Advanced Polyolefin Separators for Li-ion Batteries used in Vehicle Applications

W. Wood, R. Waterhouse, D. Spitz, D. Wandera,
A. Wimer, D. Lee and R.W. Pekala

ENTEK Membranes LLC, Lebanon Oregon 97355

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Project ID: ES289

OVERVIEW:

Timeline:

- Start Date: June, 2015
- End Date: June, 2017
- 50% Complete

Project Goals to Address Barriers:

- Improved energy density:
  - Voltage oxidation resistance up to 5V
- Improved abuse tolerance:
  - High temperature dimensional stability above 180°C
  - Shutdown Features
- Reduced Cost

Budget:

- Total Project Funding (50/50)
  - USABC Share: $1,042,745
  - ENTEK/Farasis Share: $1,042,745
- FY15 Funding:
  - USABC Share: $281,150
  - ENTEK/Farasis Share: $281,150

Partners/Subcontractors:

- Farasis Energy
- Mobile Power Solutions
- Portland State University

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RELEVANCE AND PROJECT OBJECTIVES:

Relevance:

- Mass adoption of electric vehicles requires improved lithium ion cell performance, improved safety, and reduced cost. This project addresses these challenges through inorganic filled and ceramic coated separator development.

Project Objectives:

- Improve energy density
  - High voltage oxidation resistance up to 5 V.
- Improve cell abuse tolerance with the following separator features:
  - High temperature dimensional stability above 180°C.
  - Shutdown
- Reduce separator cost through:
  - Reduced electrolyte fill times, by improving separator wetting by electrolyte solution.
  - Reduced materials costs of coatings, by minimizing coating mass required to reach high temperature dimensional stability.
  - Reduced manufacturing costs, by developing coating technologies that can be implemented continuously in-line with base separator production

MILESTONES:

Date	Milestones	Status
October, 2015	Production trial for reduced shutdown temperature: **8°C reduction in shutdown temperature**	Complete
December, 2015	Production trial for inorganic filler screening: **>20% improvement in wetting (USABC Target)**	Complete
December, 2015	USABC Separator Deliverables 1 and 2 sent to Farasis Energy for cell testing	Complete
February, 2016	Production trial for silica loading level optimization: **Achieved porosities greater than 60%, MacMullin Number less than 4 (USABC target for power cells)**	Complete
January-February, 2016	Developed test methods for evaluating voltage oxidation resistance of separators	Initial development complete. Testing is ongoing
February-Present	Screen/develop coating technologies to demonstrate continuous in-line coating with base separator	Ongoing

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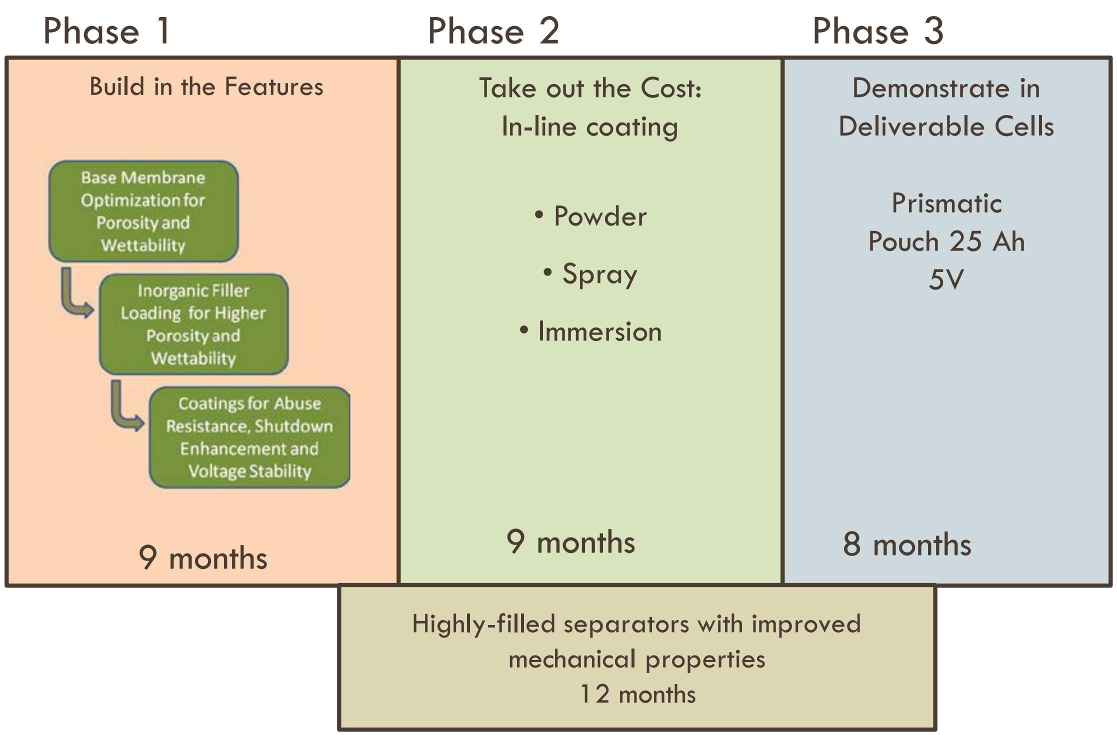
APPROACH AND STRATEGY:

