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Structure-Property Relationships of Ceramic-Modified Separators

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International Battery SEMINAR & EXHIBIT

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OUTLINE

- Ceramic-Modified Separators
  - Inorganic filler distributed throughout bulk structure
  - Inorganic coating on one or both sides of separator

- Coating chemistry
  - Particle size
  - Loading level
  - Binder content

- Structure-Property Relationships
  - High temperature dimensional stability
  - Particle penetration
  - Wicking rate
  - Moisture content

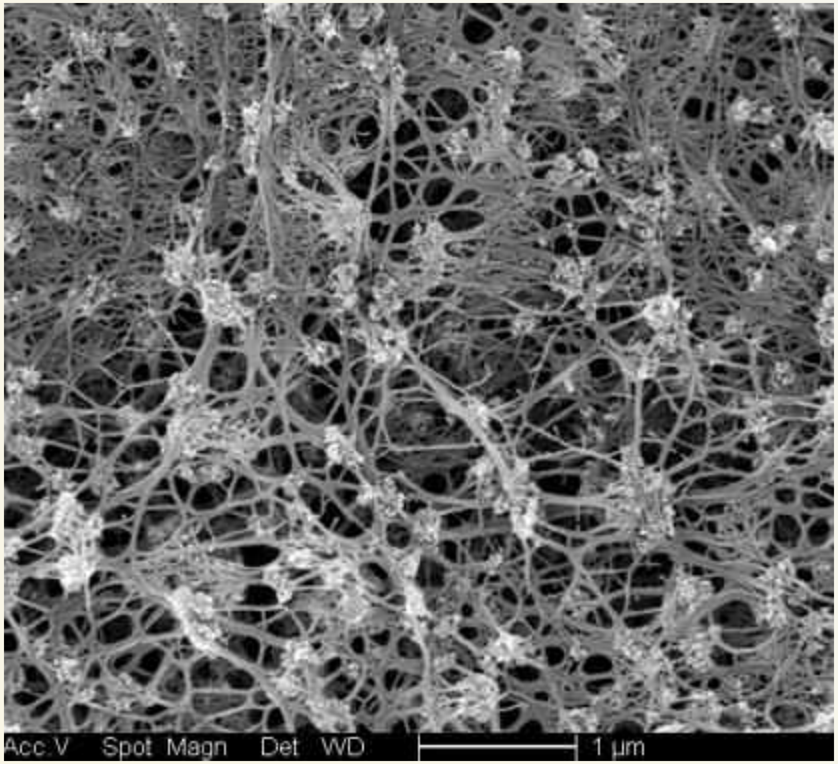
- Future opportunities

CERAMIC-FILLED SEPARATORS

1. Mix Preparation
   - Silica
   - UHMWPE
   - Process oil
2. Extrusion
3. Calendering
4. Biaxial Orientation
5. Extraction & Drying
6. Heat Treatment
7. Slit & Wind

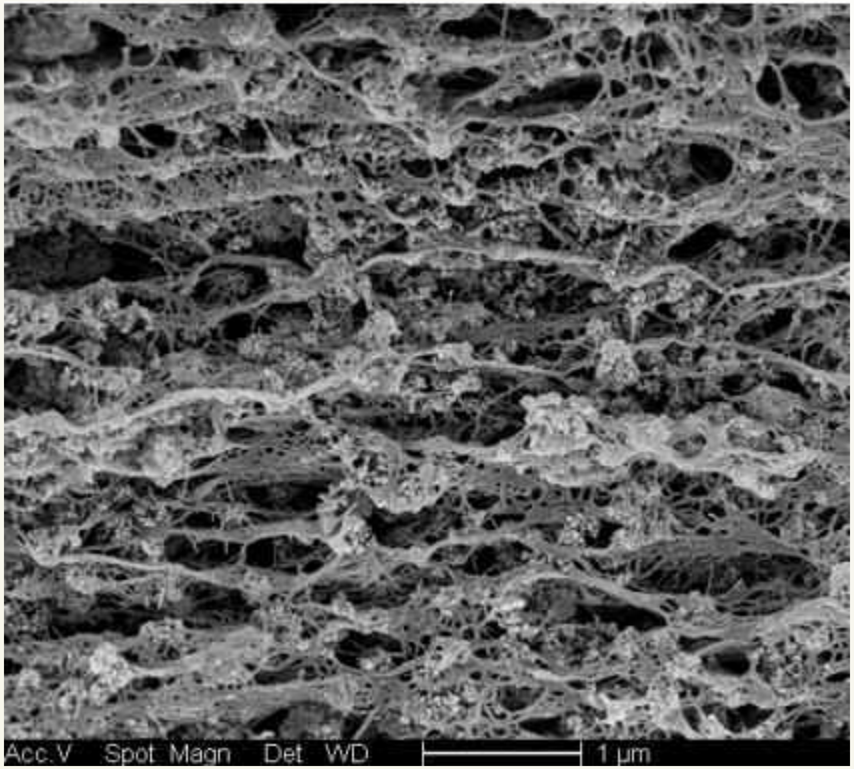
SURFACE & FRACTURE SEM - SILICA

2.3:1 Silica:PE, Surface



Polymer rich surface layer with open porosity

2.3:1 Silica:PE; XMD fracture

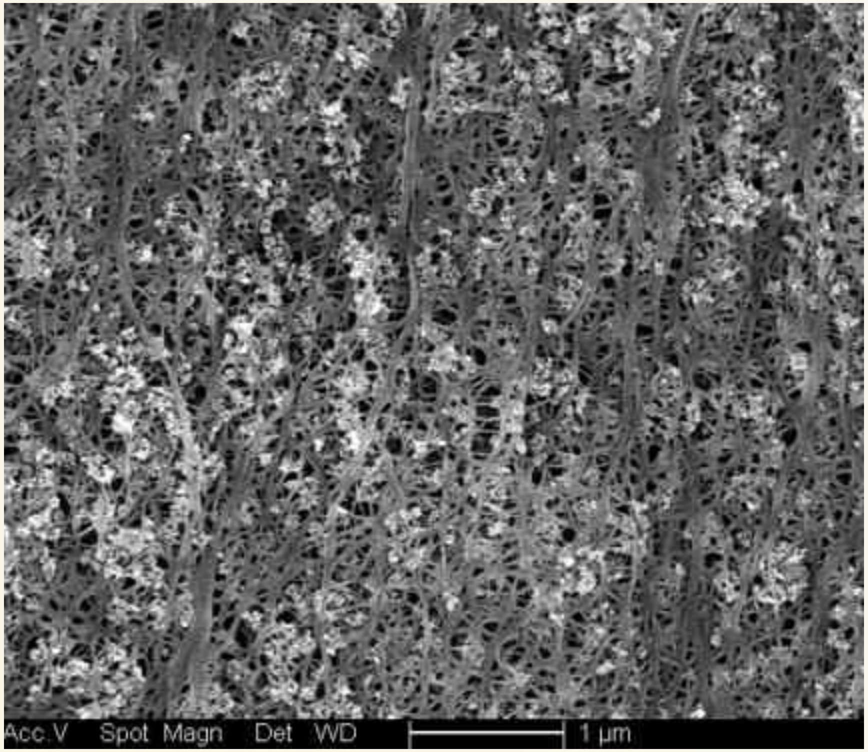


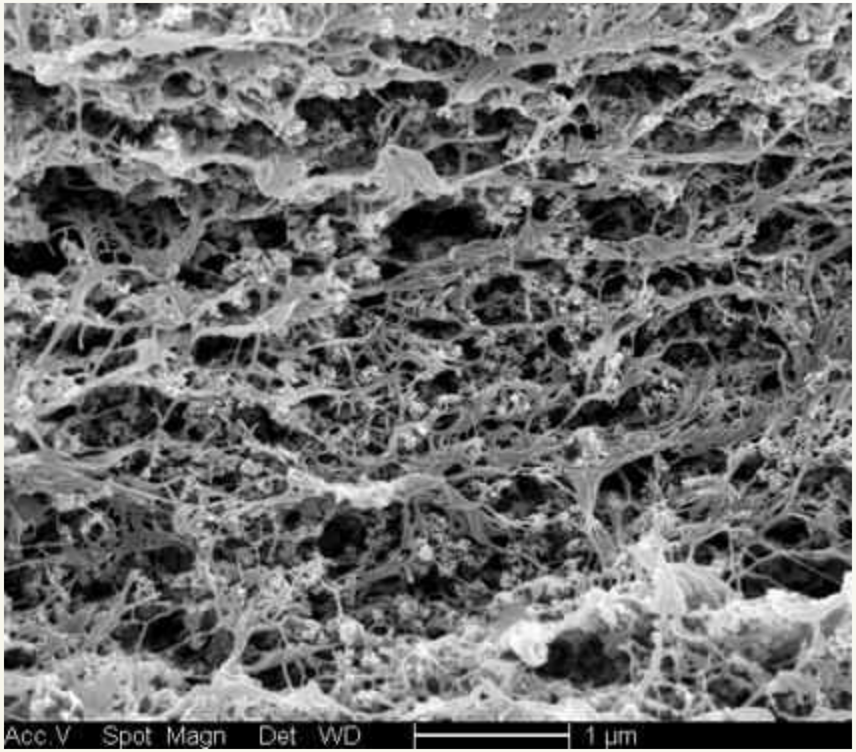
Highly porous bulk structure with pore size < 1 um

