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

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Project ID # ES008

Overview

Timeline

- Start – Feb 2010
- Finish – June 2011
- Percent complete – 90 %

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 - $ 748,404
  - Entek share - $ 748,404
- Funding received in FY2010 - $339,752
- Funding for FY 2011- $ 408,652

Partners

- Portland State University - Electron microscopy
- PPG, Evonik, Cabot - Inorganic fillers
- Parkinson -Equipment and materials processing
- Am. Lithium Energy Corp. – Cell builds

Project objectives

Operating Assumptions

- Maintenance of electrode separation under abuse conditions is vital for HEV/PHEV battery safety
- Overcharge, over-discharge, and high rate discharge are controlled at the system level by the Battery Management System

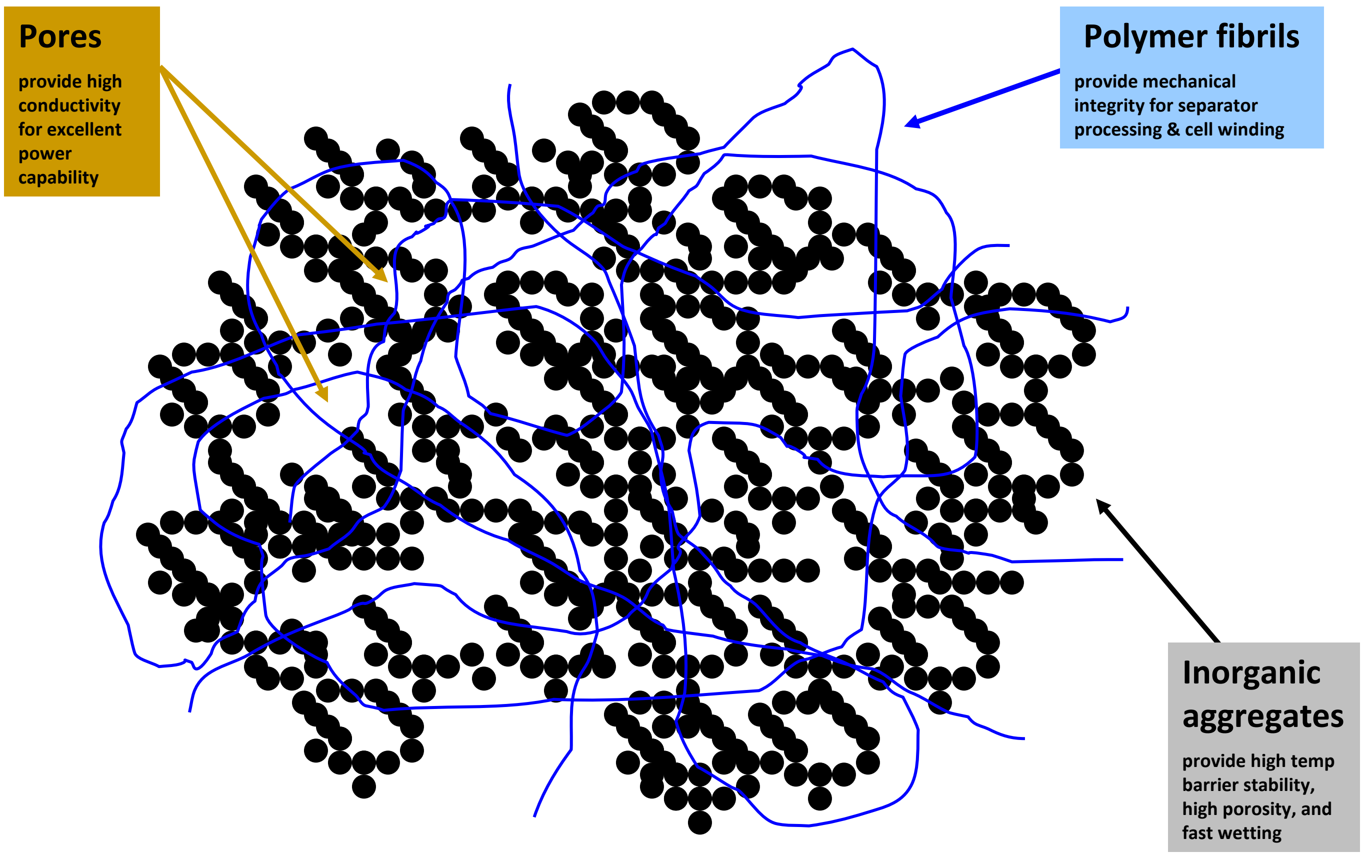
High temperature mechanical and dimensional stability of the separator, whether it exhibits shutdown or not, is the key to safety in large format, HEV/PHEV Li-ion cells regardless of cathode chemistry

Objectives of the study

- **Define optimum process parameters to achieve inorganic-filled separators with consistent properties for enhanced battery performance and abuse tolerance**
- **Demonstrate good performance and stability of inorganic-filled separators in 18650 cells**
- **Develop scale-up plan that can meet cost objectives**