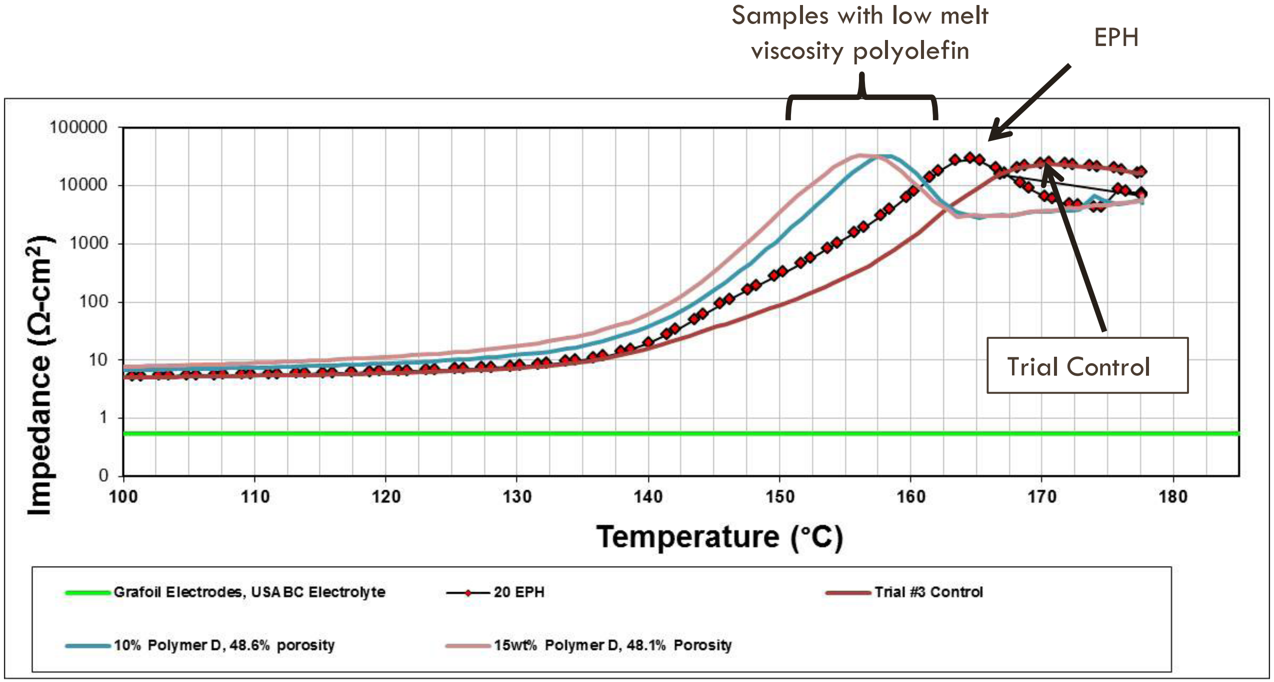
- **Phase 1**: Build-in the features with inorganic filler and ceramic/polymer coatings
  - Improve wetting, ionic conductivity, voltage oxidation resistance, and safety features (low shrinkage, shutdown)
- **Phase 2**: Take out the cost
  - Reduce electrolyte fill time, demonstrate in-line coating technologies, optimize coating to minimize material costs
- **Phase 3**: Demonstrate technology in large format cells



TECHNICAL PROGRESS: BASE SEPARATOR OPTIMIZATION

Sample Description	Porosity	Calculated Thickness	Emveco Thickness	Basis Weight	Gurley Number	Puncture	120°c shrinks 30 min	120°c shrinks 30 min	MD Tensile	XMD Tensile	MD Elong.	XMD Elong.
	%	µm	µm	g/m²	s/100cc	gf	MD	XMD	kg/cm²	kg/cm²	(%)	(%)
20 EPH	48.9	20.2	21.0	9.9	148	463	10.4	3.9	1081	585	134	248
Trial #3 Control	48.2	20.0	22.0	10.0	177.5	556.0	10.5	6.0	1208.3	797.5	80.8	316.8
10wt% Polymer D	48.6	21.2	21.7	10.5	157.0	489.8	11.4	6.1	1210.8	660.8	102.5	393.8
15wt% Polymer D	48.1	19.3	19.5	9.6	156.8	420.0	13.5	8.6	1018.3	626.3	126.8	367.3

- Shutdown temperature defined as the temperature at which impedance reaches 1000 times that at 100°C
- Shutdown temperature reduced by 7°C compared to control by adding a low melt viscosity polyolefin to the formulation



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TECHNICAL PROGRESS: INORGANIC FILLER SCREENING

- Various fillers were screened for ability to process on the ENTEK lithium ion separator production line:

Set	Filler	Silane Treatment?
1	Alumina	No
2	Alumina	Yes
3	Silica	Yes
4	Silica	No
5	Alumina + Polymer D	No

- Filler levels: 2.5vol%
- Results from the trial are shown below:

F.O.	GEM Set	Sample Description	Anneal Temperature	TDO Stretch	Porosity	Calculated Thickness	Basis weight	Gurley Number	Puncture	MD Tensile	XMD Tensile	MD Elong.	XMD Elong.
			°C	%	%	µm	g/m²	s/100cc	gf	kg/cm²	kg/cm²	(%)	(%)
1975	7	20EPH Control	Low	Medium	48.7	20.0	9.9	144.8	500.0	1190.8	762.5	109.3	286.3
1888	2	20EPX Control	Low	High	54.5	20.5	9	91	452	861	664	100	329
1975	8	Treated Alumina filler	Low	Low	54.3	20.0	9.8	114.0	472.5	1128.8	593.8	70.8	312.3
1975	9	Treated Alumina filler	High	Low	52.4	19.9	10.1	123.3	481.0	1370.8	593.5	87.0	299.5
1975	12	Treated Silica filler	High	Low	52.1	20.7	10.1	131.0	515.5	1508.5	596.0	67.5	353.3
1975	13	Untreated Silica filler	High	Low	54.0	24.5	11.5	114.3	494.8	907.3	542.5	93.5	364.8
1975	14	Untreated Alumina + Polymer D	High	Low	54.1	19.4	10.4	173.2	434.1	1162.8	549.8	87.8	398.8