SURFACE & FRACTURE SEM - AL_2O_3

2.7:1 Al2O3:PE, Surface

2.7:1 Al2O3:PE, XMD Fracture





Polymer rich surface layer with open porosity

Highly porous bulk structure with pore size < 1 um

CERAMIC-FILLED SEPARATORS

Separator Properties

- High temperature dimensional stability (< %5 Shrinkage @ 180 C)
- High porosity (> 70 -80 %)
- Ultralow impedance
- Rapid wetting with electrolyte
- Low tensile modulus & strength
- No shutdown

Roll ID	Base roll	Filler	Filler:PE	Thickness	Areal Resistance	Resistivity	MacMullin Number
				um	Ω-cm²	Ω-cm	
Inorganic Filled Separators							
DY110217.002	59	Silica	2.1	19	0.59	308	2.6
DY110224.004	261	Silica	2.3	22.8	0.85	373	3.1
DY110303.001	260	Silica	2.3	24.1	0.59	247	2.1
DY110131.025	202	Alumina	2.7	25.9	1.06	410	3.4
DY110214.003	202	Alumina	2.7	22.3	0.88	396	3.3

Battery Performance

- High voltage stability
- Improved cycle life
- High power demonstrated at low temperature

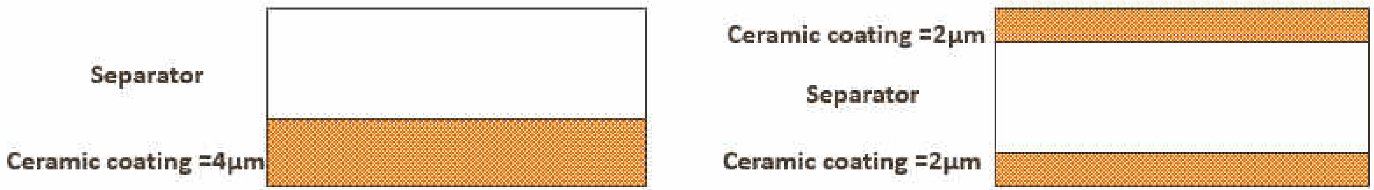
INORGANIC COATINGS

- Microporous coatings have commonly been used as ink jet receptive layers on paper or polymer substrates
- US 5,605,750 (Eastman Kodak)
  - Filed December 29, 1995
  - Patent Date February 2, 1997
  - Claim 1
    - An opaque image-recording element for an ink-jet printer which comprises an opaque substrate having on at least one surface thereof a lower layer of a solvent-absorbing microporous material… and an upper imaging layer of porous, pseudo-boehmite having an average pore radius of from 10 to 80 Angstroms
- WO 1999007558 A1 (3M)
  - Filed December 11, 1997
  - Publication Date February 18, 1999
  - Claim 1
    - An inkjet receptor medium, comprising: a microporous medium having one major surface an imaging layer comprising a coating of amorphous precipitated silica and binder

ENTEK COATING STRATEGY

- Water-based coatings
  - Dip coating process
- Inorganic oxide nanoparticles
  - Alumina
  - Silica
- Inter-particle crosslinks
  - Hydrogen bonding approach
    - Small molecule
    - Polymers
  - Ultralow polymer content
    - < 5 wt. %
  - Inorganic chemical reactions

CERAMIC-COATED SEPARATOR PROPERTIES



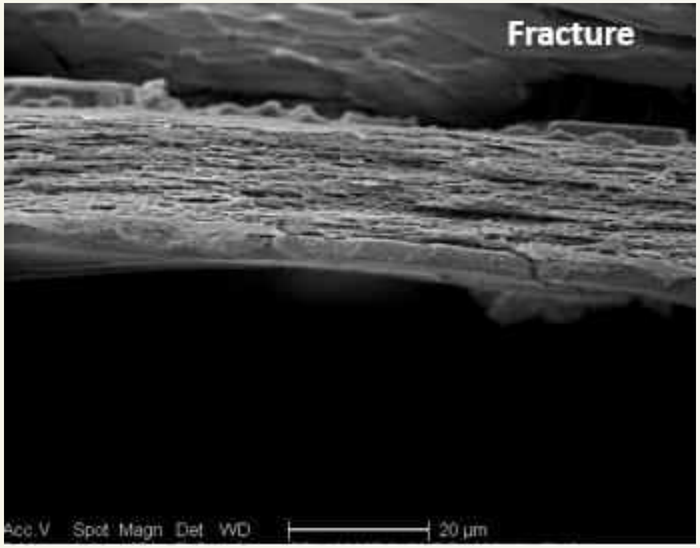
Single side coated

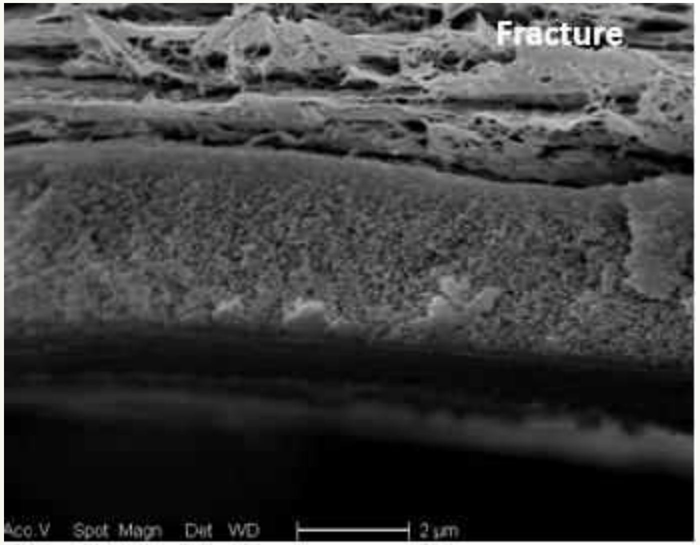
Both sides coated

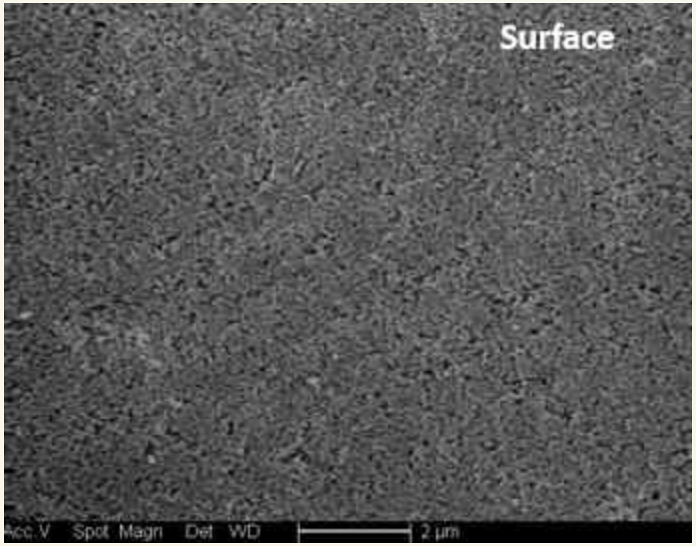
Base Thickness (µm)	Base Grade	Base + Coating thickness (µm)	Base layer Gurley (sec/100ml)	Coated separator Gurley (sec/100ml)	Thermal shrinkage @180°C
9	EP	12	140	215	<5%
12	EP	16	160	260	<5%
12	EPH	16	110	210	<5%
16	EPH	20	140	240	<5%