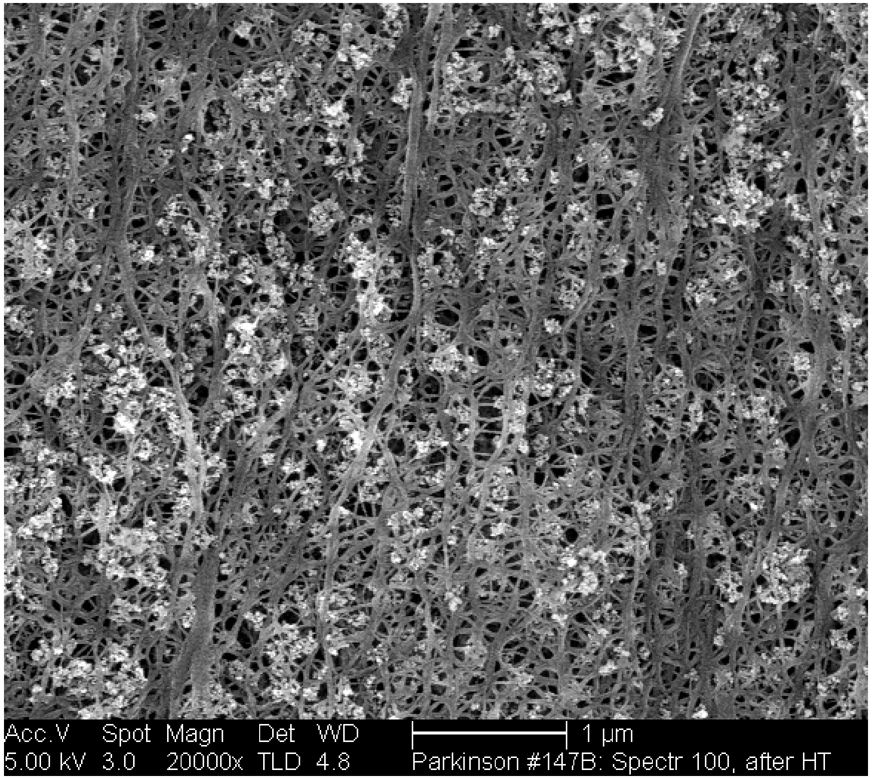
Approach

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



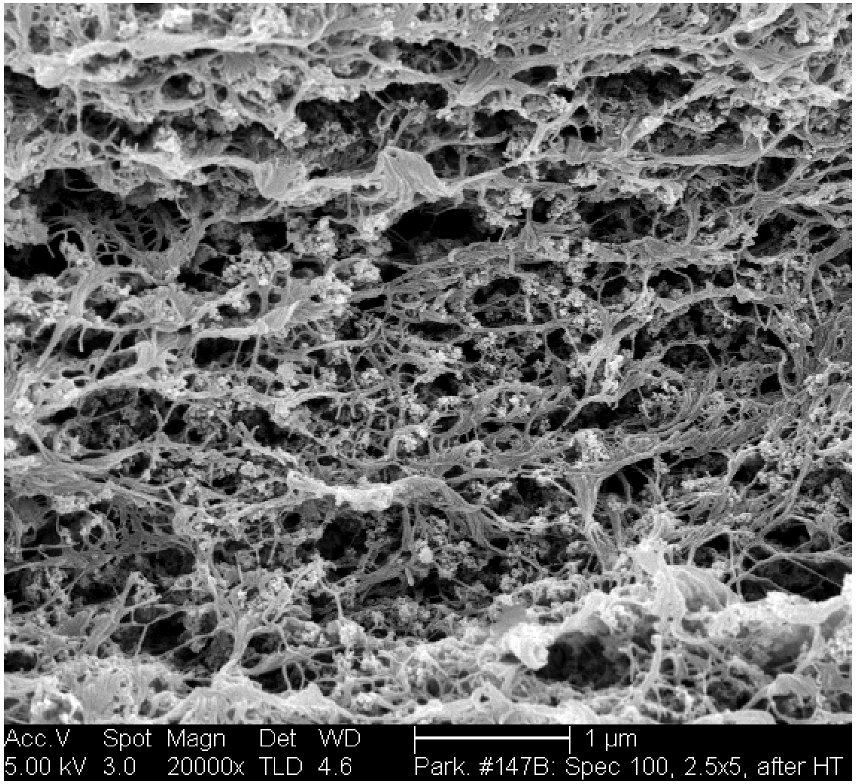
Surface & Fracture SEM --- Al_2O_3

2.7:1 Al2O3:PE, Surface



Polymer rich surface layer with open porosity

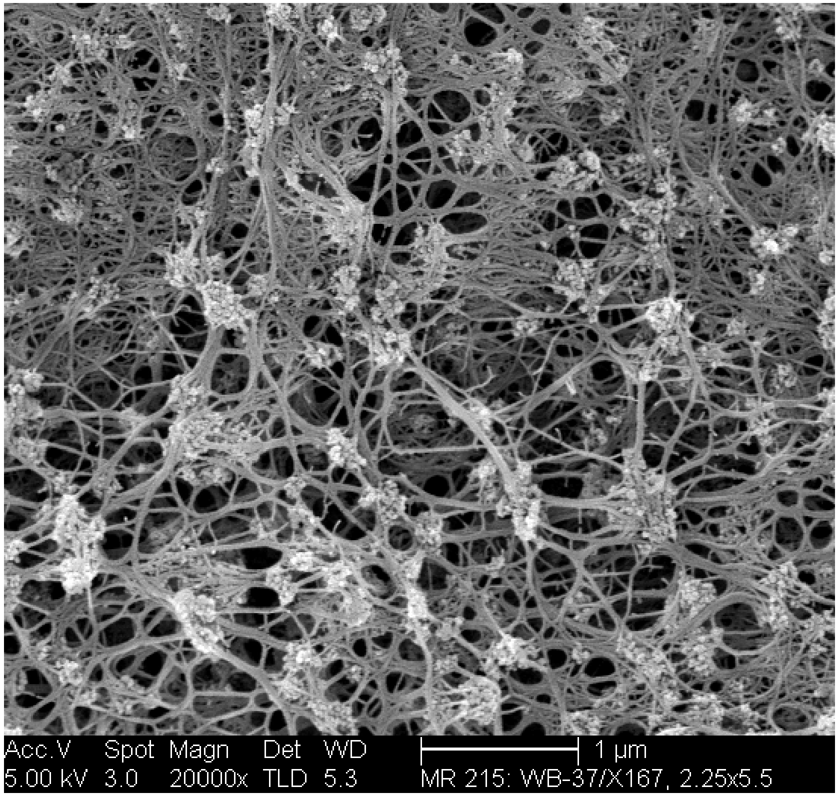
2.7:1 Al2O3:PE, XMD Fracture



Highly porous bulk structure with pore size < 1 um

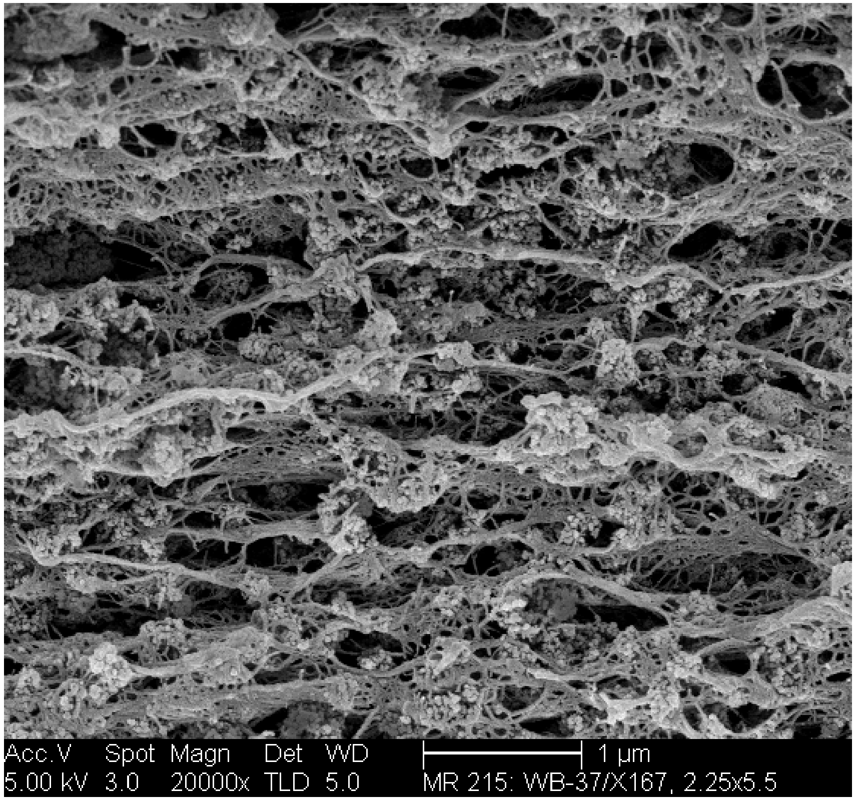
Surface & Fracture SEM --- Silica

2.3:1 Silica:PE, Surface



Polymer rich surface layer with open porosity

2.3:1 Silica:PE; XMD fracture



Highly porous bulk structure with pore size < 1 um

Technical accomplishment: excellent dimensional stability

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
DY110221.001	263	2.3	25.3	4.67	4	7.8	230
DY110301.003	260	2.3	23.8	4.2	3.5	7.2	224
DY110302.002	260	2.3	23.3	4	3.5	7.4	244
DY110303.002	260	2.3	25.1	4.5	3.7	7.6	214
DY110218.002	64	2.6	21.3	6.5	2.67	5.3	192

Alumina filled separator

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
DY110214.003	202	2.7	20.8	6.33	2.5	12	386

USABC Goal :   < 5% shrinkage at 200 °C

Achieved with more than one formulations and different inorganic fillers

Technical accomplishment: exceptionally low impedance

- Rapid wetting with electrolyte
- Enhanced power capability and low temperature performance

Roll ID	Base roll	Filler	Filler:PE	Thickness	Areal Resistance	Resistivity	MacMullin Number
				Microns	Ω-cm²	Ω-cm	
Inorganic Filled Separators							
DY110217.002	59	Silica	2.1	19	0.59	308	3.6
DY110224.002	263	Silica	2.3	23.8	0.63	266	3.2
DY110224.004	261	Silica	2.3	22.8	0.85	373	4.1
