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

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Project ID # ES008

Overview

Timeline

- Start – Feb 2010
- Finish – April 2011
- Percent complete – 13 %

Barriers

- High temperature (200 °C) melt integrity
- Shutdown
- Electrolyte compatibility
- Low cost (goal - $\$1/m^2$)

Budget

- Total project funding
  - DOE share - $ 748,404
  - Entek share - $ 748,404
- Funding received in FY2010 - $908,696
- Funding for FY 2011- $ 588,111

Partners

- Portland State University - Electron microscopy
- Rhodia - Inorganic fillers
- ENTEK Manufacturing Inc -Equipment and materials processing

Project objectives

<u>Operating Assumptions</u>

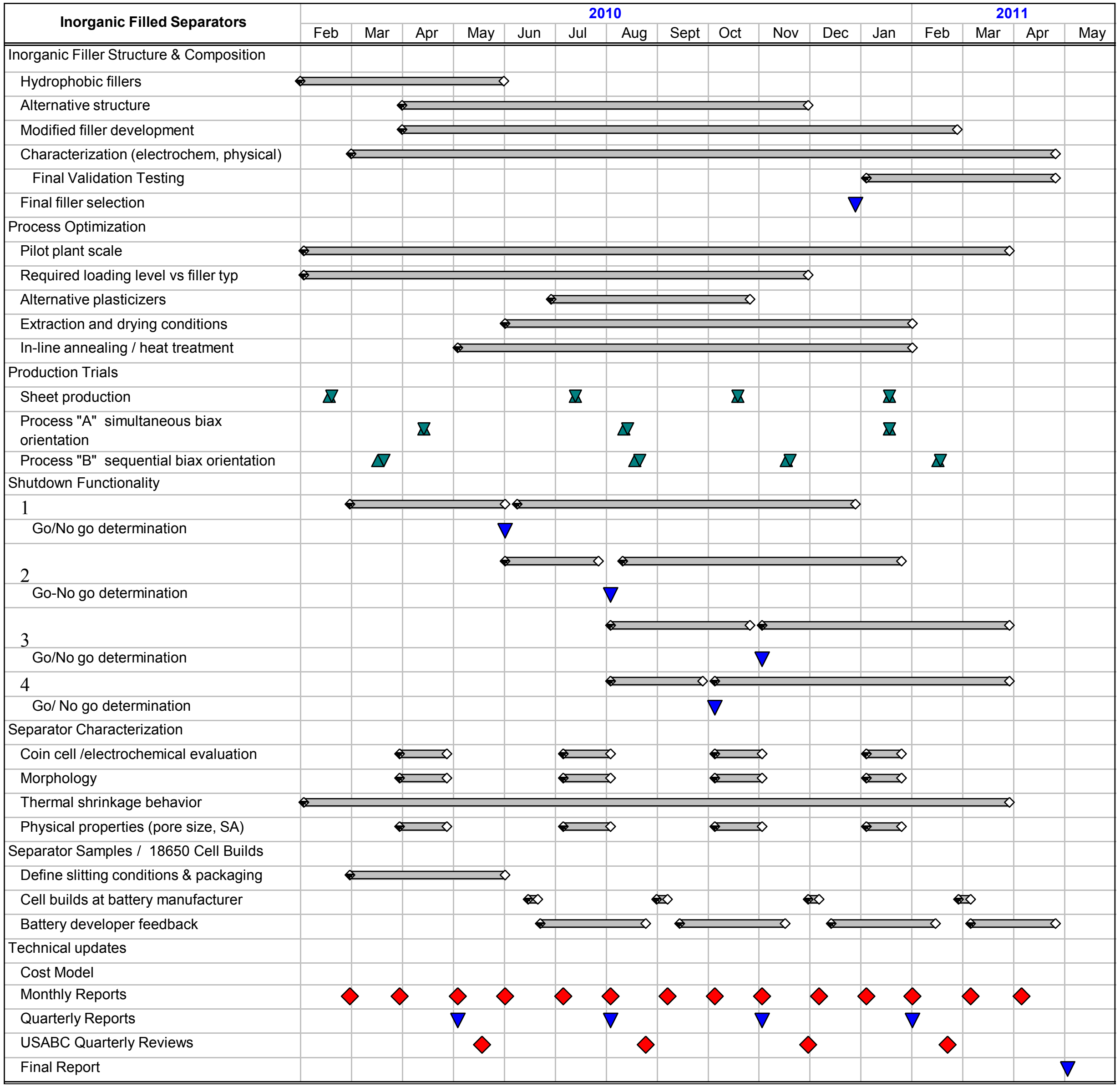
- Separator performance under abuse conditions is vital for HEV/PHEV battery safety, but shutdown is not necessarily required.
- Overcharge, over-discharge, and high rate discharge are controlled by BMS
- Thermal protection & management is handled at system level.