- Based on ease of processing and reduced material costs, silica filler was further evaluated at different loading levels

TECHNICAL PROGRESS: SILICA FILLER CONCENTRATION

- Silica filler was further evaluated at concentrations up to 20wt% loadings
  - Untreated vs silane treated silica
  - Powder vs pellet fed

F.O.	GEM Set #	Sample Description	Filler Feed type	Porosity	Calculated Thickness	Basis Weight	Gurley Number	Puncture	120°C shrinkage 30 min	120°C shrinkage 30 min	MD Tensile	XMD Tensile	MD Elong.	XMD Elong.
				%	µm	g/m²	s/100cc	gf	MD	XMD	kg/cm²	kg/cm²	(%)	(%)
1996	4	EPH control, 20µm	-	48.1	19.80	9.9	179	571	14.1	9.8	1163	773	79.0	272
1996	6	5wt% Treated Silica, 20µm	Powder	50.4	20.25	9.9	154	533	14.8	9.6	1154	722	75.0	263
1996	7	10wt% Treated Silica, 20µm	Powder	54.9	20.12	9.2	121	511	15.6	13.1	1142	725	81.3	238
1996	8	10wt% Treated Silica, 16µm	Powder	53.2	16.6	7.9	112	455	15.5	12.6	1014	765	62.8	206
1996	9	10wt% Untreated Silica, 16µm	Powder	57.9	14.2	6.1	84	347	13.1	13.1	1011	711	50.3	222
1996	10	10wt% Untreated Silica, 20µm	Powder	59.0	20.9	8.7	95	440	16.2	11.9	815	722	72.8	198
1996	11	10wt% Untreated Silica, 20µm, Pellet	Pellet	57.6	20.7	8.9	95	452	14.9	11.0	850	720	87.8	291
1996	12	20wt% Untreated Silica, 20µm, Pellet	Pellet	63.6	22.7	8.9	67	379	14.9	13.7	818	619	72.3	277
1996	13	20wt% Untreated Silica, 20µm	Powder	65.3	20.63	7.8	75	393	17.4	14.0	803	532	57.0	241

- Increasing filler loading level resulted in:
  - Increased porosity
  - Decreased Gurley Numbers
  - Decreased mechanical properties
    - Comparable to commercial product. Still within USABC Target
- Pellet fed, untreated silica showed the best sheet quality

