Advanced Cathodes and Electrolytes for High Energy and Safe of Li-ion Cells

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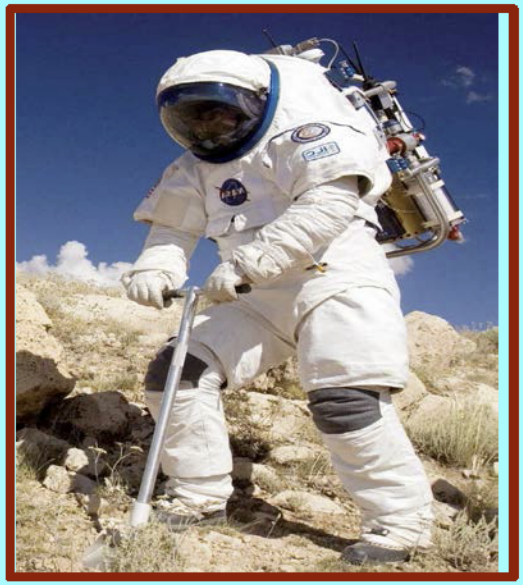
High Energy Li-Ion Cells for Future Space Missions

- **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.
  - 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

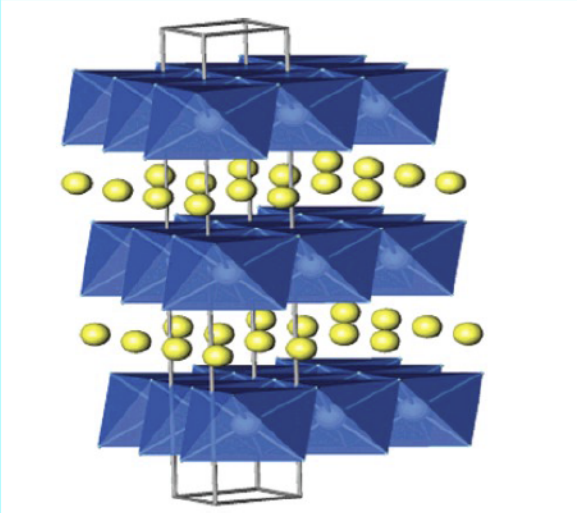
Lander

High Specific Energy Cathode Materials

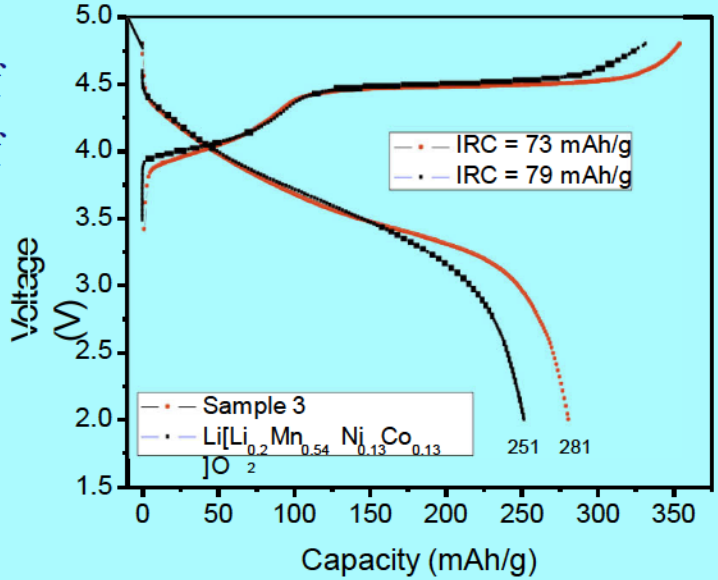
- Li-excess Layered-Layered composites (Li rich Mn rich layered-layered oxide)
  - Layered oxide compositions belonging to the series layered-layered composite $Li[Li_{1/3}Mn_{2/3}]O_2$ (commonly designated as Li_2MnO_3) and $LiMO_2$ ($M = Mn_{0.5}Ni_{0.5}$)

    $x\ Li[Li_{1/3}Mn_{2/3}]O_2 + (1-x)\ Li\ (Mn, Ni, Co)O_2$

    e.g.,$0.5\ Li[Li_{1/3}Mn_{2/3}]O_2 + 0.5\ Li\ (Mn_{0.33}, Ni_{0.33}, Co_{0.34})O_2$
  - Loss of oxygen around 4.5 V during charge,, which creates oxygen vacancies, reduction of nickel to Ni^{+2} and an overall rearrangement of the lattice.
  - The plateau corresponding to oxygen loss is absent in subsequent charges.
  - Typical capacities are as high as 250 mAh/g on cycling them from 4.8 – 2.0 V.



- Layered structure of $LiNi_yMn_yCo_{1-2y}O_2$, showing the Li^+ between the transition-metal oxide/sulfide sheets.



