



# Advanced Lithium-ion Batteries With High Specific Energy and Improved Safety for NASA's Missions

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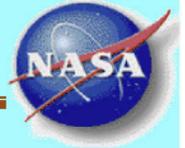
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**International Battery Association (IBA) and Pacific Power Source Symposium  
Hilton Waikoloa Village, Waikoloa, Hawaii**

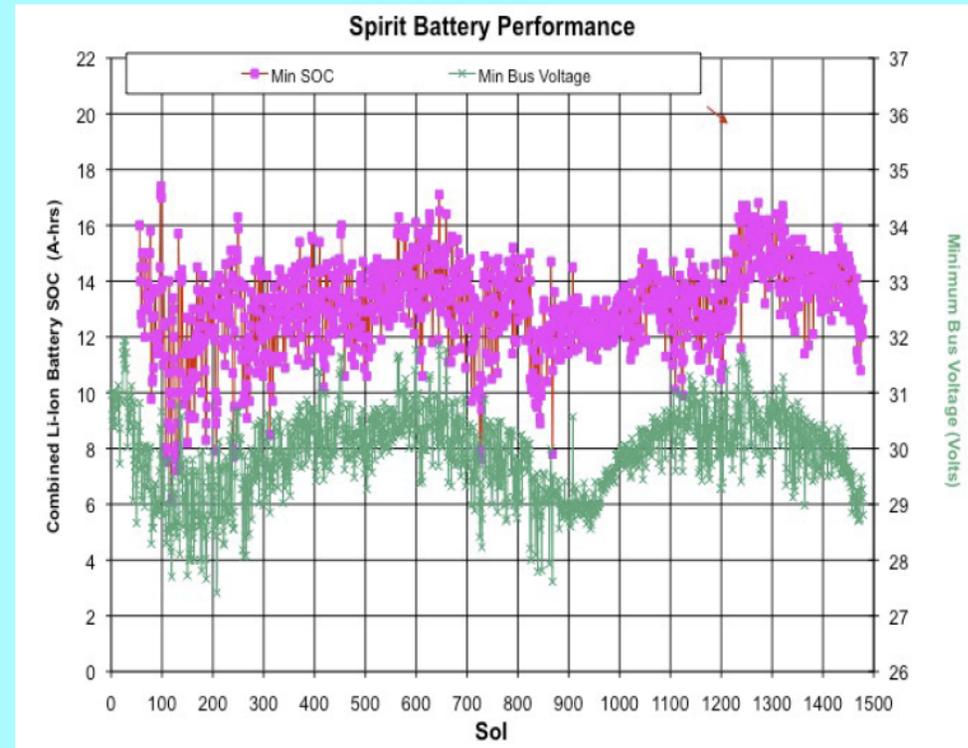
**January 12, 2012**

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# Lithium-Ion Batteries in Space

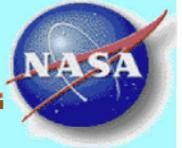


- Large-format cells
  - Li-ion batteries ( 30 V, 20 Ah) have been successfully powering the Mars Exploration rovers, Spirit and Opportunity for about years (Seven years in space and eight years after fab).
  - Li-ion batteries (30 V, 60 Ah) have successfully supported Mars Phoenix Lander mission in 2005.
- Small cells (18650)
  - Kepler, Aquarius, and Lunar orbiters
  - Several European satellites



- Chemistry (developed with Yardney)
  - MCMB and  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$
  - Electrolyte: 1.0 M  $\text{LiPF}_6$  in EC:DEC:DMC
  - True Prismatic cells
  - Qualified for (-30°C to +40°C)
- Laboratory tests show ~ 85% capacity retention
- Validates the technology for long-life applications.

# Mars Science Laboratory- "Curiosity"



Launched on Nov 26, 2011

- **Science Goals:**

- To determine Mars' "habitability."
- The biggest, most advanced suite of instruments ever sent to the Martian surface.
  - *Alpha Particle X-Ray Spectrometer*
  - *ChemCam -Laser-Induced Remote Sensing*
  - *SAM (Sample Analysis at Mars) - Quadrupole Mass Spectrometer (QMS), Gas Chromatograph (GC), and Tunable Laser Spectrometer (TLS)*
- Geology of Martian rocks,
- Analyze soil/rock samples for building blocks of life (e.g., forms of carbon) on Mars.

- **Landing:** Parachute assisted descent followed by power descent, lowered on tether sky crane.

- **Mobility:**

- Able to roll over obstacles up to 75 cm high and travel up to 90 meters/hour

- **Power**

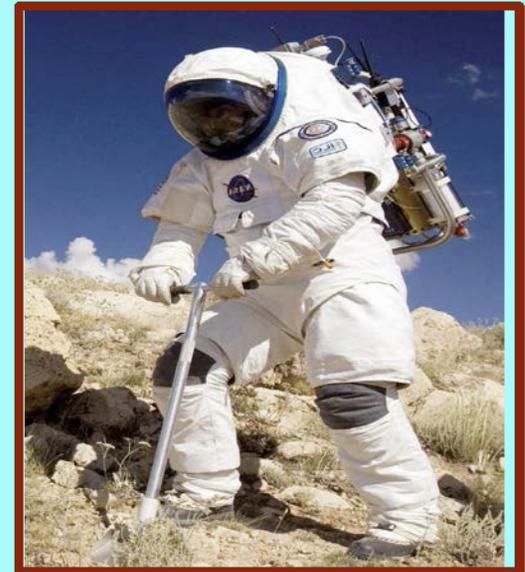
- Plutonium-based RTG as a primary energy source on the rover
- Operating lifespan of a full Martian year (687 Earth days) or more
- exploration of a much larger range of latitudes and altitudes.



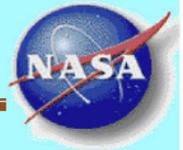
# High Energy Li-Ion Cells for Future Space Missions



- **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)
  - Combination of high energy cathode, safe electrolyte with a carbonaceous anode with known heritage and performance
- **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, and a high energy lithium alloy anode (Li-Si)

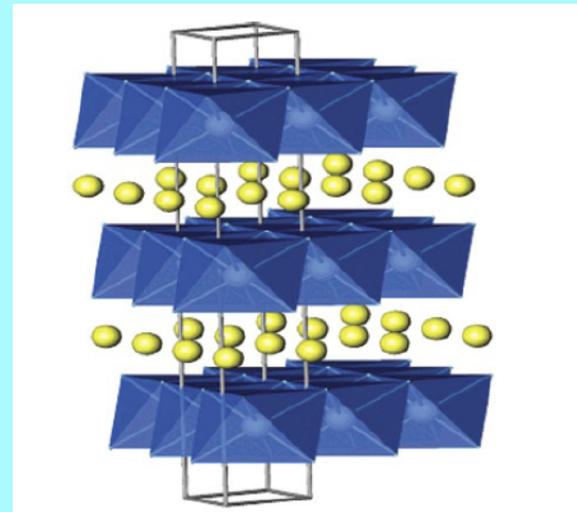


# High Specific Energy Cathode Materials

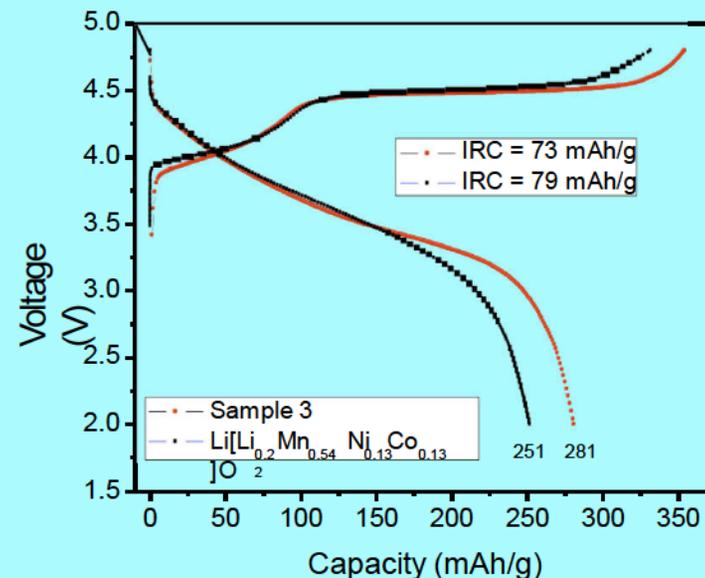


- Li-excess Layered-Layered composites
  - Layered oxide compositions belonging to the series layered-layered composite  $\text{Li}[\text{Li}_{1/3}\text{Mn}_{2/3}]\text{O}_2$  (commonly designated as  $\text{Li}_2\text{MnO}_3$ ) and  $\text{LiMO}_2$  ( $M = \text{Mn}_{0.5}\text{Ni}_{0.5}$ )
  - $x \text{Li}[\text{Li}_{1/3}\text{Mn}_{2/3}]\text{O}_2 + (1-x) \text{Li}(\text{Mn}, \text{Ni}, \text{Co})\text{O}_2$
  - e.g.,  $0.5 \text{Li}[\text{Li}_{1/3}\text{Mn}_{2/3}]\text{O}_2 + 0.5 \text{Li}(\text{Mn}_{0.33}, \text{Ni}_{0.33}, \text{Co}_{0.34})\text{O}_2$
  - Loss of oxygen around 4.5 V during charge,, which creates oxygen vacancies, reduction of nickel to  $\text{Ni}^{+2}$  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.

*cf: Dahn et al, Thackeray et al*



- Layered structure of  $\text{LiNi}_y\text{Mn}_y\text{Co}_{1-2y}\text{O}_2$ , showing the  $\text{Li}^+$  between the transition-metal oxide/sulfide sheets.



