Energy Goals and Challenges for Future Space Exploration

J. Jeevarajan, Ph.D.
NASA-Johnson Space Center, Houston, TX
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Outline

- Power Needs for Exploration
- Technology Programs to Achieve Safe and High Energy Power Goals
- Summary and Conclusions

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Power Goals and Challenges

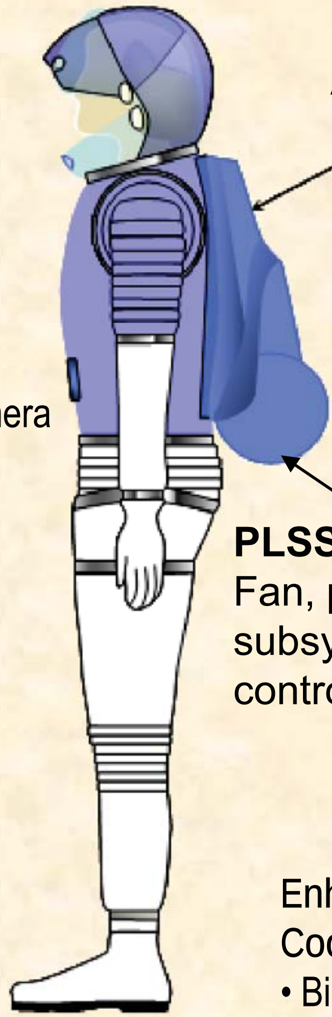
- Future exploration needs include very high energy density (~500 Wh/kg) batteries
- Batteries need to be safe under credible off-nominal conditions (no venting, fire, thermal runaway)
- Need modular power systems to go across different applications
  - Space vehicles
  - Astronaut Suit
  - Surface mobility systems
  - Habitats

Surface Systems (Mobility)
Pressurized Rover

Preliminary Power Requirements:
Safe, reliable operation
>150 Wh/kg at battery level
~ 500 cycles
270 V
Operation Temp: 0 to 30 C
Maintenance-free operation

(Advanced) Extravehicular Activity (EVA) Suit

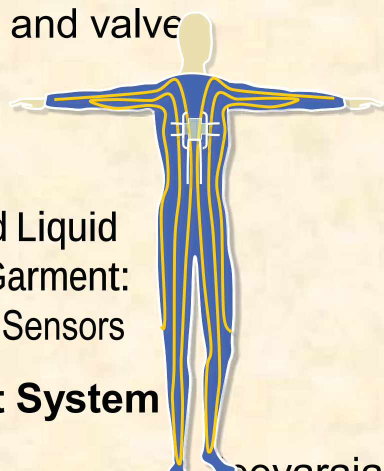
Enhanced Helmet Hardware:
- Lighting
- Heads-Up-Display
- Soft Upper Torso (SUT) Integrated Audio



Power / Communications, Avionics & Informatics (CAI):
- Cmd/Cntrl/Comm Info (C3I) Processing
- Expanded set of suit sensors
- Advanced Caution & Warning
- Displays and Productivity Enhancements

Video:
Suit Camera

PLSS:
Fan, pump, ventilation subsystem processor; Heater, controllers, and valve



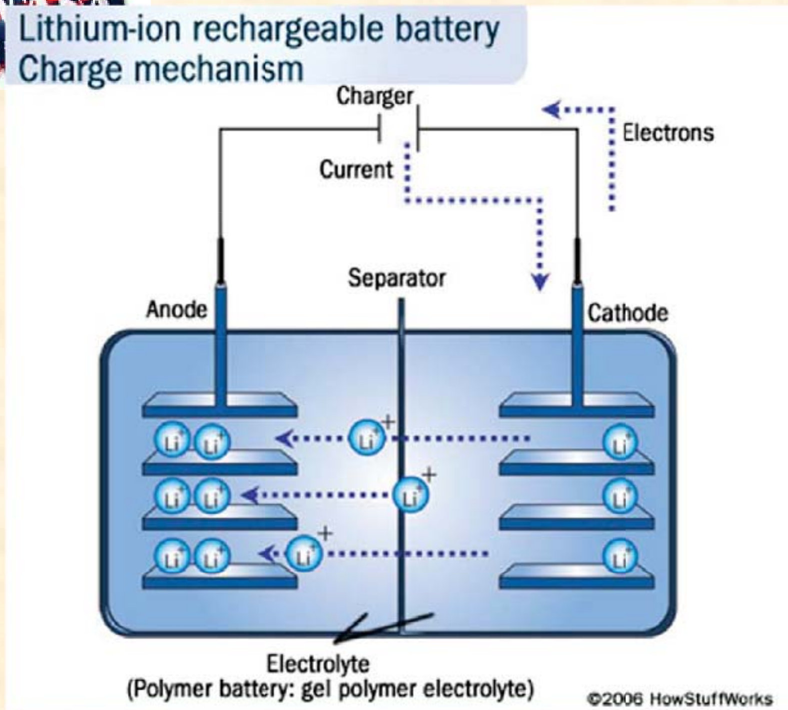
Enhanced Liquid Cooling Garment:
- Bio-Med Sensors

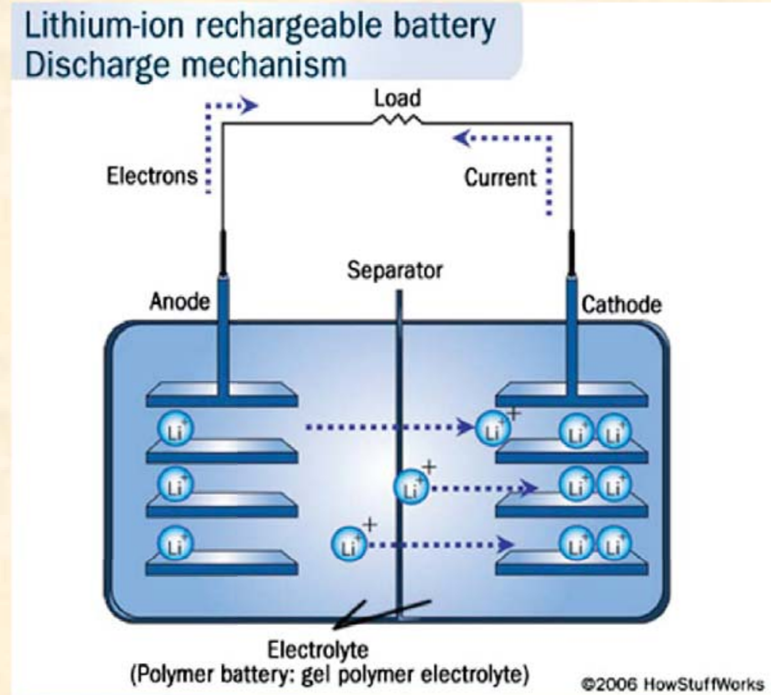
PLSS: Primary Life Support System

- Power to support 8-hour EVA provided by battery in Portable Life Support System
- Preliminary battery design goals:
  - Human-safe operation
  - 144 W (average) and 233 W (peak) power
    Assumes 1% connector loss and 30% margin for growth in power requirements
  - No more than 5 kg mass and 3 liter volume
  - 100 cycles (use every other day for 6 months)
  - 8-hour discharge to at most 85% depth-of-discharge
  - Temperature controlled to 0 to +30 °C
- Secondary batteries are considered critical for EVA Suit 2.

Current Suit Batteries:
EMU: 20.5 V; min 26.6 Ah (7 hr EVA), 9A peak, 5 yr, <15.5 lbs, 30 cycles
SAFER:42 V; 4.2 Ah (in emergency only)
REBA: 12.5 V, 15 Ah, (7 hr EVA); 5 yr, ~6 lbs
EHIP:6 V, 10.8 Ah; (7 hr EVA); 5 yr, ~1.8 lbs

Lithium-ion Chemistry





The half reactions are:

Cathode: $LiMO_2 \rightarrow Li_{1-x}MO_2 + xLi^+ + xe^-$

Anode: $C + xLi^+ + xe^- \rightarrow Li_xC$

The overall reaction is: $LiMO_2 + C \Leftrightarrow Li_xC + Li_{1-x}MO_2$

Cathode: Lithium metal oxide ($LiCoO_2$, $LiNi_{0.3}Co_{0.7}O_2$, $LiNiO_2$, LiV_2O_5, $LiMn_2O_4$, $LiNiO_{0.2}Co_{0.8}O_2$)

Anode: Carbon compound (graphite, hard carbon,etc. or Li titanate or Sn alloy, Si alloy or Si/C)

Electrolyte: $LiPF_6$ and a combination of carbonates

Separator: PE or PP/PE/PP

Key Performance Parameters for Battery Technology Development

Customer Need	Performance Parameter	State-of-the-Art	Current Value	Threshold Value	Goal
Safe, reliable operation	No fire or flame	Instrumentation/control-lers used to prevent unsafe conditions. There is no non-flammable electrolyte in SOA	Preliminary results indicate a moderate reduction in the performance with flame retardants and non-flammable electrolytes	Benign cell venting without fire or flame and reduce the likelihood and severity of a fire in the event of a thermal runaway	Tolerant to electrical and thermal abuse such as over-temperature, over-charge, reversal, and external short circuit with no fire or flame
Specific energy Lander: 150 – 210 Wh/kg 10 cycles Rover: 150 – 200 Wh/kg EVA: 200 – 300 Wh/kg 100 cycles	**Battery-level** specific energy*	90 Wh/kg at C/10 & 30 C 83 Wh/kg at C/10 & 0 C (MER rovers)	130 Wh/kg at C/10 & 30 C 120 Wh/kg at C/10 & 0 C	**135** Wh/kg at C/10 & 0 C "High-Energy"** **150** Wh/kg at C/10 & 0 C "Ultra-High Energy"**	**150** Wh/kg at C/10 & 0 C "High-Energy" **220** Wh/kg at C/10 & 0 C "Ultra-High Energy"
	Cell-level specific energy	130 Wh/kg at C/10 & 30 C 118 Wh/kg at C/10 & 0 C	150 Wh/kg at C/10 & 0°C	**165** Wh/kg at C/10 & 0 C "High-Energy" **180** Wh/kg at C/10 & 0 C "Ultra-High Energy"	**180** Wh/kg at C/10 & 0 C "High-Energy" **260** Wh/kg at C/10 & 0 C "Ultra-High Energy"
	Cathode-level specific capacity $Li(Li,NiMn)O_2$	140 – 150 mAh/g typical	$Li(Li_{0.17}Ni_{0.25}Mn_{0.58})O_2$: 240 mAh/g at C/10 & 25°C $Li(Li_{0.2}Ni_{0.13}Mn_{0.54}Co_{0.13})O_2$: 250 mAh/g at C/10 & 25°C 200 mAh/g at C/10 & 0°C	**260** mAh/g at C/10 & 0 C	**280** mAh/g at C/10 & 0 C
	Anode-level specific capacity	320 mAh/g (MCMB)	320 mAh/g MCMB 450 mAh/g Si composite	**600** mAh/g at C/10 & 0 C with Si composite	**1000** mAh/g at C/10 0 C with Si composite
Energy density Lander: 311 Wh/l Rover: TBD EVA: 240 – 400 Wh/l	**Battery-level** energy density	250 Wh/l	n/a	**270** Wh/l "High-Energy" **360** Wh/l "Ultra-High"	**320** Wh/l "High-Energy" **420** Wh/l "Ultra-High"
	Cell-level energy density	320 Wh/l	n/a	**385** Wh/l "High-Energy" **460** Wh/l "Ultra-High"	**390** Wh/l "High-Energy" **530** Wh/l "Ultra-High"
Operating environment 0°C to 30°C, Vacuum	Operating temperature	-20°C to +40°C	-50°C to +40°C	**0°C** to **30°C**	**0°C** to **30°C**

Assumes prismatic cell packaging for threshold values. Goal values include lightweight battery packaging.

