Multifunctional, Inorganic-Filled Separators for Large Format, Li-ion Batteries

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Overview

Timeline

- Start – Aug 2011
- Finish – Dec 2012
- Percent complete – 40 %

Barriers Addressed

- Abuse tolerance, reliability and ruggedness
  - High temperature (200 °C) integrity
  - Cell performance and life
- Low cost (goal - $\$1/m^2$)

Budget

- Total project funding
  - DOE share - $ 715,722
  - ENTEK share - $ 715,722
- Funding timing
  - FY2011 - $45,464
  - FY 2012 - $1,161,121
  - FY 2013 - $224,859

Partners/collaborations

- Portland State University - Electron microscopy
- Parkinson -Equipment and processing
- American Lithium Energy Corp. – Small cells
- Johnson Controls – Large cells
- Mobile Power Solutions – Abuse/cycle testing
- Sandia National Labs – Abuse testing

Project objectives and relevance

Develop an inorganic-filled separator that will increase abuse tolerance, ruggedness and reliability while improving cell performance and reducing cost.

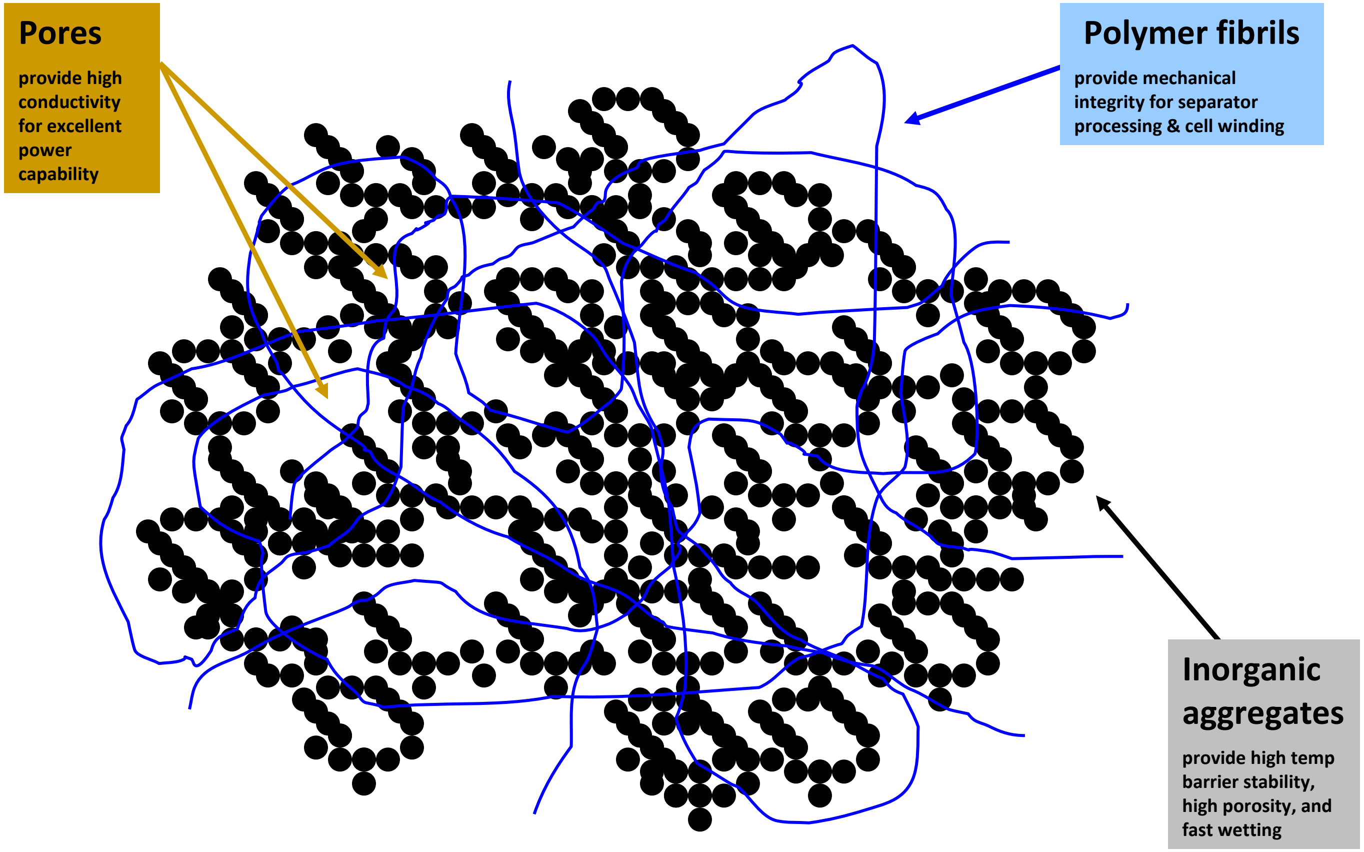
- **Continue pilot production of silica-filled separator film with an emphasis on improving mechanical strength and reducing variability.** **Reliability, life and cost**
- **Characterize the moisture absorption properties of the silica-filled separator and develop handling and drying recommendations for cell manufacturers.** **Reliability, life and cost**
- **Demonstrate good electrical performance and chemical stability of inorganic-filled separators in 18650 cells, pouch cells, and larger format (>7Ah) cells.** **Reliability and life**
- **Characterize abuse resistance of cells with silica-filled separator.** **Abuse tolerance and ruggedness**

Milestones

Milestone Date	Milestone Description
Sep-11	Flatsheet precursor production runs using ENTEK's commercial extrusion line.
Dec-11	
Mar-12	
Jun-12	
Sep-12	
Oct-11	Biaxial stretching trials and optimization of key separator characteristics.
Jan-12	
Apr-12	
Jul-12	
Oct-12	
Oct-11	Production runs of 18650 cells and small pouch cells for performance and abuse testing.
Feb-12	
Jun-12	
Oct-12	
Jul-12	Deliver 18650 cells to USABC for testing