DY110303.001	260	Silica	2.3	24.1	0.59	247	3.1
DY110218.002	64	Silica	2.6	20.5	0.48	232	2.9
DY110131.025	202	Alumina	2.7	25.9	1.06	410	4.4
DY110214.003	202	Alumina	2.7	22.3	0.88	396	4.3
Unfilled Separators							
Teklon® HPIP		Unfilled		25	2.15	869	8.2
Teklon® Gold LP		Unfilled		12	1.85	1460	13.2
Coated Unfilled Separator							
Coated Teklon®		Alumina		14	2.4	1668	14.9

USABC Goal : MacMullin # < 11

Achieved with all formulations

Technical accomplishment: 18650 Cell Builds

- Purpose: To characterize the performance of cells with inorganic-filled separators and compare them to control cells with microporous polyethylene separator.

- Primary concerns:
  - Adsorbed H_2O on the fillers
  - Stability of fillers in contact with positive and negative electrodes.

- Cell build campaigns
  - Cells built by American Lithium Energy Corp.
    - NMC positive electrodes, graphite negative electrodes, high rate design
  - Build #1: April 2010, 20 cells, control and silica-filled separators
  - Build #2: August 2010, 40 cells, four different inorganic fillers
  - Build #3: December 2010, 20 cells, silica repeat and alumina

Generic Test Plan for Cell Builds

Build 18650 Cells
American Lithium Energy Corp.
• 10 cells for each separator formulation

7-day OCV screening test

Initial Performance Characterization
8 cells
• 1C discharge, room temp
• 1C discharge, -30°C
• HPPC, room temp.

2 cells reserved for future tests.

Calender Life Test
60°C, 100% SOC
• 4 cells each formulation
• Repeat RPT every 4 wks

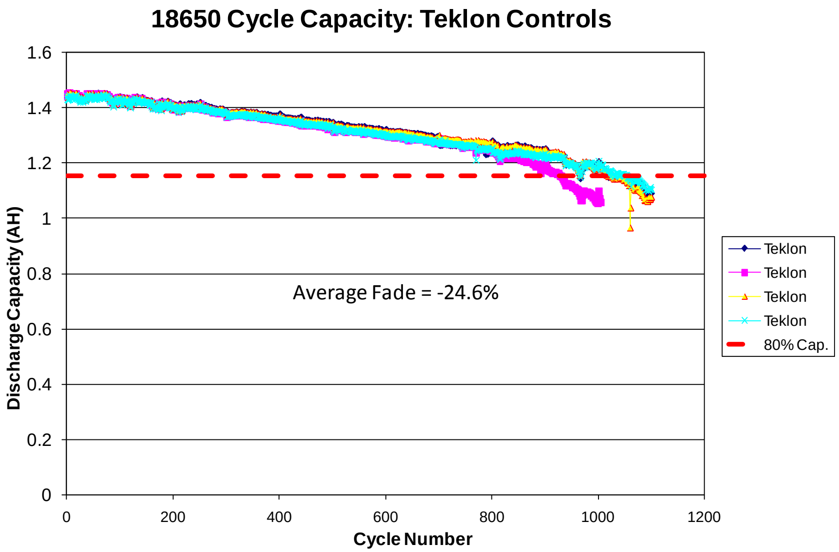
Cycle Life Test
Room Temp., 1C with 2C pulse
• 4 cells each formulation