LMR-LLC Cathode Materials

- Lithium rich manganese rich layered layered composite
  - **Li_2MnO_3 : $LiMO_2$ (M = $Mn_{0.5}Ni_{0.5}$)**

    $0.5\ Li[Li_{1/3}Mn_{2/3}]O_2 + 0.5\ Li\ (Mn_{0.33}, Ni_{0.33}, Co_{0.34})O_2$
- Issues
  - Irreversible capacity loss, especially in the uncoated cathodes
    - About 30% (~100 mAh/g) vs ~30% compared to 7-10% for SOA cathode)
    - Non-availability of lithium at the anode for the irreversible capacity
    - Impedance build up at the anode
  - Low Power densities
    - High capacity only at low rates (C/20-C/10) and at ambient temperatures.
    - Poor electrochemical kinetics and low Li^+-diffusion coefficients (10^{-12} cm^2/s)
  - Broad voltage profile with more capacity available between 3.0 V and 2.5 V, even at moderate rates.
  - Voltage slump during cycling
  - Transition Metal Dissolution

Refinement of Synthesis

Improvement in tap density and Performance

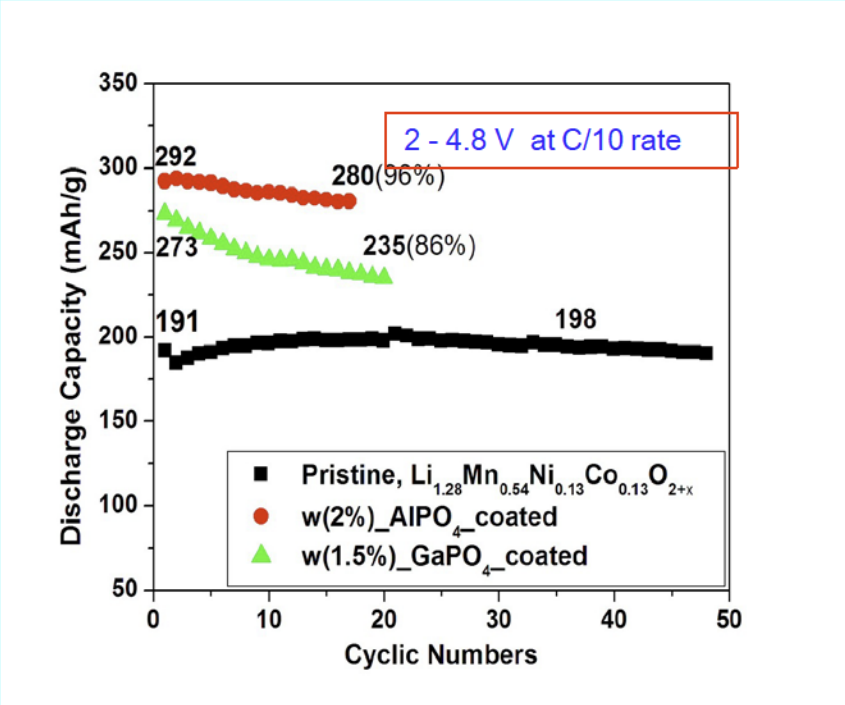
- High capacity > 250 mh/g achieved from optimized composition of transition metal ratio and Li content
- High tap densities (1.5-2.0 g/cc) and spherical morphology realized from hydroxide precursor synthesis.
- Demonstrated improved performance (high reversible and low irreversible capacity, and cyclic and thermal stability.

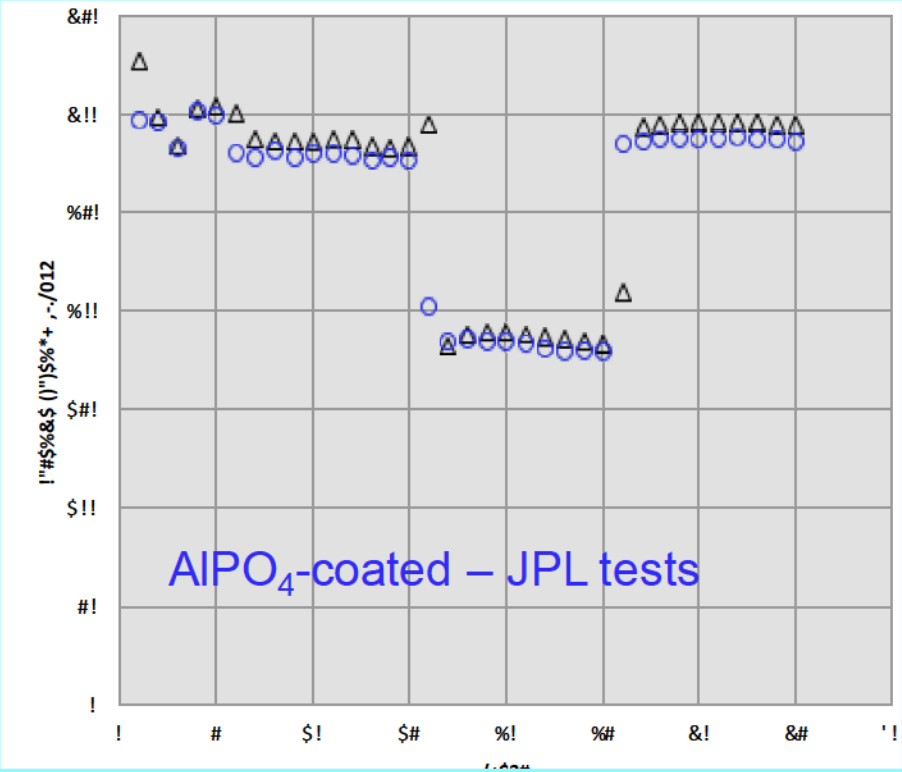
Characteristics	11 month (Al_2O_3-coated)	18 month ($AlPO_4$-coated)	23 months	
			($AlPO_4$-coated)	($GaPO_4$-coated)
Tap Density (g/cc)	1.17	1.99	2.02	2.01
First Cycle Discharge capacity (C/20) -2V	276	256	264	274
First Cycle Discharge capacity (C/20) -3V	255	216	209	243
First cycle Irreversible capacity (mAh/g)	48	34	35	35
OC discharge at C/10 - to 2V	184	163	174	150
OC discharge at C/10- to 3V	116	108	126	105