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 (FY 2010)

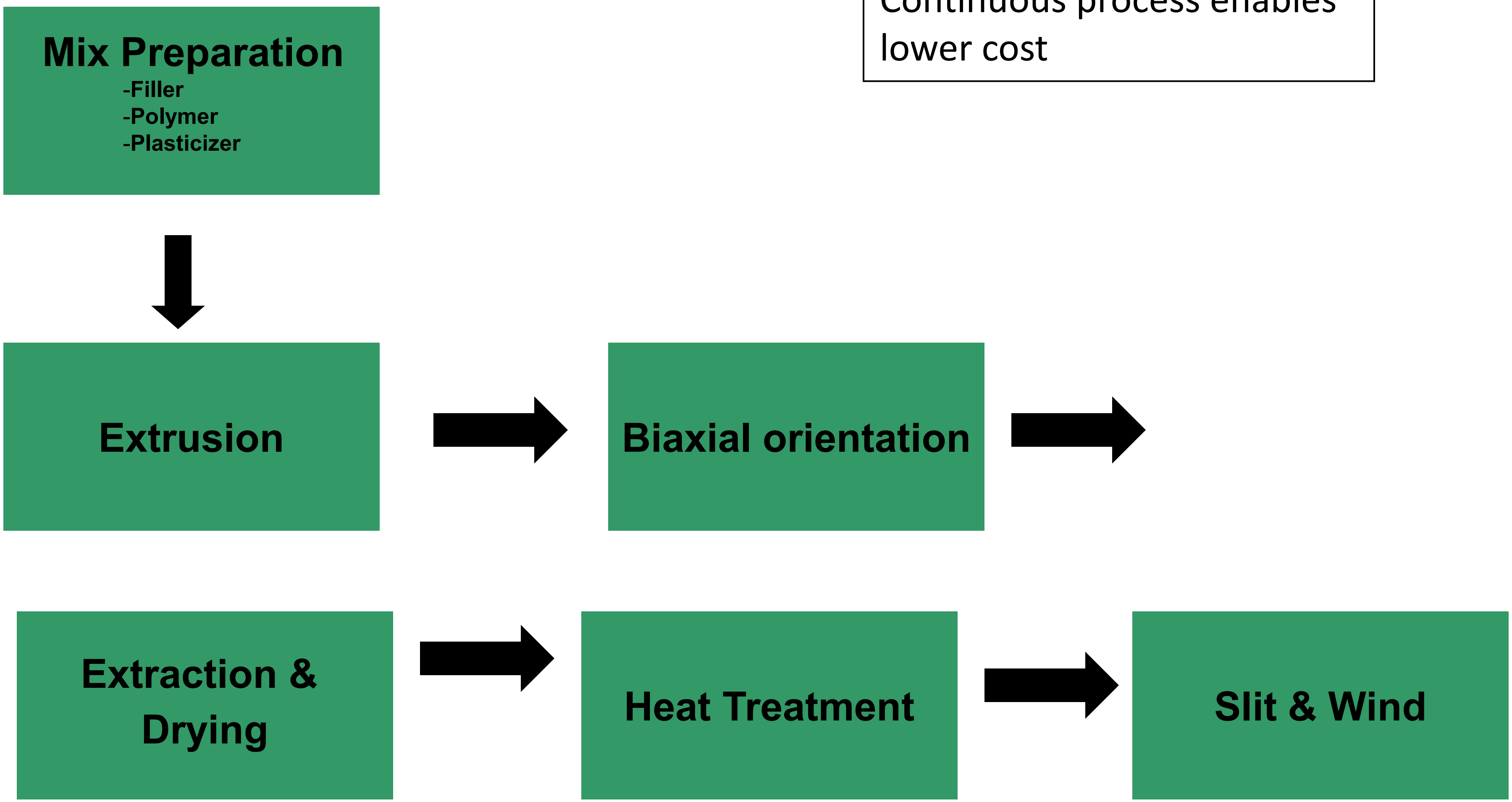
- **Selection of electrochemically stable, dispersible and economical inorganic filler**
- **Process optimization to achieve highly filled separator films with consistent properties**
- **Demonstration of performance and stability of highly filled separators in a standard wound cell design**