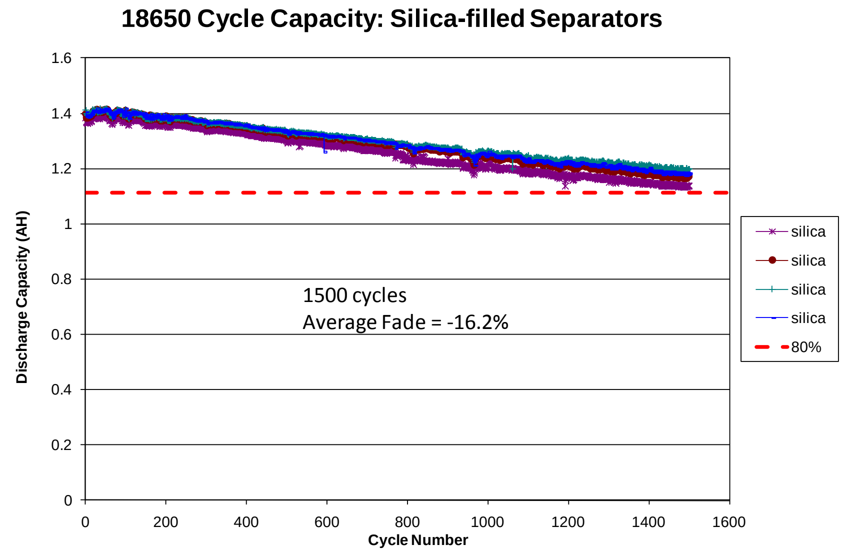
18650 Cell Build #1 – April 14, 2010

20 cells built: two different separators.

Group Designation	Separator Formulation
A & B	Control, Teklon XP, 20 micron
C & D	Precipitated silica, PR 59, 20 micron)

Cycle Testing: Control vs. Silica-filled Separator

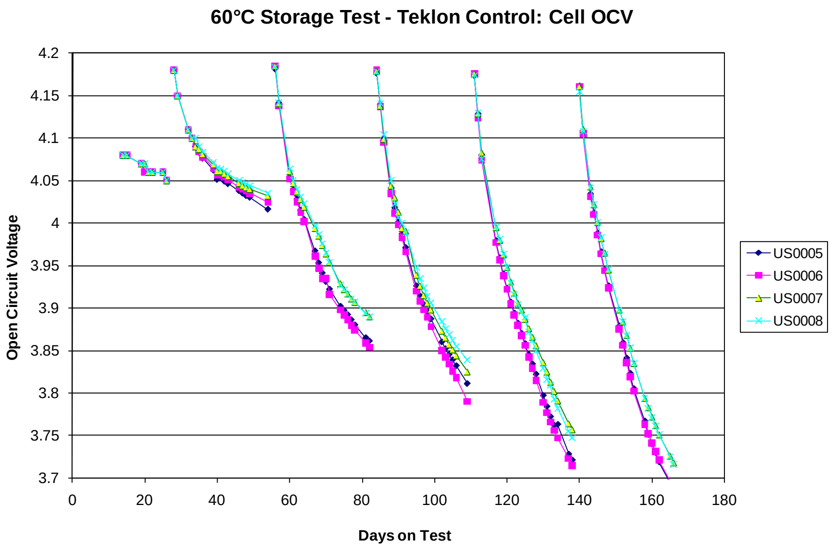


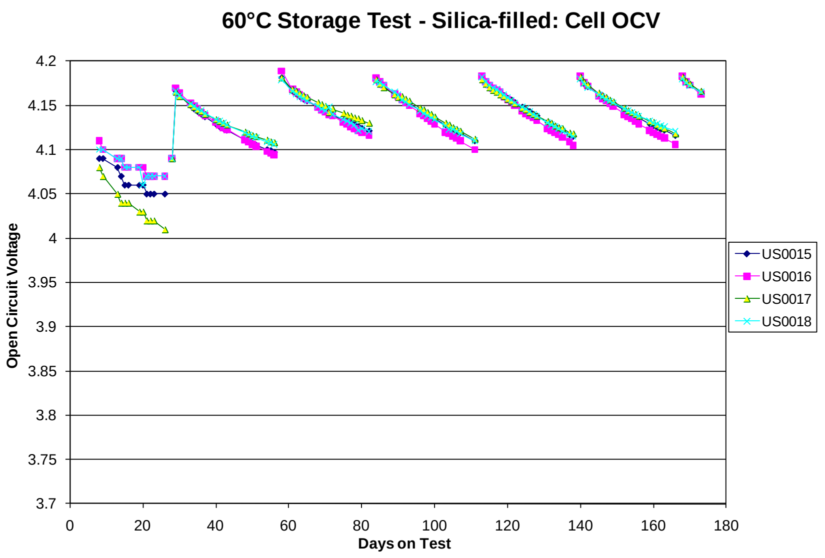


- Room temperature, 100% DOD, 1C rate.
- Control cells reached 80% of initial capacity at 1000-1100 cycles.
- Cells with silica-filled separator are still cycling with 84% of initial capacity after 1500 cycles.

Cells with silica-filled separator have demonstrated greater cycle life than controls.