Materials synthesized at UT Austin

Surface-modified Sample from Hydroxide Synthesis

Materials synthesized at UT Austin

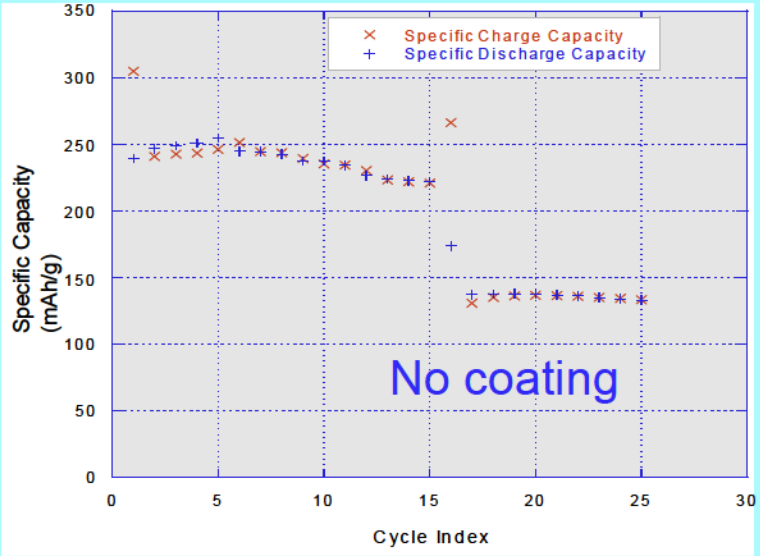


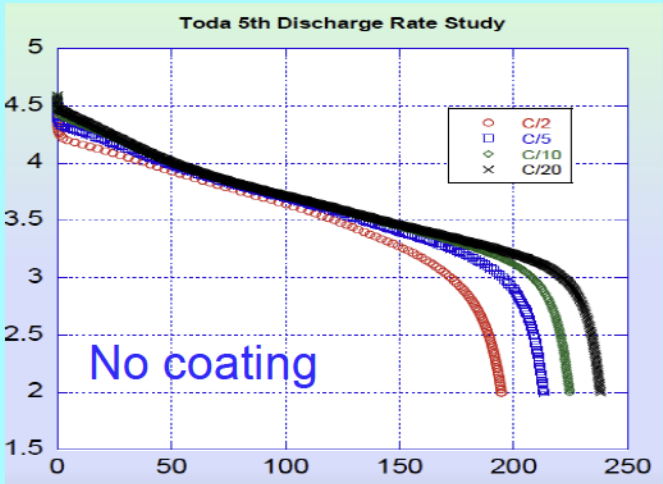


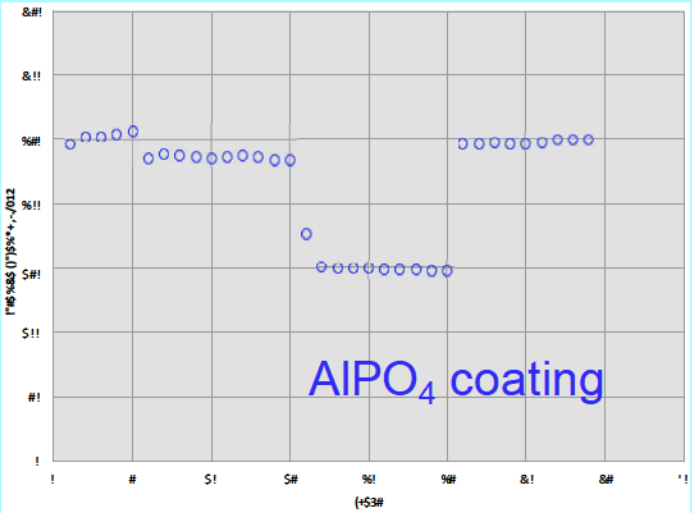
- Both the $AlPO_4$- and $GaPO_4$-coated samples show higher capacities
- $AlPO_4$-coated sample shows high capacity with good cycle life