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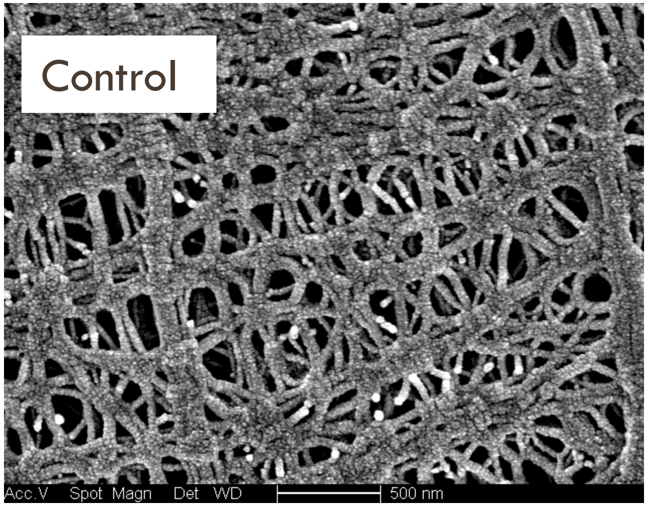
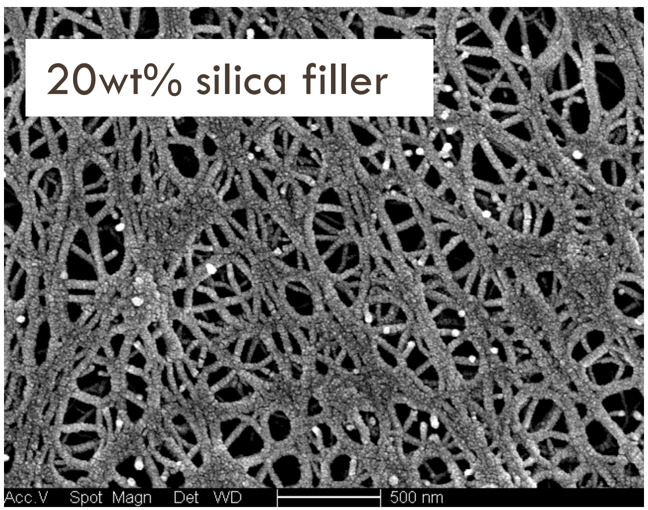
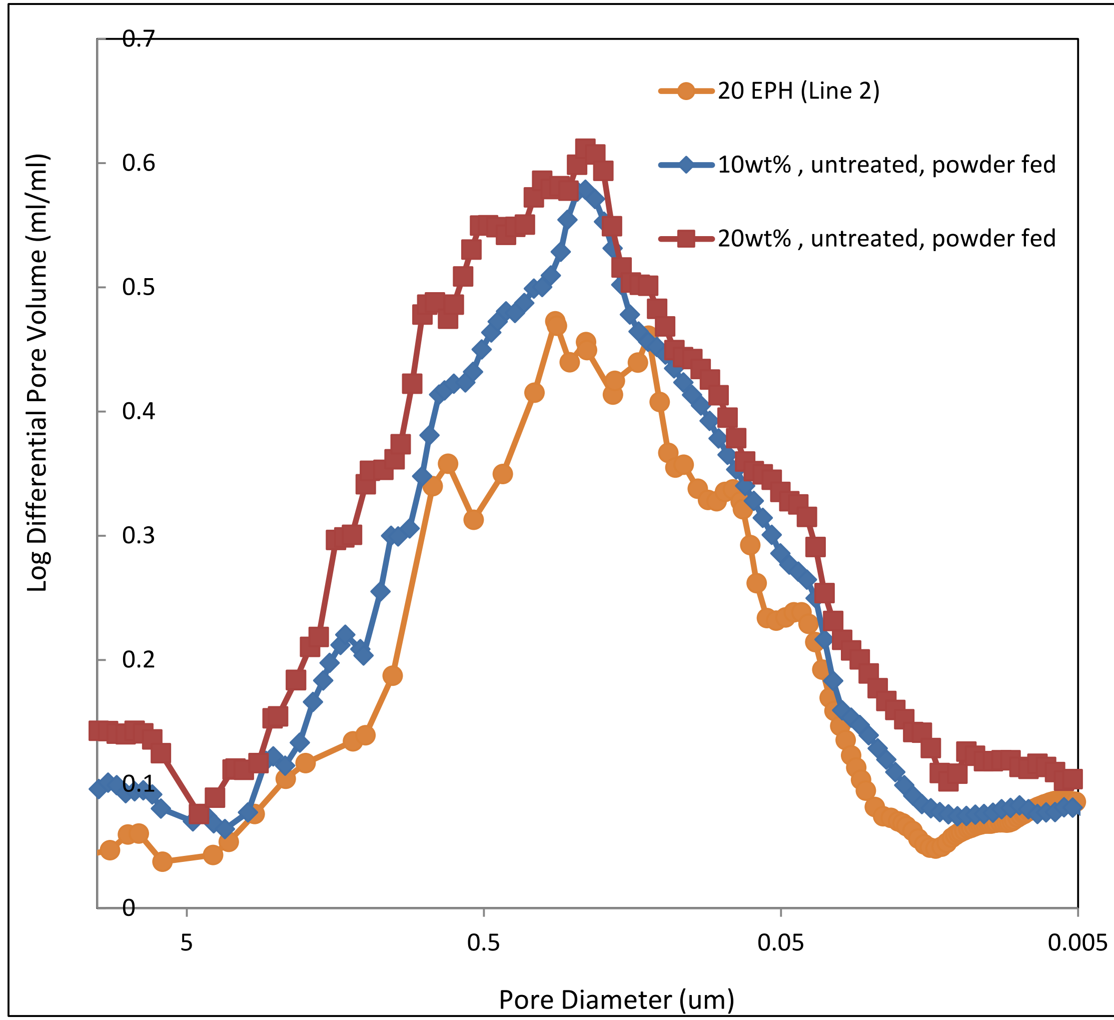
TECHNICAL PROGRESS: SILICA FILLER PORE STRUCTURE