Project plan & key decision points



Generic production process

Continuous process enables lower cost



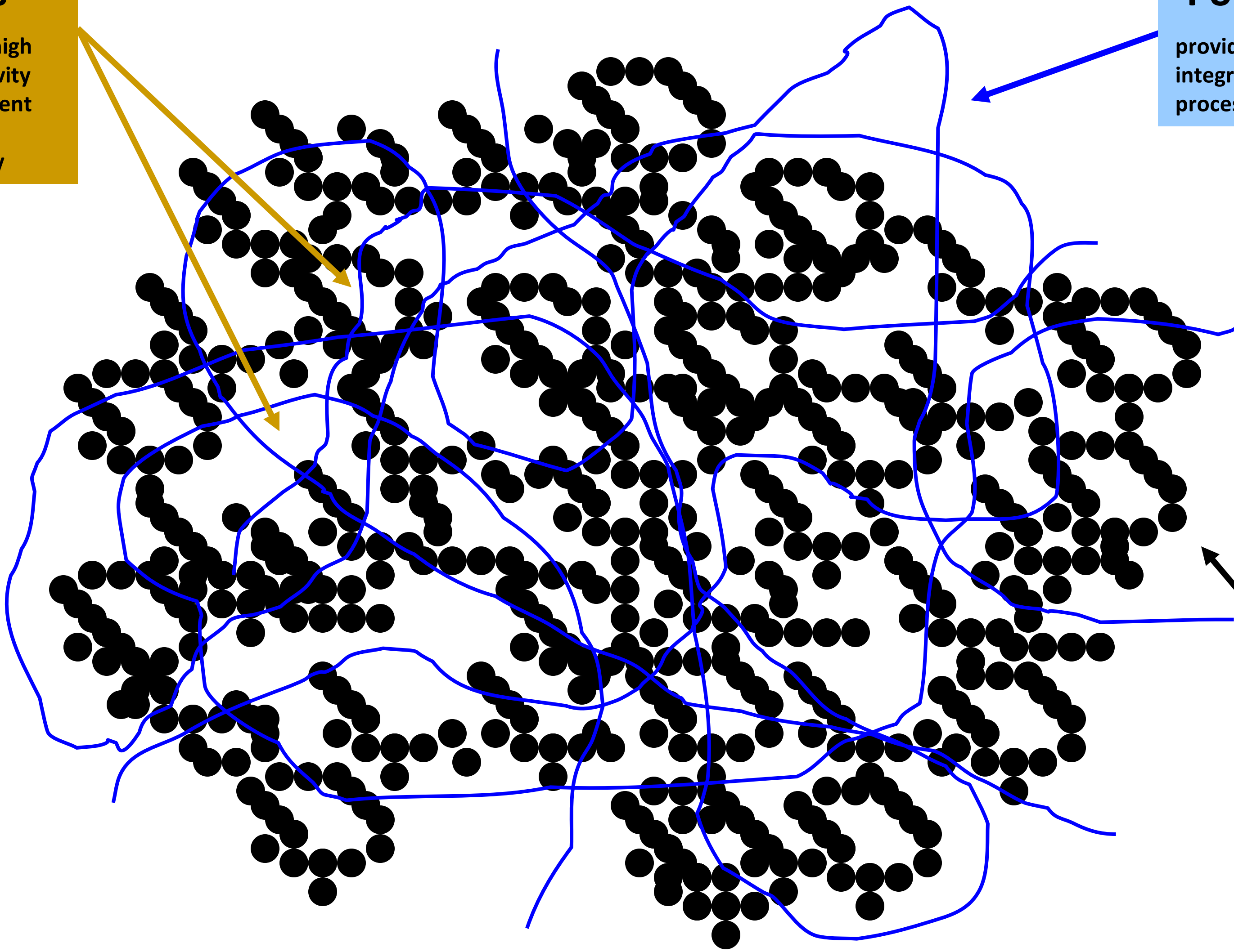
Inorganic-filled separator schematic

Pores

provide high conductivity for excellent power capability

Polymer fibrils

provide mechanical integrity for separator processing & cell winding