# High Specific Energy Cathode Materials

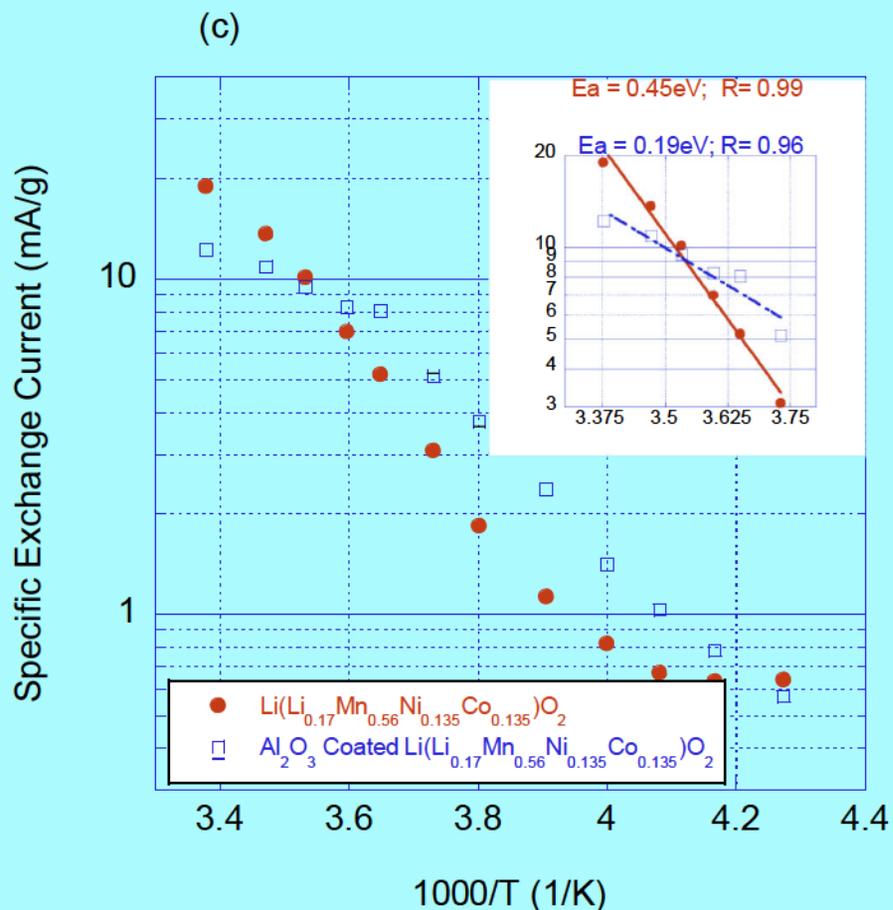


- Issues

- Irreversible capacity loss, especially in the uncoated cathodes
  - 50 – 100 mAh/g in the first cycle (~30% compared to 7-10% for SOA cathode)
  - Non-availability of lithium at the anode for the irreversible capacity and impedance build up at the anode
- Cation Disorder (transition metal ions, typically nickel, occupying the Li sites) and interfering with Li<sup>+</sup> ion diffusion
- Low Tap densities (0.6 to 2.0 g/cc)
  - Strongly dependent on the synthetic conditions and morphology
- Low Power densities
  - High capacity is realizable only at low rates (C/20-C/10) and at ambient temperatures.
- Broad voltage profile with more capacity available between 3.0 V and 2.5 V, even at moderate rates.



# Reaction Kinetics in LNMC cathodes (from Tafel Measurements)

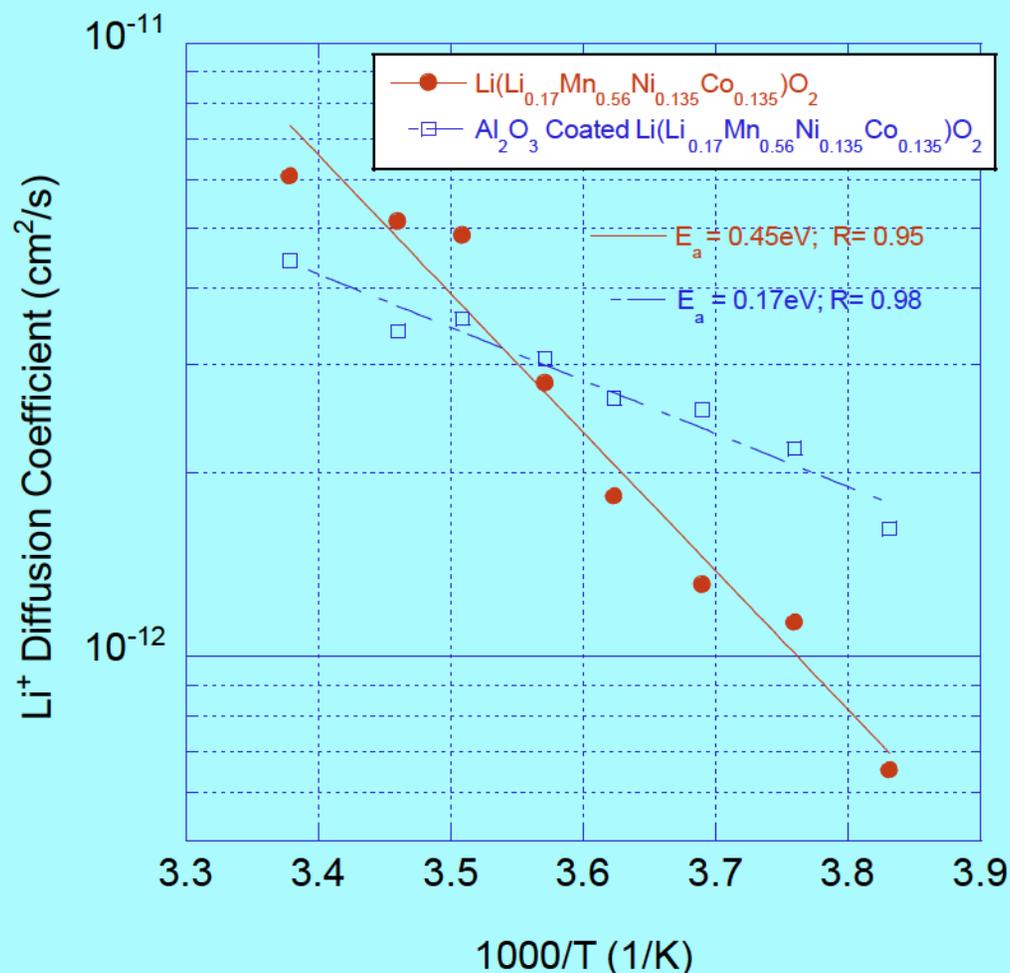


West et al J. Electrochem. Soc., Volume 158, Issue 8, pp. A883-A889 (2011)

- The kinetics for the Li intercalation into the cathode seem to be improved with surface coating ( $\text{Al}_2\text{O}_3$ ), especially at low temperatures.



## Li<sup>+</sup> Diffusion Coefficient From PITT (Potentiostatic Intermittent Titration Technique)

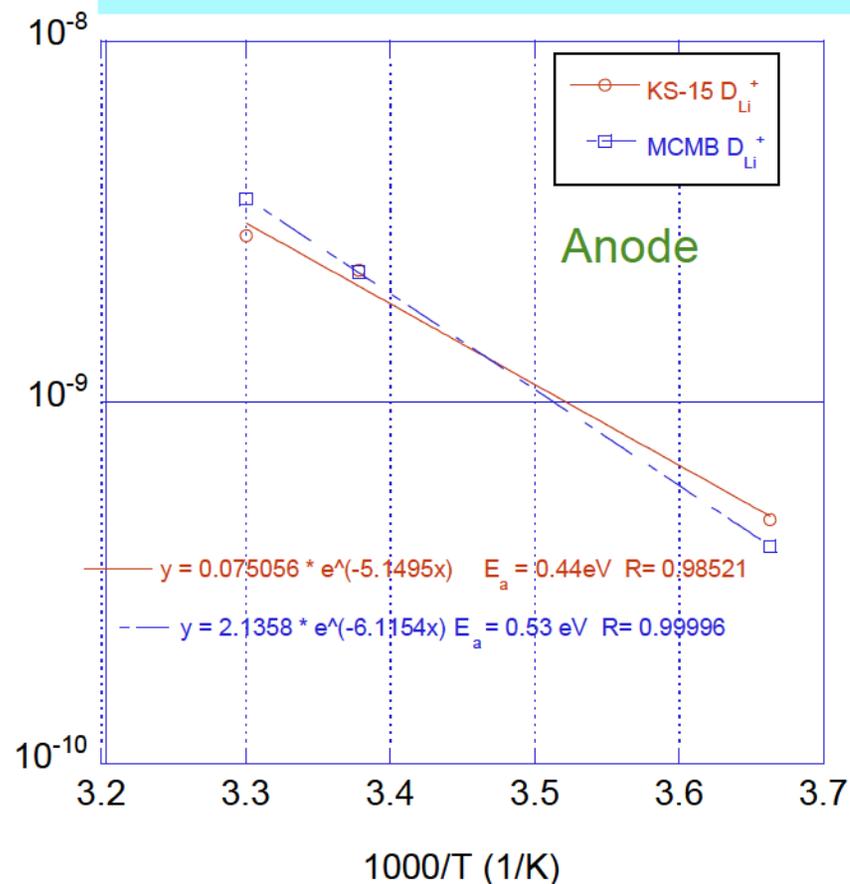
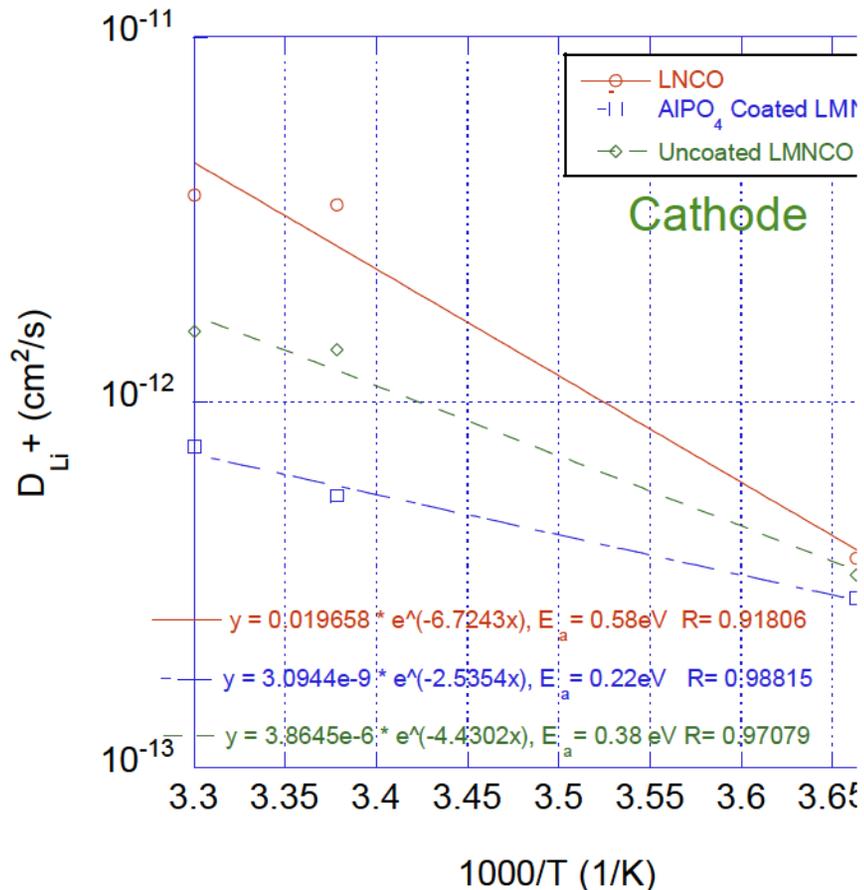