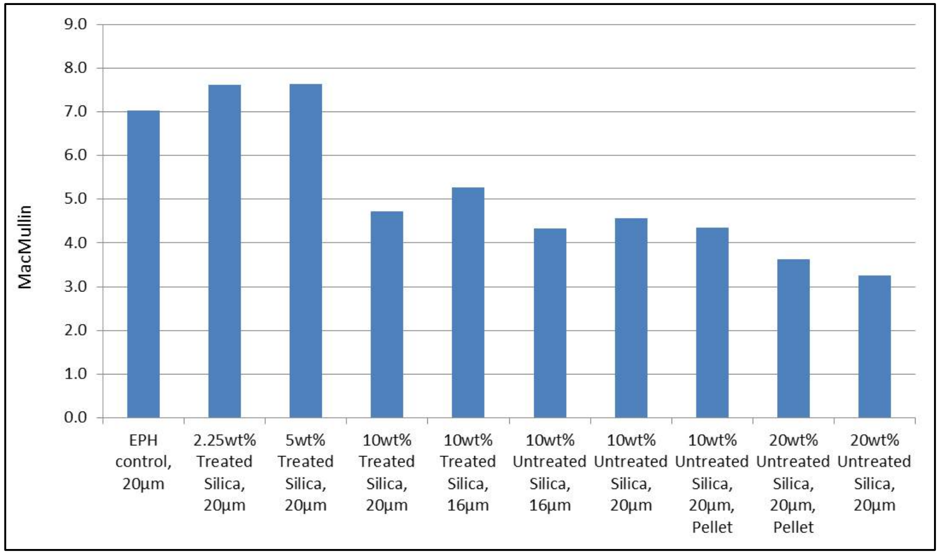


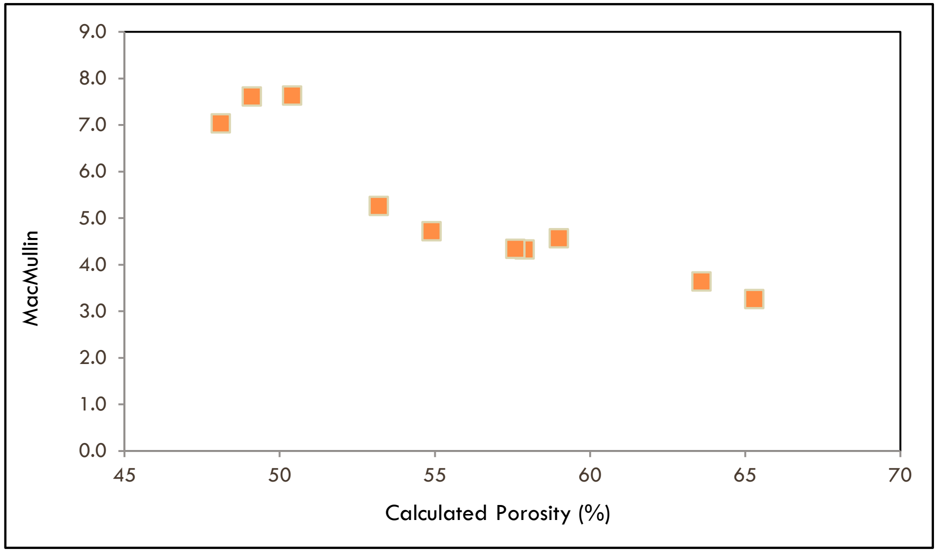


- Despite much higher porosity, the inorganic filled separator pore size was similar to that of the control sample

TECHNICAL PROGRESS: SILICA FILLED IONIC CONDUCTIVITY

- For given process conditions, ionic conductivity increased (decrease in Macullin) with increasing silica loading level
- At 20wt% loading levels, the MacMullin Number was below 4 **(USABC goal for power applications)**
- Direct correlation between ionic conductivity and separator porosity

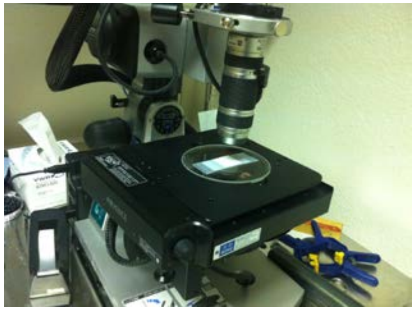


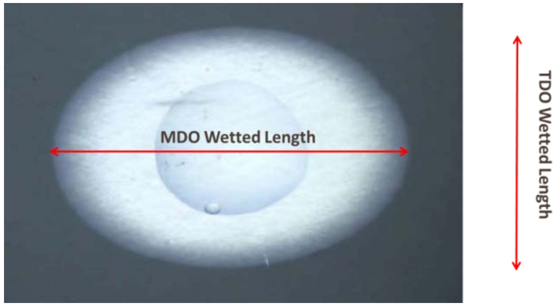


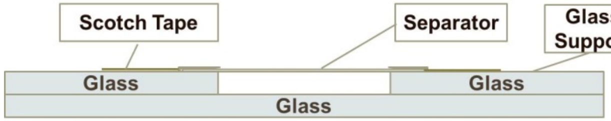
TECHNICAL PROGRESS: SILICA FILLER WETTING IMPROVEMENT

Droplet Wetting Method:

- Separator suspended in air to prevent solvent wicking on glass
- 5ul droplet placed on separator by micro-pipette. Wetted area measured after **5 minutes**.
- Solvent: propylene carbonate/tri(ethylene glycol) dimethyl ether = 1/1 (vol.)

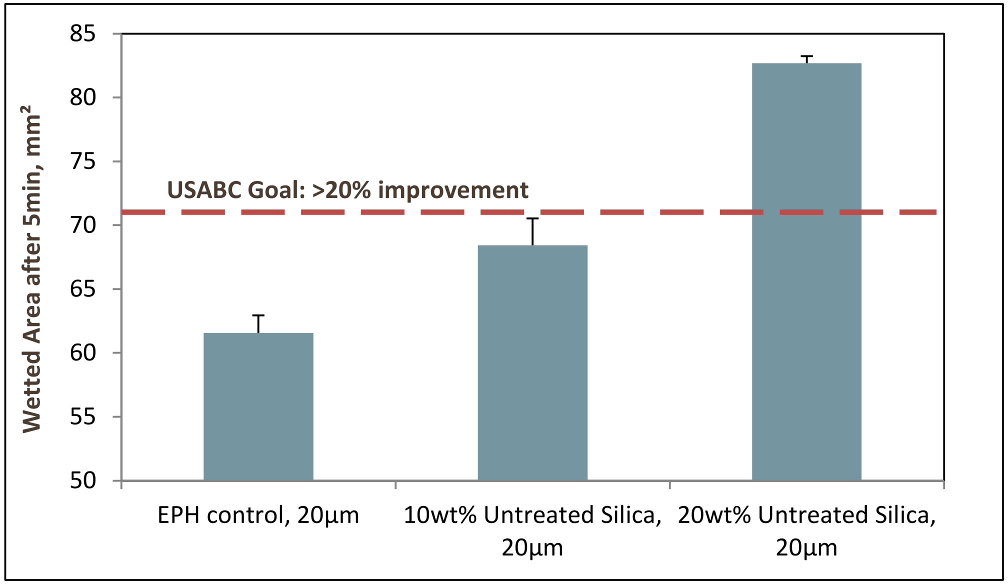






Results:

- Inorganic filled separator with 20 wt% loading showed a ***34% improvement in wetting*** in the droplet wetting test