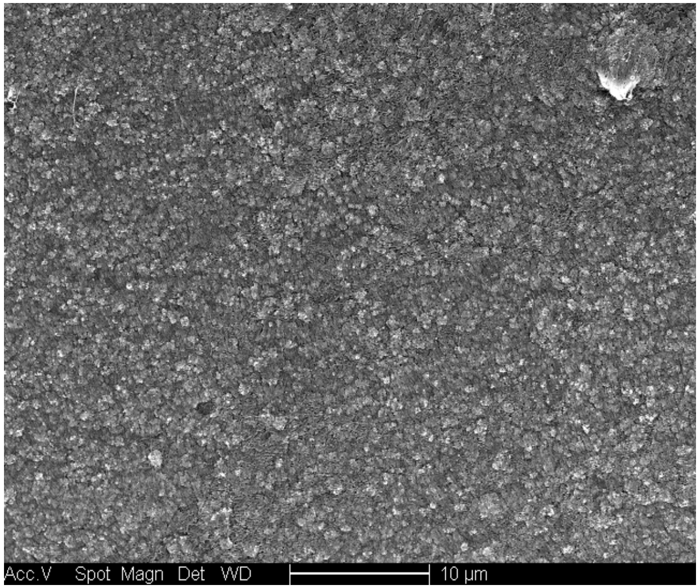


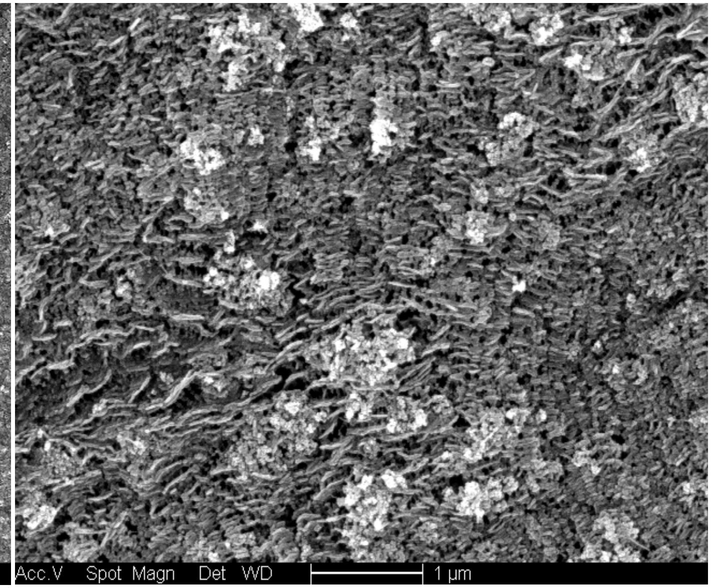
Inorganic aggregates

provide high temp barrier stability, high porosity, and fast wetting

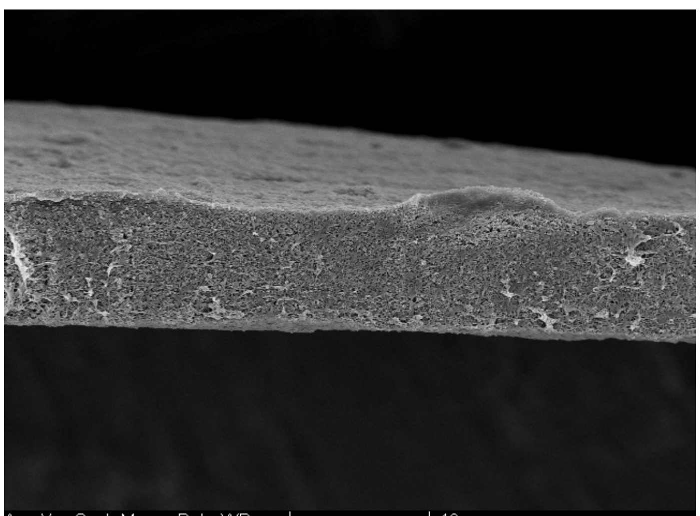
Separator morphology --- 67% Al_2O_3

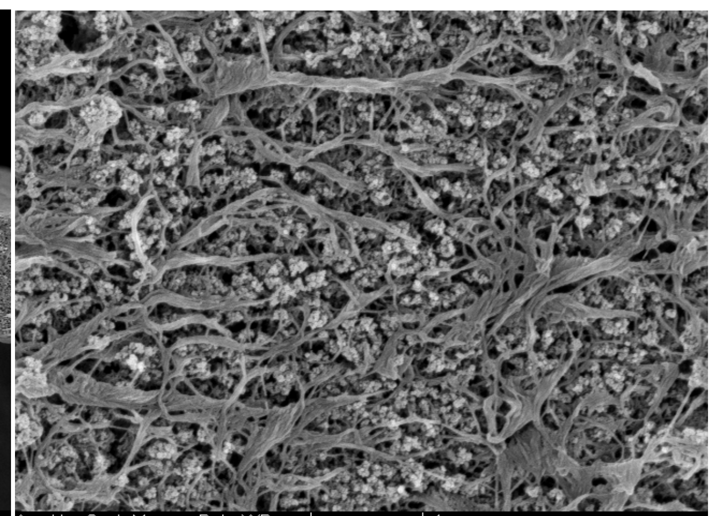
Surface



