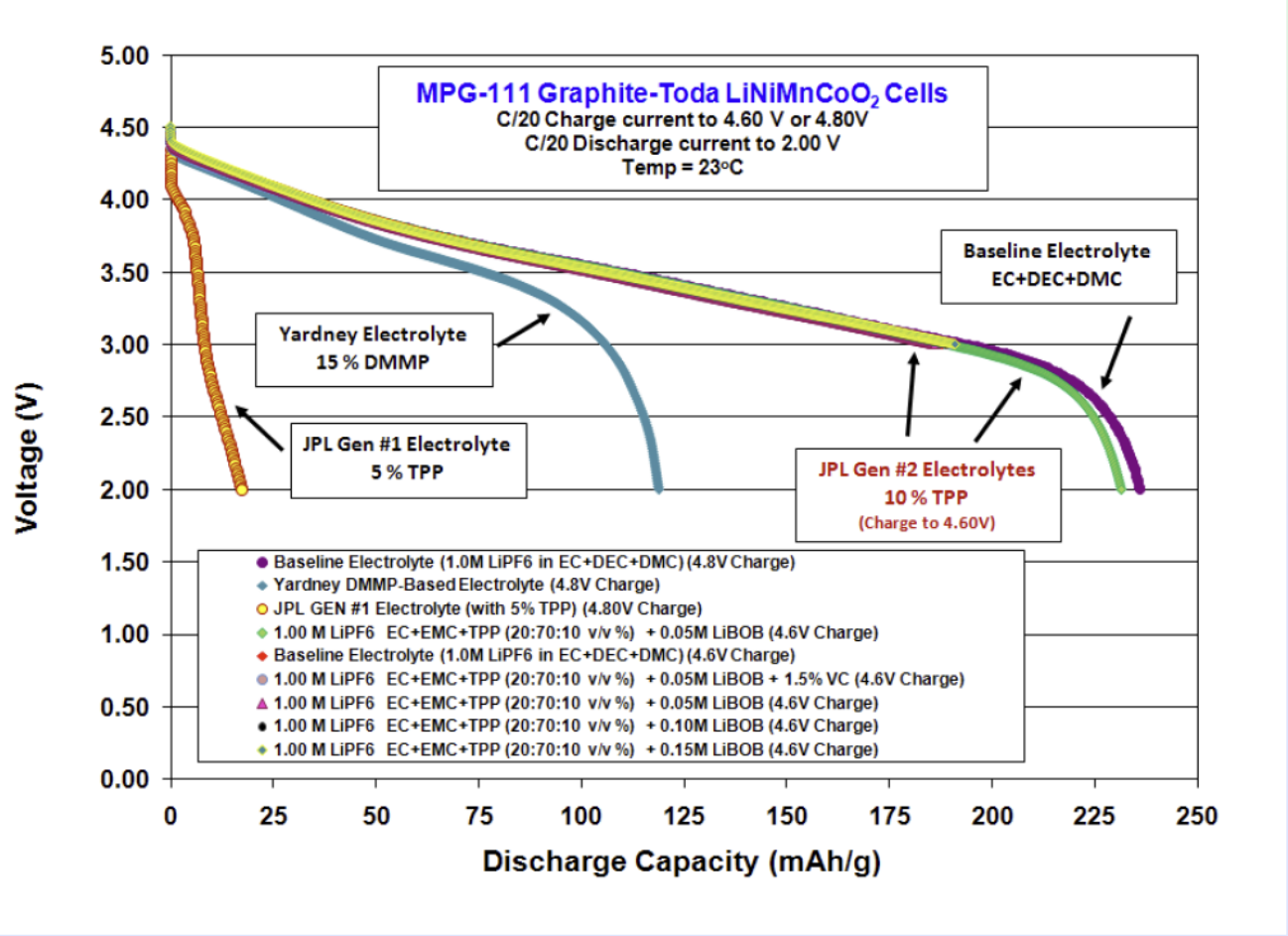
Quallion MCMC-$LiNiCoAlO_2$ Prototype Cells Initial Characterization at 20°C



- A cell containing an electrolyte with 15% TPP is observed to perform at low temperatures.
- Rate characterization testing over the full range of temperatures and rates is in progress.