West et al J. Electrochem. Soc., Volume 158, Issue 8, pp. A883-A889 (2011)

- At room temperature, the diffusion coefficient for uncoated  $\text{Li}_{1.17}\text{Mn}_{0.56}\text{Ni}_{0.135}\text{Co}_{0.135}\text{O}_2$  is slightly higher than that for the  $\text{Al}_2\text{O}_3$  coated material.
- The diffusion coefficient decreases much more steeply with decreasing temperature for the uncoated material relative to the  $\text{Al}_2\text{O}_3$  material.



# Li<sup>+</sup> Diffusion Coefficient From PITT (Potentiostatic Intermittent Titration Technique)



Cathode	D <sub>Li<sup>+</sup></sub> (30°C) (cm <sup>2</sup> /s)	D <sub>Li<sup>+</sup></sub> (23°C) (cm <sup>2</sup> /s)	D <sub>Li<sup>+</sup></sub> (0°C) (cm <sup>2</sup> /s)	E <sub>a</sub> (eV)
LNCO	3.68x10 <sup>-12</sup>	3.48x10 <sup>-12</sup>	3.73x10 <sup>-13</sup>	0.58
AlPO <sub>4</sub> coated LMNCO	7.56x10 <sup>-13</sup>	5.53x10 <sup>-13</sup>	2.91x10 <sup>-13</sup>	0.22
Uncoated LMNCO	1.56x10 <sup>-12</sup>	1.39x10 <sup>-12</sup>	3.37x10 <sup>-13</sup>	0.38

Carbon	D <sub>Li<sup>+</sup></sub> (30°C) (cm <sup>2</sup> /s)	D <sub>Li<sup>+</sup></sub> (23°C) (cm <sup>2</sup> /s)	D <sub>Li<sup>+</sup></sub> (0°C) (cm <sup>2</sup> /s)	E <sub>a</sub> (eV)
MCMB	3.65x10 <sup>-9</sup>	2.29x10 <sup>-9</sup>	3.98x10 <sup>-10</sup>	0.53
KS-15	2.88x10 <sup>-9</sup>	2.31x10 <sup>-9</sup>	4.72x10 <sup>-10</sup>	0.44

# Refinement of Synthesis

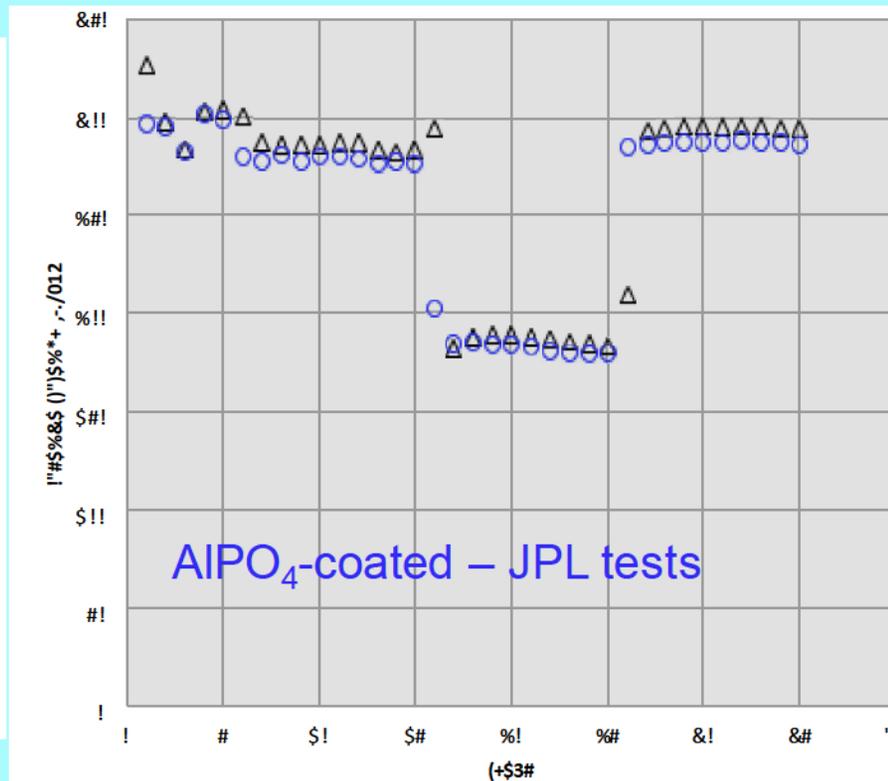
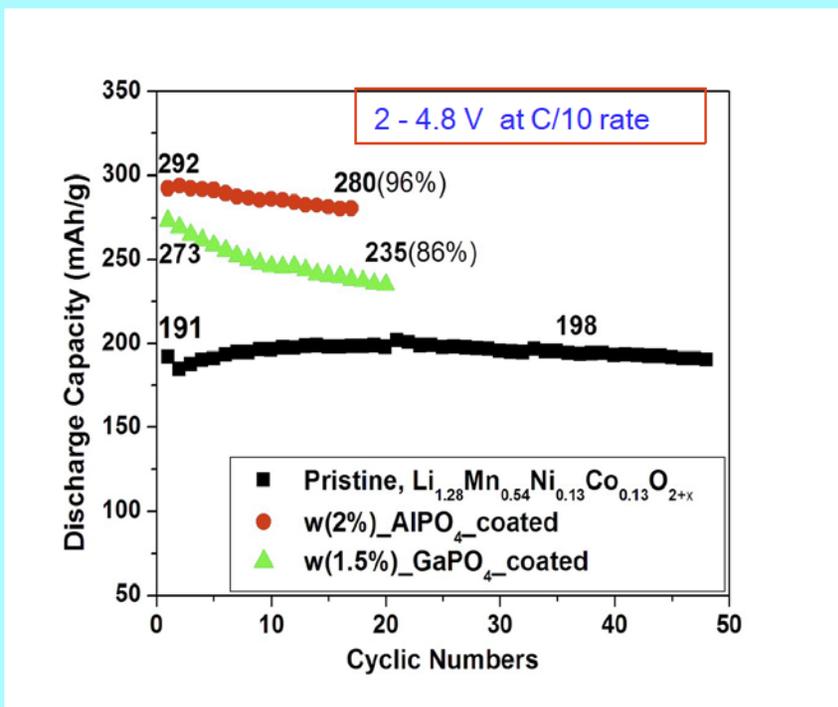


## Improvement in tap density and Performance

Characteristics	11 month (Al <sub>2</sub> O <sub>3</sub> -coated)	18 month (AlPO <sub>4</sub> -coated)	23 months	
			(AlPO <sub>4</sub> -coated)	(GaPO <sub>4</sub> -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

- Spherical morphology preferred for high tap density.
- An increase in the tap density is generally accompanied by decreased rate capability.