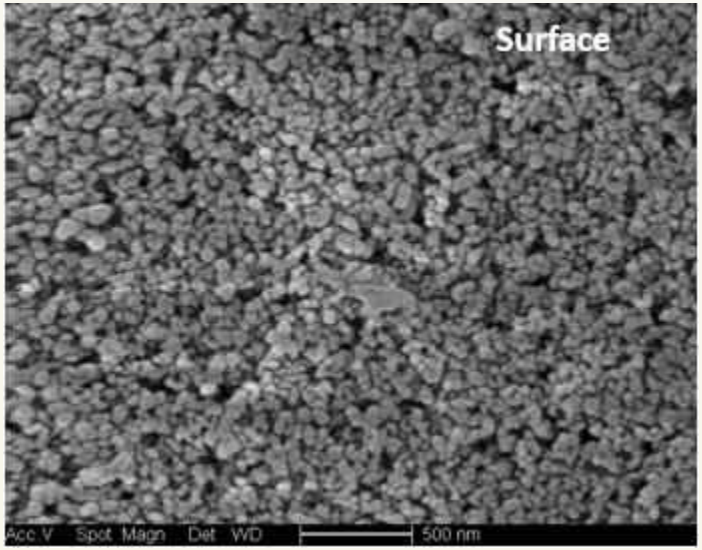
These data only show typical properties

SEM – SILICA COATING / DOUBLE SIDE









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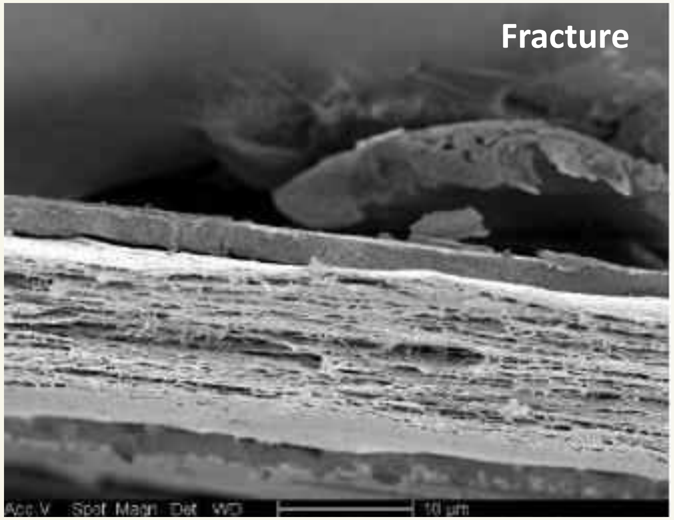
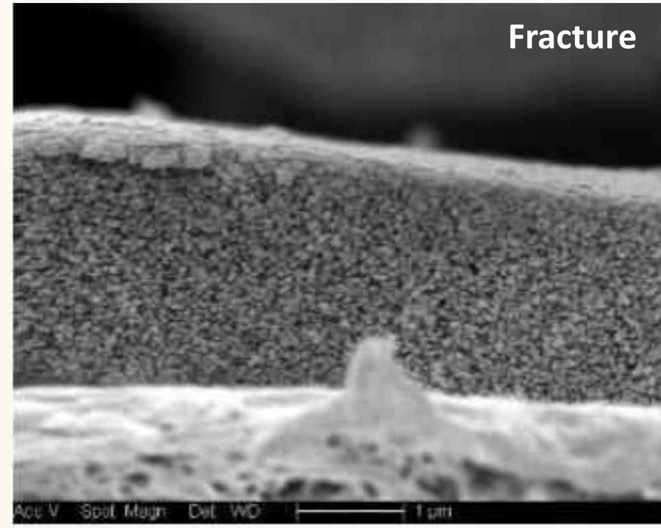
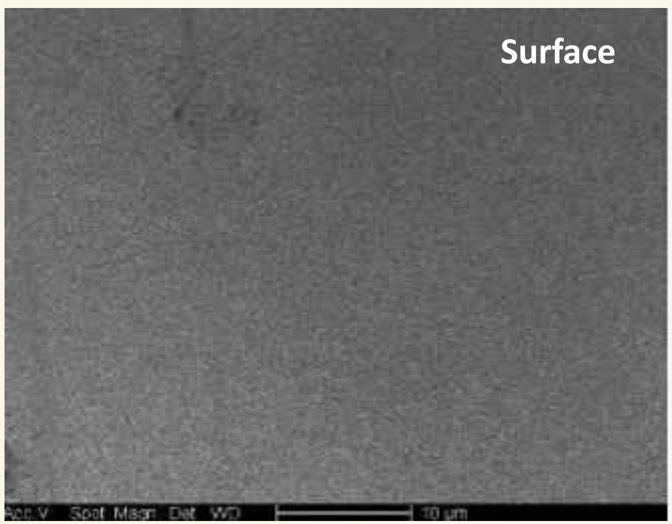
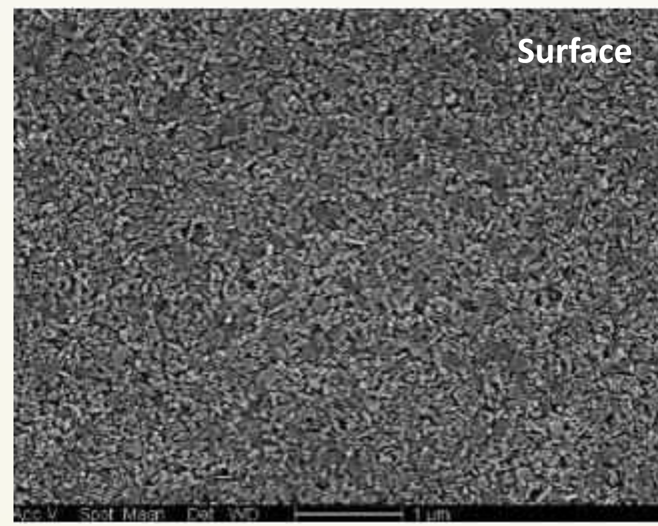
SEM – ALUMINA COATING / DOUBLE SIDE