* Battery values are assumed at 100% DOD, discharged at C/10 to 3.0 volts/cell, and at 0°C operating conditions

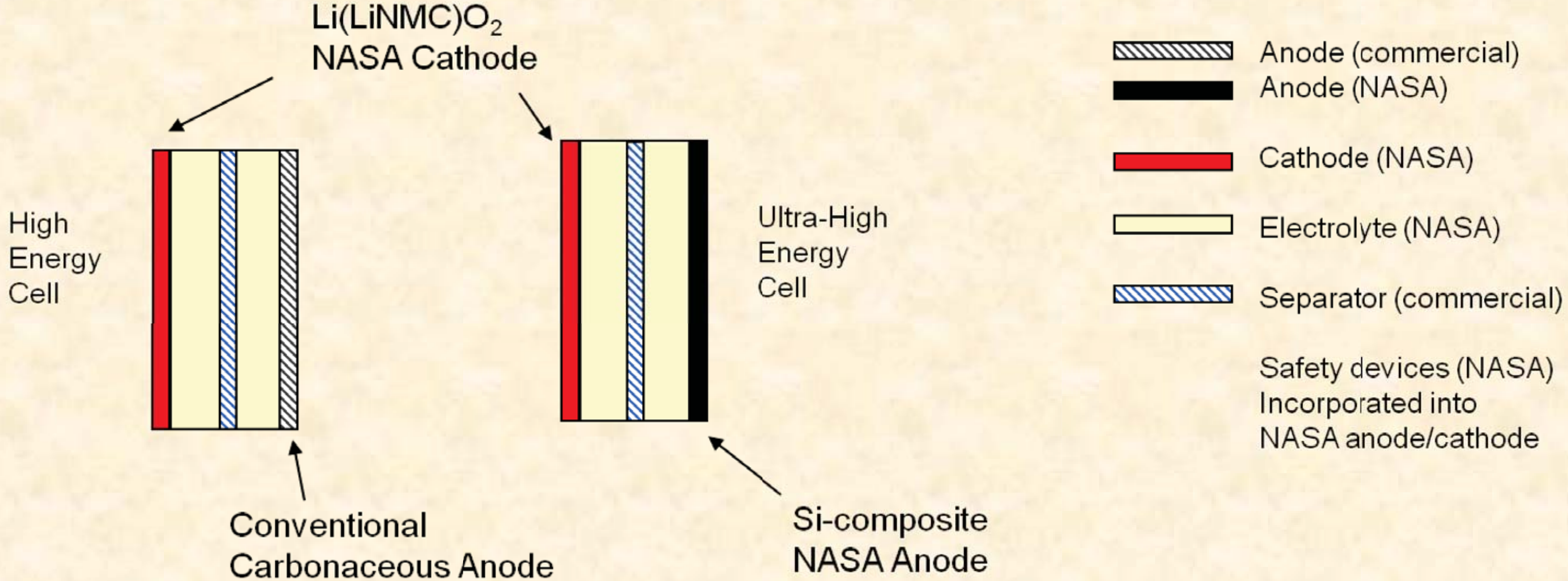
** "High-Energy" = Exploration Technology Development Program cathode with MCMB graphite anode
"Ultra-High Energy" = Exploration Technology Development Program cathode with Silicon composite anode

Revised 06/02/2008

Space Power Systems (SPS) Li-ion Cell Development

- **Component-level goals** are being addressed through a combination of NASA in-house materials development efforts, NASA Research Announcement contracts (NRA), and grants
- Materials developed will be delivered to NASA and screened for their electrochemical and thermal performance, and compatibility with other candidate cell components
- Other activities funded through NASA can be leveraged – NASA Small Business Innovative Research (SBIR) Program and Innovative Partnership Program (IPP)
- Leveraging off other government programs (DOD, DOE) for component-level technology
- Leveraging off other venues through Space Act Agreements (SAA) that involve partnerships with industry partners such as Exxon; non-profit organizations such as Underwriters Laboratory (UL), etc.

Energy Storage Project Cell Development for Batteries



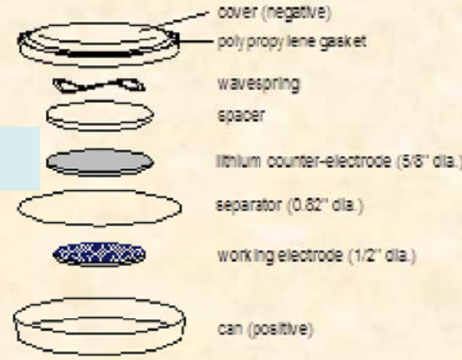
"High Energy" Cell
Baseline for EVA and Rover
Lithiated-mixed-metal-oxide cathode / Graphite anode
$Li(LiNMC)O_2$ / Conventional carbonaceous anode
150 Wh/kg (100% DOD) @ battery-level 0^0C C/10
80% capacity retention at ~**2000** cycles

"Ultra-High Energy" Cell
Upgrade for EVA and Altair, possibly Rover
Lithiated-mixed-metal-oxide cathode / Silicon composite anode
$Li(LiNMC)O_2$ / silicon composite
220 Wh/kg (100% DOD) @ battery-level 0^0C C/10
80% capacity retention at ~**200** cycles

Cell Development

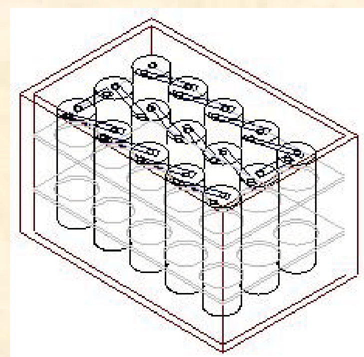
- **Assess components**
  - Build and test electrodes and screening cells (Coin and Pouch)
  - Provide manufacturing perspective from the start
- **Scale-up components**
  - Transition components from the lab to the manufacturing floor
- **Build baseline cells (10 Ah):**
  - graphite anode (MPG-111) with nickel-cobalt cathode (NCA)
  - Determine baseline performance
- **Build and test evaluation cells (10 Ah):**
  - Determine component interactions
  - Determine cell-level performance

Coin Cell



Pouch Cell

DD Cells



Cathode Development
Led by JPL

- **Goals:**
  - Specific capacity of 280 mAh/g at C/10 and 0°C to 3.0 V
  - High voltage operation to 4.8 V
  - Improved thermal stability over conventional Li-ion cathodes

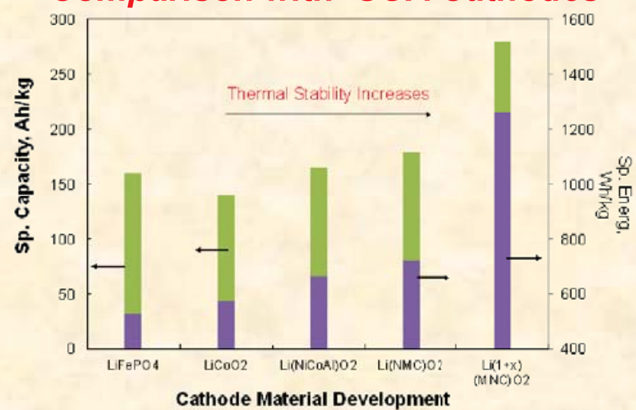
Technology Challenges	Current Project Approaches to Address
High specific capacity at practical discharge rates	•Vary stoichiometry to determine optimum chemical formulation •**Reduce particle size** •Experiment with different synthesis methods to produce materials with physical properties such that their specific capacity is retained on production scale
Low volume per unit mass	•Vary cathode synthesis method to optimize properties that can: •Improve energy density •Improve ability to cast cathode powders •Facilitate incorporation of oxide coatings, which have the potential to increase rate capability and reduce capacity fade to extend cycle life
Minimize 1st cycle irreversible capacity loss and irreversible oxygen loss	•Surface modification via coatings to improve cathode-electrolyte interfacial properties •Improves capacity retention •Reduces capacity fade

High Specific Energy Cathodes for Li-ion cells

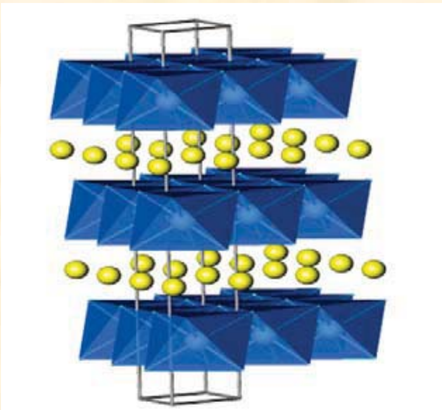
Lithium- excess Layered-Layered composites of Li_2MnO_3 and $Li(Mn,Ni,Co)O_2$.

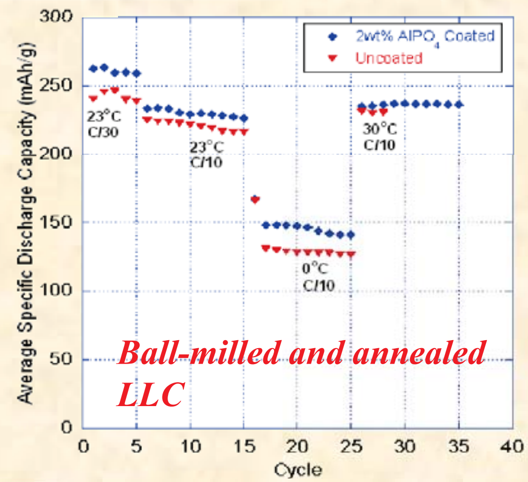
- High capacity > 250 mAh/g achieved from optimized composition of transition metal ratio and Li content
- High tap densities (1.5-2.0 g/cc) and spherical morphology realized from hydroxide precursor synthesis.
- Demonstrated improved performance (high reversible and low irreversible capacity, and cyclic and thermal stability with surface coatings, ($AlPO_4$ & $LiCoPO_4$)
- Developed new 'mechanical' method (ball milling) for high specific energy and high (tap density) cathodes.
- Understood the First cycle irreversible capacity (Oxygen evolution without Li)
- Developed new efficient coatings amenable for scale-up
- Evaluated cathode material of similar composition from several commercial sources.
- Cathode material scale-up been partly successful (Li content higher than desired, which contributed to poor performance)