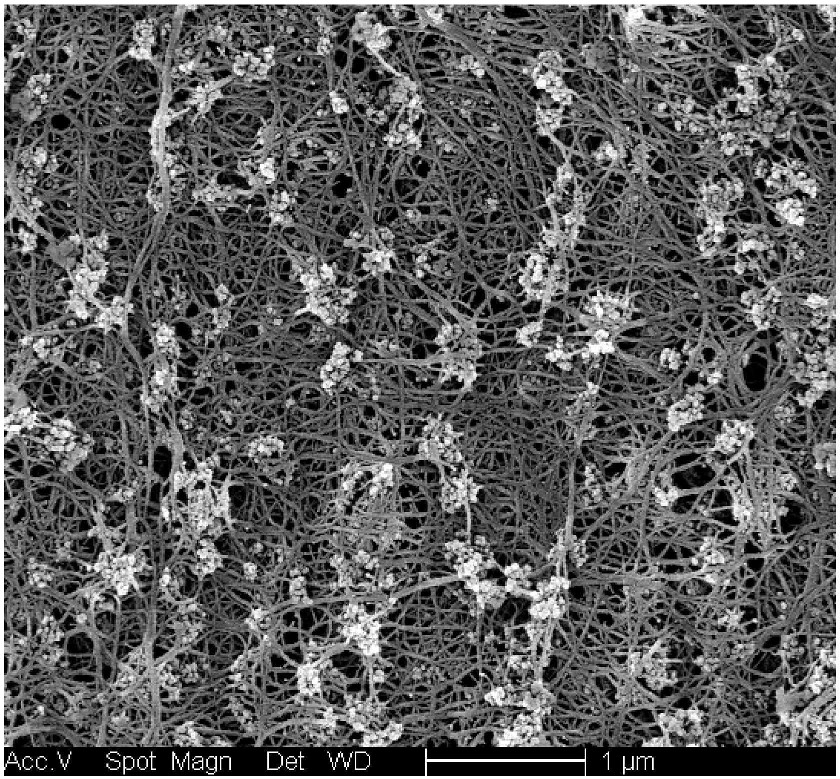
Technical Approach

- Inorganic-filled separators
  - Extrusion of inorganic filler / UHMWPE / oil mixtures
    - Inorganic filler content > 65 wt. %, Silica = preferred filler
  - Biaxial orientation to achieve thin films (20-25 um)
  - Extraction and thermal annealing to ensure high temperature dimensional stability

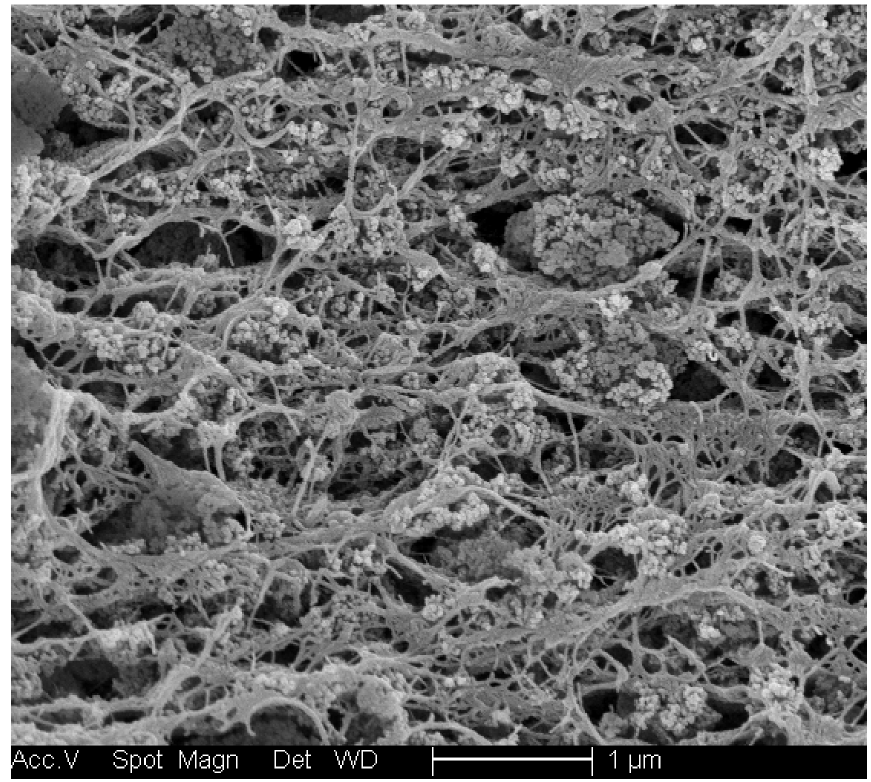


Surface & Fracture SEM --- Silica

2.3:1 Silica:PE, Surface



2.3:1 Silica:PE; XMD fracture



Polymer rich surface layer with open porosity

Highly porous bulk structure with pore size < 1 um

Prior accomplishments: Thermal Stability and Resistance

Thermal Stability -- USABC Goal met: < 5% shrinkage at 200 °C

Achieved with more than one formulations and different inorganic fillers

Silica filled separator

Roll ID	Base roll	Filler:PE	Thickness (avg)	200 C Shrinkage %		Gurley	Puncture
			µm	MD	XMD	sec/10ml	gf /25 u
DY110217.002	59	2.1	18.7	5.87	4	6.8	280
DY110302.002	260	2.3	23.3	4	3.5	7.4	244
DY110218.002	64	2.6	21.3	6.5	2.67	5.3	192

Alumina filled

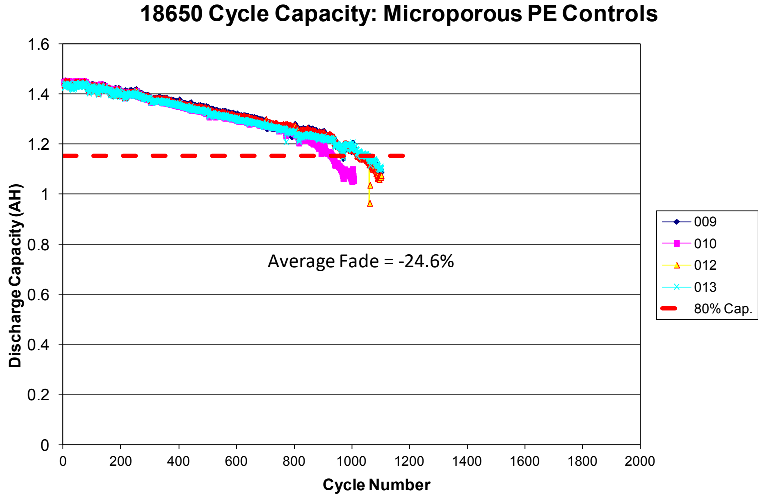
Roll ID	Base roll	Filler:PE	Thickness (avg)	200 C Shrinkage %		Gurley	Puncture
			µm	MD	XMD	sec/10ml	gf /25 u
DY110131.025	202	2.7	25.4	5	1	12.7	391