Coated from aqueous dispersion with ~ 3% polymer

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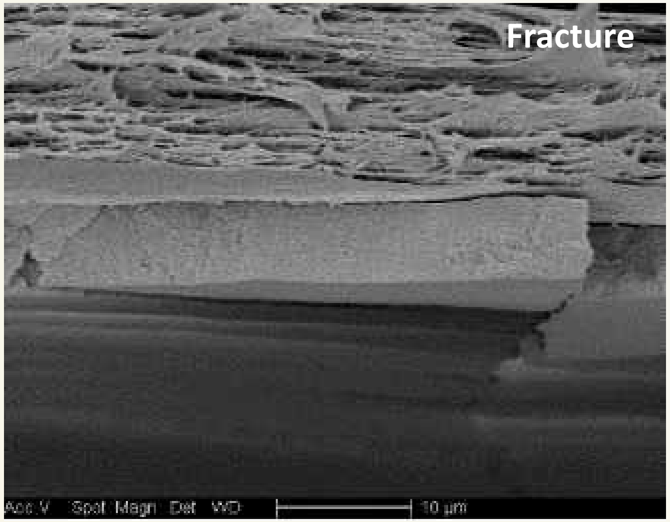
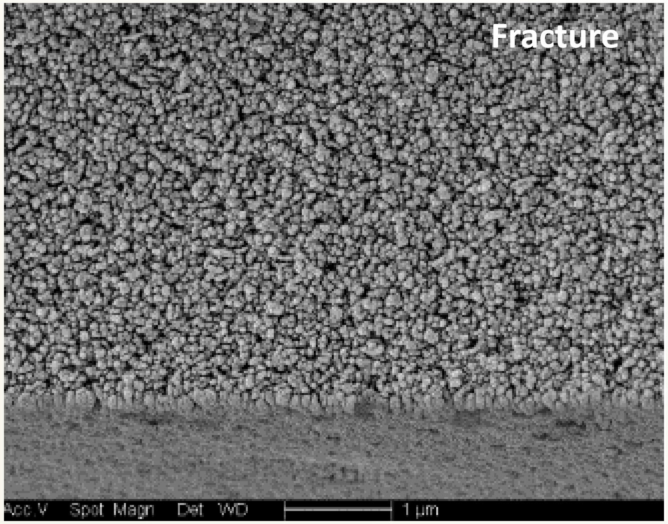
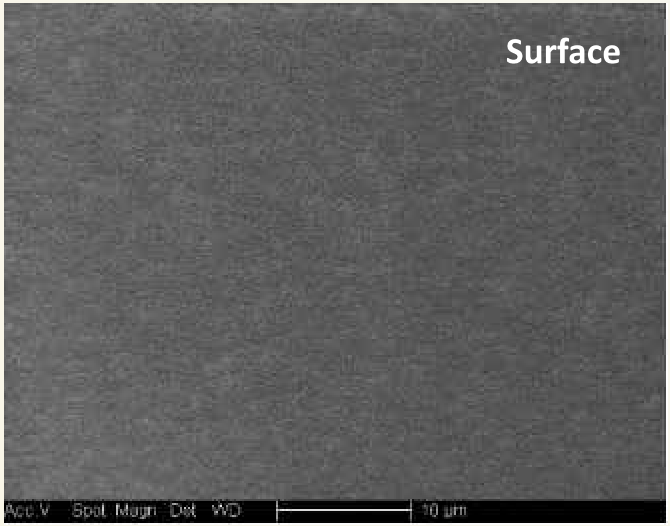
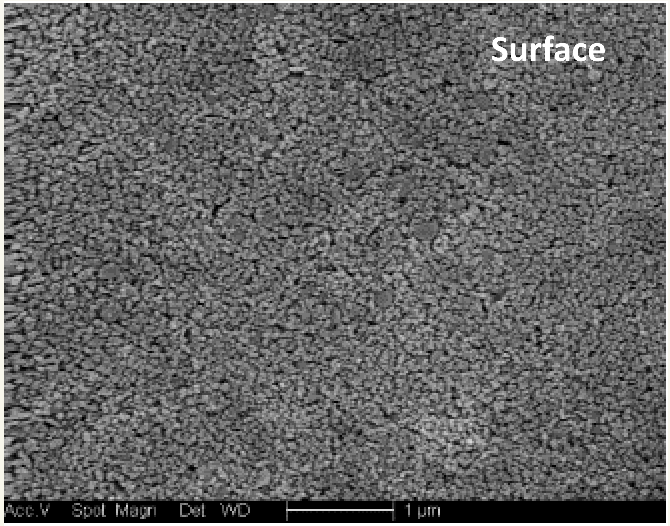
SEM – ALUMINA COATING / SINGLE SIDE

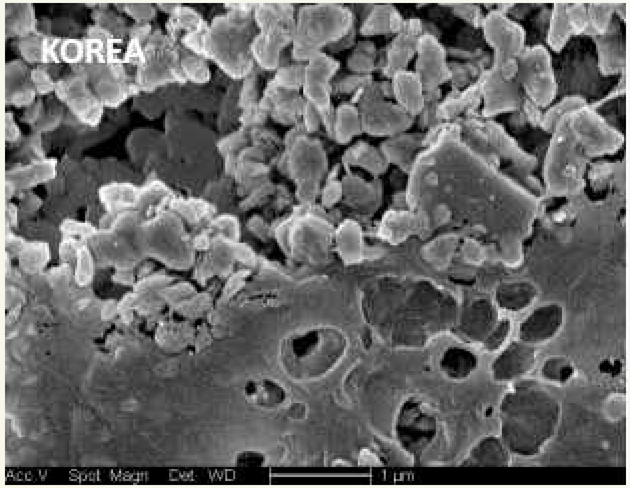


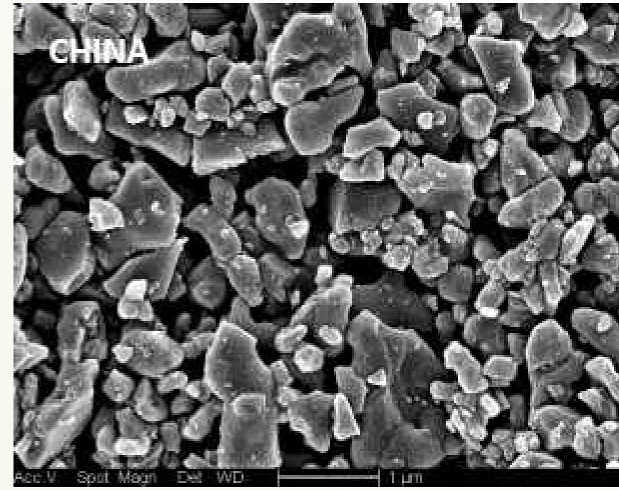


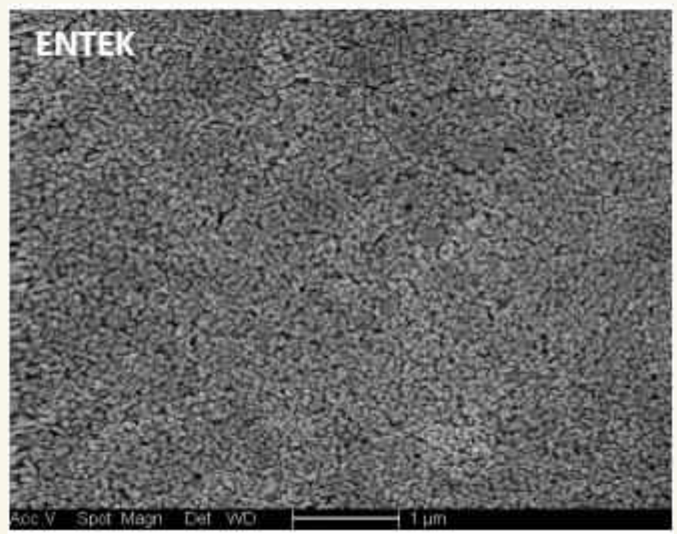




SURFACE SEM COMPARISON OF AL_2O_3-COATED SEPARATORS







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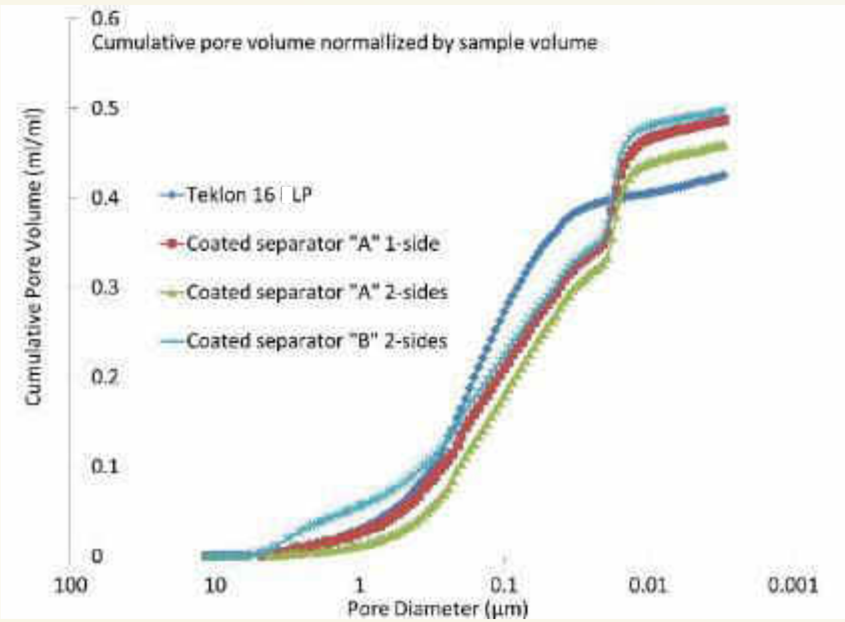
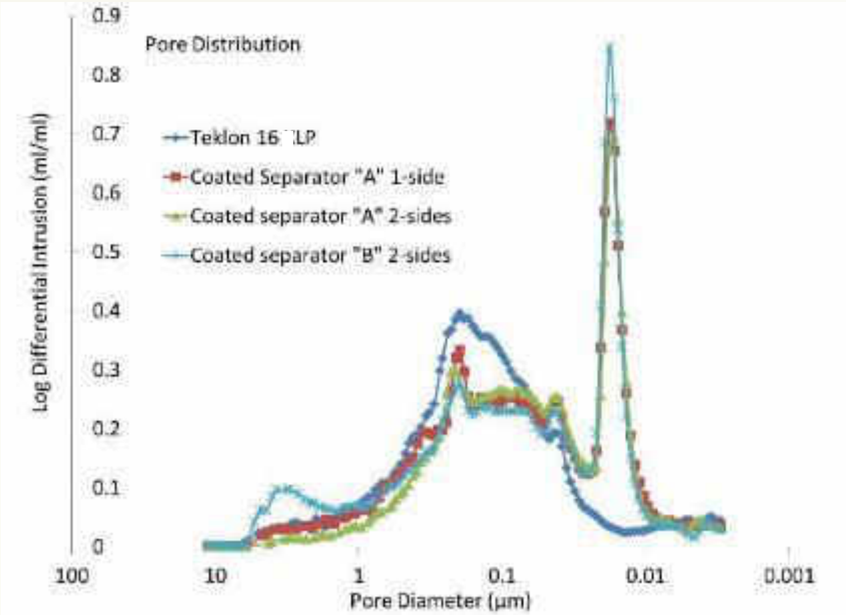
MERCURY POROSIMETRY