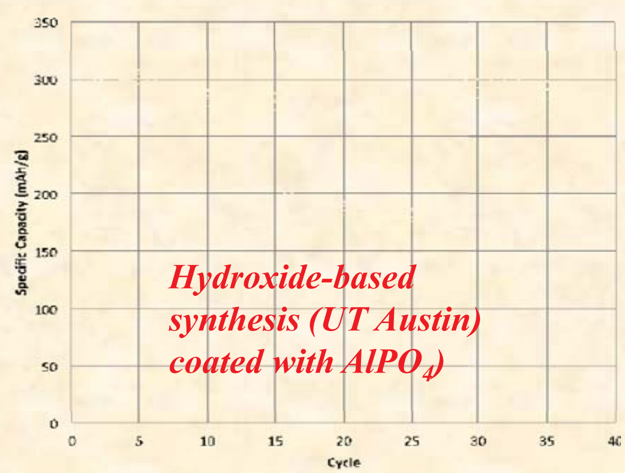
Comparison with SOA Cathodes

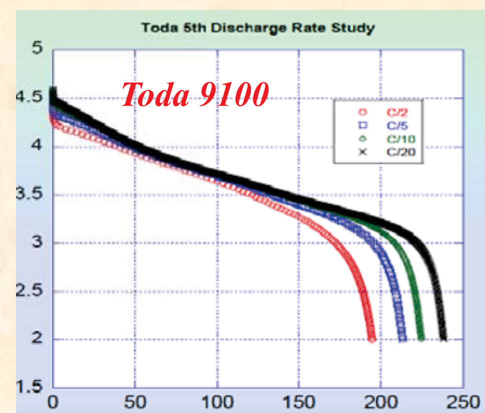


Layered Structure







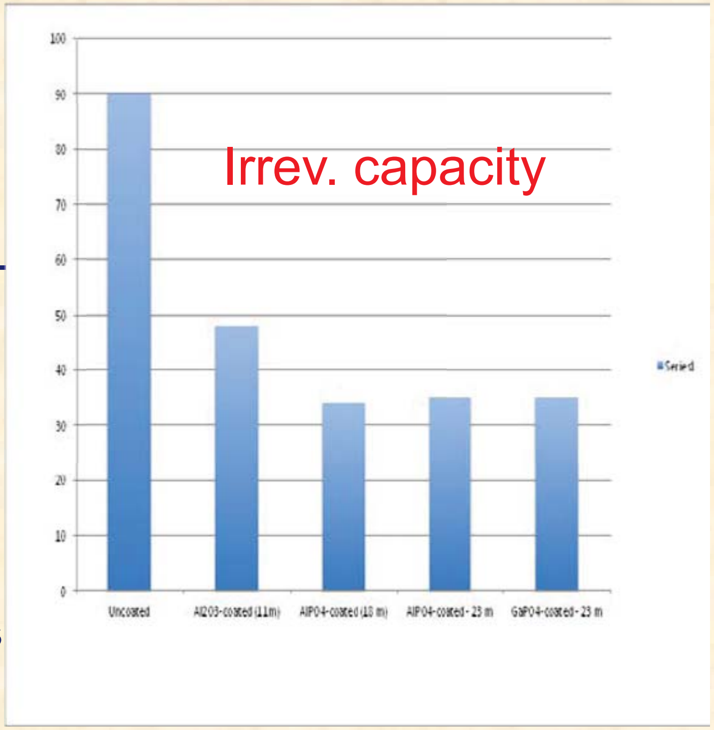


Proposed Activities to improve NMC material: Coatings

It is well known that **coatings reduce irreversible capacity and can improve cycle life / kinetics.**
We currently use $AlPO_4$ coatings as our baseline.

The following two ideas can improve performance if needed -

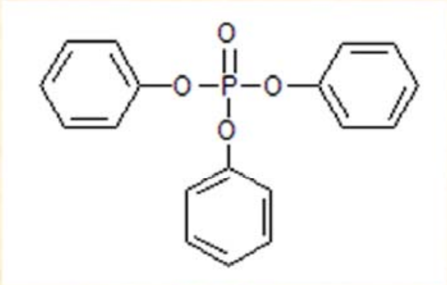
- **Dual coating of graphene and $AlPO_4$** can improve rate capability
  - Graphene provides electrically conductive layer between lithiated material and $AlPO_4$
  - This should improve the flow of ions, providing better performance at C/10
  - Has also been shown to provide better cyclic stability, perhaps because it creates a more conformal coating.



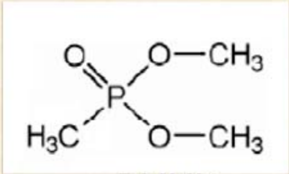
- **Fluorination of dry powders** can improve scale up
  - Metal fluorides formed via direct fluorination of dry powders can provide a more uniform coating.
  - Simpler process helps with scale up.
  - Uniformity is important because reactive surfaces should not be exposed to the electrolyte. Unwanted electrolyte reactions can cause deposits that increase impedance.
  - Uniform coating should reduce metal dissolution out of cathode particles.

Key Accomplishments: Electrolytes

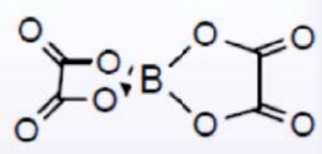
- Developed new electrolytes with reduced flammability (and thus enhanced safety) and high voltage compatibility for Li-ion cells.
  - Developed low –flammability electrolytes capable of operating at high voltages.
  - Various amounts of flame retardant additive (triphenyl phosphate – 5-15%) with ‘no 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.
  - Delivered ~ 3 liters of Gen-2 and Gen-3 electrolytes to Saft for insertion into prototype cells (and to GRC for laboratory testing).
  - 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.



TPP
(triphenyl phosphate)

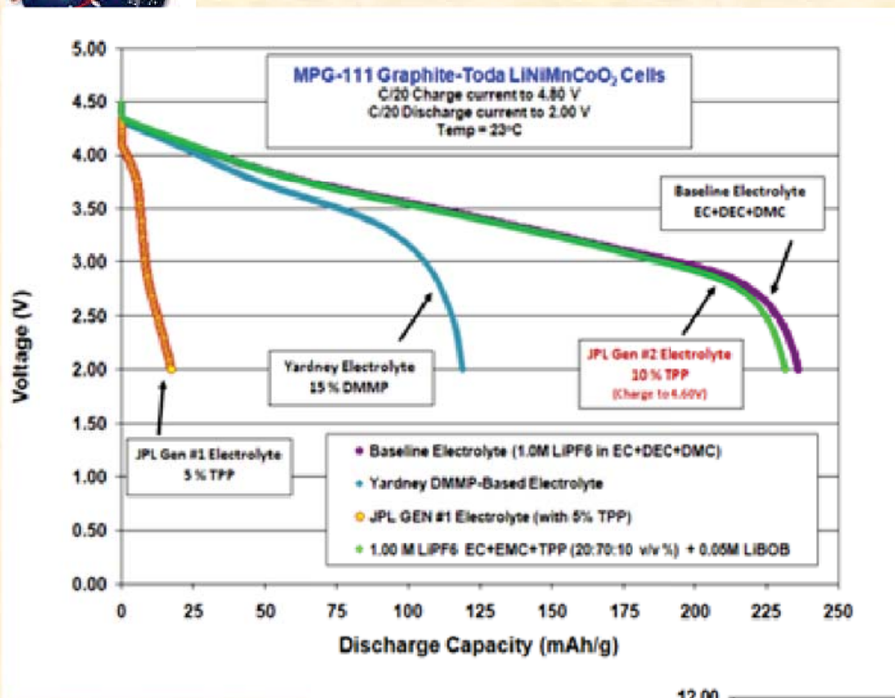


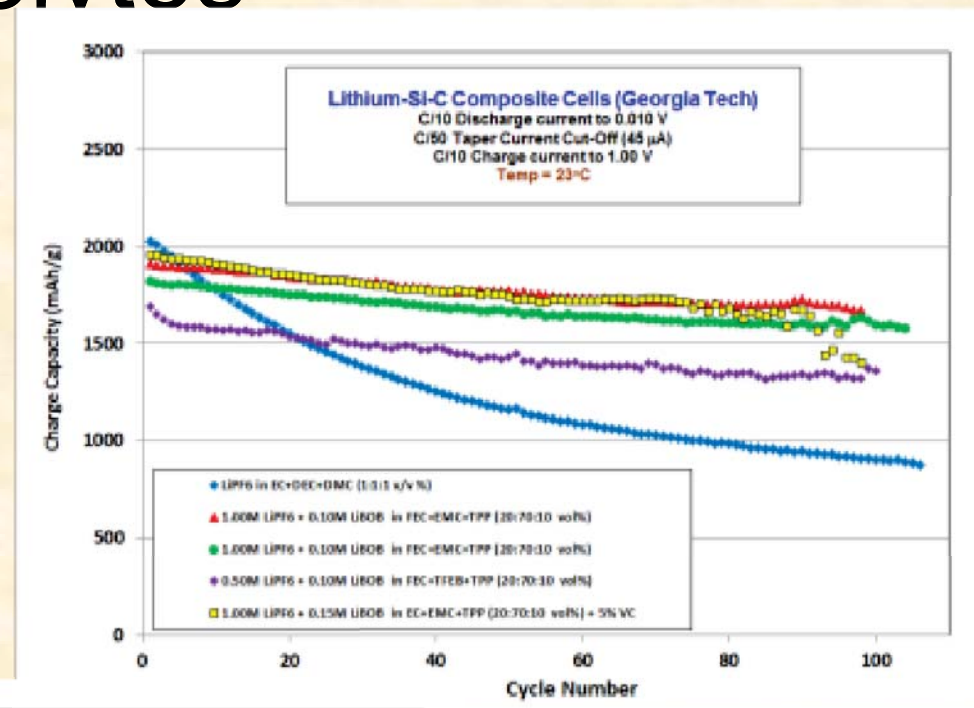
DMMP
(Dimethyl methyl phosphanate)

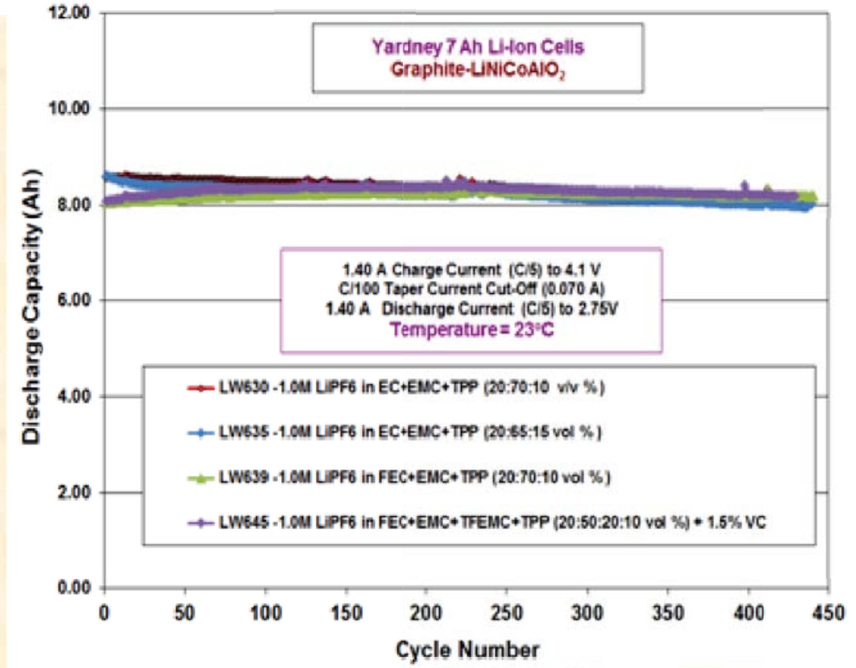


$LiB(C_2O_4)_2$ (LiBOB)