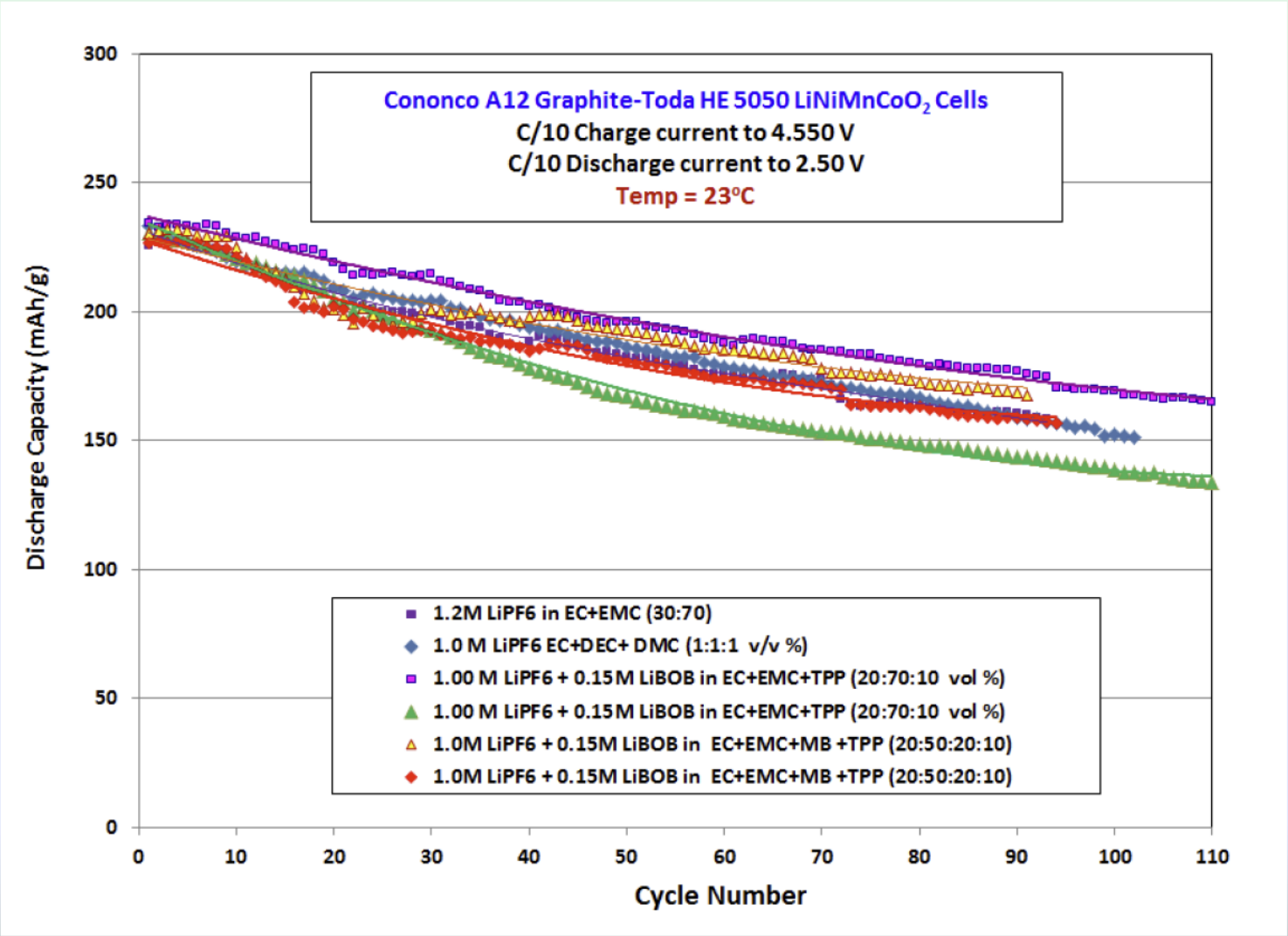
Results from Electrolytes Evaluated in the MPG-111-Toda System

Comparison of Electrolyte Types (After Formation)



- **Comparable performance was obtained with the JPL Gen #2 electrolytes (containing LiBOB) compared with the baseline solution.**

Argonne Conoco A12 Graphite-Toda HE 5050 $LiNiMnCoO_2$ Cells
Cycle Life Performance in Coin Cells at 23°C



SUMMARY and CONCLUSIONS

- **Performance in experimental three electrode MCMB-$LiNiCoO_2$ Cells and Graphite-$LiNiCoAlO_2$ Cells**
  - Many electrolytes containing flame retardant additives were observed to perform well in experimental MCMB-$LiNi_xCo_{1-x}O_2$ cells.
  - 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-$LiNiCoO_2$ 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-$LiNiCoAlO_2$ 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 NCO-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).

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