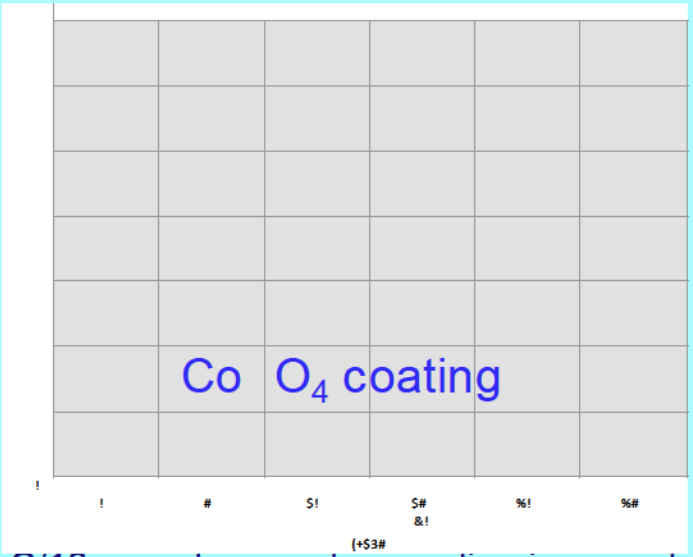
- JPL studies validate the improved performance
- Initial discharge capacity to 2V = 300 mAh/g
- At C/10 RT: 281 mAh/g (2V) & 242 mAh/g (3V)
- Irreversible capacity : 35 mAh/g

Toda 9100 Cathode with and without surface stabilization



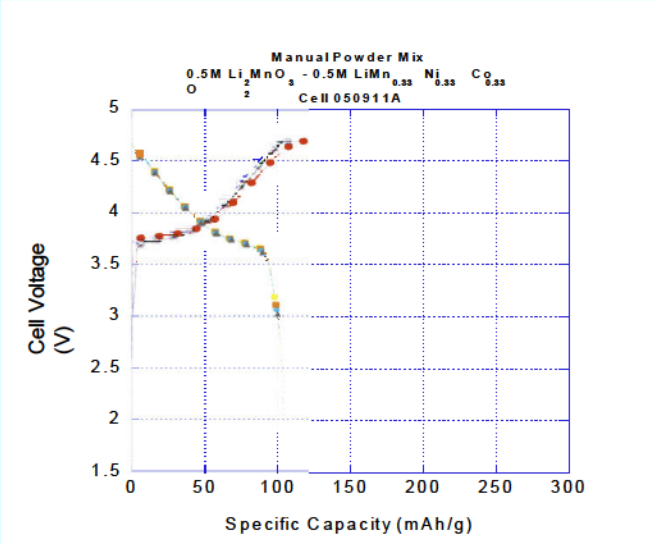


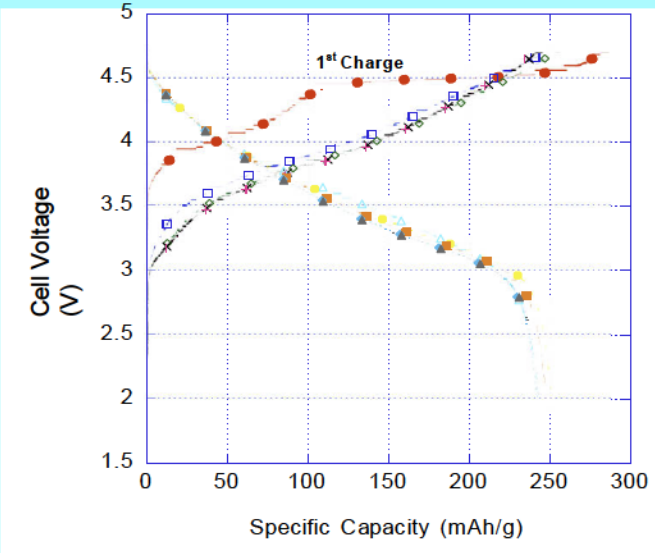


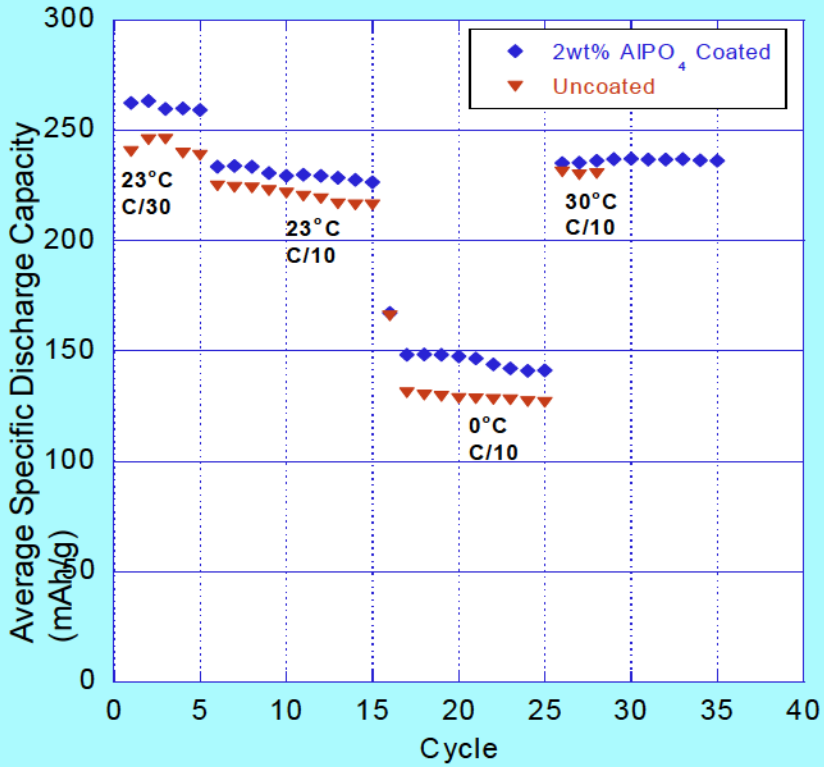


- Capacity appears to experience significant fade in C/10 room temperature cycling in uncoated cathodes following room temperature formation.
- Surface coating helps improve the cyclic stability and also lowers the irreversible capacity from ~ 90 mAh/g to 35 mAh/g