Electrolytes







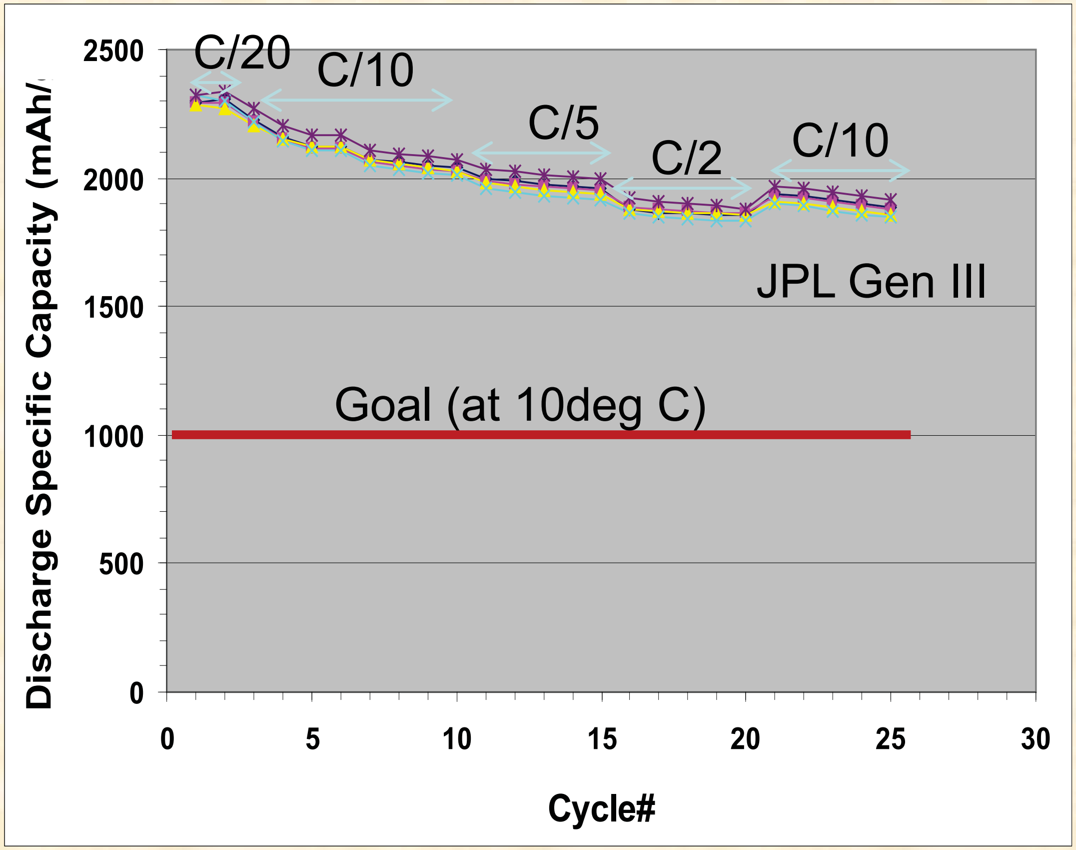
Anode Development
Led by NASA GRC

- **Goal:** 1000 mAh/g at C/10 (10 hour discharge rate) and 0°C
  - Over 3 times the capacity of SOTA (State-of-the-art) Li-ion anodes
  - Threshold value = 600 mAh/g at C/10 and 0°C

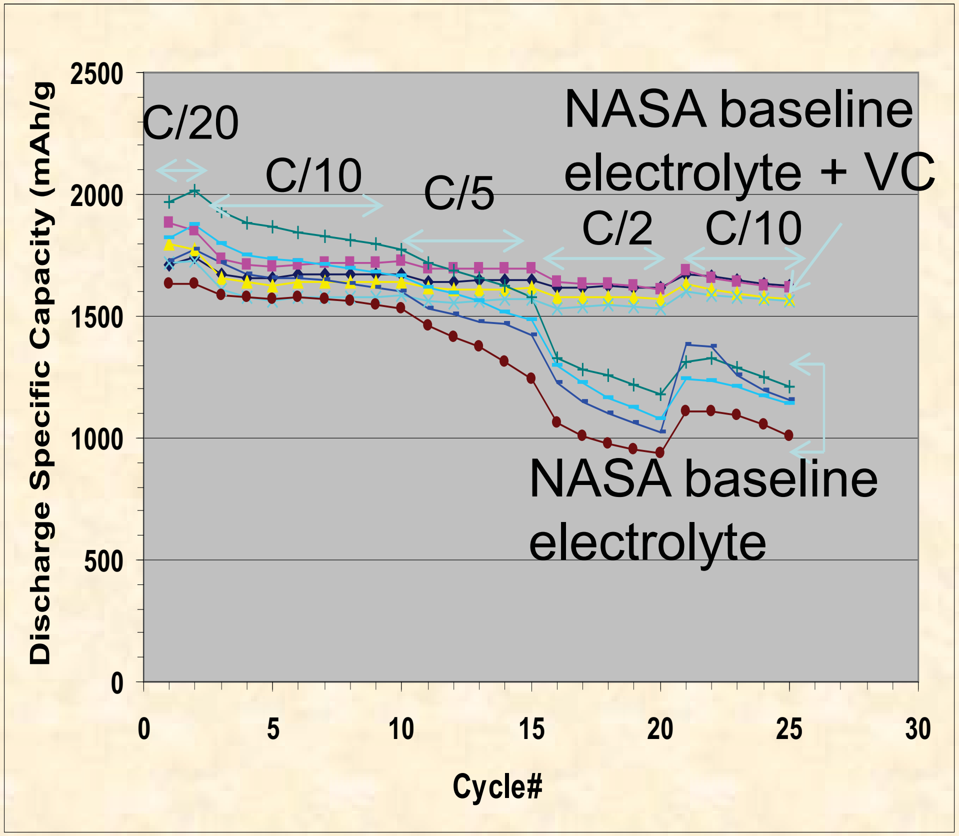
Technology Challenges	Current Approaches to Address
Minimize volume expansion during cycling	•Pursuing various approaches to optimize the anode structure to accommodate volume expansion of the silicon •Nanostructured Si composite absorbs strain, resists active particle isolation on cycling •Incorporation of elastic binders in Si –graphite and Si-C matrices •Improvement of mechanical integrity by fabricating structure to allow for elastic deformation
Minimize irreversible capacity loss	•Protection of active sites with functional binder additives •Pre-lithiation approaches are possible •Nanostructured Si resists fracture and surface renewal
250 cycles	Loss of contact with active particles reduces cycle life. Addressing volume changes and improvement of mechanical integrity will improve cycle life

Si Anode Successfully Scaled up by Saft Rate Characterization at Coin Cell Half Cell

Si Anode made by Saft (2nd, calendared)



Si Anode (GT-4B)



- Saft successfully scaled up Si anode:
  Si anode made by Saft shows the highest capacity and excellent rate capability cycling which is much higher than 1000 mAh/g (the goal)
- VC in baseline electrolyte improves rate capability cycling

The Path Forward - Silicon/NCA showing progress

In-Work:

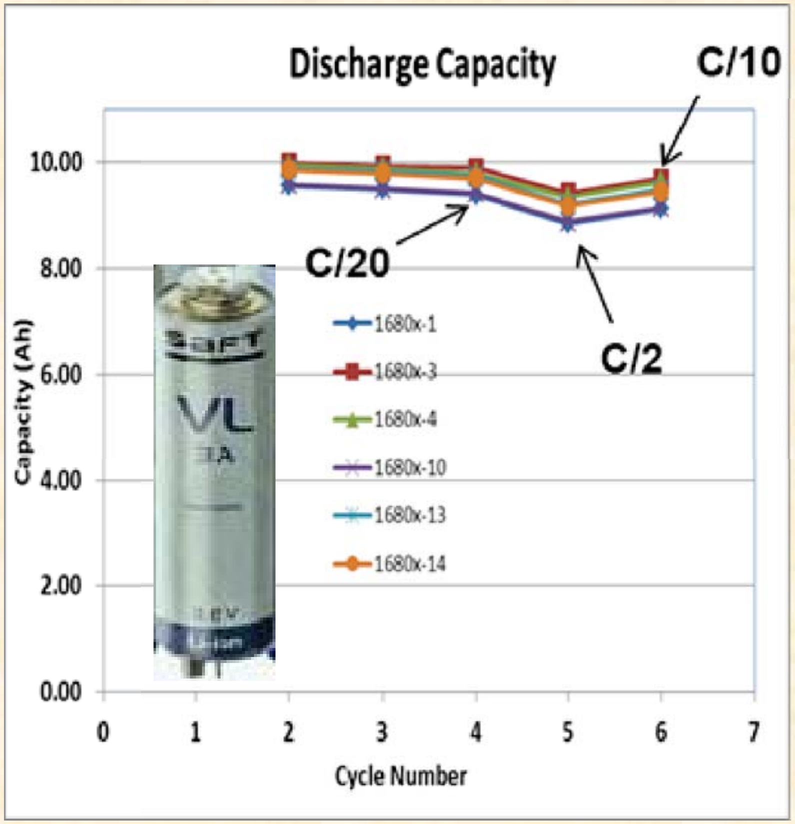
Silicon-composite anode cells being built with NCA

(Saft Cell Build #3)

- Projection shows 168 Wh/kg in VL3A using "low loaded" anode
  - Projected to achieve 211 Wh/kg in large capacity optimized cells (52Ah)
  - Performance will increase with higher loading.
- Cell assessment will include performance, safety, and life.

Proposed:

- Fabricate cells using the highly loaded Si-composite anode. 50 Ah prismatic cells would be a good option.
- Work with two vendors for anode development.
- 1000 mAh/g should exceed 500 cycles; if only 200 cycles are needed, higher loading can increase performance (Wh/kg). Target 1400 mAh/g.