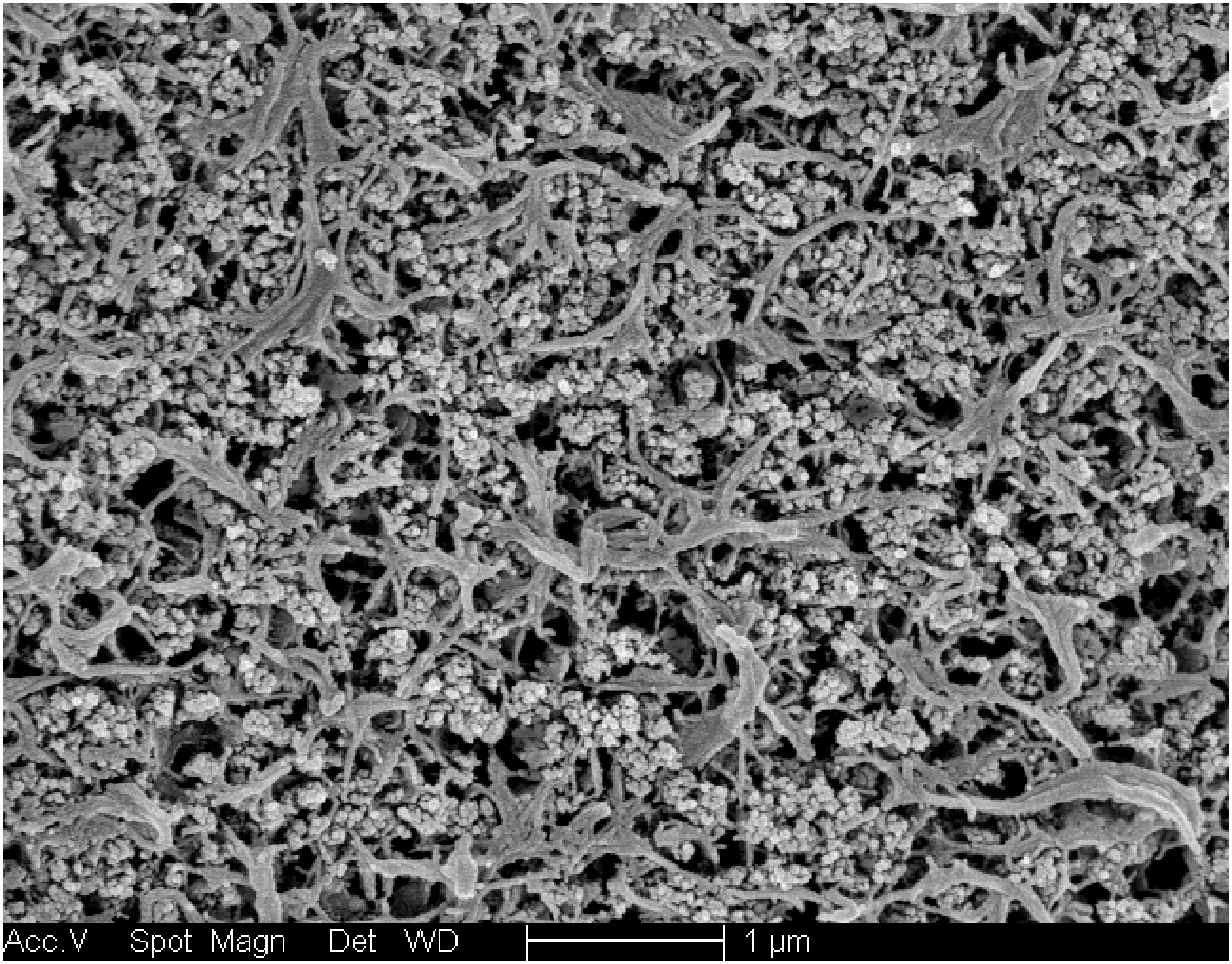


Fracture



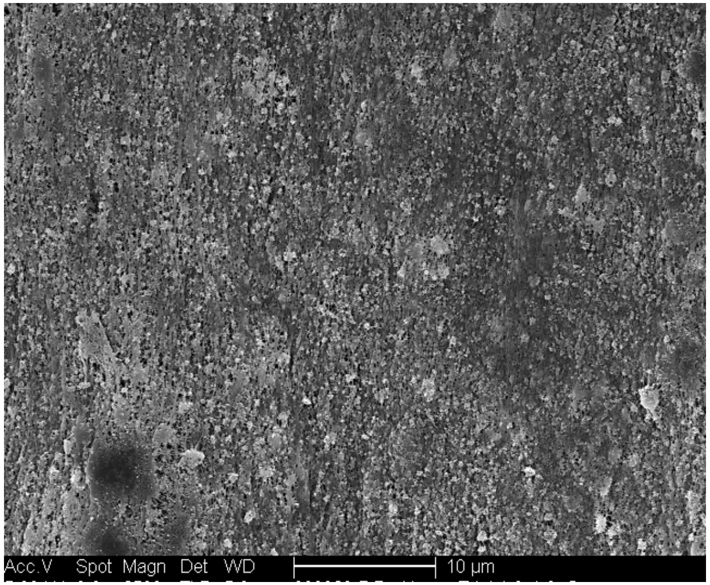


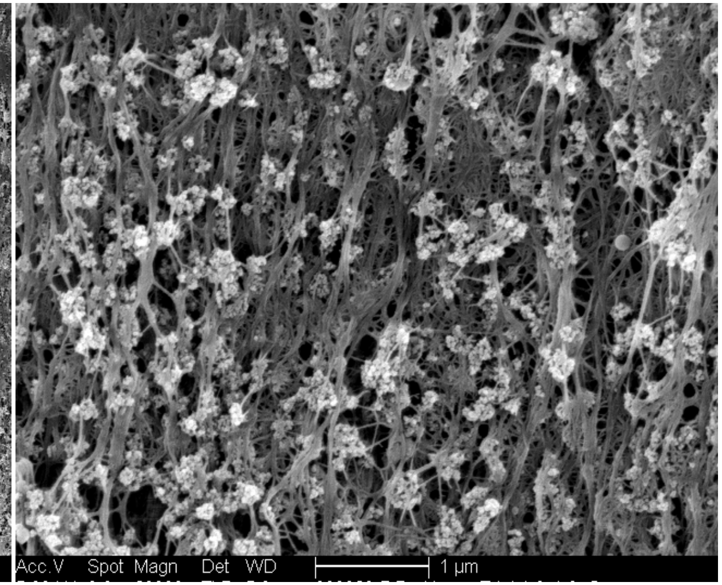
Fracture SEM --- 67% Al_2O_3



Separator morphology --- 69% SiO_2

Surface





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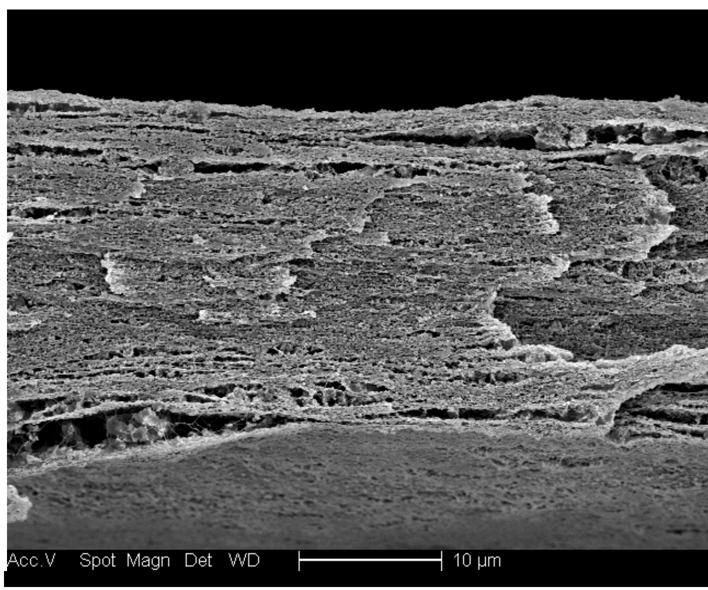