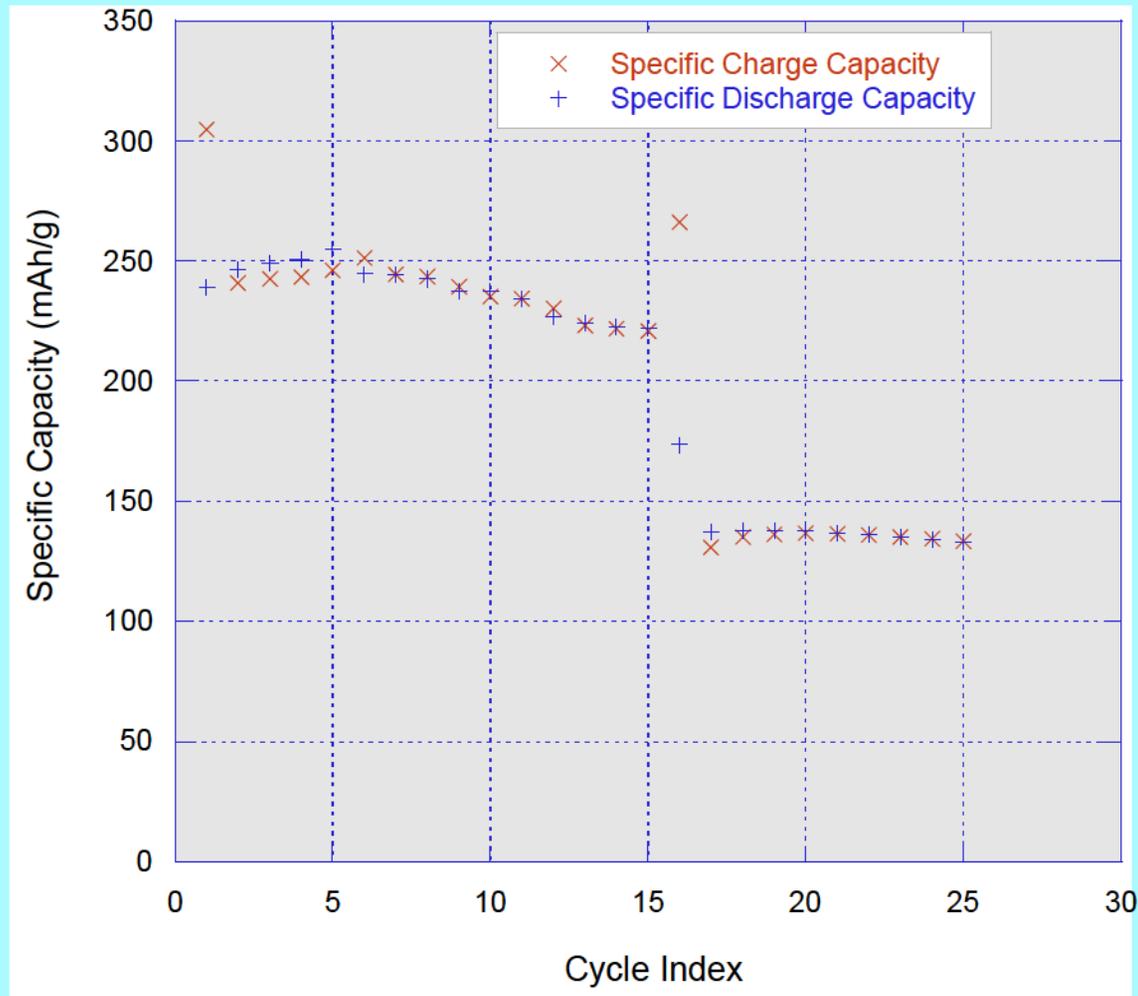
# Surface-modified Sample from Hydroxide Synthesis



- Both the AlPO<sub>4</sub>- and GaPO<sub>4</sub>-coated samples show higher capacities
- AlPO<sub>4</sub>-coated sample shows high capacity with good cycle life

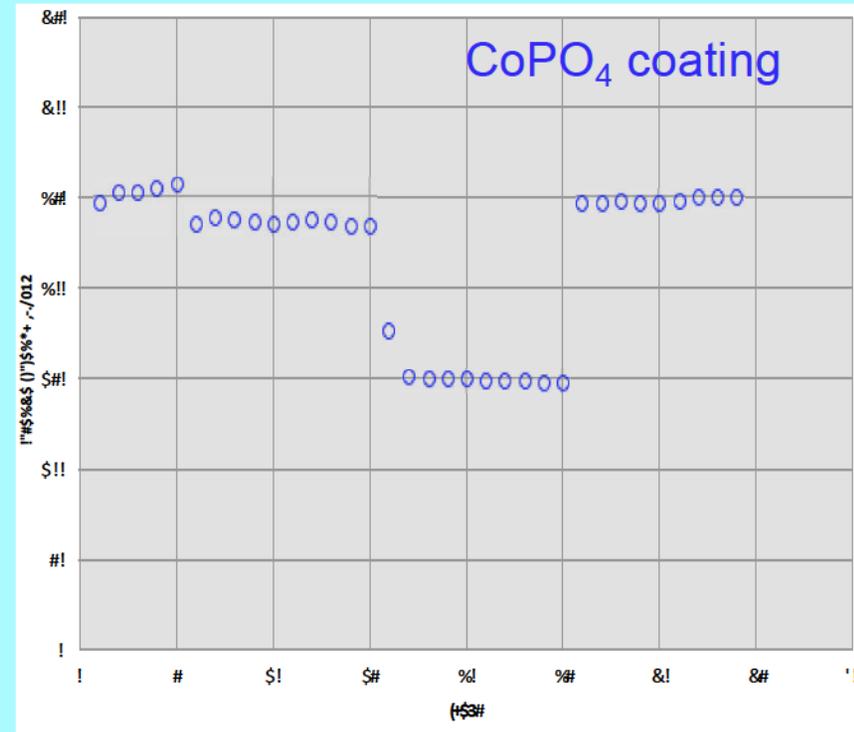
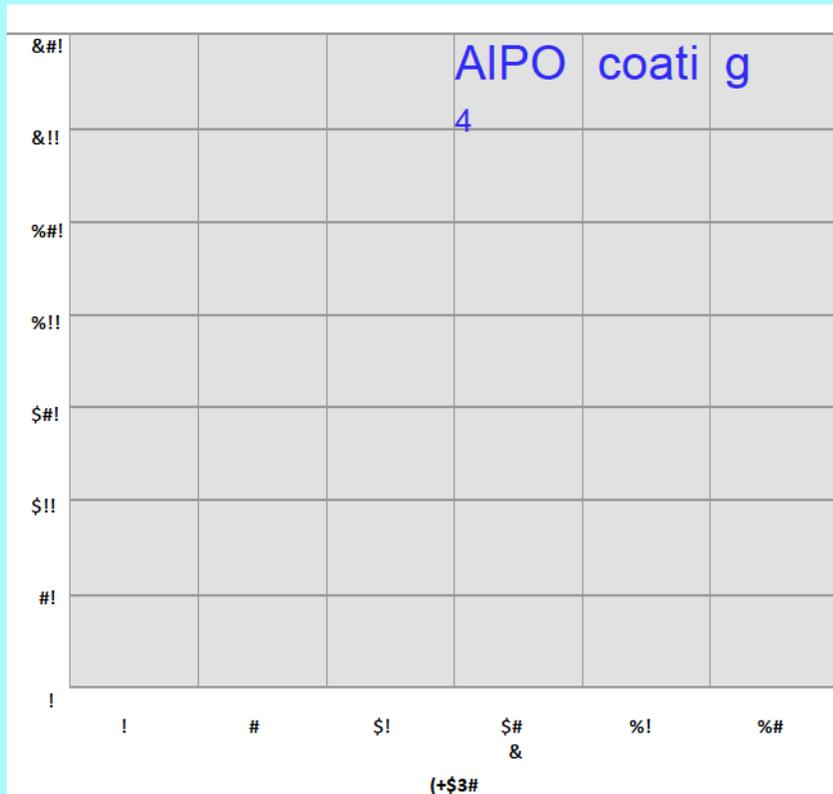
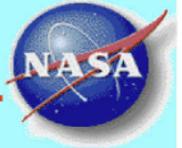
- JPL studies validate the improved performance
- Initial discharge capacity to 2V = 300 mAh/g
- At C/10 RT: 281 mAh/g (2V) & 242 mAh/g (3V)
- Irreversible capacity : 35 mAh/g.
- **Material being scaled up at NEI Corp**

# Toda 9100 Cathode From DD Cells-Half cells



- Capacity in half cell configuration looks good initially.
- Capacity appears to experience significant fade in C/10 room temperature cycling following room temperature formation

# Toda 9100 Cathode with Surface Coatings



Coated at Physical Sciences

- Surface coating helps improve the cyclic stability and also lowers the irreversible capacity from ~ 90 mAh/g to 35 mAh/g

# Ball Milled and Annealed $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Co}_{0.13}\text{Ni}_{0.13}\text{O}_2$



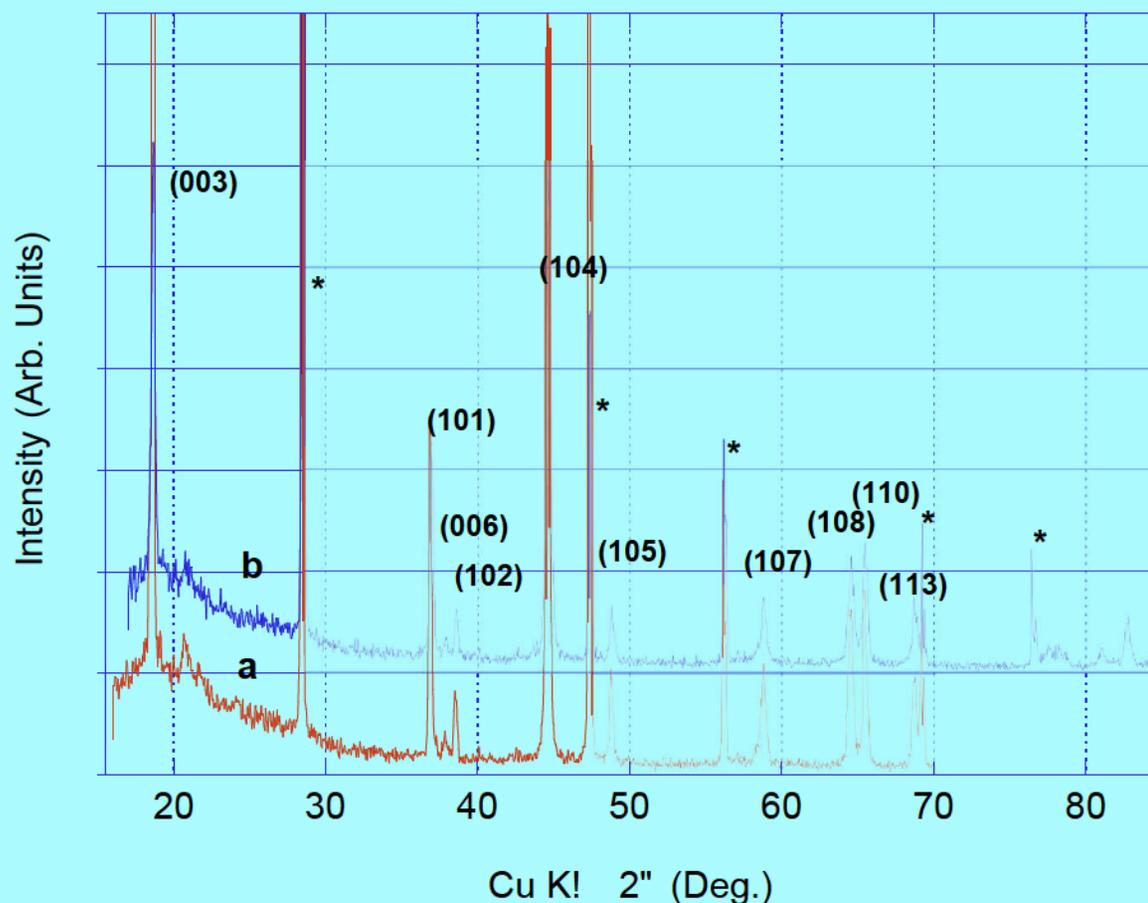
*...a new method of synthesizing LLC cathode*