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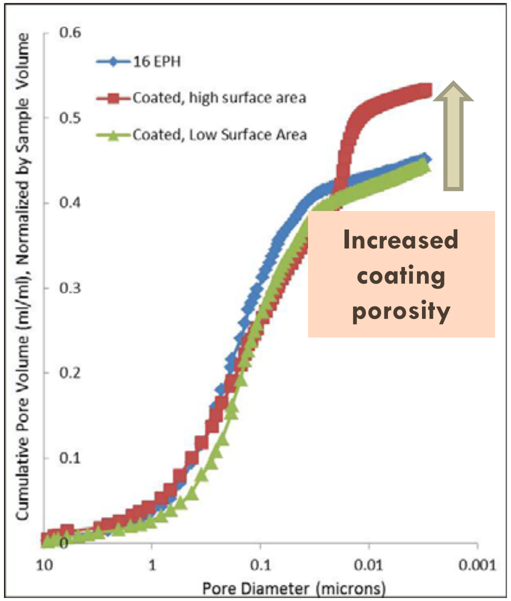
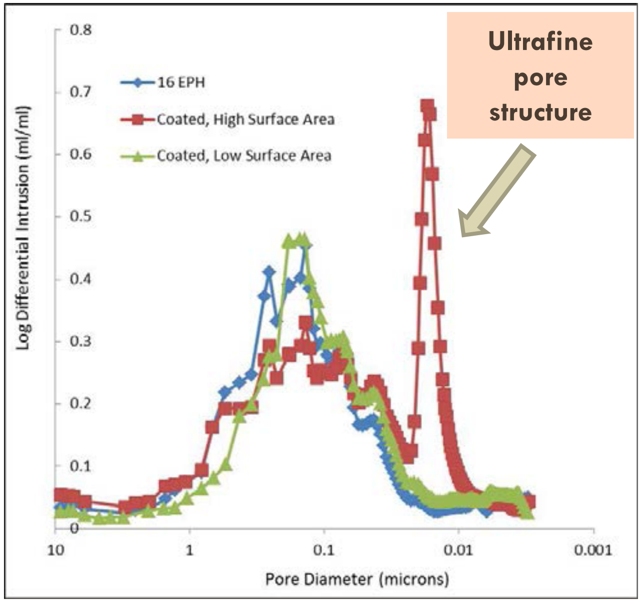
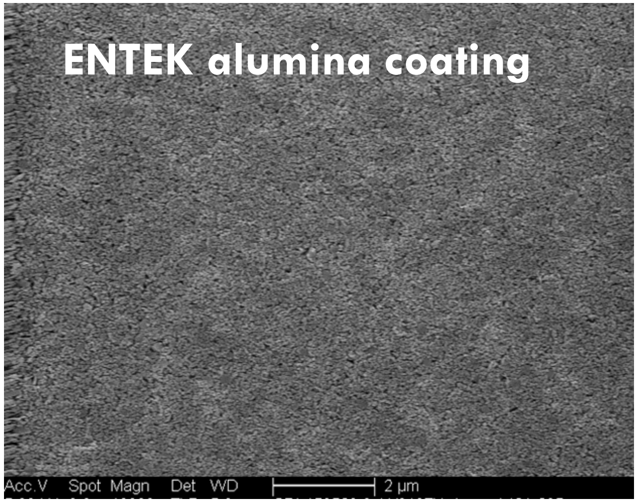
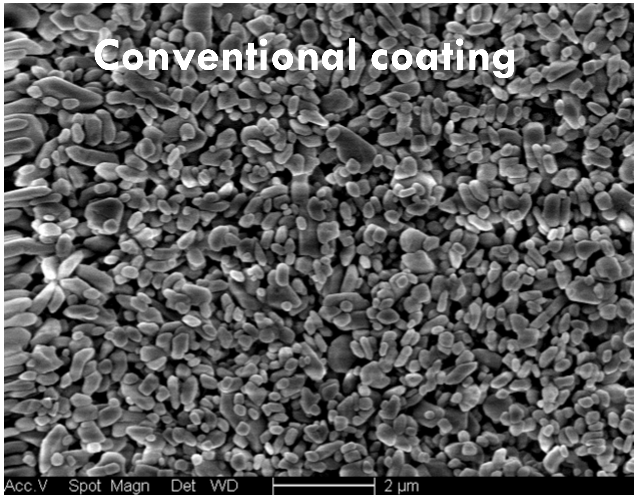
TECHNICAL PROGRESS: COATED SEPARATOR DEVELOPMENT

- ENTEK's approach: alumina coatings with nanostructure, high surface area
  - Excellent dimensional stability, improved safety
  - Very thin, uniform coatings can be applied for improved energy density
- Challenge:
  - Higher moisture content than conventional coated separator