60°C Storage Test: Control vs. Silica-filled Separator

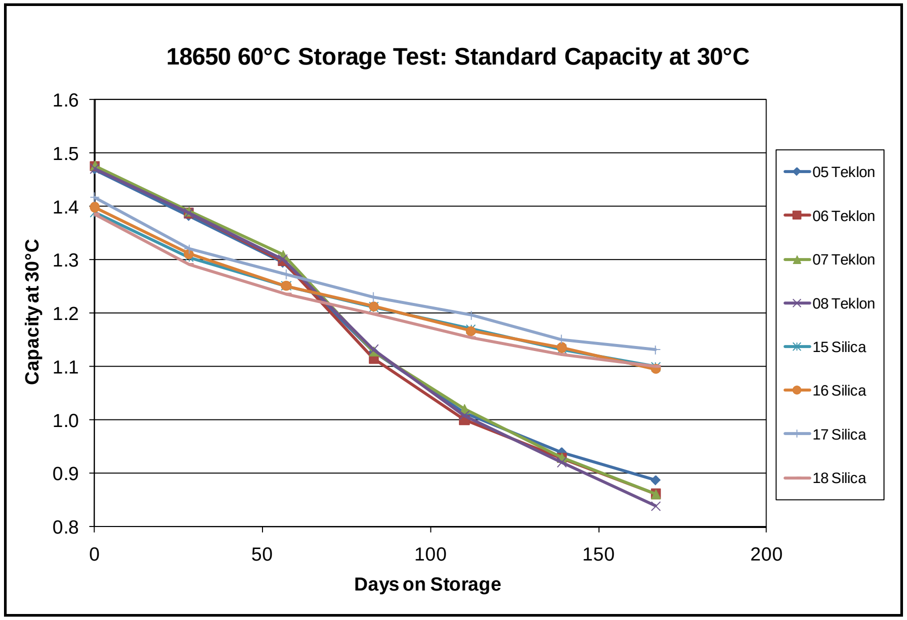


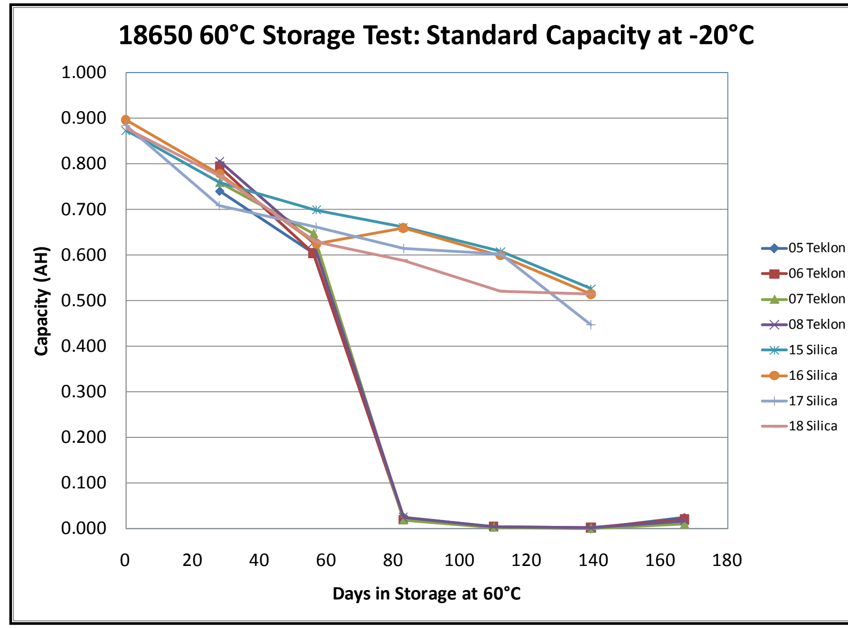


- Fully charged (4.2V), 60°C, characterization test every 4 weeks.
- Control cells exhibited increasing OCV fade rate over time.
- Cells with silica-filled separator had lower, stable OCV fade rate.

Silica-filled separator contributes to lower rate of self discharge.

60°C Storage Test: 30°C and -20°C Capacity



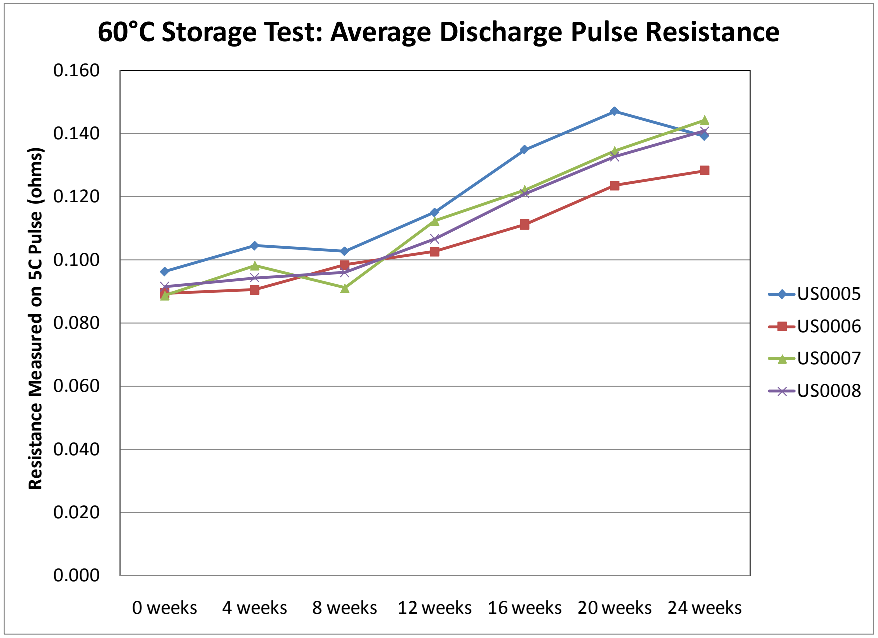


The rate of capacity loss is greater for the controls and less for the cells with silica-filled separator.

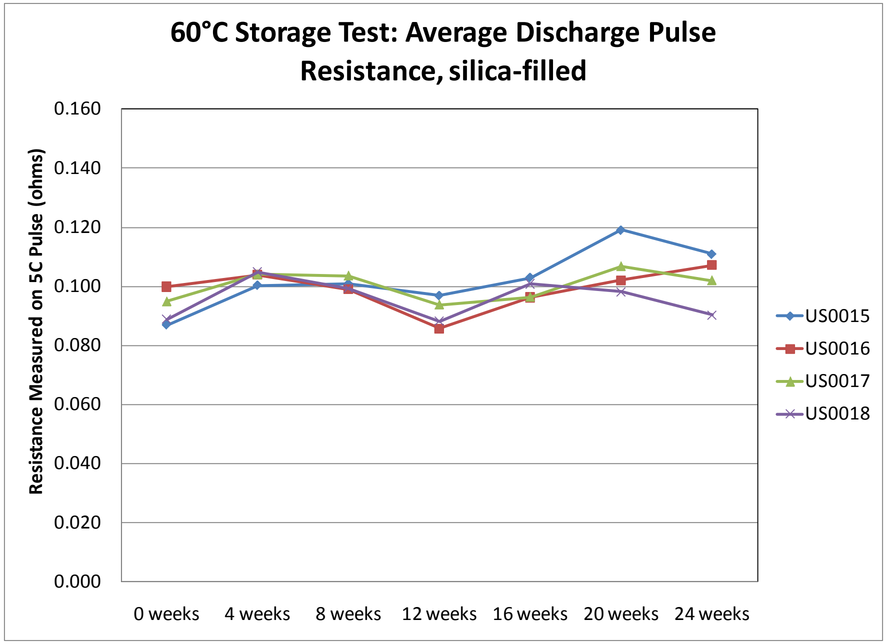
The control cells are unable to support 1C discharge at -20°C after 12 weeks of storage. The silica-filled cells continue out to 20 weeks.