Mechanical Method: $Li_{1.2}Mn_{0.4}Co_{0.08}Ni_{0.32}O_2$





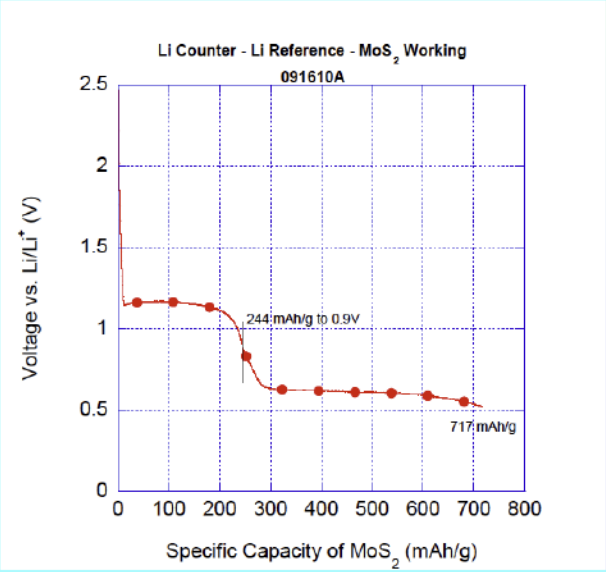


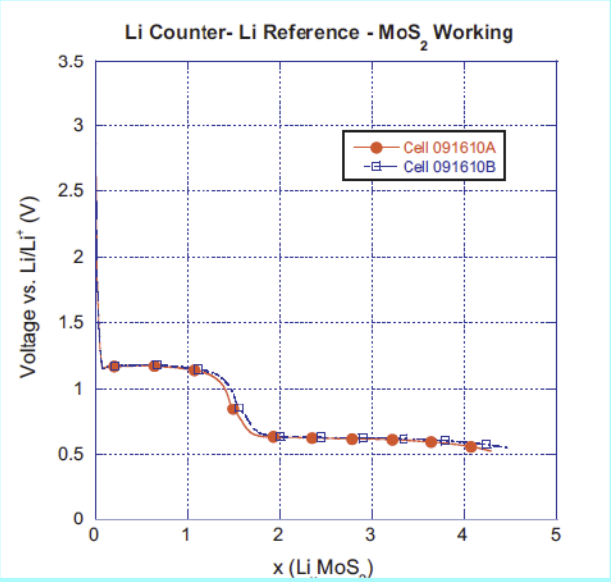
- Simple mixing does not activate the Li_2MnO_3 phase
- Voltage profile similar to the chemically-synthesized materials with plateau at 4.5 V plateau on first charge comparable discharge capacity.
- Performance improved upon coating with $AlPO_4$ and is comparable to the analogous cathode from solid state methods. Irreversible capacity is only 25 mAh/g

W. C. West, J. Soler, and B. V. Ratnakumar J. power Sources (in press)

Quantification of Li transported to anode during 1st charge

- $Li_{1.2}Ni_{0.175}Co_{0.1}Mn_{0.52}O_2$ as a cathode.
  - 1st cycle charge capacity : 324 mAh/g, discharge capacity :236 mAh/g. Irrever. Capacity: 88 mAh/g.
- Two separate approaches to determine lithium release at the anode
  - With MoS_2 as the anode,
    - No complications associated with the SEI
    - MoS_2 has easily identifiable lithiation plateaus at about 1.2 V and 0.6 V vs. Li/Li+ Analytical determination of Li at the anode.
  - Analytical determination of Li in the graphite anode.





Summary of experimental data from Li titration studies.

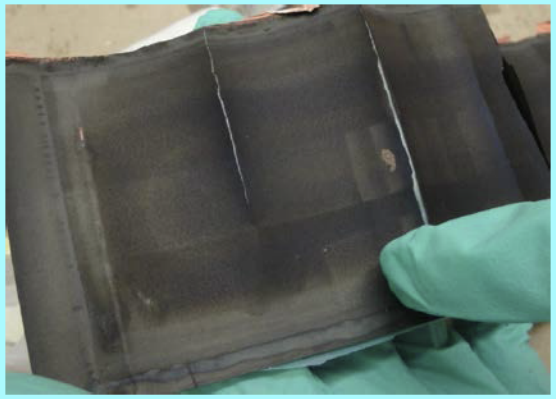
Description	Cell ID: 77-1	Cell ID: 77-3	Average	Units
Total of 6 charges (ΣC)	1387	1467	1427	$mAh\,g^{-1}$
Total of 5 discharges (ΣD)	1014	1091	1053	$mAh\,g^{-1}$
Carbon SEI	42	40	41	$mAh\,g^{-1}$
Summation of capacity (sum) = $\Sigma C - \Sigma D$ – SEI	331	336	334	$mAh\,g^{-1}$
Volume of H_2 gas (corrected for STP)	17.8	19.3	18.6	ml
Li in anode as calculated from vol. of H_2 gas (Li)	234	246	240	$mAh\,g^{-1}$
Irreversible capacity not producing SEI or H_2	97	90	94	$mAh\,g^{-1}$