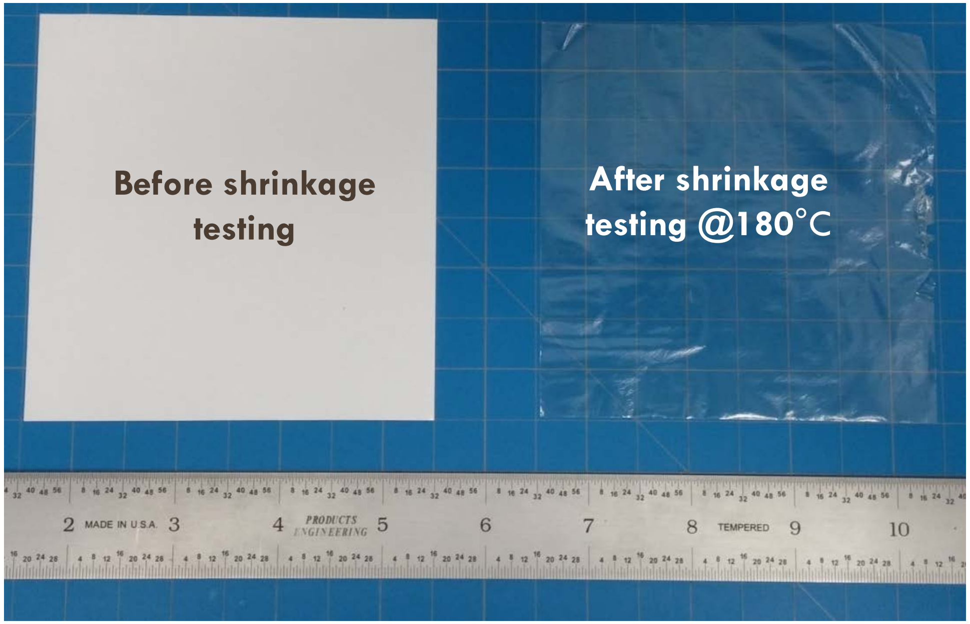


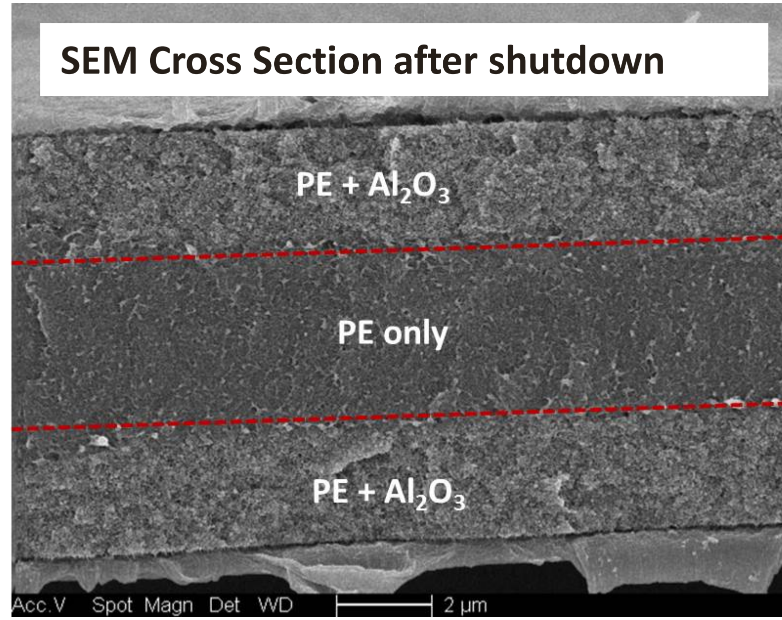




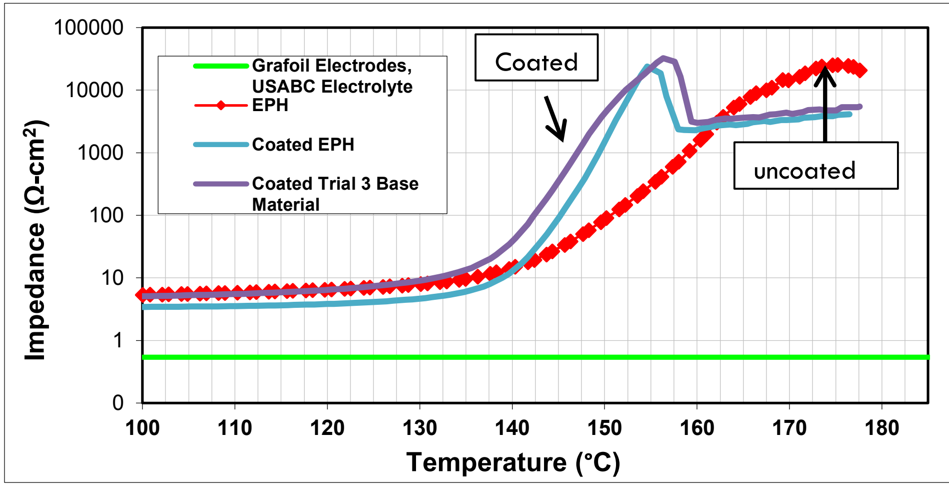
- ENTEK uses nan-particulate alumina with ultrafine pore structure to improve safety

TECHNICAL PROGRESS: COATED SEPARATOR SAFETY FEATURES





- Alumina coated separator yields improved high temperature dimensional stability (<5% shrinking at 180°C) and lower shutdown temperature