Separator Resistance -- USABC Goal met: MacMullin # << 11 for all fillers

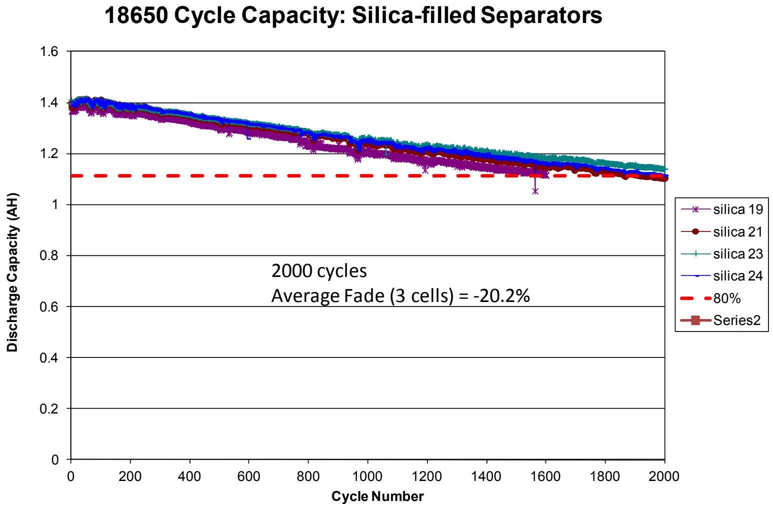
Roll ID	Base roll	Filler	Filler:PE	Thickness	Areal Resistance	Resistivity	MacMullin Number
				Microns	Ω-cm²	Ω-cm	
DY110217.002	59	Silica	2.1	19	0.59	308	2.6
DY110303.001	260	Silica	2.3	24.1	0.59	247	2.1
DY110218.002	64	Silica	2.6	20.5	0.48	232	1.9
DY110214.003	202	Alumina	2.7	22.3	0.88	396	3.3

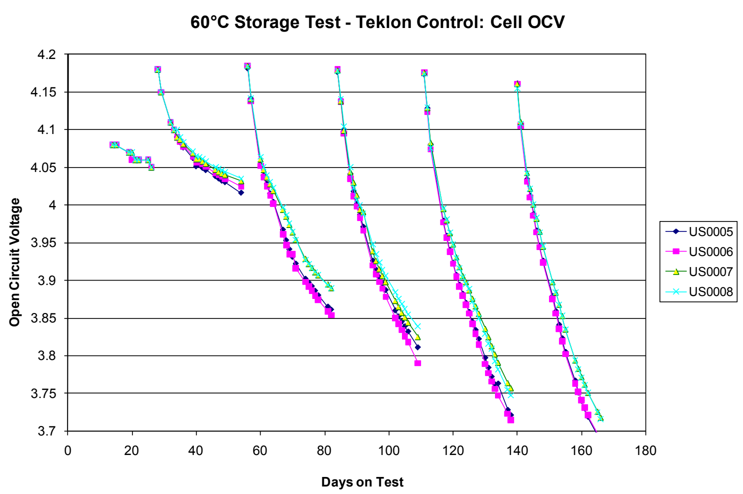
Prior accomplishments: Improved Cycle Life

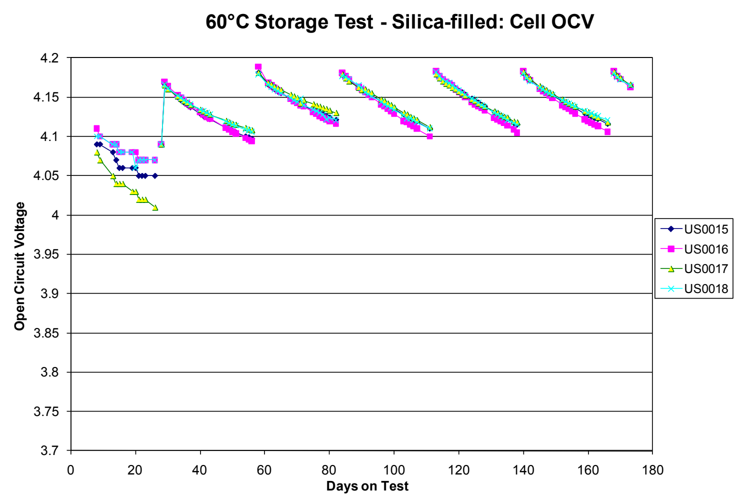
Microporous PE



Silica-filled separator





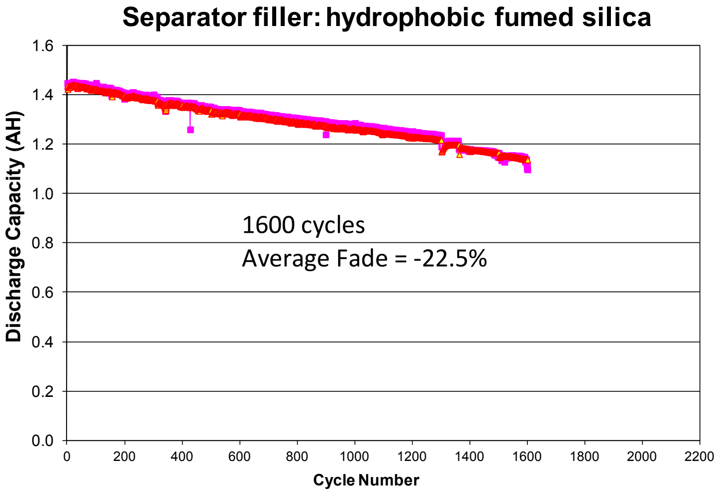


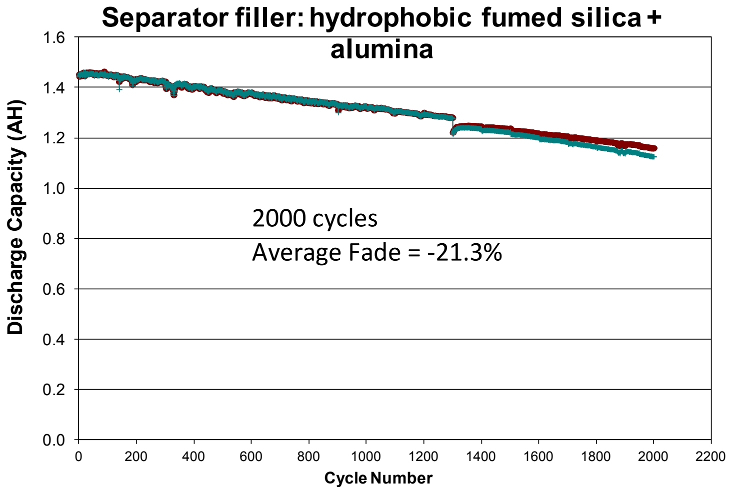
In 18650 cells with NMC/graphite, silica-filled separator increases cell cycle life 80% and decreases self-discharge 90% compared to the control micro-porous PE.