LLC oxide cathode combined with Graphite anode

Data provided by SAFT

- Anode dry out during formation
  - Anode shows unusual dryness, even with excess electrolyte.
  - Dry regions facilitated lithium plating detected in the cells failed prematurely.
- Metal Dissolution during formation cycling
  - Dissolution of transition metal ions (Mn, Ni and Co) from the cathode and their redeposit ion on the anode.

Metal Content: [ppm] = [mg/kg]	Sample 1 (Anode) of July 2011	Sample 2 (pure MPG 111) of July 2011	Sample 3 (Anode) of December 2011
Co	27	< 2	14
Fe	217	22	130
Li	8896	Not analyzed	3680
Mn	370	< 2	70
Ni	97	2	70
P	1891	12	700
Alkalinity [g Li2CO3 /kg]	50.9	Not analyzed	15



Electrolytes with Low Flammability and 5 V Stability

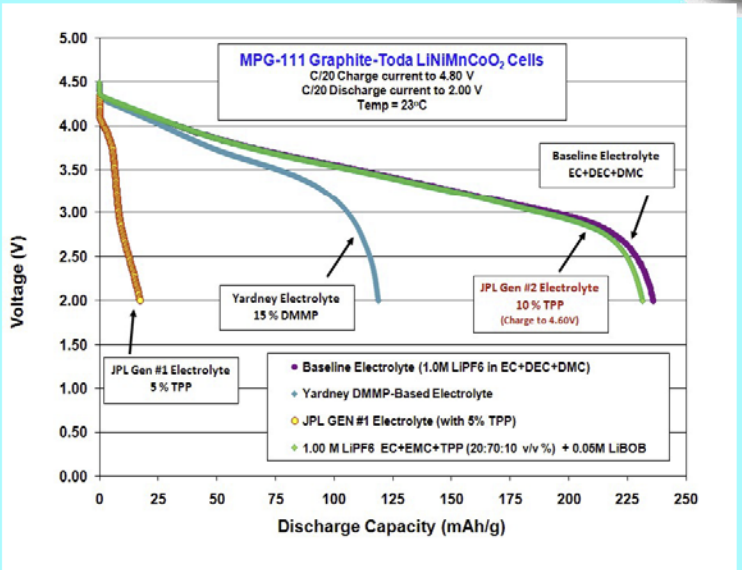
Development Strategies

- Retain the carbonate solvent mixture, add small but adequate amounts of FRAs (Flame Retardant Additives) to the electrolyte and assess their electrochemical compatibility.
  - Triethyl phosphate, triphenyl phosphate, tributyl phosphate, triphenyl phophite, Tris(2,2,2-trifluoroethyl) phosphate, Bis-(2,2,2-trifluoroethyl) methyl phosphonate and Diethyl phenyl phosphonate.
- Substitute fluorinated carbonates or esters as co-solvents for the conventional carbonates (EC, EMC) for reduced flammability.
  - FEC and trifluro ethylene carbonate
- Evaluate compatibility in conjunction with various chemistries (different anodes and cathodes) individually and modify their stability with additives, if required.

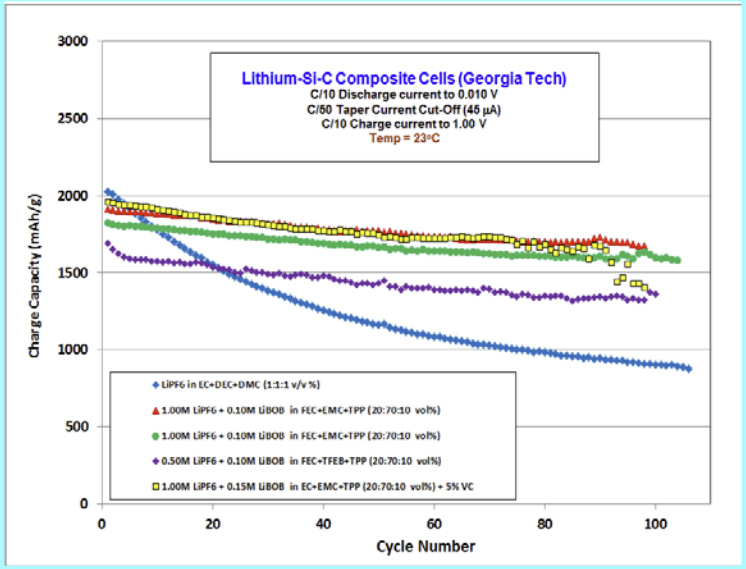
Smart et al ECS Fall Meeting, Vienna, Austria, Oct 2009; IBA Meeting, Hawaii, January 2012

Low-Flammability & 5V Electrolytes for Li-Ion Cells

- Various amounts of flame retardant additive (triphenyl phosphate – 5-15%) with 'no loss' in performance.
- Developed low flammability electrolytes with improved performance over baseline electrolytes with Si anodes, while also providing enhanced safety.
- Reduced (to ~30%) flammability achieved from electrolyte solutions.