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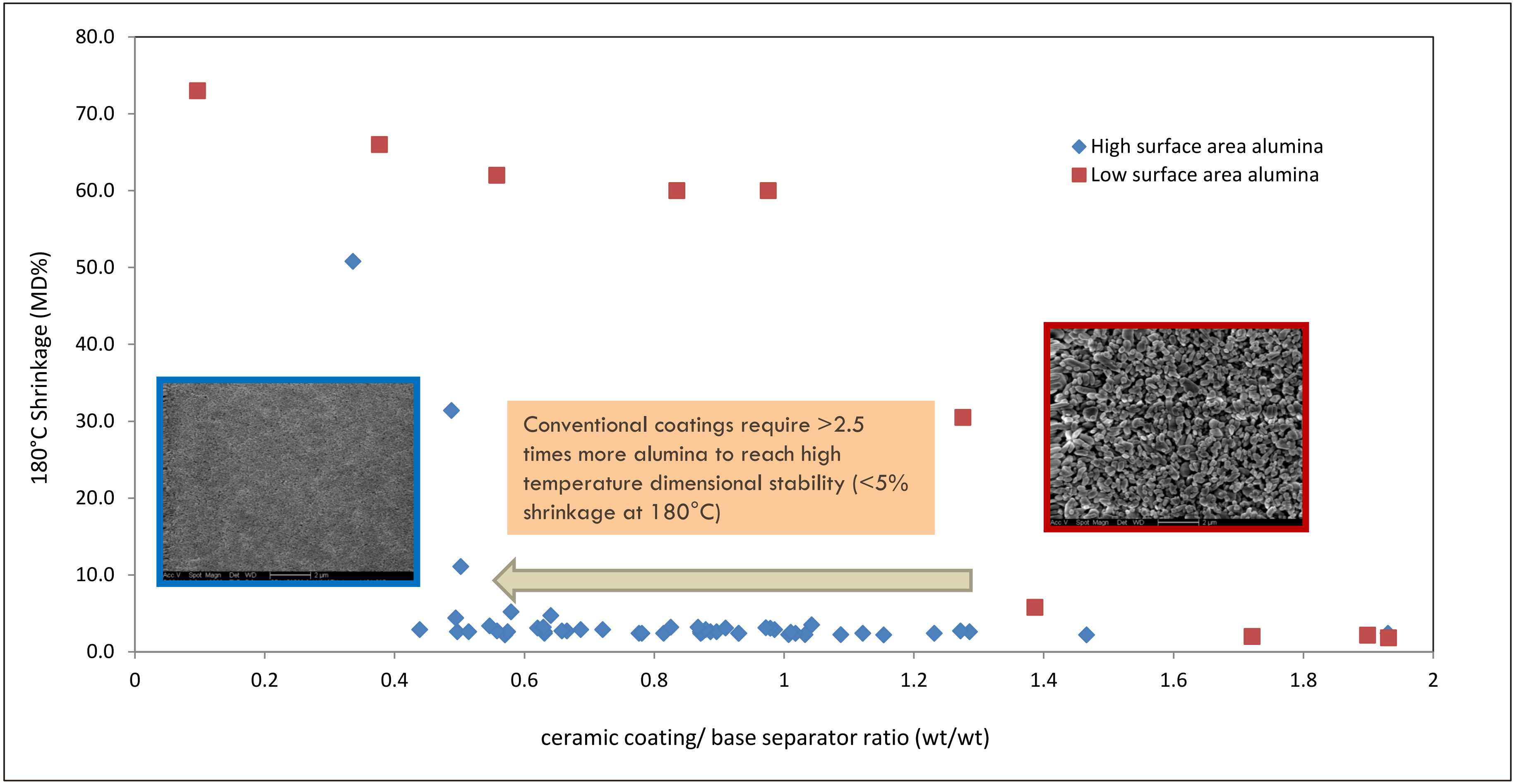
TECHNICAL PROGRESS: COATED SEPARATOR REDUCED COST



- Alumina coated separators with higher surface area require a much lower loadings in order to reach low thermal shrinkage below <5% @180°C.
- ~60% materials cost reduction assuming similar alumina pricing.

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RESPONSE TO COMMENTS FROM PREVIOUS YEAR

- This is the first Annual Merit Review for this project.

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PARTNERSHIPS AND COLLABORATIONS

- **Farasis Energy** (Project Partner)
  - High voltage cell development
  - Cell builds for separator development
- **Mobile Power Solutions**
  - Subcontractor for cell performance testing
- **Portland State University**
  - Scanning electron microscopy and other auxiliary testing

CHALLENGES AND BARRIERS

- Development of separators for high voltage cells
  - Requires the proper selection and integration of electrodes, electrolyte, and separator
  - Methods for voltage oxidation resistance screening are being developed. Optimized coated separator will be integrated in cathode/electrolyte development at Farasis Energy.

- High moisture in high surface area alumina coated separator
  - Various methods for removing moisture, such as drying/packaging, formulation change, or surface modification will be evaluated.

- In-line coating for reduced costs
  - Requires specific coating speeds and path lengths for a given production line. Technical and economic feasibility for in-line coating will be addressed in the upcoming months.

PROPOSED FUTURE WORK

- **Perform abuse testing on cells built with inorganic filled and ceramic coated separator**

- **Evaluate voltage oxidation resistance of alumina/polymer coatings**
  - Integrate the optimized ceramic coated separator with a high voltage cathode and electrolyte into an operating cell.

- **Electrolyte fill time experiments**
  - Significant improvements in wetting were demonstrated for both inorganic filled and ceramic coated separators
  - Future experiments will investigate the correlation between electrolyte fill times and improvements in wetting

- **Evaluate methods for moisture removal from high surface area alumina coated separator**
  - Drying methods and ceramic coating formulation optimization will be evaluated

- **Demonstrate technologies that can integrate continuous in-line coating with base separator production**
  - Evaluate the feasibility of continuously coating separator using immersion, spray coating, and powder coating systems

SUMMARY:

Inorganic filled separator development:

- Incorporating inorganic filler into the separator resulted in:
  - Wetting improvement greater than 20% (droplet)
  - MacMullin Number less than 4
  - Pore structure similar to unfilled control samples

Coated separator development:

- Coating the base separator with a high surface area alumina resulted in:
  - High temperature dimensional stability (<5% shrinkage @180°C)
    - Less coating required to reach high temperature dimensional stability compared to conventional alumina coatings
  - Wetting improvement greater than 50%

- Future work will include further evaluation of separator voltage oxidation residence and coating techniques for reduce cost