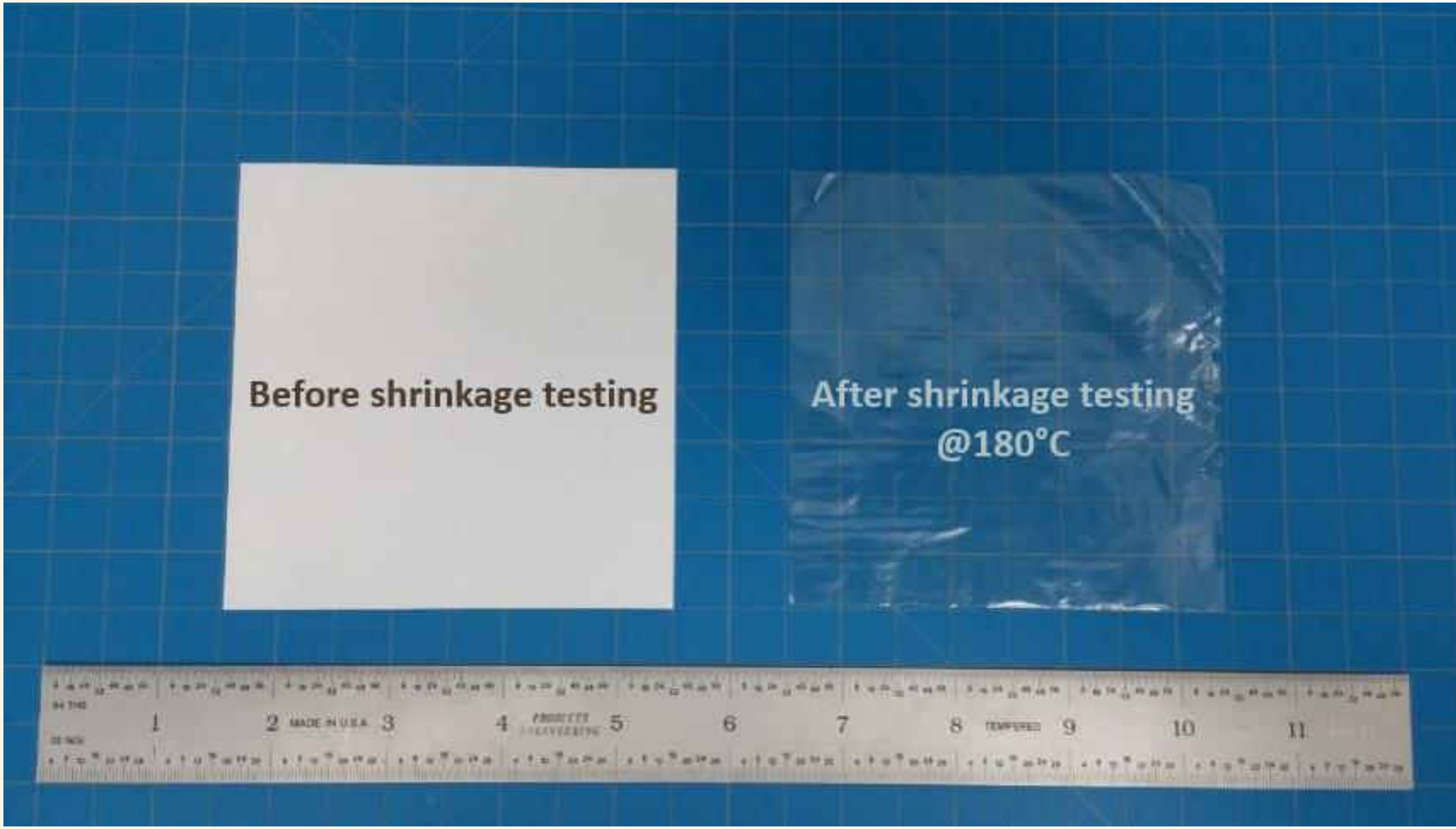
Description	Basis Wt (g/m²)	Thickness (µm)	Bulk density (g/cc)	Porosity (%)	Ave. Pore Dia. (µm)	Calculated coating porosity (%)
16 µm LP	9.0	16.1	0.59	42.5	0.052	-
Coated Separator A, 1-side	16.0	22.0	0.77	48.7	0.032	65.6
Coated Separator A, 2-sides	15.2	18.9	0.76	45.9	0.031	65.5
Coated Separator B, 2-sides	16.1	20.7	0.75	49.7	0.034	74.9





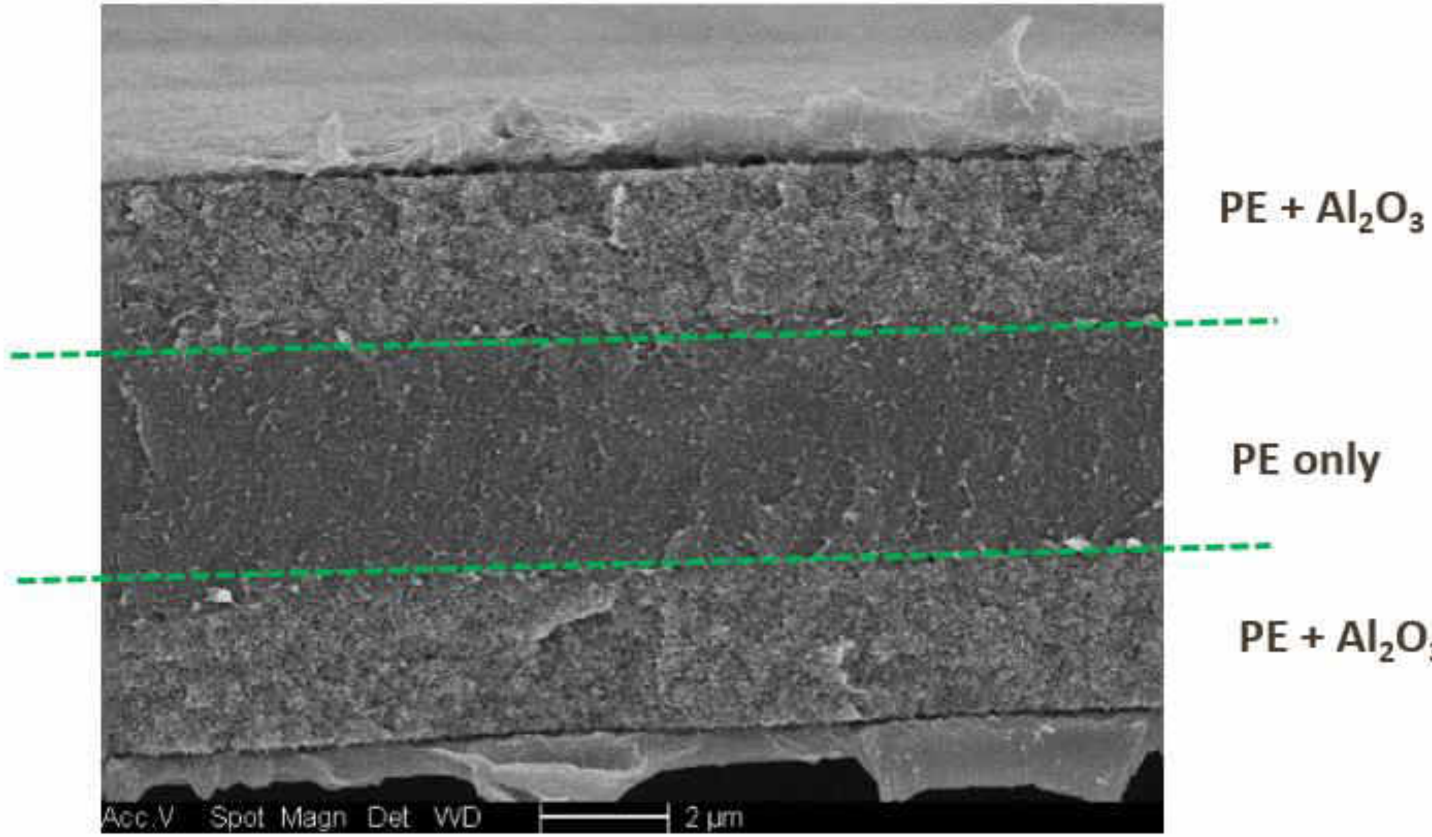
Pore size distribution of base layer and ceramic coating can be differentiated.