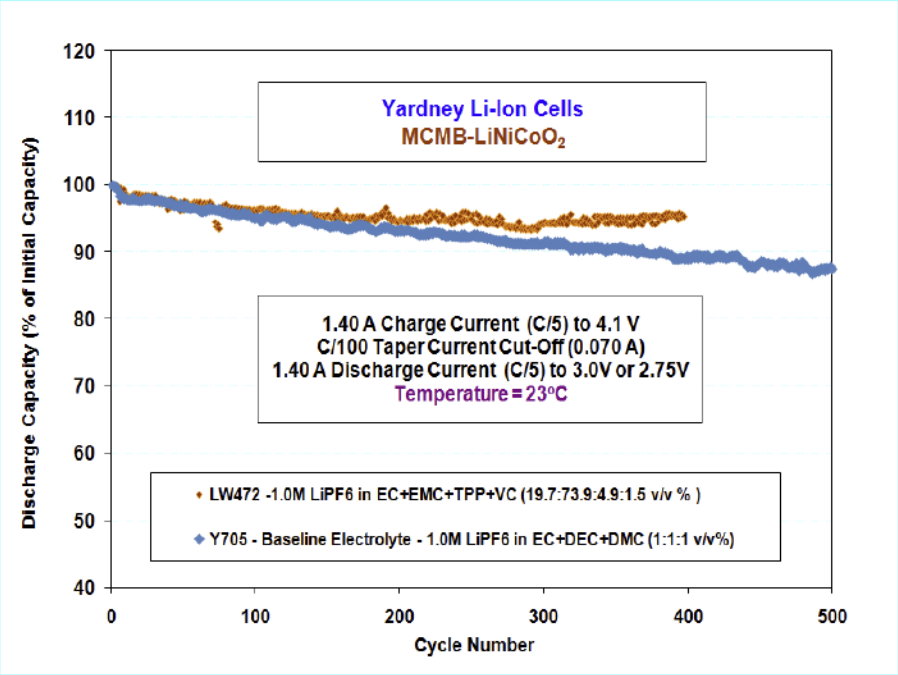


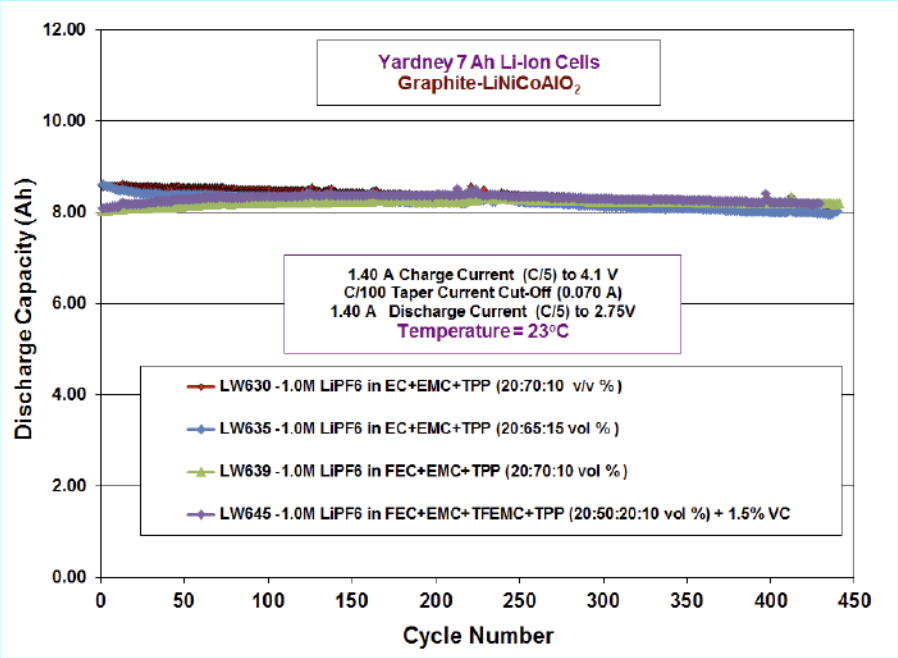
Electrolyte	SET, S	Standard Deviation
1.0M (95% LiPF6+ 5% LiBOB) in EC/EMC/DMMP (3/5.5/1.5)	1.8	1.5
1.0M LiPF6 in EC/EMC/TPP (2/6.5/1.5)	3.78	1.2
1.0M LiPF6 in EC/EMC/TPP (2/7/1)	9.57	0.9
1.0M LiPF6 in EC/EMC/TPP (2/7.5/0.5)	22.45	2.3
1.0M LiPF6 in EC/EMC (3:7)	33.4	3.4
1.0M (95% LiPF6+ 5% LiBOB) in EC/EMC/DMMP (3/5/2)	0.4	0.4