Silica-filled separator demonstrates less capacity fade, especially at low temperature.

60°C Storage Test: HPPC Test – Discharge Pulse Resistance



Control Cells



Cells with silica-filled separator

The resistance of the control cells increased with storage while the resistance of the cells with silica-filled separator stayed relatively stable.

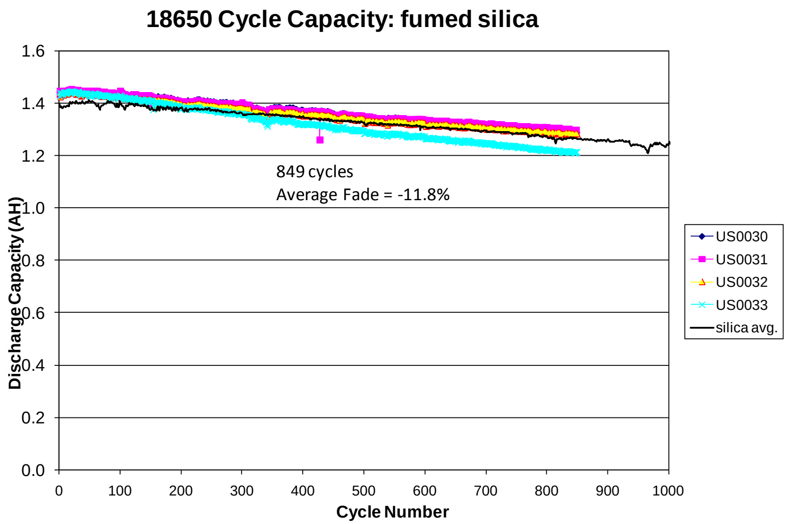
Cells with silica-filled separator show less resistance growth than controls.

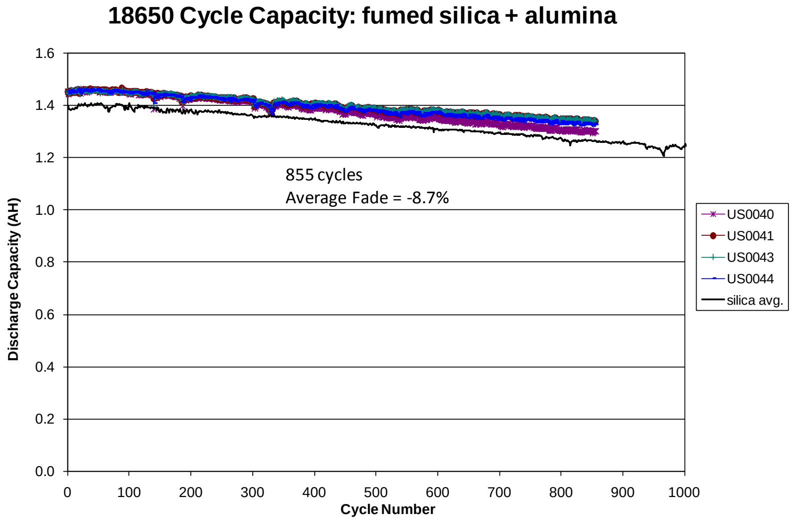
18650 Cell Build #2 – August 10, 2010

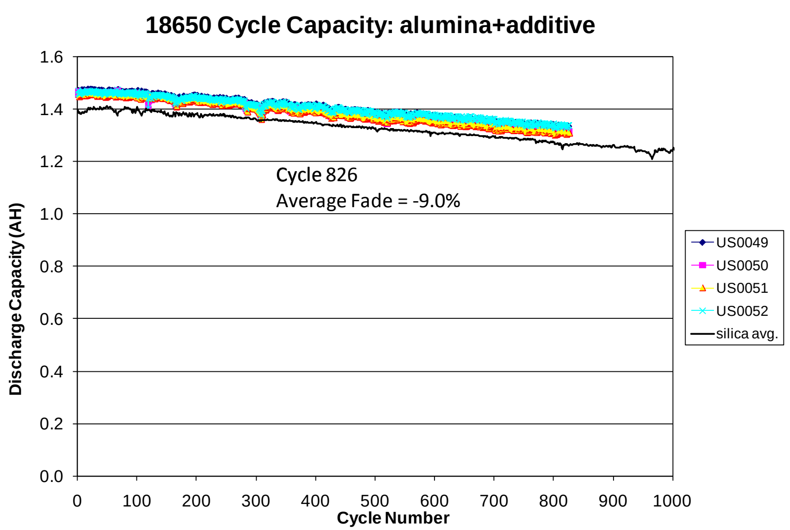
40 cells built: 10 each with four different separators.

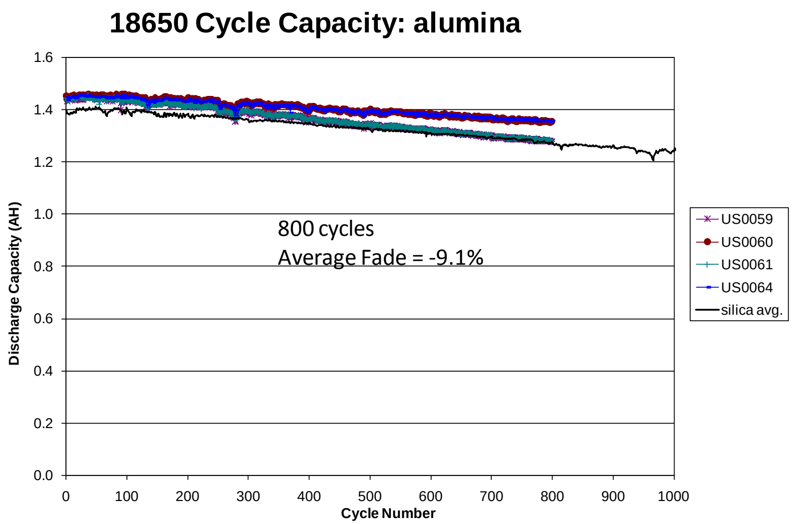
Group Designation	Separator Formulation
E & F	Surface-treated, fumed silica (hydrophobic)
G & H	Surface-treated, fumed silica + fumed alumina
I & J	Fumed alumina + additive (processing aid)
K & L	Fumed alumina