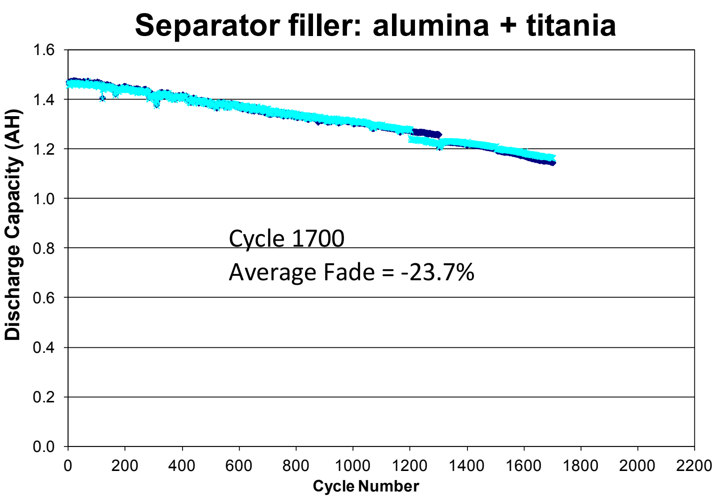
New Technical Accomplishments

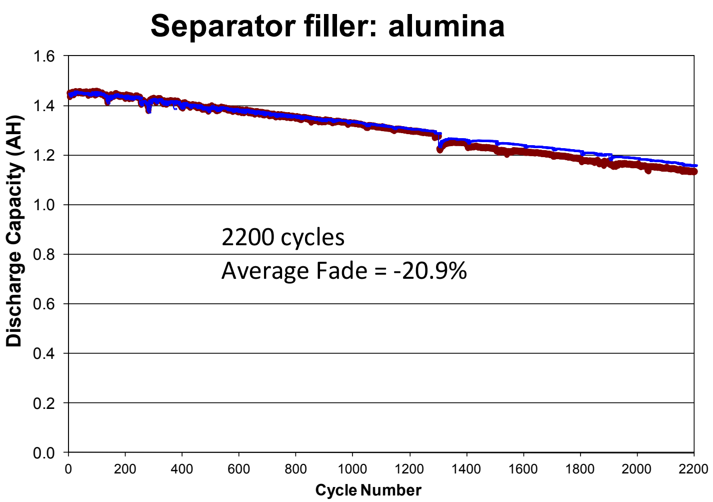
- Pilot production: material produced from May 2011 to March 2012.
  - Biaxially-oriented film: 50,000 m^2; Extracted: 5,000 m^2; Annealed 2,000 m^2
- Further demonstration of cycle life improvements in cells with different filler combinations. Up to 2200 cycles demonstrated.
- Characterization of adsorbed water content in filled separator and conditions for drying.
  - Cells built with different drying procedures
  - 1C cycle testing and 60°C storage testing in process
- Characterization of electrolyte wetting properties of inorganic filled separator. Filled separators wet out faster than unfilled.
- Preliminary abuse test results in 18650 cells
  - Oven ramp, overcharge, short circuit, blunt nail crush
- Prismatic pouch cells built with silica-filled separator
  - Small cells (2.2 Ah), American Lithium Energy Corp.
  - Large cells, JCI