Low-Flammability & 5V Electrolytes for Li-Ion Cells

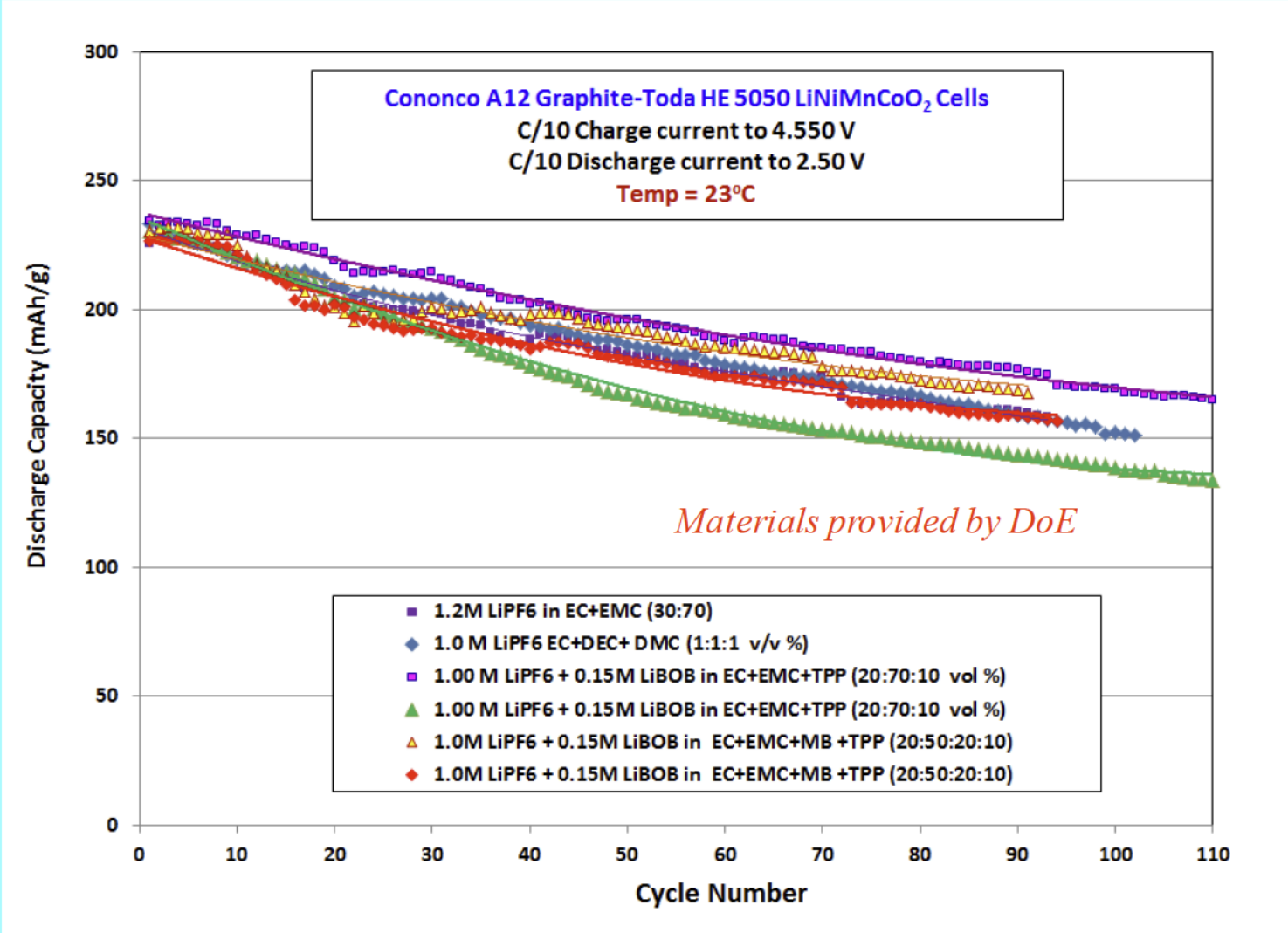
- Demonstrated excellent cycle life and good rate capability of low flammability electrolytes in various aerospace cells (Yardney, Quallion and now SAFT)
  - > 500 cycles with <5% loss in capacity.
  - Good rate capability and low temperature performance





Cycle Life Performance of the Cathode

Conoco A12 Graphite-Toda HE 5050 $LiNiMnCoO_2$ (coin) Cells



Summary and Conclusions

- **High Energy Materials (Cathodes, anodes and high voltage and safe electrolyte are required to meet the needs of the future space missions.**
  - **Cathodes**
    - The layered layered composites of of Li_2MnO_3 and $LiMO_2$ are promising
    - Power capability of the materials, however requires further improvement.
    - Surface coatings help in the interfacial kinetics and stability.
  - **Electrolytes**
    - Small additions of Flame Retardant Additives improves flammability without affecting performance (Rate and cycle life).
    - 1.0 M in EC+EMC+TPP was shown to have good performance against the high voltage cathode; Performance demonstrated in large capacity prototype MCMB-$LiNiCoO_2$ Cells. Formulations with higher proportions are looking promising.
    - FEC-containing electrolyte blends perform well with Si anodes.

Acknowledgments

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