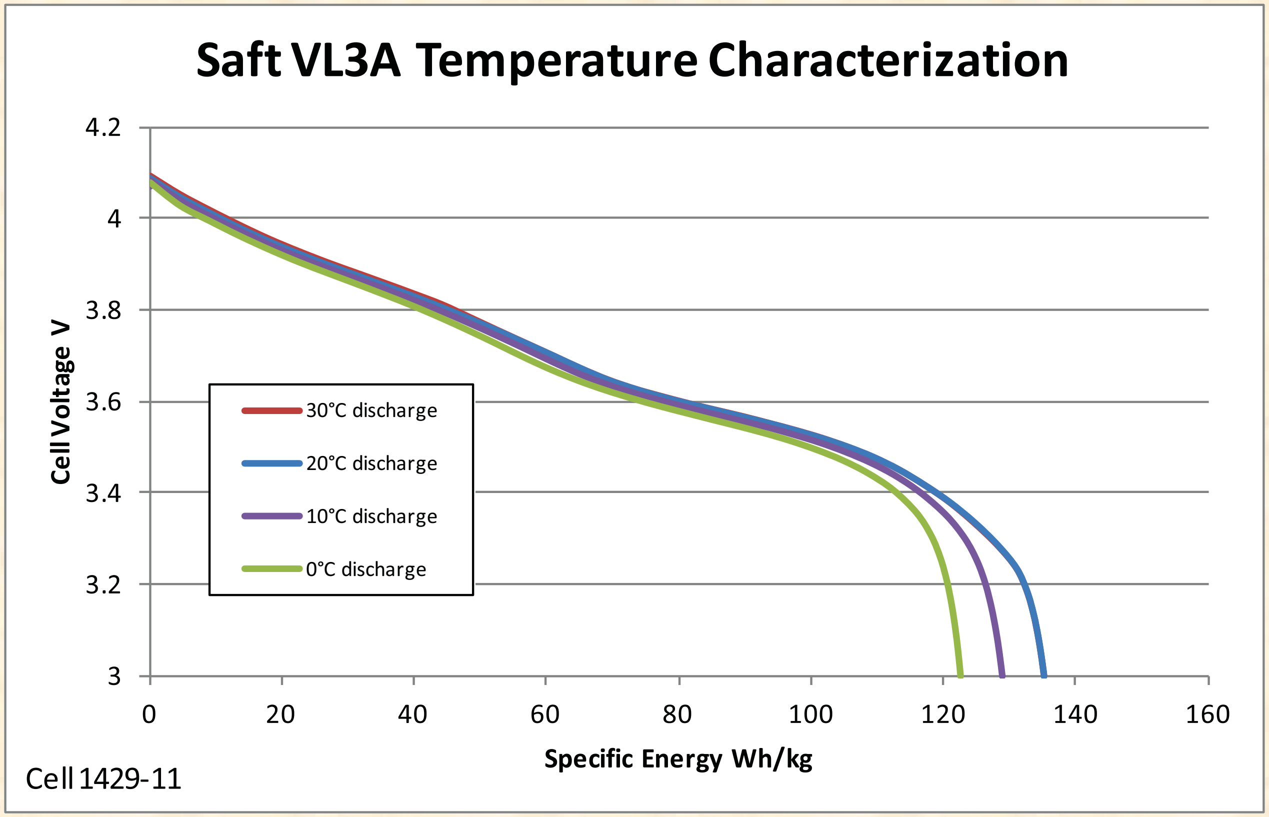


VL3A cells built with "low loading" GIT anode, JPL Gen III electrolyte, and NCA cathodes. Compare to commercial VL3A cells which yield only 3 Ah.

6/21/2012 data from Saft

Characterization of Saft VL3A Baseline Cells

- VL3A baseline cells were cycled under same profile as DD baseline cells
- Among 11 cells, an average of 135 Wh/kg was delivered at 20°C
  - Cells delivered 90.8% of 20°C capacity when tested at 0°C
  - Performance at 20°C and 30°C roughly overlaps
  - Variability among the 11 cells was minimal
  - Rate characterization of remaining 9 cells is ongoing



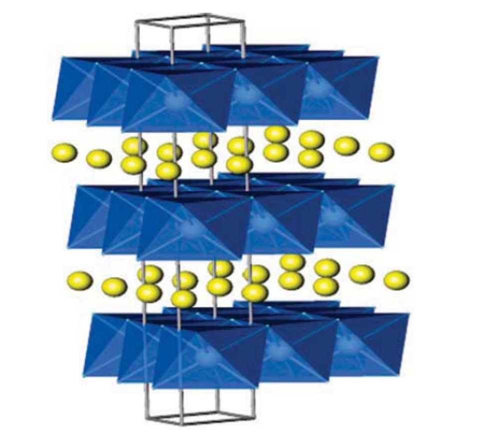
Opportunities Exist to Improve Components

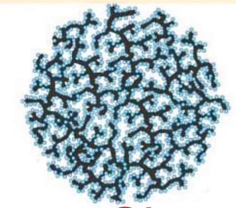
- **High Energy NMC Cathodes**
    - Scale up of the NASA-process
    - High Irreversible capacity loss, especially with uncoated cathode
        - Non-availability of lithium at the anode for the irreversible capacity.
    - Electrolyte consumption (and anode dry out) due to O_2 evolved in formation
    - Transition metal dissolution in electrolytes (Mn, Ni and Co)
    - Low power densities, more noticeable with high electrode loadings
    - Voltage slump during cycling due to “spinel formation”

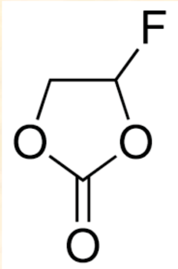
- **Si composite anodes**
    - Limited cycle life (< 500)
    - High irreversible capacity (10-20%) and poor coulombic efficiency
    - Unknown compatibility with the high energy cathode (dissolved metal?)

- **Electrolytes**
    - Changes to the cathode or anode may require electrolyte modification

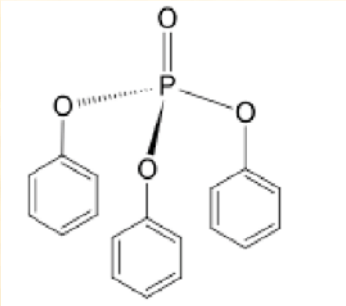
- **Cell Design**
    - Electrolyte dry out at the anode, when combined with HE-NMC cathode


HE-NMC Cathode


Nano-Si anode



FEC



Triphenyl phosphate (TPP)

Current State for Safety of Li-ion Batteries

Although the chemistry is one that can provide very high energy density at this time, it is not the safest

- NASA human-rated safety requirement is two-fault tolerance to catastrophic failures – leakage of electrolyte (toxicity hazard), fire, thermal runaway

Hazards are encountered in Li-ion cells/ batteries typically during

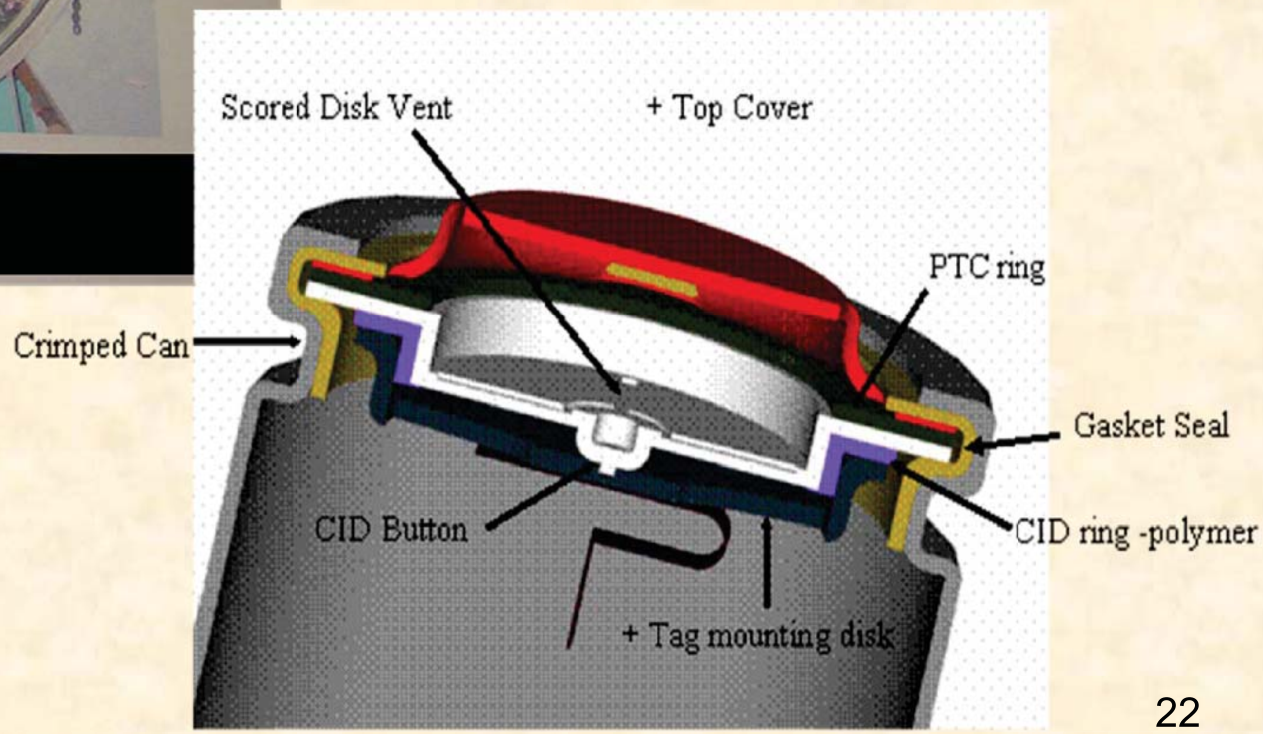
- Overcharge/overvoltage
- External shorts
- Repeated overdischarge with subsequent overvoltage
- High thermal environments
- Internal Shorts

Overcharge of Li-ion Cell Module

41S 5P

[redacted]

Overcharge limit: 5.5 V/Cell
Thermal runaway after 4.8 V/Cell
Highest temp Observed before thermal runaway: 248 ºC