Cycle Life of cells with different fillers in the separator





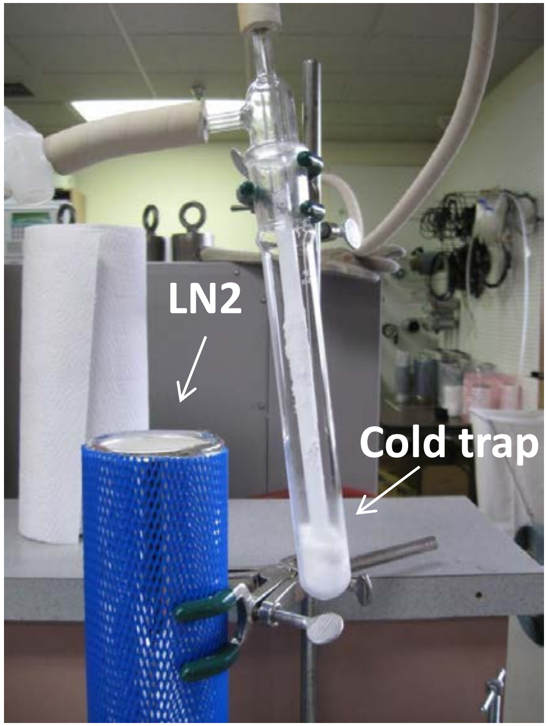


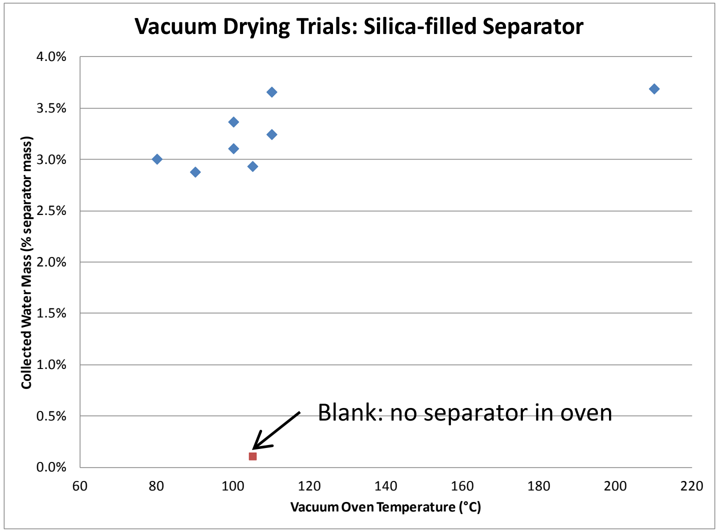


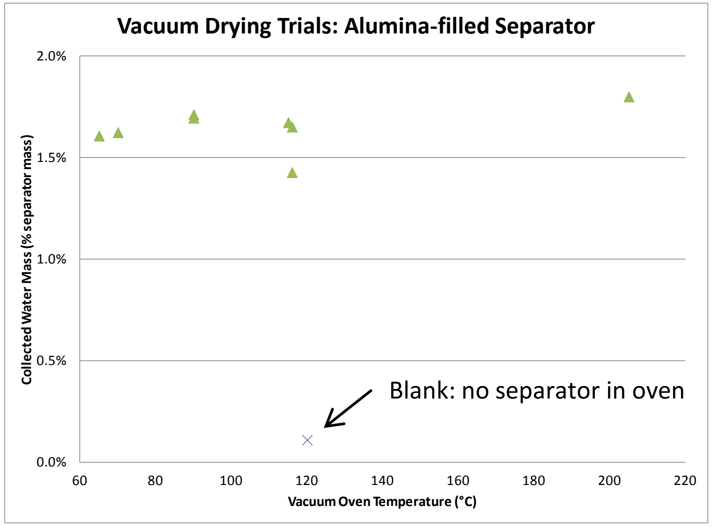
- All four groups have better cycle life than the control.
- No filler combination appears better than precipitated silica.

Vacuum Drying Trials

- Separators filled with silica and alumina were dried under vacuum at different temperatures for 6-9 hours.
- Moisture removed was trapped cryogenically and weighed.
- Results show water can be removed at modest temperatures and times under vacuum.

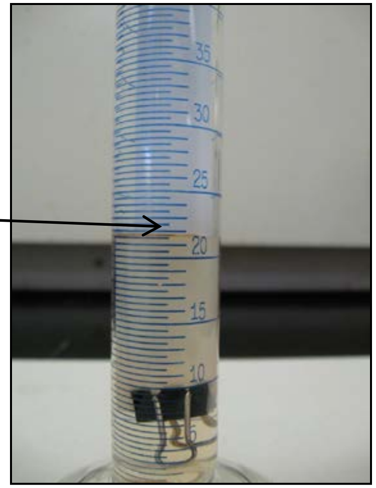




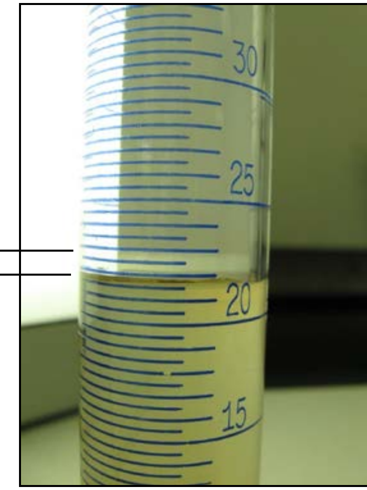


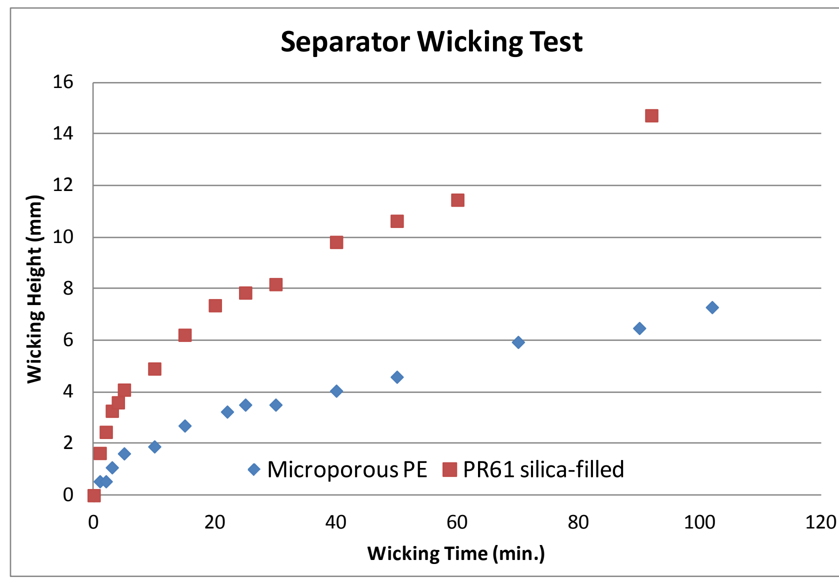
Separator Wetting Characterization

Separator suspended in electrolyte in a graduated cylinder with binder clip weight.



Wicking height at 30 minutes





Wicking rate measurements are repeatable.

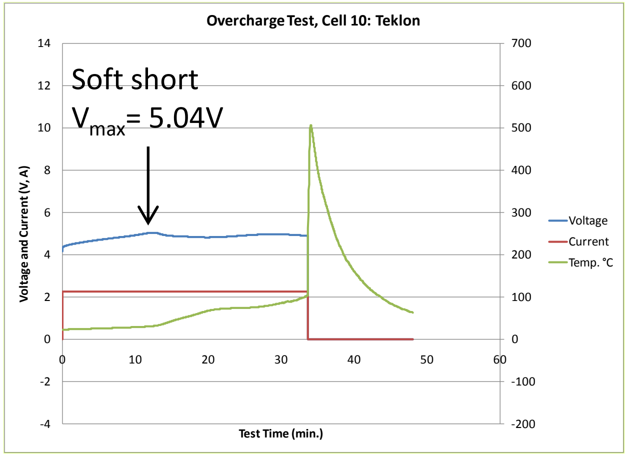
Silica-filled separator wicking rate is over twice the rate of porous PE.