THERMAL SHRINKAGE TEST - DRY



Ceramic coated separators exhibit < 5% shrinkage in both the machine and transverse directions after being heated for 1 hr at 180 C.

SEM: X-SECTION AFTER 180C SHRINKAGE TEST



THERMAL SHRINKAGE TEST - WET

- Samples:
  - Uncoated
  - 97/3 Alumina/polymer A
  - 90/10 Alumina/Box
- Wetted with Electrolyte
  - DMC/EMC/LiPF6
- Used Aluminum/PP seal to make pouches
- Heated at 150°C for 30 minutes

Sample	Shrinkage (%)	
	MD	TD
Uncoated	70	61
97/3 Alumina/polymer	2.6	1.6
90/10 Alumina/ BOx	2.1	0.6

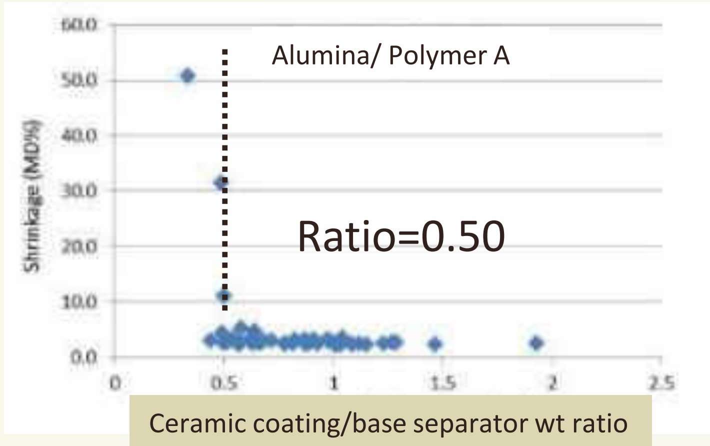
Sealed aluminum pouch for shrinkage testing in electrolyte

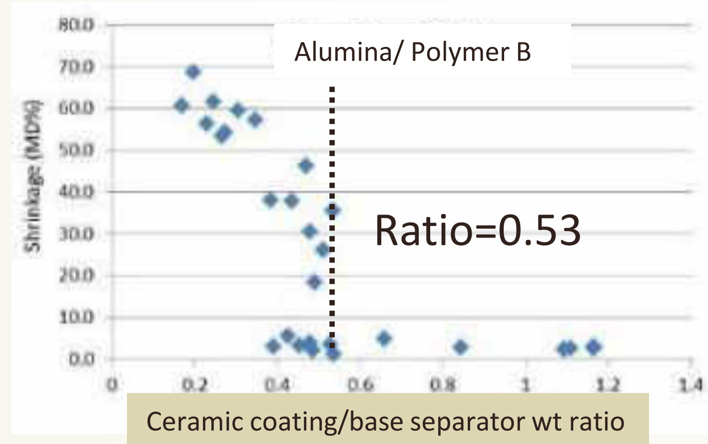
Uncoated

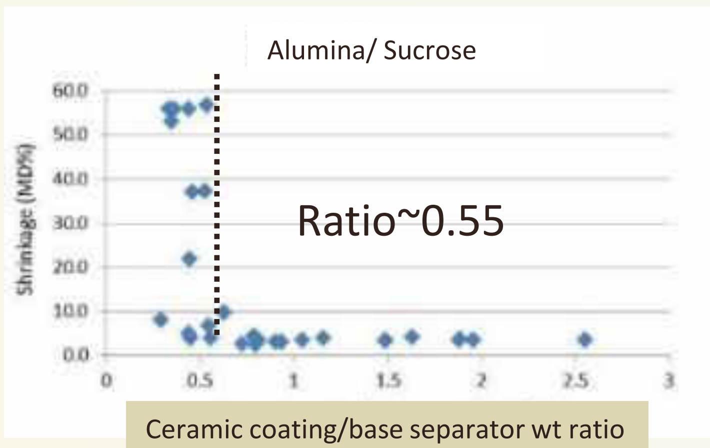
Alumina/polymer A

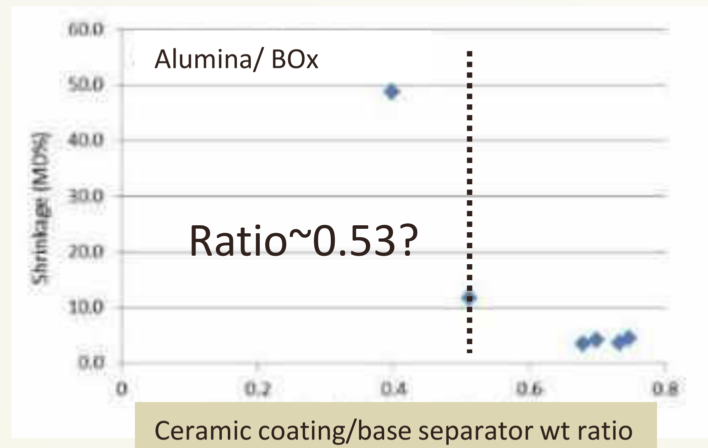
Alumina/BOx

SHRINKAGE TESTING – VARIOUS COATED SEPARATORS









A critical [coat weight / PE basis weight] ratio has been identified for achieving high temperature dimensional stability, independent of the formulation used.

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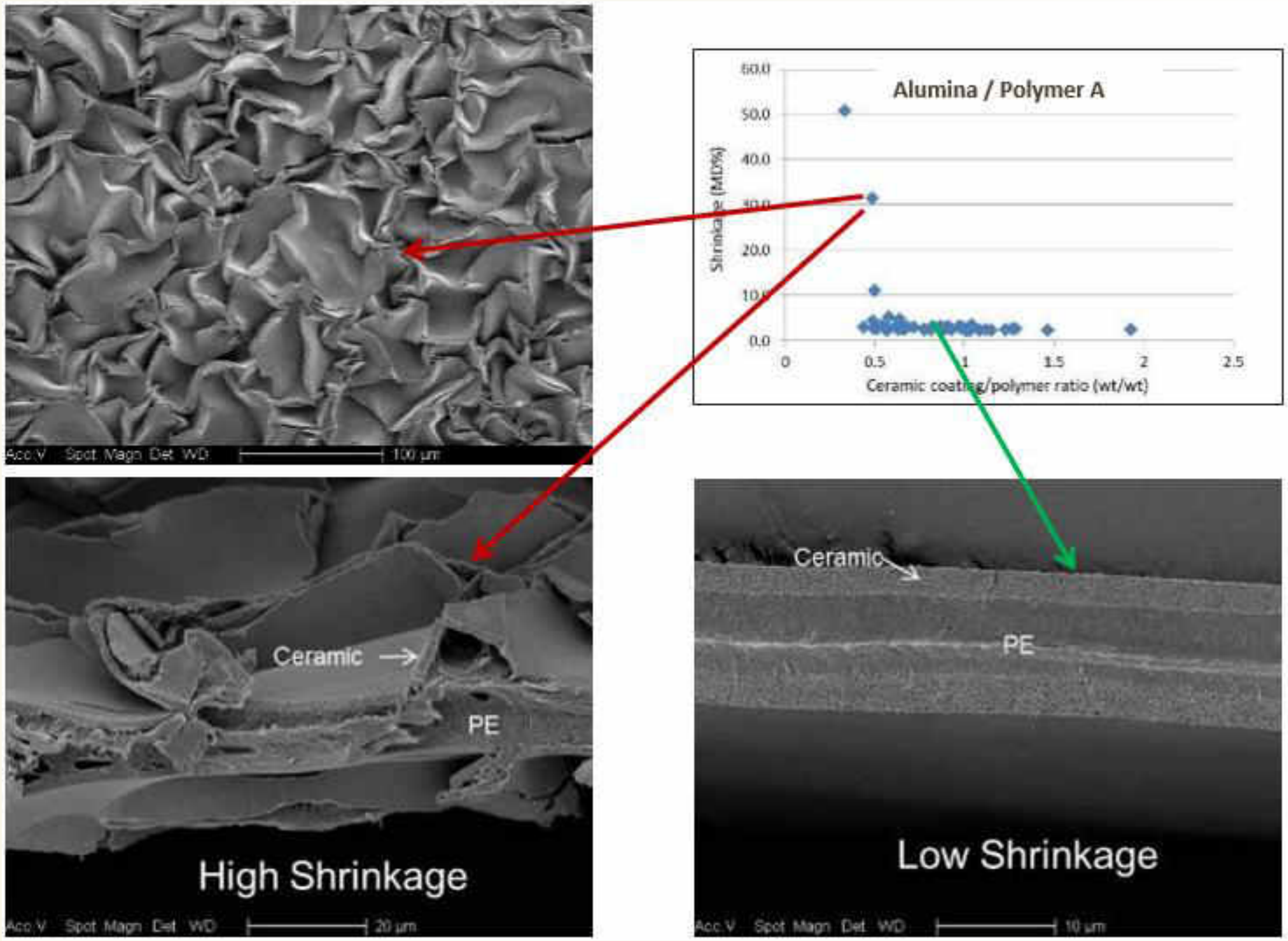
MICRO-BUCKLING OF COATED SEPARATOR