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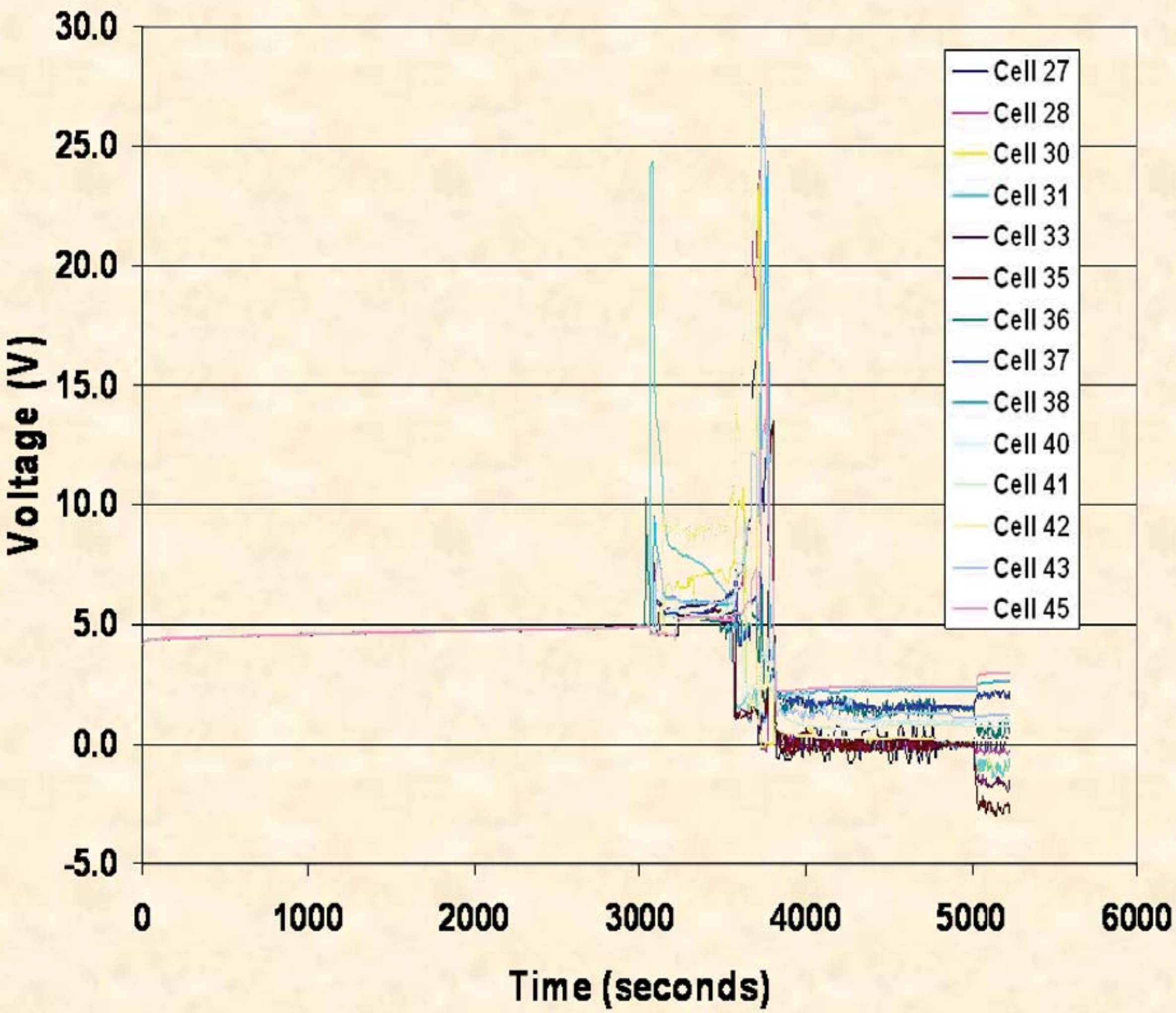
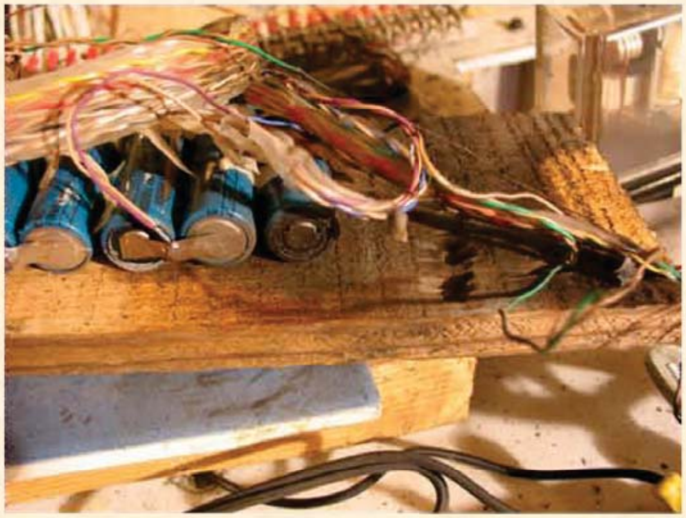
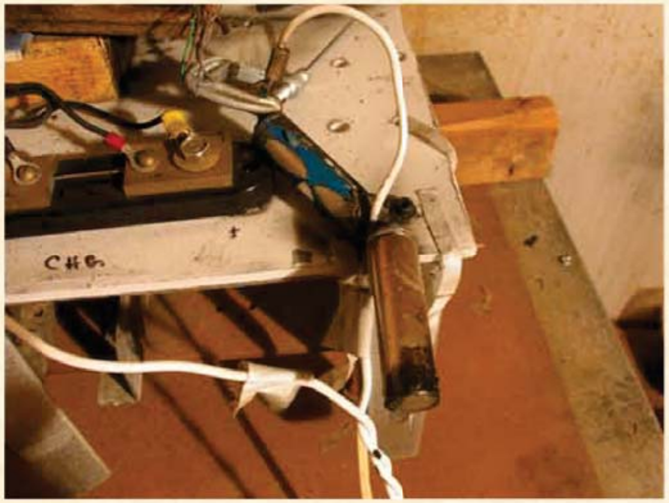
Overcharge Test on a 14-Cell String Showing Cell Voltages for the Sony Li-ion Cells



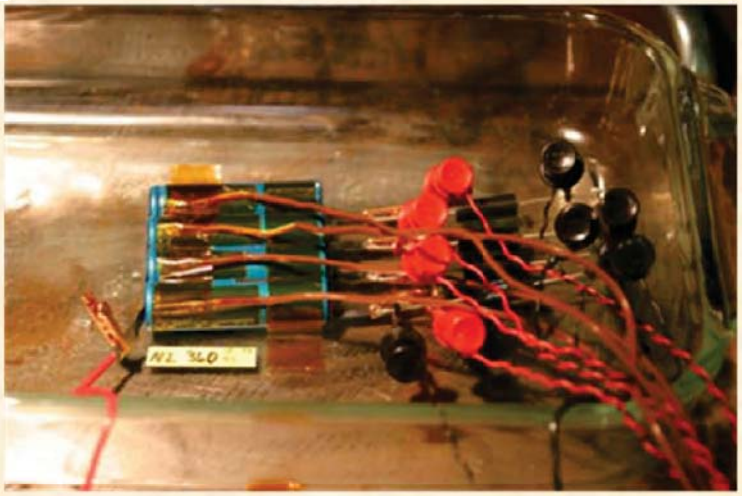


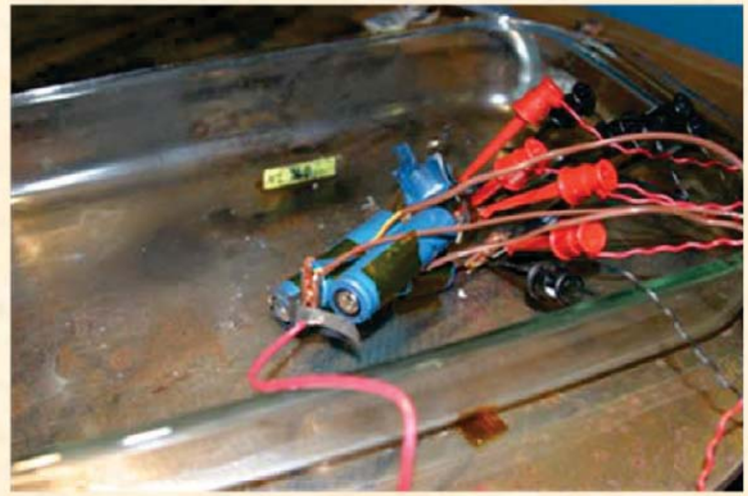


Missing : 27, 28, 30 and 31

Cells 37, 38 and 45 showed no visible Signs of venting

48V 6A Overcharge on 4P Battery





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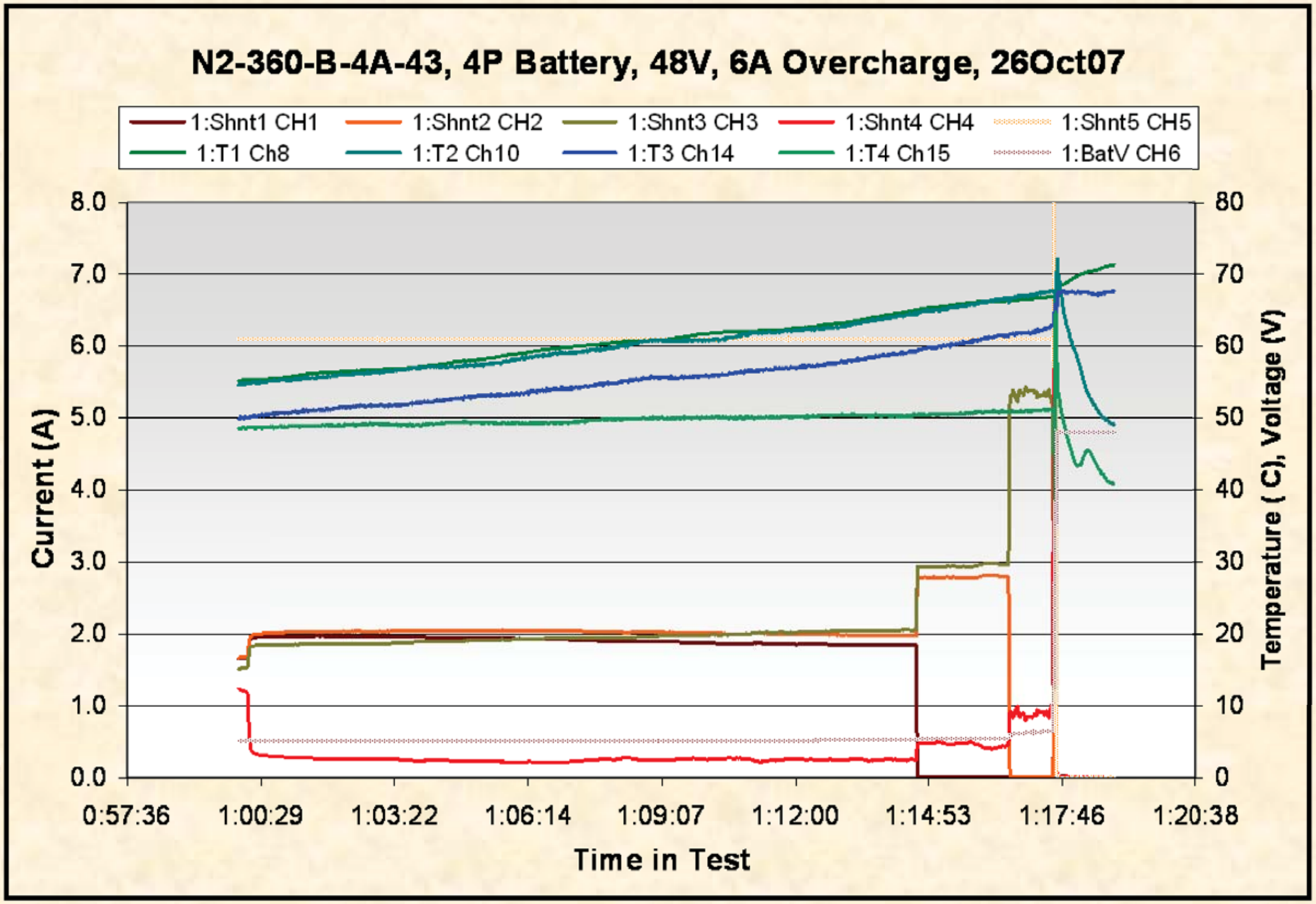
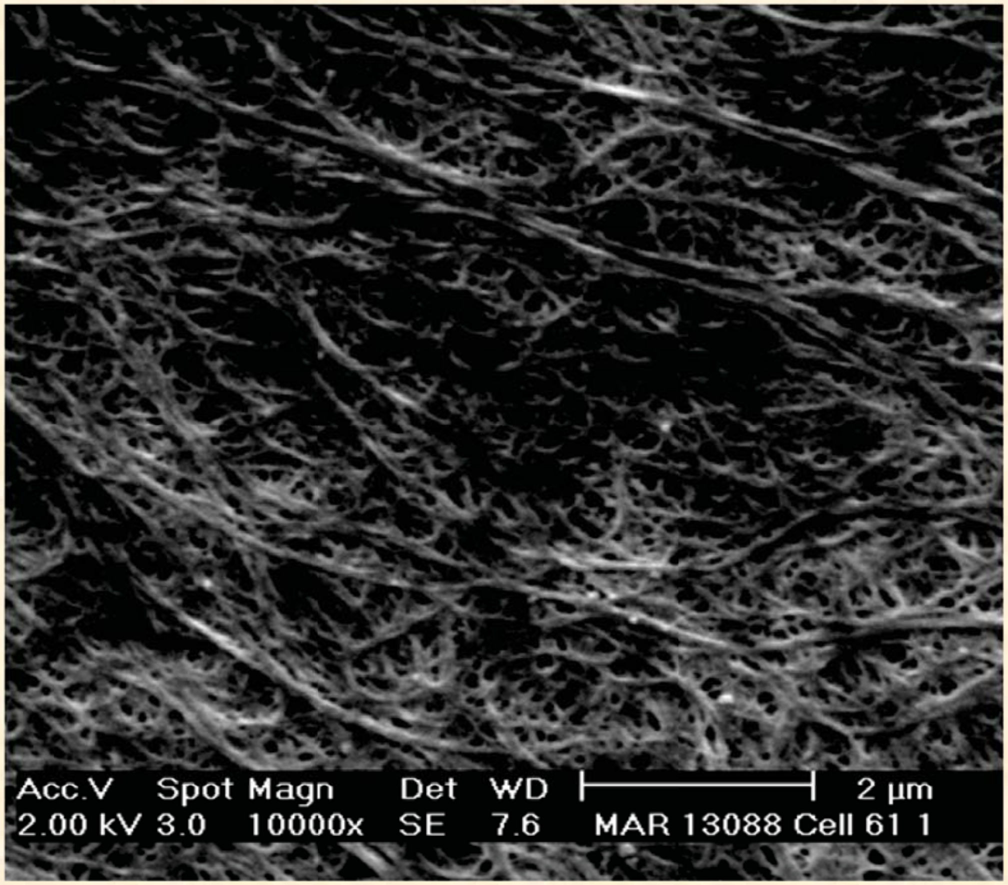
48V 6A Overcharge on 4P Battery