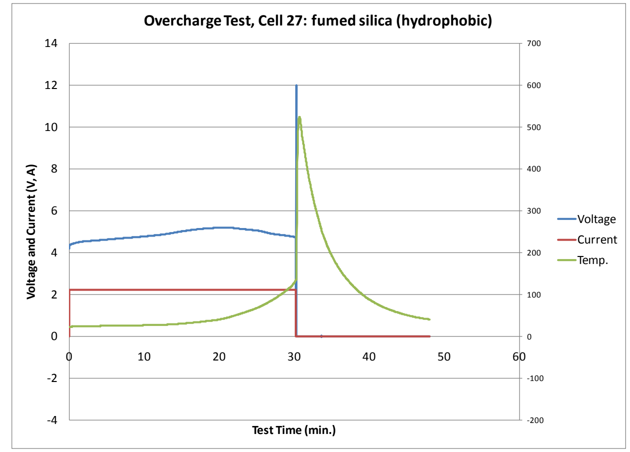
Abuse Testing of 18650 Cells

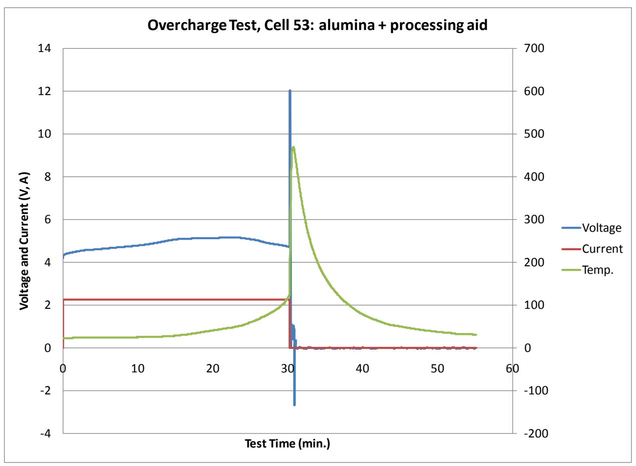
- Overcharge (Mobile Power Solutions)
  - 1 control cell, 3 cells with different fillers in the separator
  - Overcharge (1.5C for 1.5 h or until failure): V, I, T sampled 1/sec.
- Overcharge (Sandia)
  - 2 control cells (fresh & cycled), 2 cells with silica-filled separator (fresh & cycled)
  - Overcharge (1.0C for 1.5 h or until failure): V, I, T sampled 1/sec.
- Oven Ramp (Mobile Power Solutions)
  - 1 control cell, 3 cells with different fillers in the separator
  - 100% SOC, Heat 5°C/min with 30 min dwell at 130°, 160°, and 250°C.
- Oven Ramp (Sandia):
  - 2 control cells (fresh & cycled), 2 cells with silica-filled separator (fresh & cycled)
  - 100% SOC, Heat 5°C/min, no dwell
- Short Circuit (Mobile Power Solutions):
  - 2 control cells (fresh), 2 cells with silica-filled separator (fresh)
  - 60°C, 100% SOC, 20 mΩ
- Blunt Nail Penetration: (Sandia)
  - 2 control cells (fresh), 2 cells with silica-filled separator (fresh)
  - 60°C, 3mm dia. rod with 1.5mm radius tip, pressed at 0.1mm/s until a voltage drop >100mV is detected.

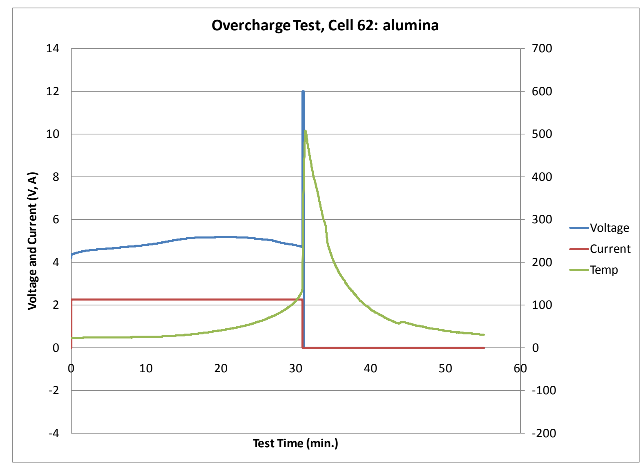
Overcharge Test: Mobile Power Solutions

Overcharge (1.5C for 1.5 h or until failure): V, I, T sampled 1/sec.





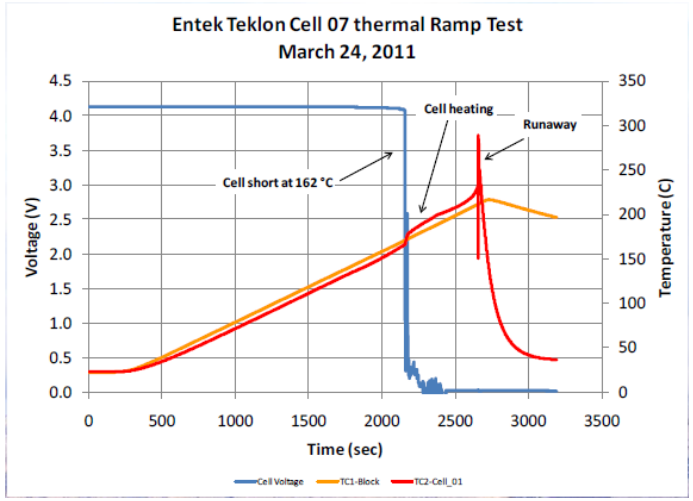


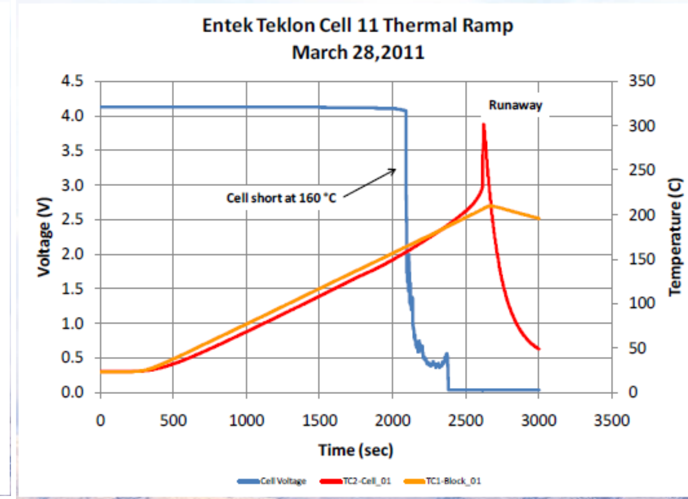


All four cells vented at approximately the same time due to pressure rise, followed by thermal runaway. Teklon cell was slightly delayed due to a “soft” internal short which reduced the rate of gas generation.