- Anticipated benefits over conventional methods
  - A novel, low cost, simple, and easily scalable alternative.
  - Can be tailored to a wide range of stoichiometries
  - Can reduce cation disorder provided starting materials have low disorder.
  - Can be Extended for the straightforward preparation of other immiscible (e.g. spinel + layered) cathode compositions as well.
- The  $\text{Li}_2\text{MnO}_3$  and  $\text{LiMn}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{O}_2$  (supplied by Quallion) powders were added in 1:1 molar ratios to a steel ball mill.
- The powders were dry milled with steel balls for a total of six hours. Following milling, the powders were fired in air at  $800^\circ\text{C}$  for 24 hours and then quenched on copper plates to room temperature.
- These powders were then re-milled for six hours and re-fired in air at  $800^\circ\text{C}$  for 24 hours and quenched to room temperature.

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

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# XRD of the LLC Cathode (mechanical vs conventional)

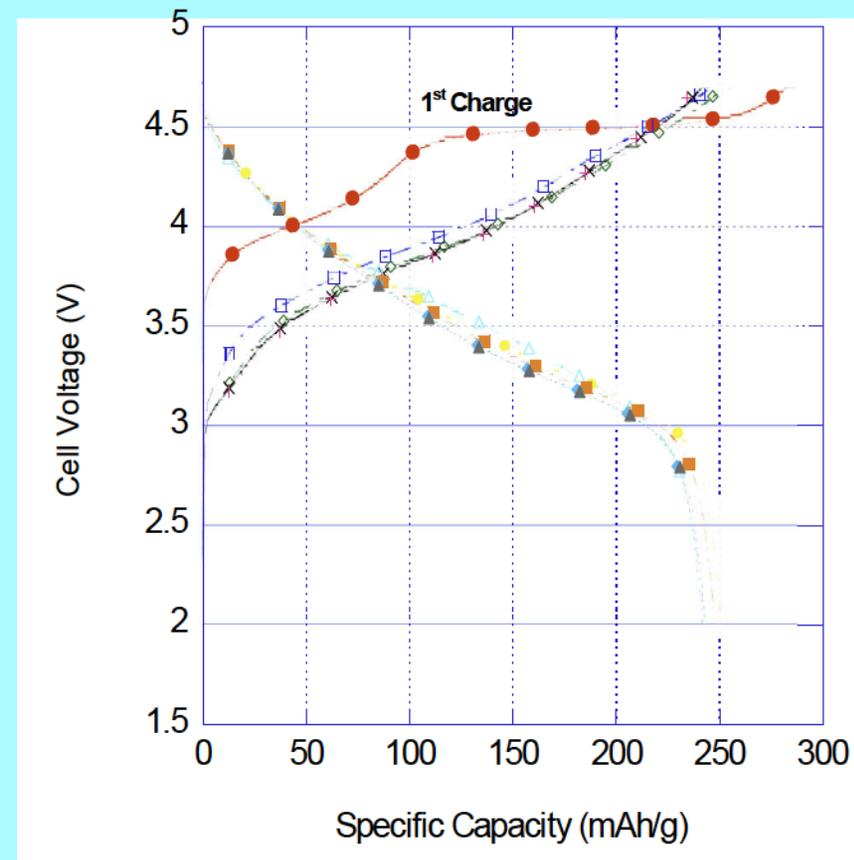
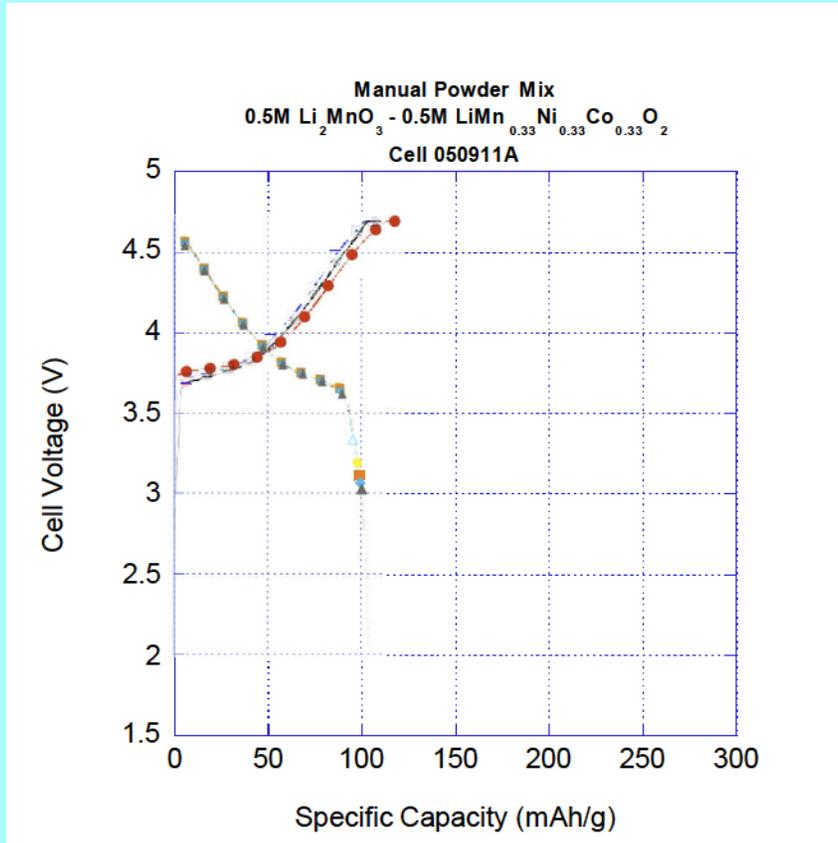
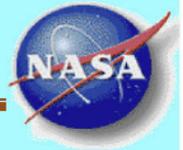


- a)  $\text{Li}_{1.17}\text{Mn}_{0.56}\text{Ni}_{0.135}\text{Co}_{0.135}\text{O}_2$  prepared by conventional carbonate synthesis route, and b) milled and annealed  $0.5\text{M Li}_2\text{MnO}_3 - 0.5\text{M LiMn}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{O}_2$  (resultant  $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ ). Asterisks indicate reflections associated with Si standard.

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

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# Mechanical Method: $\text{Li}_{1.2}\text{Mn}_{0.4}\text{Co}_{0.08}\text{Ni}_{0.32}\text{O}_2$

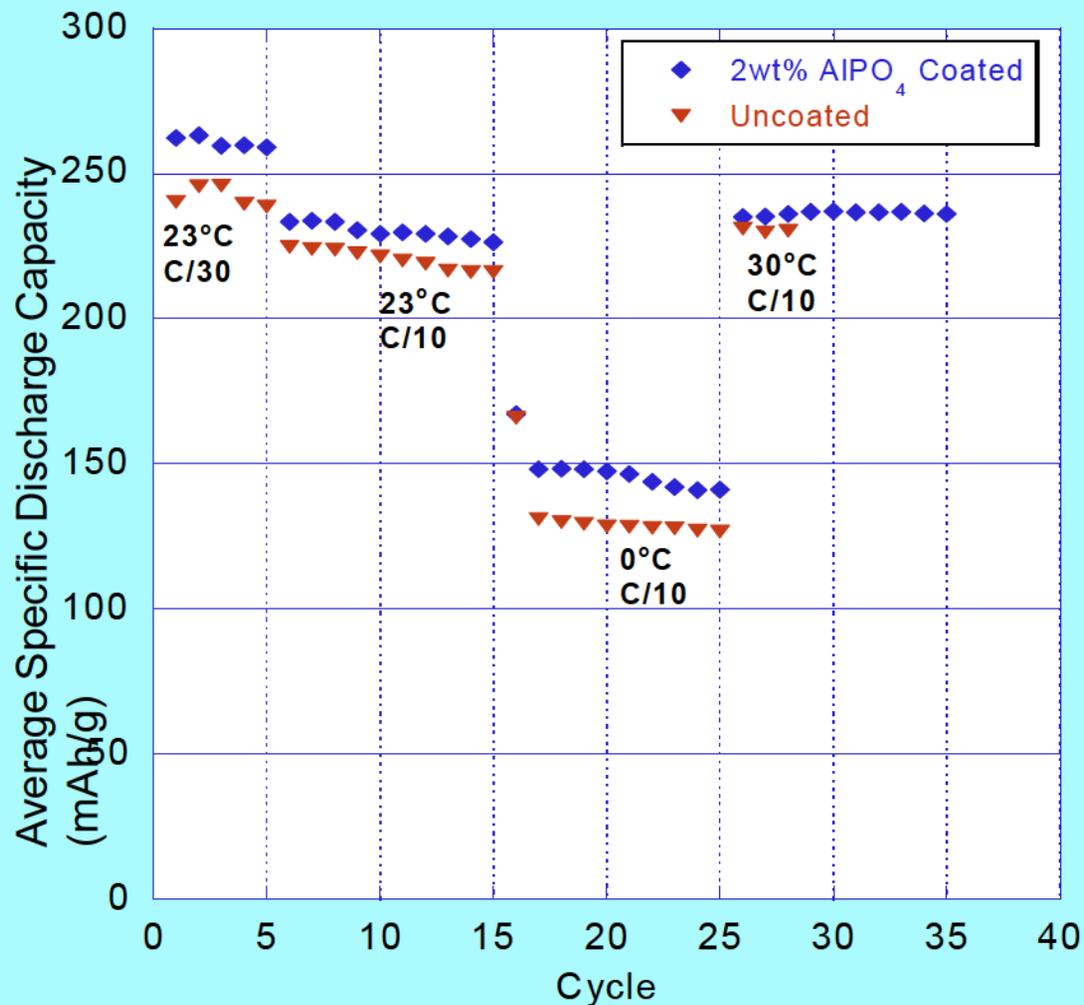


- Simple mixing does not activate the  $\text{Li}_2\text{MnO}_3$  phase
- There is no voltage plateau at 4.5 V during first charge and no improvement in the discharge capacity
- $\text{Li}_2\text{MnO}_3$  phase activated
- Voltage profile similar to the chemically-synthesized materials with plateau at 4.5 V plateau on first charge comparable discharge capacity

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

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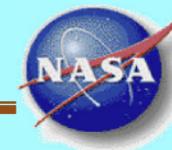
# (Mechanical) $\text{Li}_{1.2}\text{Mn}_{0.4}\text{Co}_{0.08}\text{Ni}_{0.32}\text{O}_2$ Cathode coated with $\text{AlPO}_4$



- Performance improved upon coating with  $\text{AlPO}_4$  and is comparable to the analogous cathode from solid state methods.