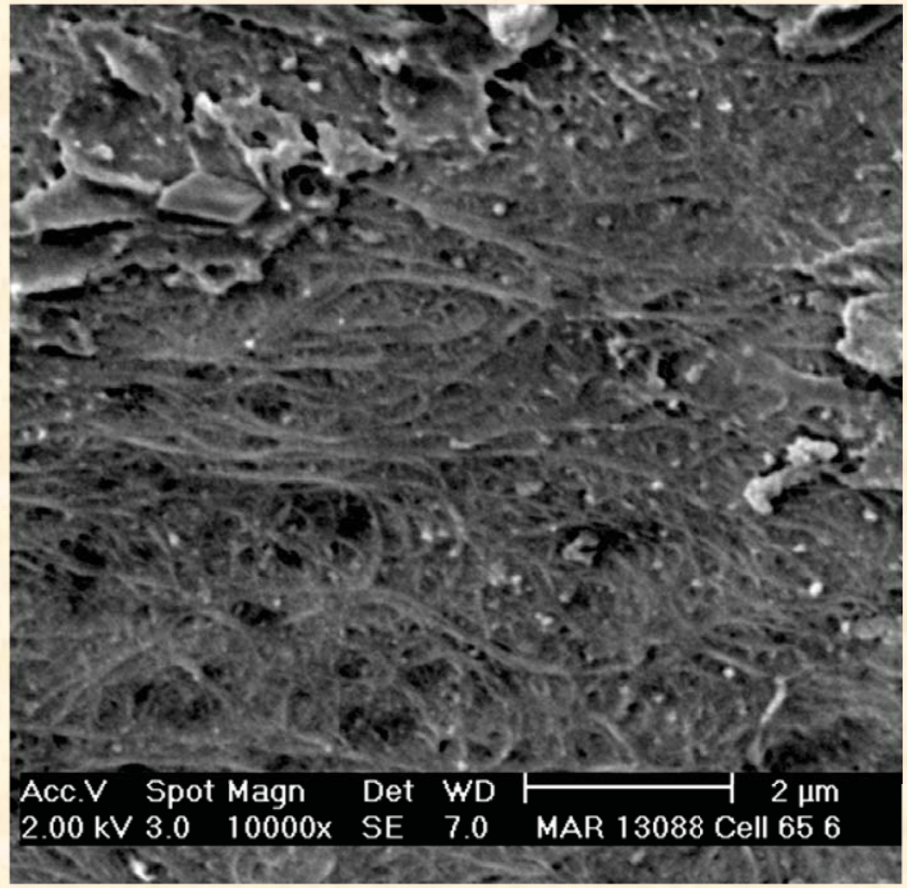


- The current on cell 4 in the parallel battery dropped low at ~1 hour into the overcharge; 14 minutes later the three other cells began to trip CID devices (a pop was audible) in sequence
- When the 3 cells dropped out, cell 4 was left carrying the 6A charge current.
- Cell 4 ruptured with flame (explosion); The cell can was split; temperature of the cell at the time of the event was 51°C

Current Separators in Commercial-off-the-Shelf Li-ion Cells



Unactivated Separator

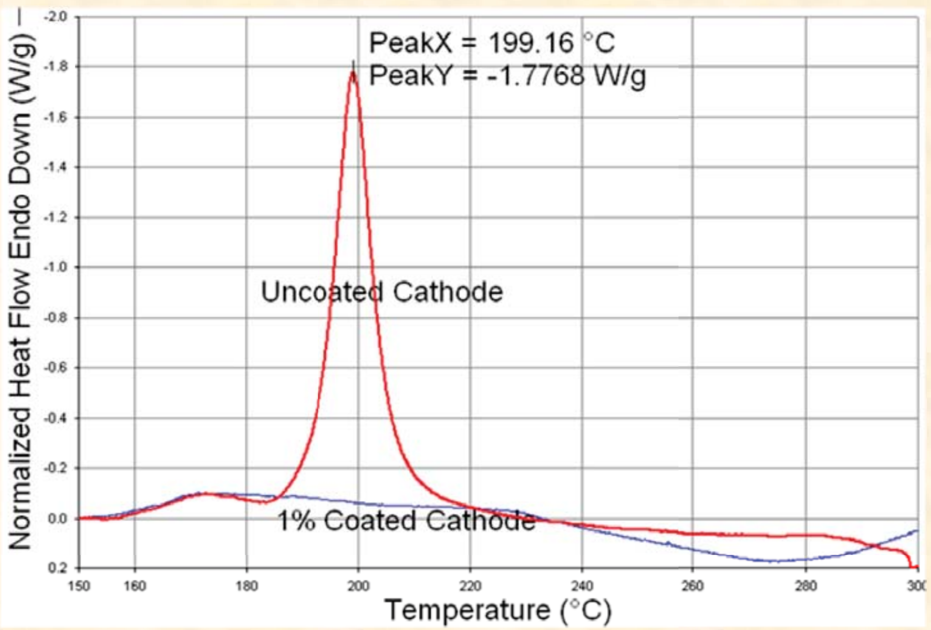


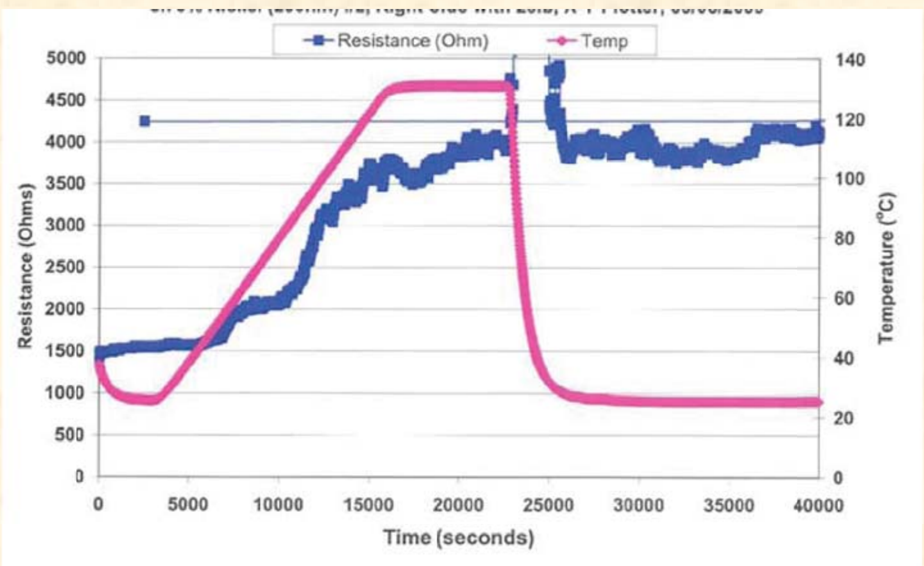
Activated Separator

Shut-down temperature is very close to temperature at which initiation of thermal runaway occurs.

Safety Component Development Led by NASA JSC

- Development of internal cell materials (active or inactive) designed to improve the inherent safety of the cell
  - Approach 1: Develop a high-voltage stable (phosphate type) coating on cathode particles to increase the safe operating voltage of the cell and reduce the thermal dissipation by the use of a high-voltage stable coating material. (Nano-sized material)
  - Approach 2: Develop a composite thermal switch to shutdown cell reactions safely using coatings on the current collector substrates (nano-particle metals)