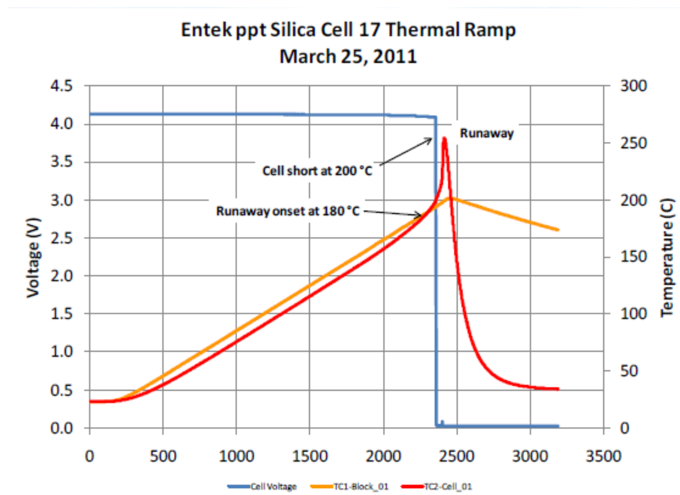
Oven Test – Sandia (ramp only, no dwell)

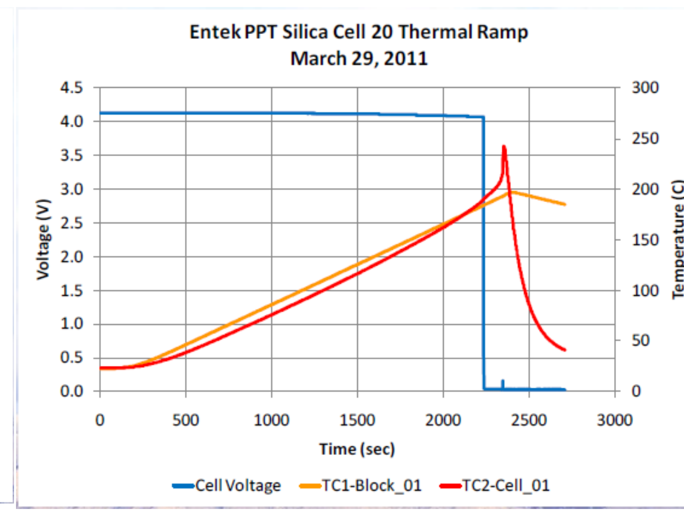
Cells with Teklon





Cells with silica-Filled separator

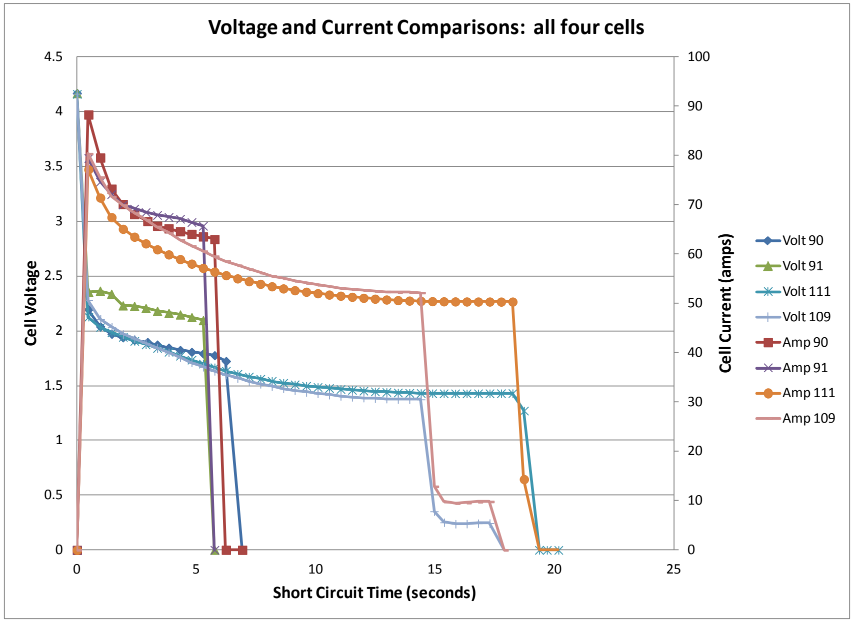


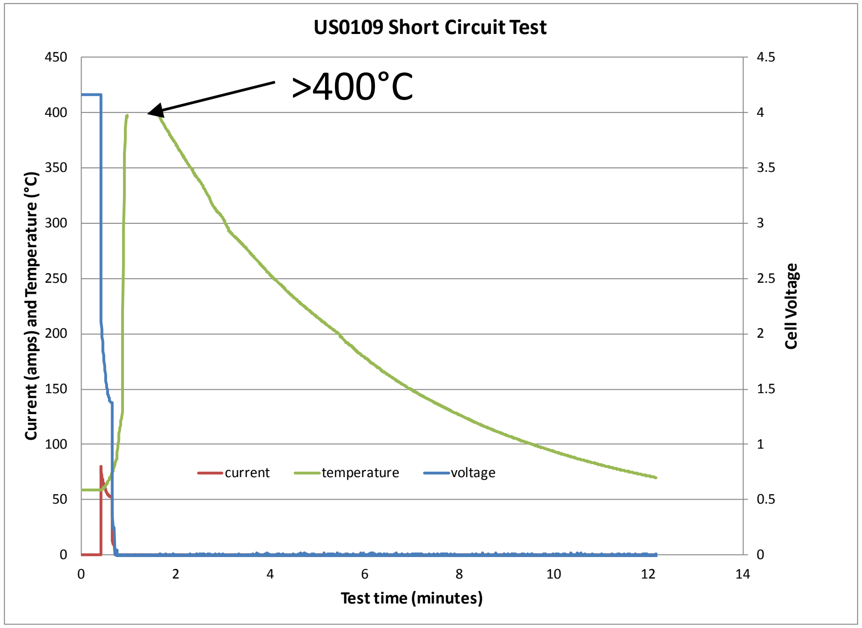


The cells with Teklon shorted out at 160°C. The cells with silica-filled separator shorted out at 185-190°C, when PP gasket melted. All cells went into thermal runaway at >200°C.