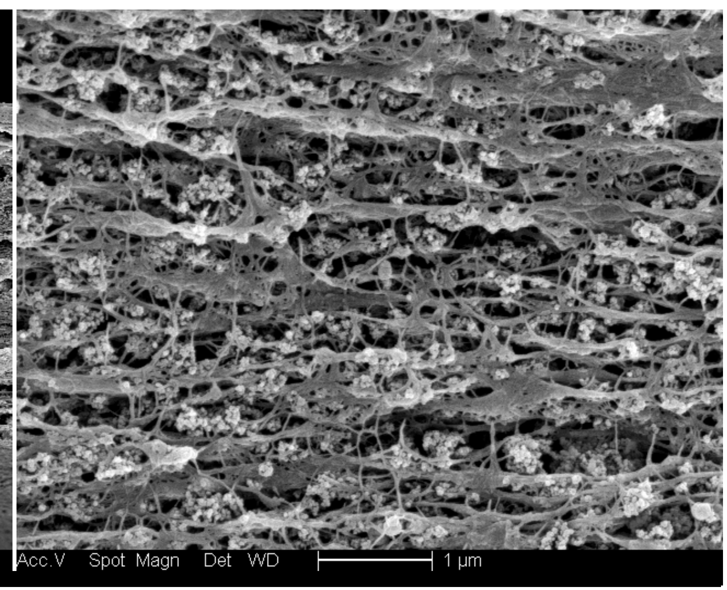

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