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

## Irreversible Capacity in High-Voltage Cathodes



- Irreversible Capacity mechanism involving the simultaneous removal of Li and O from the solid.
- The voltage plateau at 4.5 V results from the electrochemical removal of  $\text{Li}_2\text{O}$  (lithium extraction and oxygen loss) from the  $\text{Li}_2\text{MnO}_3$  component (Dahn et al)
- Evolution of oxygen was observed from mass spec, at potentials above 4.5 V (also 10% of gas being  $\text{CO}_2$  from an oxidation of the electrolyte). (Bruce et al)
  - As oxygen is evolved from the surface, lithium ions migrate from the octahedral sites in the transition metal layers into the lithium layers leaving vacancies, which are subsequently occupied through a cooperative displacement of the transition metal ions diffusing from the surface into the bulk, until all the octahedral sites vacated by the lithium ions are occupied by transition metals, at which point oxygen evolution ceases.

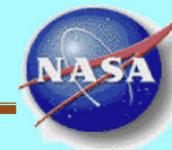
## Irreversible Capacity in High-Voltage Cathodes

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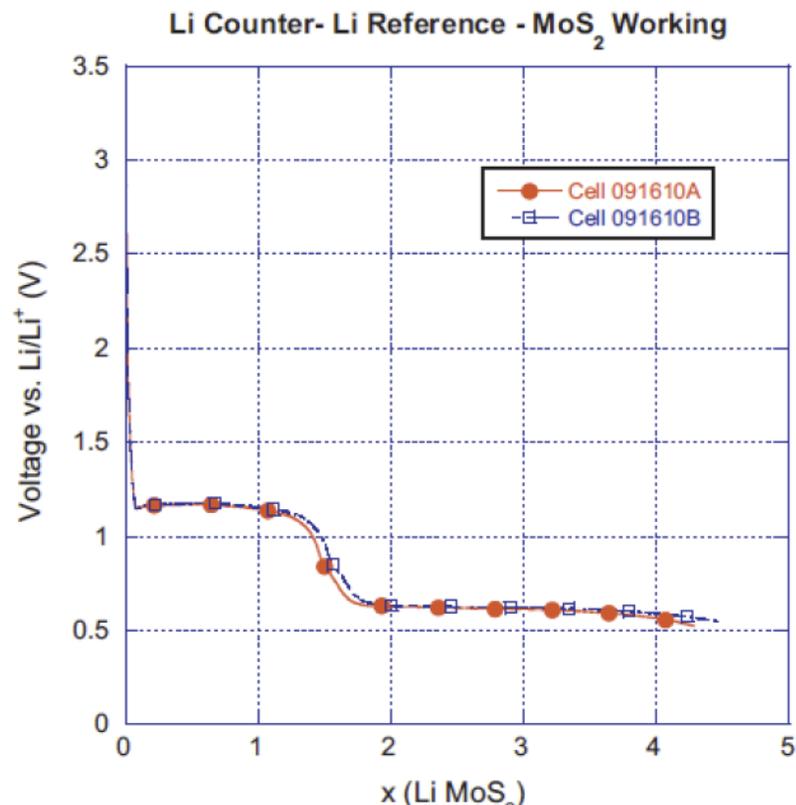
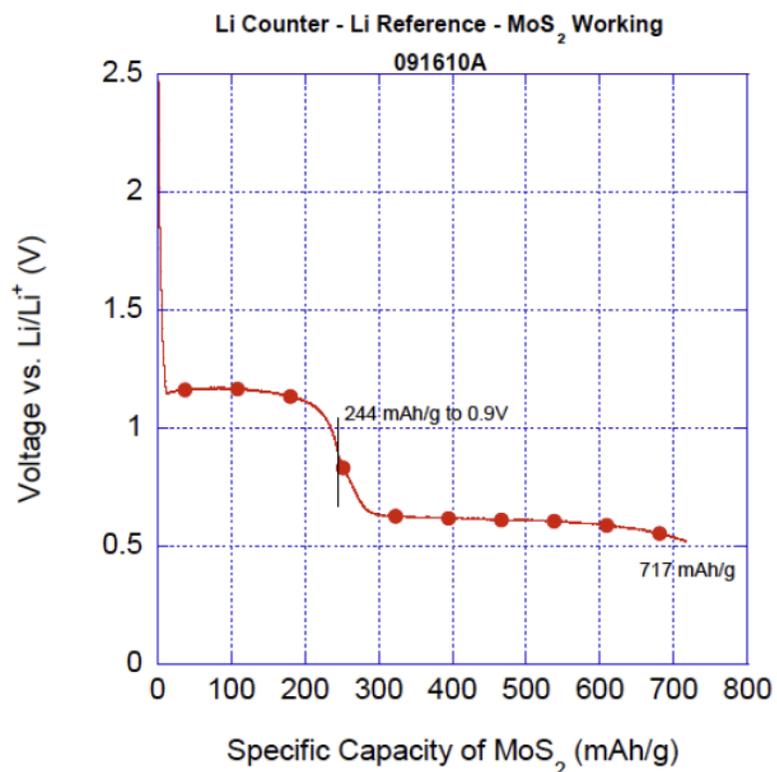
- A key question must be addressed before this materials system can be infused into a lithium-ion cell manufacturing line:
  - Cathode is the lithium source in a Li-ion cell and the cell is designed cathode-limited with the anode in excess both geometrically and in reversible capacity.
  - The anode and cathode loadings must be carefully balanced both in terms of irreversible capacities and reversible lithium capacities to maximize cell specific energy and to avoid lithium plating on the anode.
  - Given that a significant fraction of irreversible specific charge capacity, upwards by 15–40%, is generated on the first charge for these cathodes, it is imperative to understand the implications of this capacity with regard to the anode design.
  - Unfortunately, the majority of the studies that have been performed on these materials to date have involved the use of lithium metal anodes, and have not addressed the nature of the irreversible capacity loss and the implications that this has upon electrode balancing issues (i.e., cathode to anode ratio).

## Quantification of Li transported to anode during 1<sup>st</sup> charge



- $\text{Li}_{1.2}\text{Ni}_{0.175}\text{Co}_{0.1}\text{Mn}_{0.52}\text{O}_2$  as a cathode.
  - 1<sup>st</sup> cycle specific charge capacity : 324 mAh/g, specific discharge capacity : 236 mAh/g. Irreversible capacity was 88 mAh/g.
- Two separate approaches to elucidate the nature of the irreversible cathode capacity in terms of anode effects.
  - With  $\text{MoS}_2$  as the anode,
    - Due to its high lithium reduction potential, there would be no complications associated with the SEI formation from the electro-reduction of the electrolyte species.
    - $\text{MoS}_2$  has easily identifiable lithiation plateaus at about 1.2 V and 0.6 V vs.  $\text{Li}/\text{Li}^+$  with an abrupt transition near  $\text{Li}_{1.5}\text{MoS}_2$ , which can be used to accurately track the degree of lithium inserted.
  - Analytical determination of Li at the anode.
    - Harvest the charged anodes from the LNMC-graphite cells, and measure the  $\text{H}_2$  gas released upon its reaction with deionized water for a quantitative estimate of Li at the anode.