Short Circuit Test: 20 mΩ, 60°C

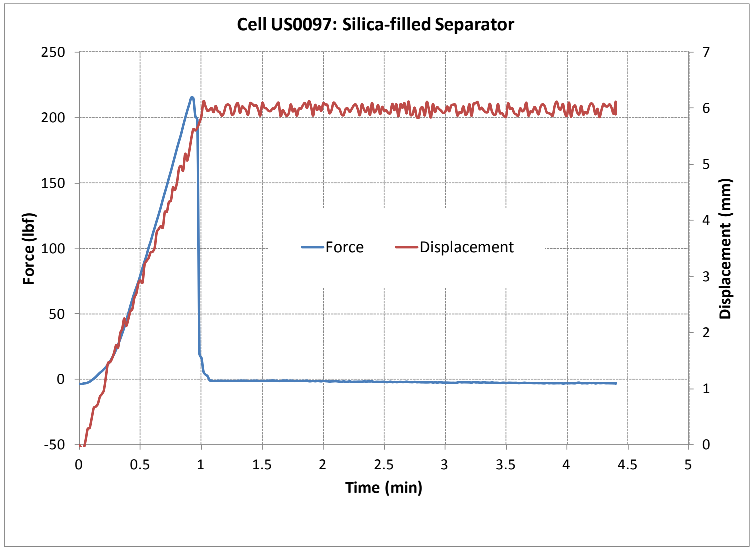
Cell No.	Separator	Peak Current	Peak Temp.	Pass/Fail	Notes
US0090	2.1:1 silica	88.3	73	Pass	
US0091	2.1:1 silica	79.5	73	Pass	
US0109	Teklon	80.4	>400	Fail	Fire
US0111	Teklon	77.2	106	Pass	



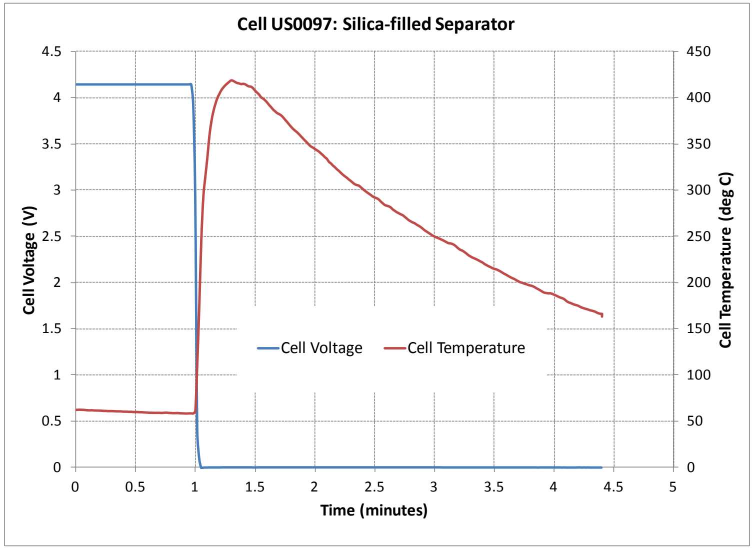


- The cells with silica separator went open quickly (6 seconds of short circuit) and reached mild peak surface temperatures.
- The Teklon cells maintained the current for longer (15-19 seconds) before going open and reached higher temperatures.
- Cell 109 went into thermal runaway shortly after going open.
- Silica-filled separators offer a marginal advantage over control separators.

Blunt Nail Penetration -- Sandia



- No drop in voltage (internal short) prior to cell penetration at 3.5-7mm.
- Penetration followed by rapid voltage drop and temperature rise to >400°C.
- Cell vented with lots of smoke, but no flame or explosion.
- No difference observed between cells with silica-filled separator and control cell with PE separator.



18650 Abuse Test Conclusions

- The inorganic filled separators do not shut down and will not prevent cell over-pressure on overcharge.
- The inorganic filled separators do not prevent thermal runaway. After 200°C runaway is inevitable.
- Filled separators do maintain mechanical integrity at high temperature.
- Filled separators do increase the margins before failure; the time or temperature at which bad things start to happen is increased.
- Cells with silica-filled separator are in better shape after short circuit testing than cells with Teklon control.
- One anticipated benefit of silica-filled separators, increased resistance to internal shorts due to defects, cannot be tested.

Gap analysis

Parameter	Units	USABC Goal	Phase II Base Line
Thickness	micron	<25	19
MacMullin#	#	<11	< 4.2
Gurley	s/10cc	< 35	7.5
Wettability		Wet out in electrolytes	Complies (fast-wetting)
Chemical Stability		Stable in battery for 10 years	Not tested
Pore Size	micron	<1	< 1
Puncture Strength, JIS 1019*	gf	>300 gf/25.4 µm	285
Thermal Stability at 200° C		<5% shrinkage	4.7% MD
			2.7% XMD
Tensile Strength		<2% offset at 1000 psi, MD	1390
Skew	mm/m	<2 mm/meter	Not measured
Pin Removal		Easy removal from all winding machines	Not measured
Shutdown	° C	As required	No Shutdown
Selling price	$/m^2	1.00	1.0**

Future work (mid-March – December 2012)

- Three precursor runs and three stretching trials.
  - Improved filler dispersion
  - Improved mechanical strength
  - Develop full scale equipment requirements
  - Refine cost model
- Cell builds
  - 18650: 60 cells
  - Small prismatic: 30 cells
  - Large format cells: TBD
- Cell performance testing
  - Ongoing cell tests and new cells: 1C cycle tests and 60°C storage tests
- Conduct abuse tests on 18650 and prismatic cells
  - Sandia National Labs
  - Mobile Power Solutions
- Provide separator samples for large format cell builds to interested cell manufacturers

Summary

- Separators with inorganic filled separators demonstrated significantly faster wetting with electrolyte.
- Filled separators can be dried of adsorbed moisture under vacuum at mild temperatures.
- 18650 cells with inorganic-filled separators continue to show good performance compared to control cells with microporous polyethylene separator.
  - Improved cycle life
  - Lower self discharge
  - Higher rate capability
- Preliminary abuse tests of 18650 cells demonstrate:
  - The inorganic filled separators do not prevent thermal runaway. After 200°C runaway is inevitable.
  - Filled separators increase the margin before failure; the time or temperature at which bad things start to happen is increased.
  - More abuse testing needed in prismatic cell designs that dominate the xEV battery market.