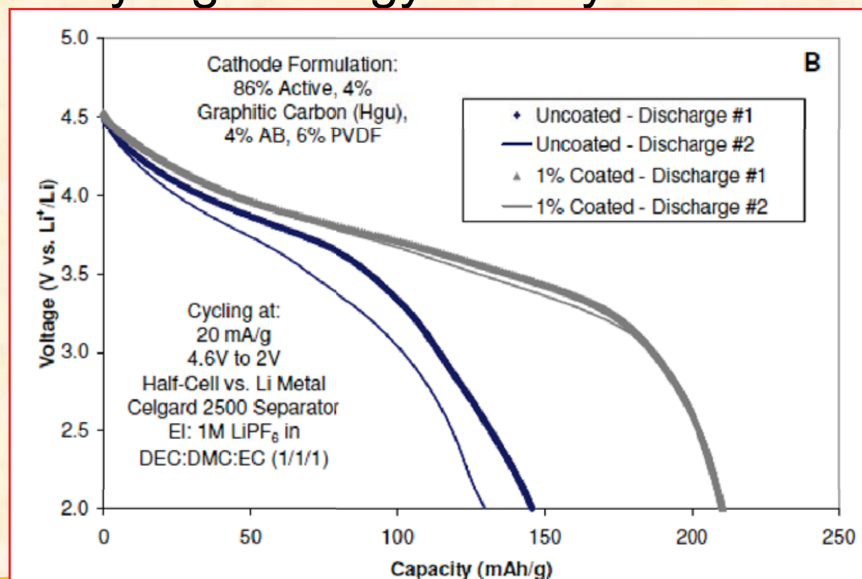
PSI

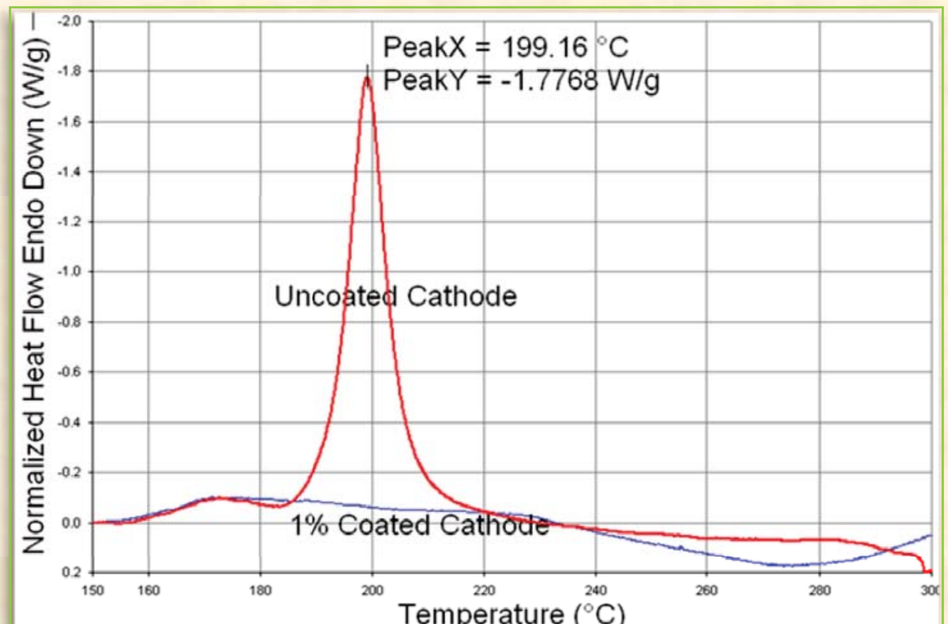
PSI formed lithium metal phosphate coatings on metal oxide cathodes by thermal treatment of a mixture of metal phosphate and the cathode.[1]

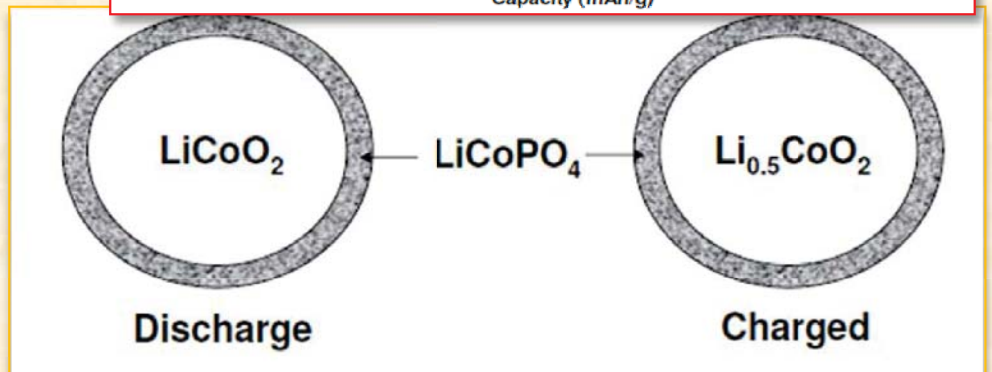
[1] H. Lee, M. Kim, J. Cho, *Electrochemistry Communications, 9 (2007) 149–154.*

Benefits of Coating:

- Coating is a lithium conductor.
- Metal phosphates offer greater stability than their metal oxide counterparts.
- Coating technique can be applied to protect any high energy density cathode material.
- Common processing steps allowing for low cost manufacturing.

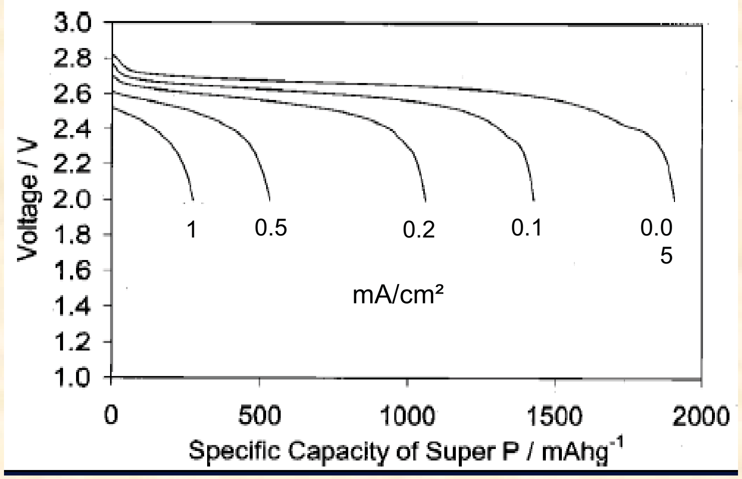






Li-O_2 and Li-air: ~ TRL 2

Characteristics:
Ultra-low mass
600 to 2200 mAh/g of cathode depending upon current density (rate)



Journal of The Electrochemical Society, **149** (9) A1190-A1195 (2002)

2.5 V avg. with 630 mAh/g carbon, 0.5

Li-O_2 and Li-air	Wh/kg	Wh/liter
electrochemical	587	880
pouch cell	473	617

2.3 V avg. with 300 mAh/g carbon, 1.0 mA/cm^2

Li-O_2 and Li-air	Wh/kg	Wh/liter
electrochemical	329	526
pouch cell	279	381

*Projections are for "free" air (neglect O2 storage)

Challenges:
•Recharge capability
•Capacity of carbon to store Li discharge products
•Rate capability

Li-S: ~ TRL 3

Characteristics:
High specific capacity (1600 mAh/g S theoretical)
2-plateau discharge

Projection for 2-plateau discharge
Assume 1000 mAh/g S

Li-S	Wh/kg	Wh/liter
electrochemical	610	864
pouch cell	474	595

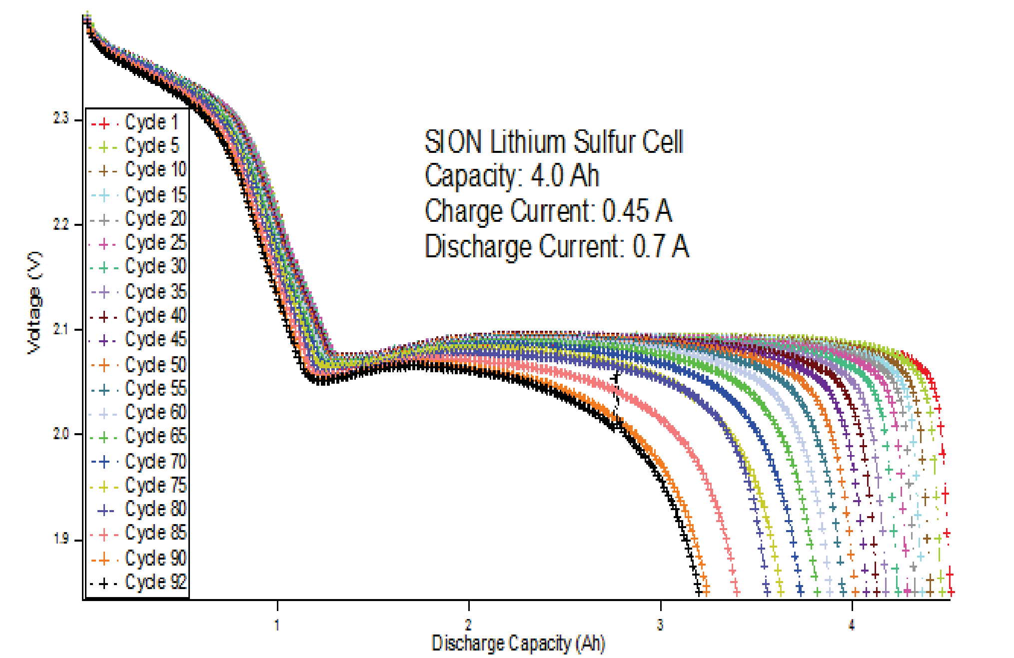


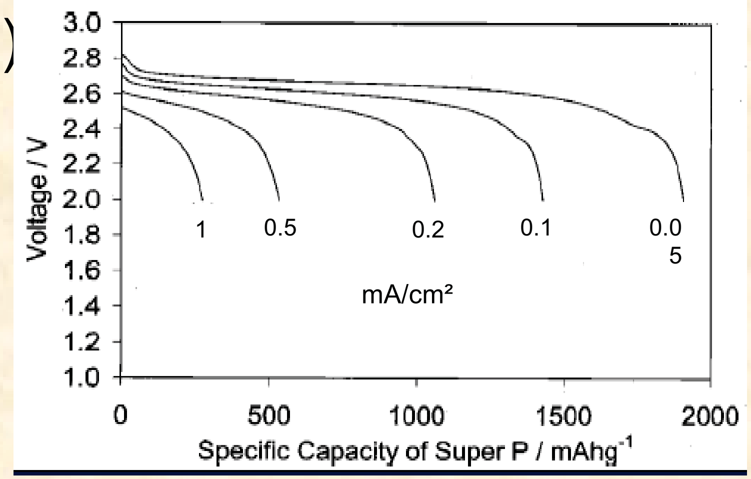
Figure 17: Sion Lithium Sulfur Cell ID# 20F Rate Capability Protocol #2 Data

Demonstrated in 4 Ah pouch cells (JSC):
BOL: 393 Wh/kg
EOL: 256 Wh/kg
75 cycles to 80% of initial capacity

Challenges:
Safety (rechargeability, lithium dendrite formation)
Cycle life

Li-O_2 with Oxygen Included: ~TRL 2

Impact of oxygen storage (mass and volume)



Journal of The Electrochemical Society, **149 (**9) A1190-A1195 (2002)

Assume:
2000 psia storage pressure
10% excess O_2
Include estimated mass of pressure vessel
Safety factor = 2
steel vs. lightweight carbon composite

Projections for pouch cell at 0.5 mA/cm²:

Oxygen storage type	Wh/kg	Wh/liter
steel	375	419
carbon composite	438	427
no storage	473	617

Greatest impact is on energy density (30% reduction)
Lightweight tank preserves 90% of the specific energy

Summary

- Exciting Future Programs ahead for NASA
- Power is needed for all Exploration vehicles and for the missions.
- For long term missions as in NEA (near earth asteroid) and Mars programs, safe, high energy/ultra high energy batteries are required.
- Component level research will provide higher energy density as well as safer lithium-ion cells for human-rated space applications.
- Collaborations with other government agencies and industry will provide good leverage.
- NRA, grants, SBIR and STTR allow us to take significantly good research into production even though space applications requires only low volume production.

Acknowledgment

- Coworkers in Power Systems Branch at JSC and other NASA Centers
- Collaborators in industry and academia