# Lithiation of MoS<sub>2</sub> - Half Cells

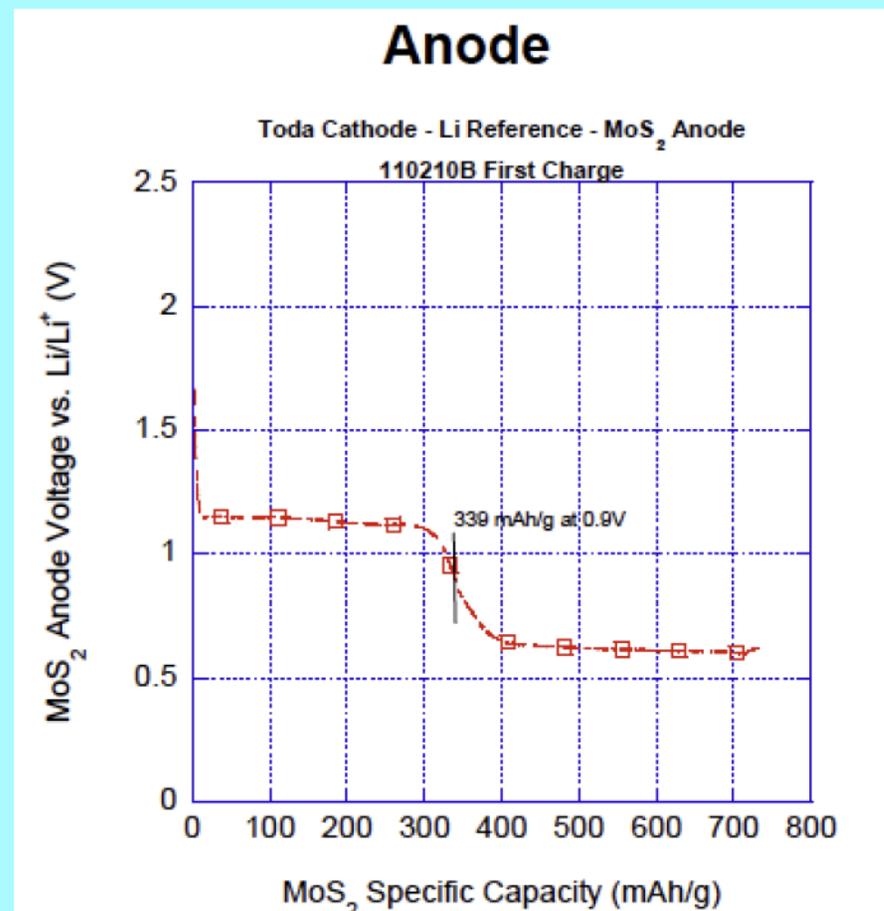
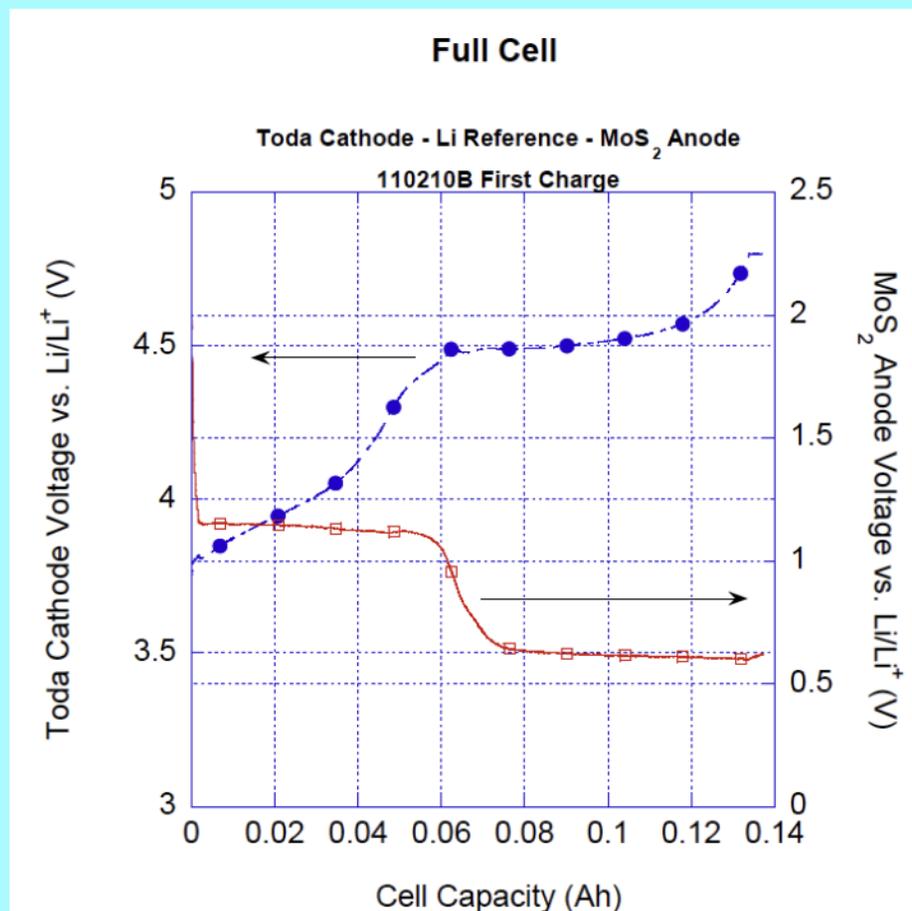


- The lithiation of MoS<sub>2</sub> at a current density of 0.74 mA cm<sup>-2</sup> resulted in two plateaus of 1.2 V and 0.6 V. The transition between the two plateaus, taken as 0.9 V vs. Li occurred at an average composition of  $x = 1.50 + 0.04$  for Li<sub>x</sub>MoS<sub>2</sub> corresponding to about 250 mAh/g.
- The transition between the two plateaus occurs at about  $x = 1.2$  (Julien et al), though others have shown that the transition and discharge profile is rate dependent [14].

# Toda Cathode-Irreversible Capacity

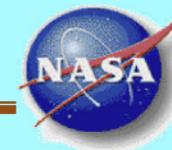


## Toda-MoS<sub>2</sub> Full Cell



The lithiation of MoS<sub>2</sub> from the Toda cathode results in two plateaus, but the transition between these plateaus (taken as 0.9V vs. Li/Li<sup>+</sup>) occurs at 339 mAh/g anode basis.

# Li Titration via Water Reaction with Lithiated Anodes



(Data generated by SAFT)

Summary of experimental data from Li titration studies.

Description	Cell ID: 77-1	Cell ID: 77-3	Average	Units
Total of 6 charges ( $\Sigma C$ )	1387	1467	1427	$\text{mAh g}^{-1}$
Total of 5 discharges ( $\Sigma D$ )	1014	1091	1053	$\text{mAh g}^{-1}$
Carbon SEI	42	40	41	$\text{mAh g}^{-1}$
Summation of capacity (sum) = $\Sigma C - \Sigma D - \text{SEI}$	331	336	334	$\text{mAh g}^{-1}$
Volume of $\text{H}_2$ gas (corrected for STP)	17.8	19.3	18.6	ml
Li in anode as calculated from vol. of $\text{H}_2$ gas (Li)	234	246	240	$\text{mAh g}^{-1}$
Irreversible capacity not producing SEI or $\text{H}_2$	97	90	94	$\text{mAh g}^{-1}$

## Quantification of Li transported to anode during 1<sup>st</sup> charge

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- It is thus clear from the two independent studies that the Li release from the LLC oxide cathode during the 1<sup>st</sup> charge is lower than estimated from its charge capacities.
- A parallel process, possibly oxygen evolution occurs through an electrochemical route on the cathode surface. There will be accompanying redistribution of vacancies within the cathode for charge neutrality. A more intriguing question is on likely reactions occurring at the anode, since the reactions involving Li species will account for only about 60–70% of the charge capacity.
- The questions then would be: What is the anodic process conjugate to the oxygen release from the cathode? Could it be recombination of oxygen at the anode or something involving the electrolyte species?
- It is difficult to speculate on the reaction products and their effects. Clearly, further studies are warranted to understand the complexities in these cathodes.



## Development Strategies

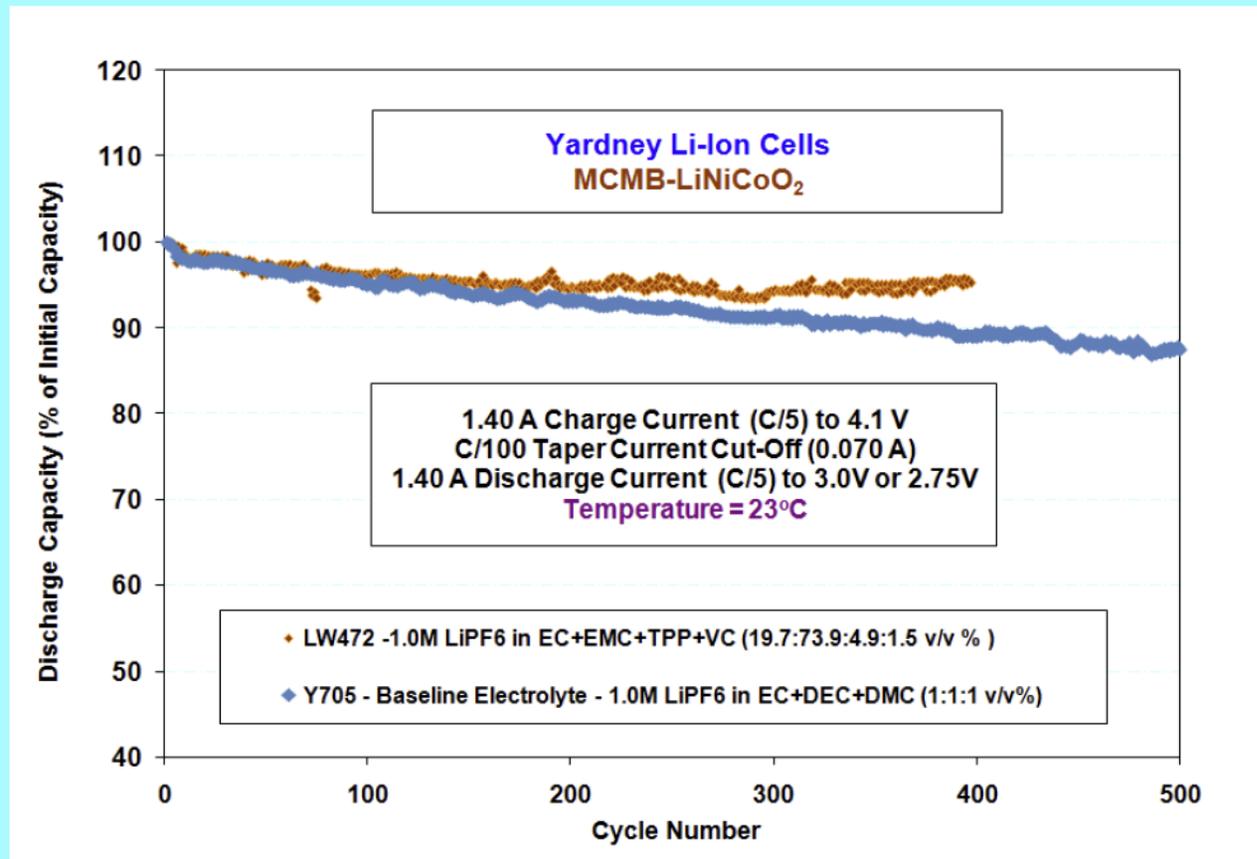
- Retain the carbonate solvent mixture, add small but adequate amounts of FRAs (Flame Retardant Additives) to the electrolyte and assess their electrochemical compatibility.
  - Triethyl phosphate, triphenyl phosphate, tributyl phosphate, triphenyl phosphite, Tris(2,2,2-trifluoroethyl) phosphate, Bis-(2,2,2-trifluoroethyl) 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 trifluoro 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 2010*