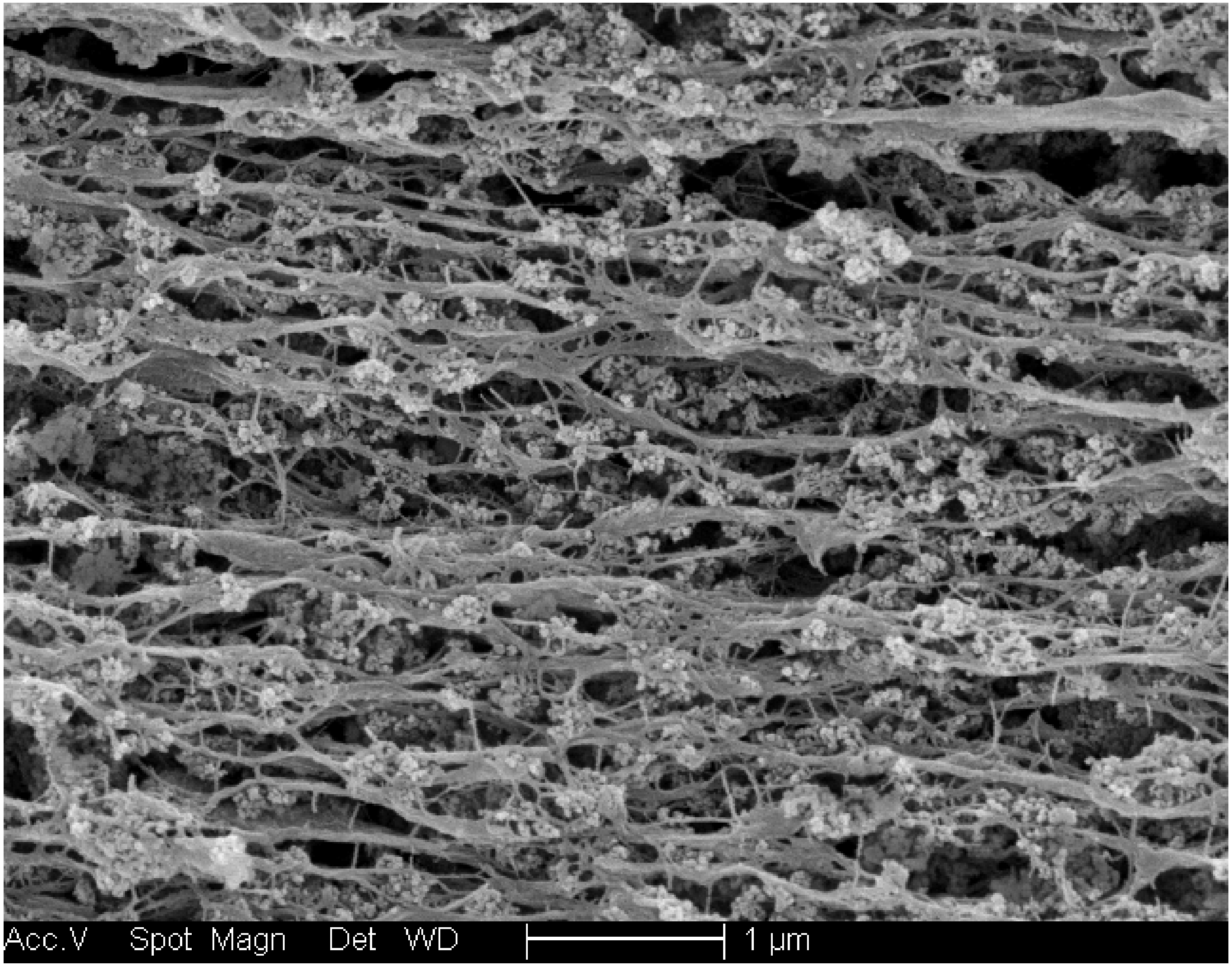
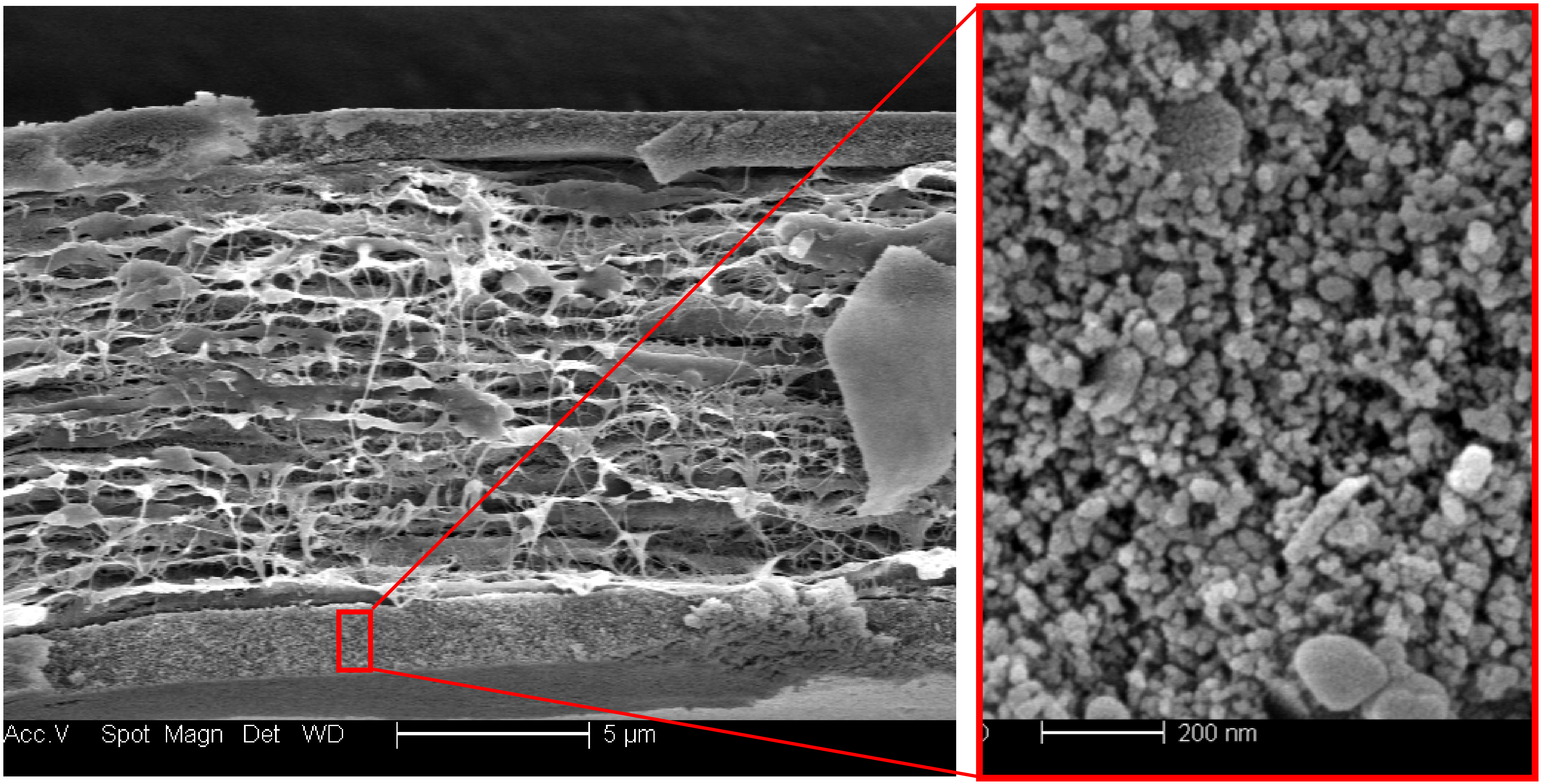