Coated separator with high shrinkage exhibits ***micro-buckling*** at the alumina-PE interface

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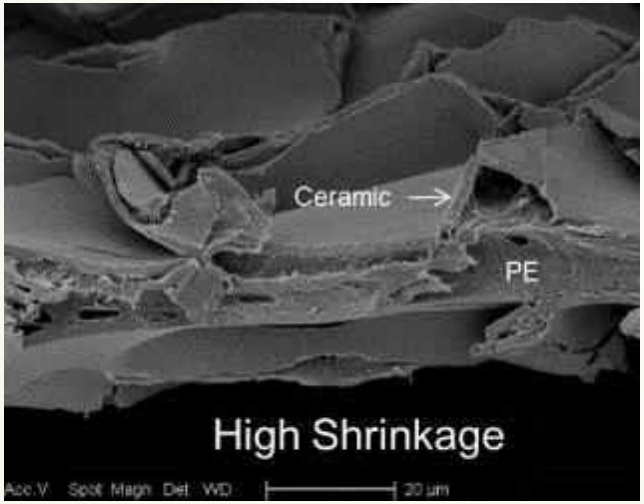
THERMAL SHRINKAGE MODEL

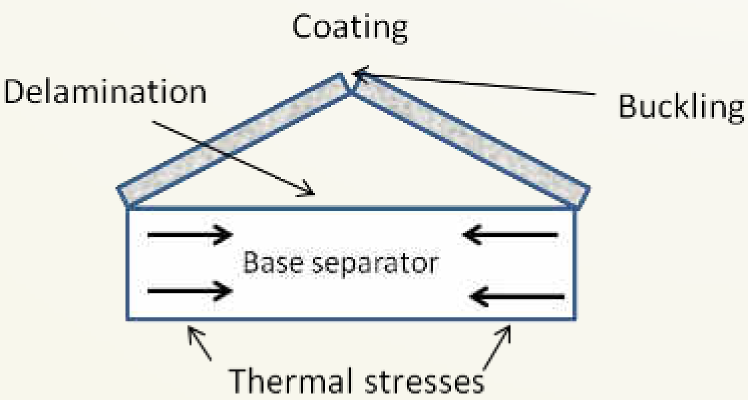
- Critical coating weight required to resist residual stresses in the separator for high temperature dimensional stability
- Micro-buckling model:

$$h_c = \frac{b}{\pi}\sqrt{\frac{12\sigma}{E_c}}$$

=> **Critical coating weight** is dictated by **coating 'stiffness'**

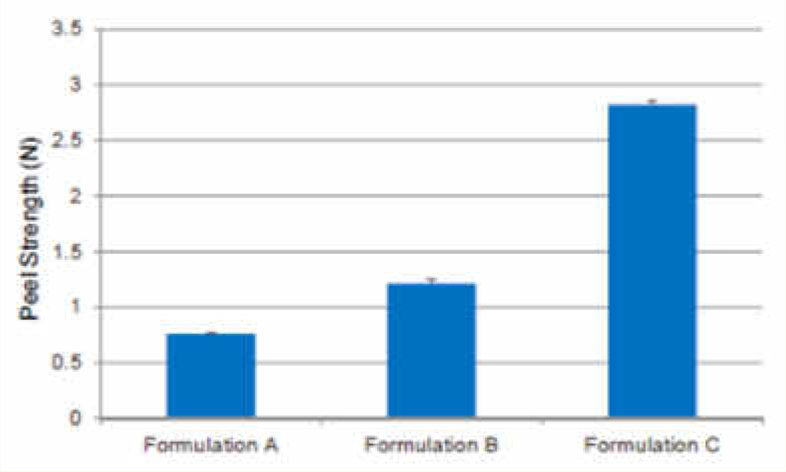
- Implications:
  - Critical coating weigh for ceramic/polymer mixtures can be predicted
  - Surface contact between ceramic particles will strongly influence the critical coating weight

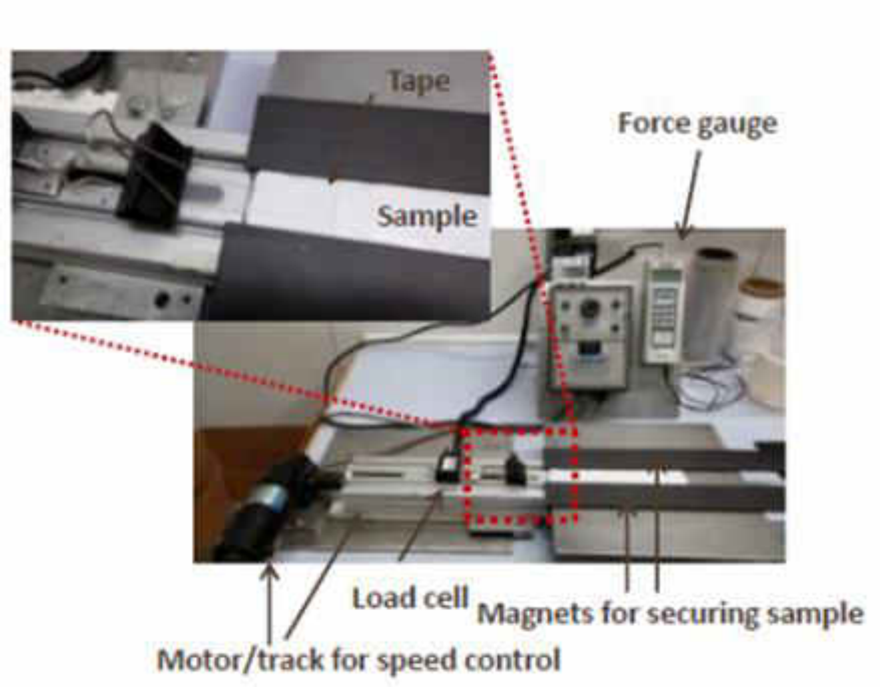




180° PEEL TEST

- A peel test was developed to quantify the adhesion strength of various ceramic-coated separators
- The load required to pull the ceramic-coated layer from the base layer was measured