# Electrolytes with FRAs in Prototype (Yardney 7 Ah) cells



## 100 % DOD Cycle Life Testing at Room Temperature

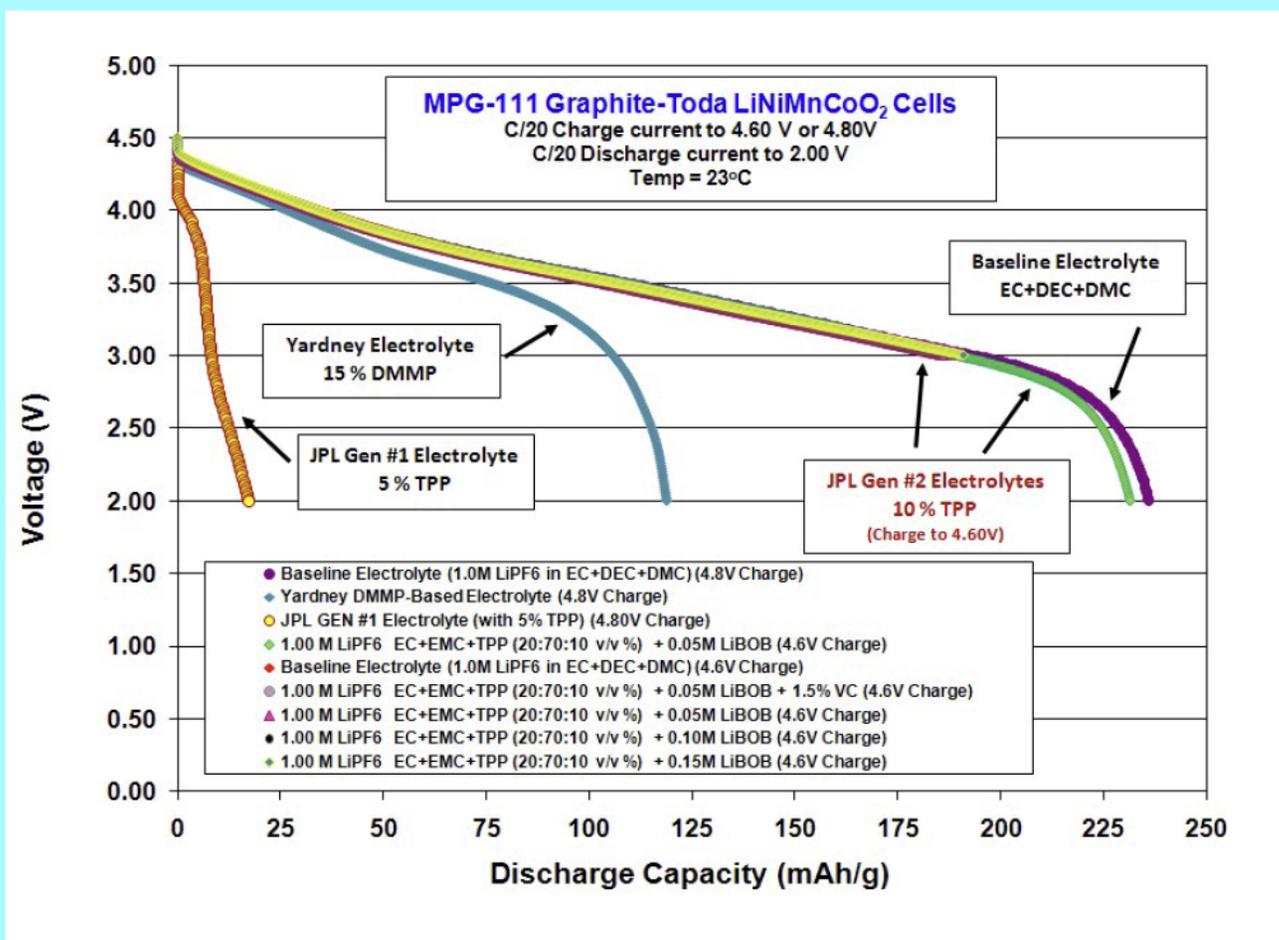


- Cells containing an electrolyte with a flame retardant additive (i.e., 1.0 M LiPF<sub>6</sub> in EC+EMC+TPP+VC) are observed to display good cycle life compared to the baseline formulation.



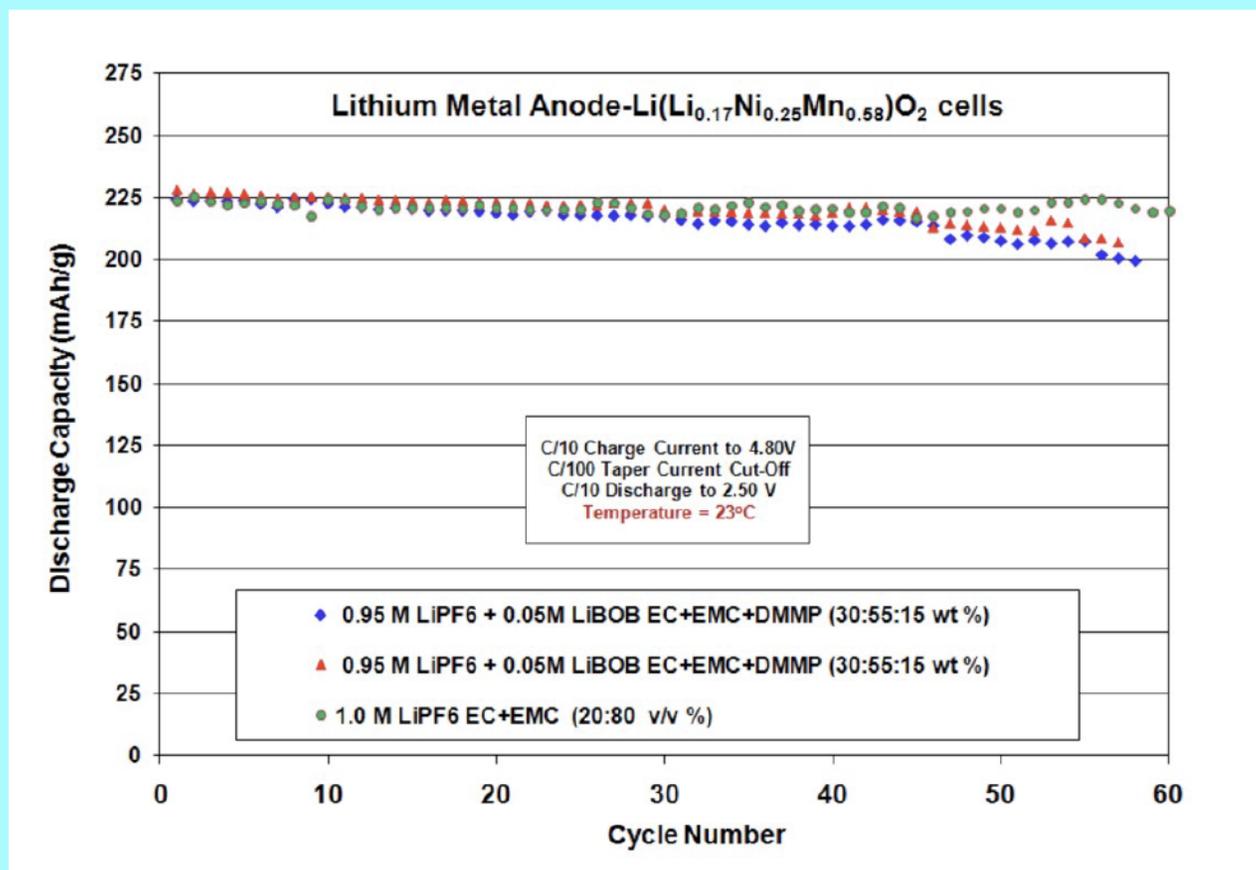
# Low-Flammability Electrolytes for the MPG-111-Toda System

## Comparison of Electrolyte Types (After Formation)



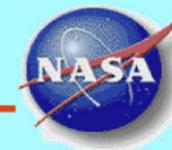
- Comparable performance was obtained with the JPL Gen #2 electrolytes (containing LiBOB) compared with the baseline solution.
- Some of these electrolytes are also compatible with Si anode, with selected additives.

# Stability of Electrolytes at 5 V



- Carbonate blends show some stability towards high voltage cathodes.
- Are they good for > 1000 cycles? Low coulombic efficiencies in general are not encouraging.
- Performance in half cells is encouraging and misleading (due to abundant counter electrode)
- Electrolyte systems needs to be tuned to the chemistry

## Electrolytes with Reduced Flammability



- Self-extinguishing time: A cotton ball-wick soaked with electrolyte. The self-extinguish time (SET) was normalized by dividing the burning time by the electrolyte mass. (cf: K. Xu, M. S. Ding, S. Zhang, J. L. Allen, T. R. Jow. – J.. Electrochem.Soc., **149**,A622 (2002))

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

- Reduced flammability with TPP-containing electrolytes.
- Similar tests are underway with higher amounts of TPP, and with other FRAs and with fluorinated so-solvents.

# 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  $\text{Li}_2\text{MnO}_3$  and  $\text{LiMO}_2$  are promising
    - Power capability of the materials, however requires further improvement.
    - Suitable morphology is critical for good performance and high tap (packing) density
    - 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<sub>2</sub> Cells. Formulations with higher proportions are looking promising.
    - Still requires further validation through abuse tests (e.g., on 18650 cells).

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