Competing approach

- 12 micron unfilled separator coated with alumina / binder layer



Good dimensional stability achieved at 200 °C

Process A 67% alumina filler

Roll#	Heat Treated	Thickness (um)	Puncture (gf)	Gurley sec/100cc	Shrinkage % MD 200° C	Shrinkage % TD 200° C
ENTEK 25.001 A	Yes	62.4	283.2	361	2.0	2.0
ENTEK 526.001	Yes	36.4	150.7	237	3.7	2.8
ENTEK 529.003	No	21.7	96.7	137	2.8	3.3

Process B 69% silica filler

Roll#	MD Stretch	TD Stretch	Thickness (um)	Puncture (gf)	Gurley sec/100cc	Shrinkage % MD 200° C	Shrinkage % TD 200° C
10	2	4	36.7	227.8	226.3	6.3%	3.3%
12	3	3	35.3	214.5	153.1	8.0%	2.4%
7	4	4	20.3	159.2	109.7	10.8%	2.7%

Ultralow impedance was observed

- High porosity (> 60%)
- Rapid wetting with electrolyte

	Thickness	Areal Resistance	Resistivity	MacMullin
	mm	Ω – cm2	Ω - cm	Number
Sample A - 67% SiO_2	0.040	0.84	209	2.7
Sample B – 67% SiO_2	0.037	0.89	238	3.0
Sample C – 67% SiO_2	0.023	0.54	231	2.9
Sample D – 67% SiO_2 (annealed at 165 C)	0.023	0.44	189	2.6
Sample E – 67% Al_2O_3	0.036	1.07	300	3.5
Sample F – 67% Al_2O_3	0.018	0.68	386	4.2
Teklon HPIP (unfilled)	0.025	2.15	869	8.2
Teklon GOLD LP (unfilled)	0.012	1.85	1460	13.2
Al_2O_3-coated Teklon	0.014	2.40	1668	14.9

Gap analysis

Parameter	Units	USABC Goal	Program Goal	Process A, 67% Al2O3	Process B, 69% Silica,
Selling price	$\$/m^2$	1.00	1.00	-	
Thickness	micron	<25	<25	**22**	**24**
MacMullin#	#	<11	<8	**< 4.5**	**< 3**
Gurley	s/10cc	< 35	< 20	**14**	**3.5**
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	**110**	**245**
Thermal Stability at 200° C		<5% shrinkage	<3% shrinkage	**2.8% MD** **3.3% XMD**	**2.8% MD** **3.3% XMD**
Tensile Strength		<2% offset at 1000 psi	<2% offset at 1000 psi	-	**6,900**
Skew	mm/m	<2 mm/meter	<2 mm/meter	-	-
Pin Removal		Easy removal from all winding machines	Easy removal from all winding machines	-	Cells Built
Shutdown	° C	As required	As required	No Shutdown	No Shutdown

Future work

- Filler selection
  - Electrolyte compatibility tests at 60 C
  - Supplier development of optimized inorganic fillers (chemistry, surface area, structure)

- Shutdown integration

- Continue pilot plant investigation of fillers that are stable in Li-ion environment
  - Identify process conditions required for new fillers and polymers
  - Quantify mechanical properties of plasticized sheet prior to biaxial stretching
  - Complete separator characterization

- Scale up
  - Identify required equipment for continuous process
  - Refine cost model

- Cell Performance
  - 18650 cell construction & testing
  - Provide separator samples to selected USABC battery companies
  - Improve separator formulation & properties as required

Summary

- Free-standing, heat resistant separators were manufactured with > 50% inorganic filler
- No particle shedding observed even at highest loading levels (> 70%)
- Inorganic filled separators exhibited good dimensional stability even after 1 hr. exposure at 200 $^{\circ}$C
  - approx. 65 $^{\circ}$C above the melting point of the polymer matrix
- Rapid wetting achieved
- Ultralow impedance (MacMullin number < 4.5) was measured for inorganic-filled separators
- Further improvements to puncture strength are required
- Shutdown approaches have been identified