Cycle Life: Cell Build #2





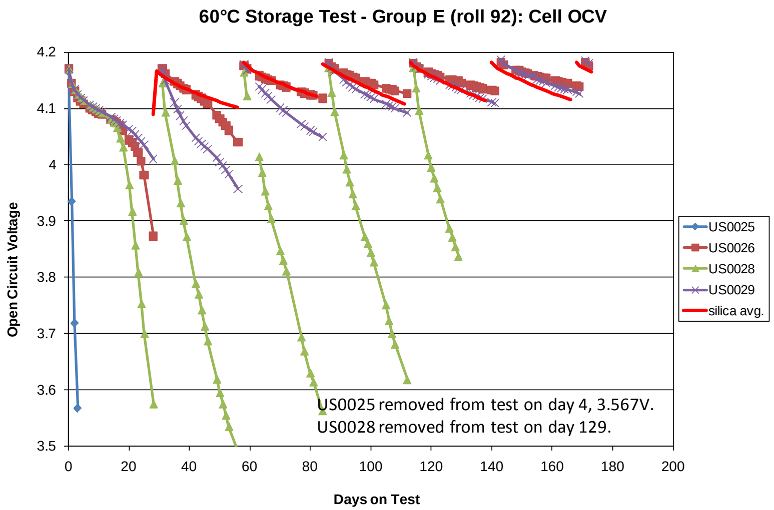




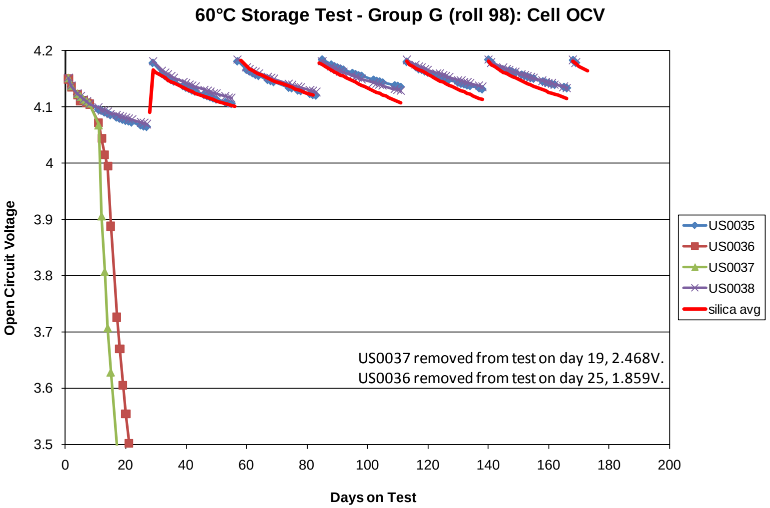
- All cell groups are cycling well at >800 cycles.
- Capacity fade rate is similar to silica-filled group in Build #1.

60°C Storage OCV – Cell Build #2

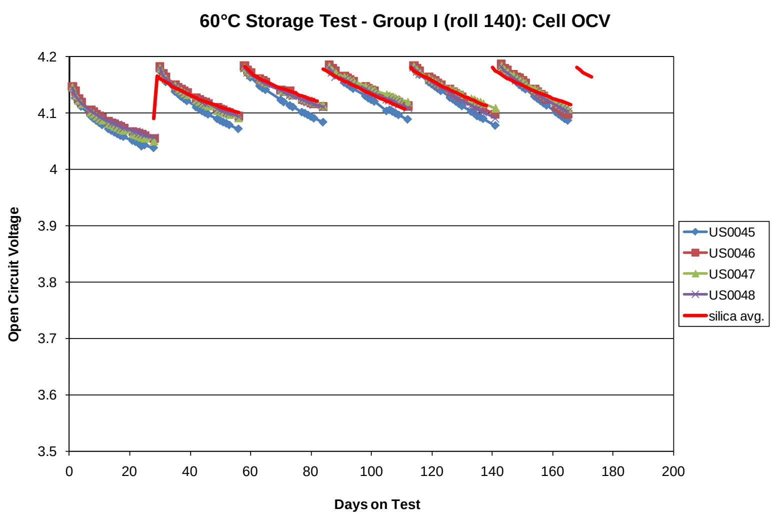
Treated, fumed silica filler



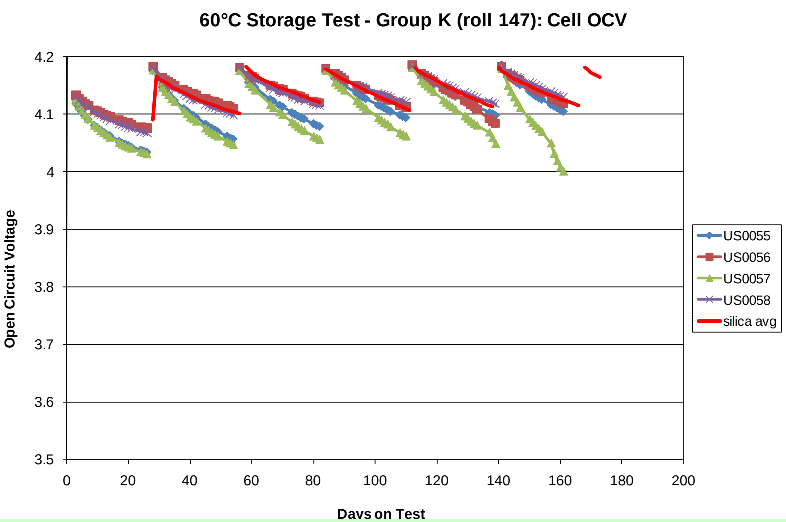
Treated, fumed silica + alumina filler



Fumed alumina + additive filler

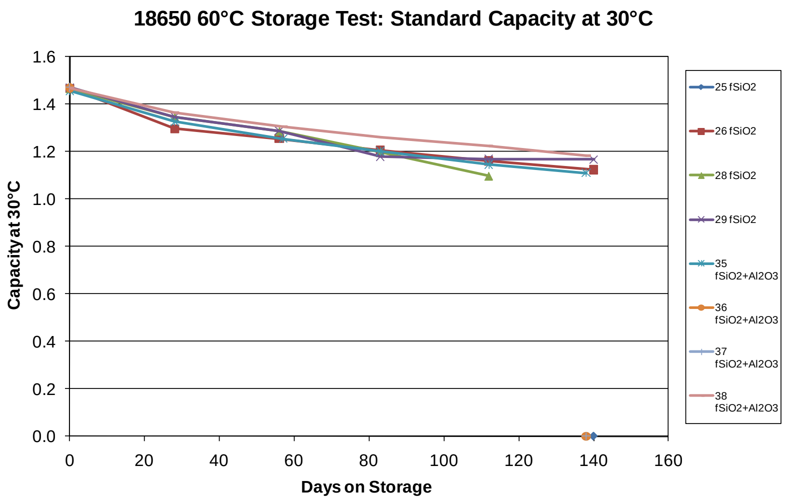


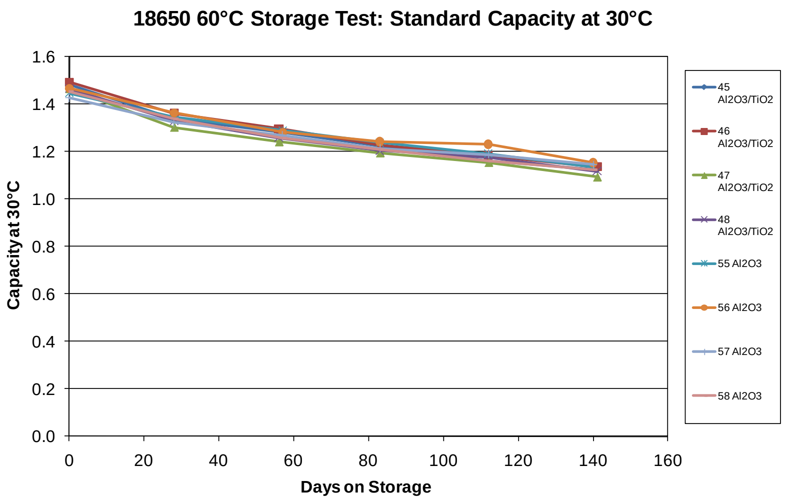
Fumed alumina filler



Except for early failures in groups E & G, OCV fade is similar to silica-filled cells in Build #1.

60°C Storage OCV – Standard Capacity





- All groups have experienced about equal capacity loss at 30°C.
- No cells are able to support -30°C discharge after 12 weeks at 60°C. All can handle -20°C.

Similar results to Build #1 confirm lack of deleterious interaction with inorganic-filled separators.

Summary for Builds 1 and 2

- Cycle testing
  - All groups cycling with stable capacity.
    - No evidence of any negative effect from the inorganic-filled separators
  - Silica-filled separator demonstrated better cycle life (>1500 cycles) than the control.
- 60°C Storage
  - Build #1:
    - Cells with silica-filled separators have lower self-discharge rate, less capacity fade and less resistance growth than control cells.
  - Build #2
    - Early failures in OCV testwere due to soft shorts/defects in the cells.
    - All remaining cells demonstrate low self-discharge, low capacity fade and low resistance growth similar to silica-filled cells in build #1.

Overall: There is no evidence that inorganic-filled separators cause negative effects. Cell performance is generally better than for controls: longer cycle life, less self discharge, and higher rate capability.

Gap analysis

Parameter	Units	USABC Goal	Program Goal	Alumina DY110131.025	Silica DY110217.002
Selling price	$/m²	1.00	1.00	-	
Thickness	micron	<25	<25	**25.4**	**18.7**
MacMullin#	#	<11	<8	**< 4.4**	**< 3.6**
Gurley	s/10cc	< 35	< 20	**12.7**	**6.8**
Wettability		Wet out in electrolytes	Wet out in electrolytes	**Complies**	**Complies**
Chemical Stability		Stable in battery for 10 years	Stable in battery for 10 years	Not tested	Not tested
Pore Size	micron	<1	<1	**< 1**	**< 1**
Puncture Strength, JIS 1019*	gf	>300 gf/25.4 µm	>300 gf/25.4 µm	**391**	**280**
Thermal Stability at 200° C		<5% shrinkage	<3% shrinkage	**5% MD**	**5.8% MD**
				1% XMD	**4% XMD**
Tensile Strength		<2% offset at 1000 psi	<2% offset at 1000 psi	1970	1170
Skew	mm/m	<2 mm/meter	<2 mm/meter	-	-
Pin Removal		Easy removal from all winding machines	Easy removal from all winding machines	-	-
Shutdown	° C	As required	As required	No Shutdown	No Shutdown

Future work (March – June 2011)

- Continue 18650 cell performance testing
  - Cycle life
  - 60 C storage

- Conduct abuse tests
  - Sandia National Labs
  - Mobile Power Solutions

- Continue pilot production of silica-filled separators
  - Identify equipment requirements for scale-up
  - Refine cost model

- Complete separator characterization
  - Drying methodology
  - Pore size distribution
  - Mechanical properties vs. UHMWPE molecular weight

- Submit separator samples for large format cell builds
  - A123
  - Dow-Kokam™
  - JCS

Summary

- Developed free-standing, dimensionally stable, inorganic-filled separators that meet USABC requirements
- Optimized web handling and annealing technology to ensure < 5% shrinkage in inorganic-filled separators at 200 $^\circ$C
- Demonstrated exceptionally low impedance in inorganic-filled separators (MacMullin number < 4.5) that allows for high power capability and low temperature performance
- 18650 cells with inorganic-filled separators show good performance compared to control cells with microporous polyethylene separator.
  - Improved cycle life
  - Lower self discharge
  - Higher rate capability
- Preliminary cost model suggests that silica-filled separators can approach target price