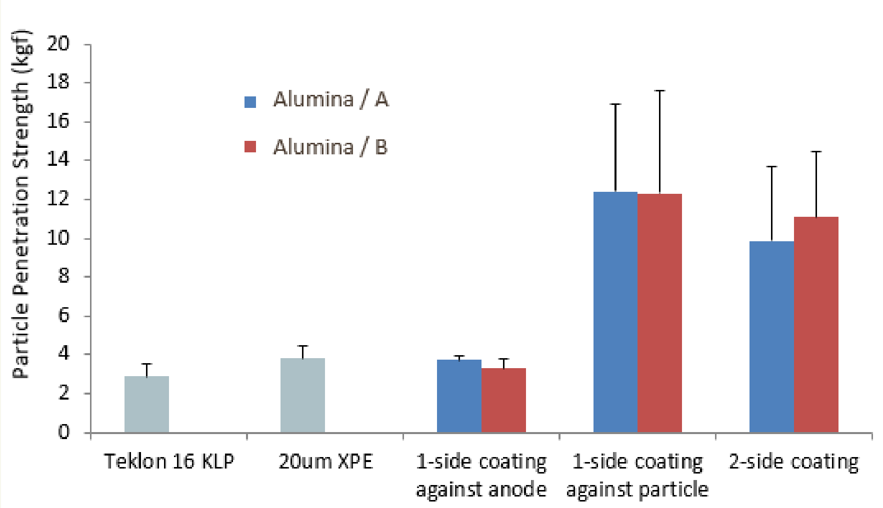


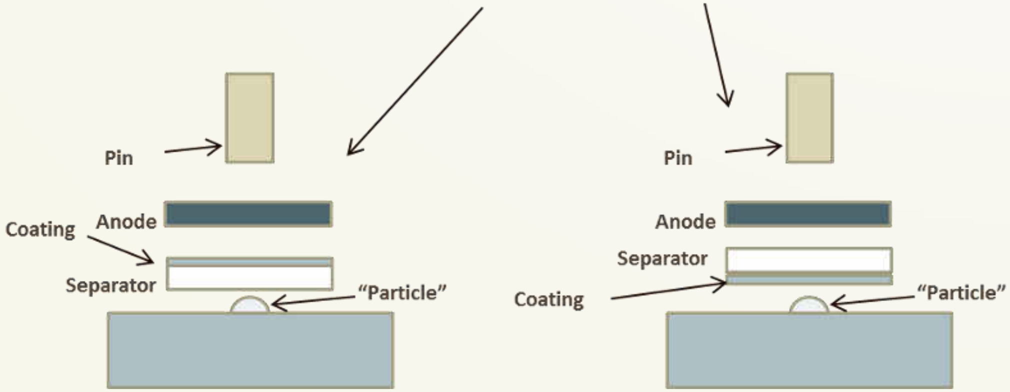


Peel strength of the ceramic coated layer can be modified as needed

PARTICLE PENETRATION: 1-SIDE VS 2-SIDE COATING

- Testing was performed under 3 different configurations:
  - Single side coated separator, uncoated side against the particle
  - Single side coated separator, with coated side against the particle
  - Double side coated separator
- For single sided separators, when uncoated side is adjacent to particle, penetration strength is similar to the base material controls
  - Coating is stressed under tension
- However, when the coating is adjacent to the particle, the penetration strength is significantly higher than controls
  - The coating is largely compressed

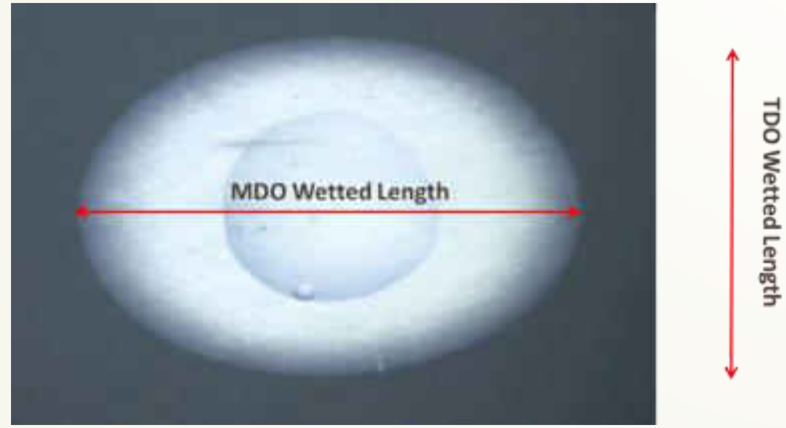


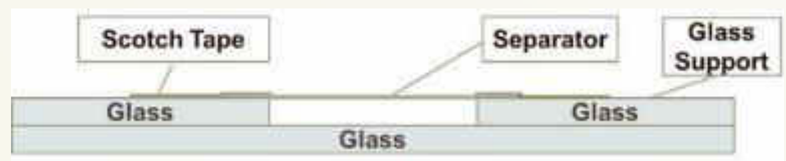


Double sided coated separator offers better protection against particle penetration

WETTING TEST METHOD

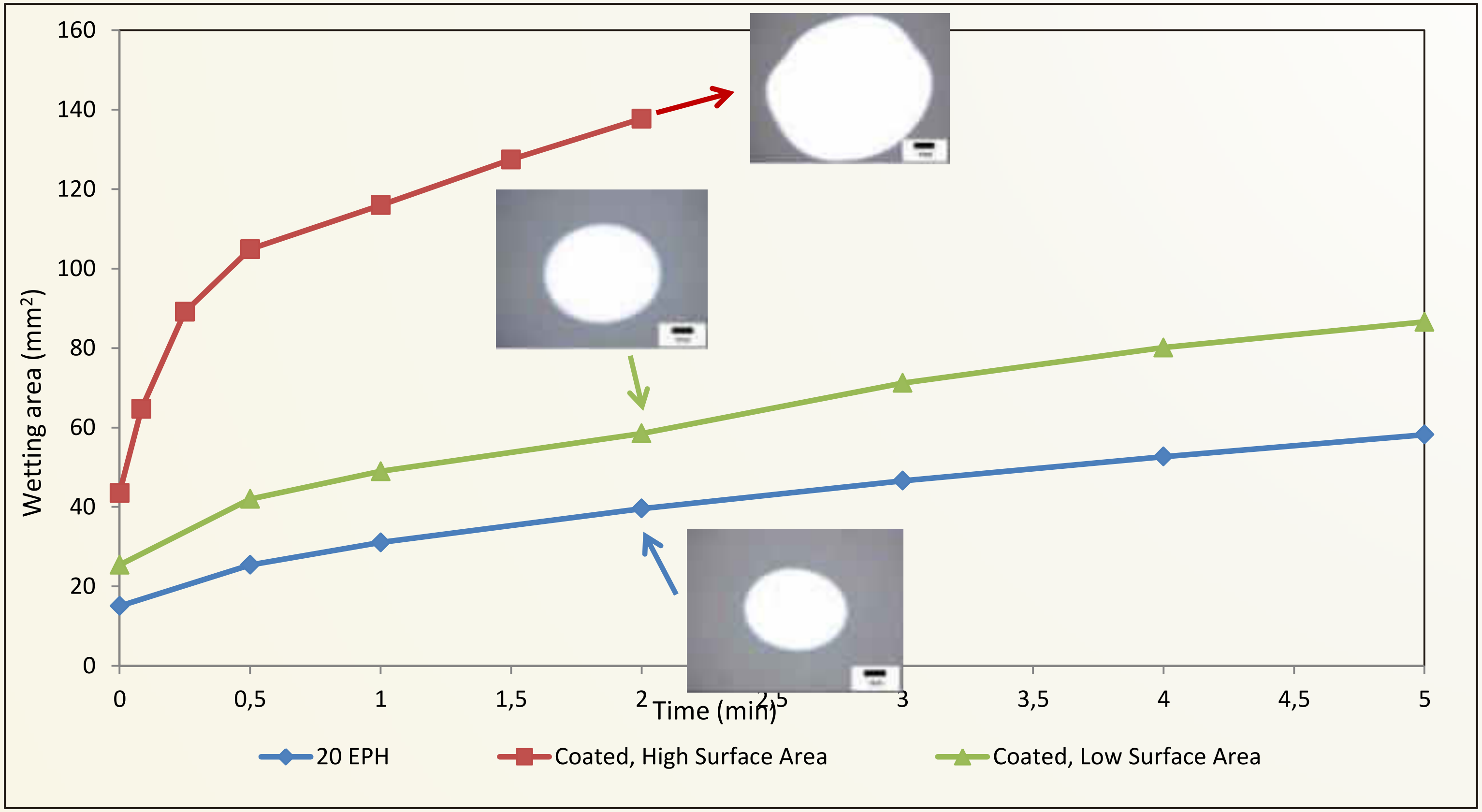
Keyence microscope used for wetting experiment





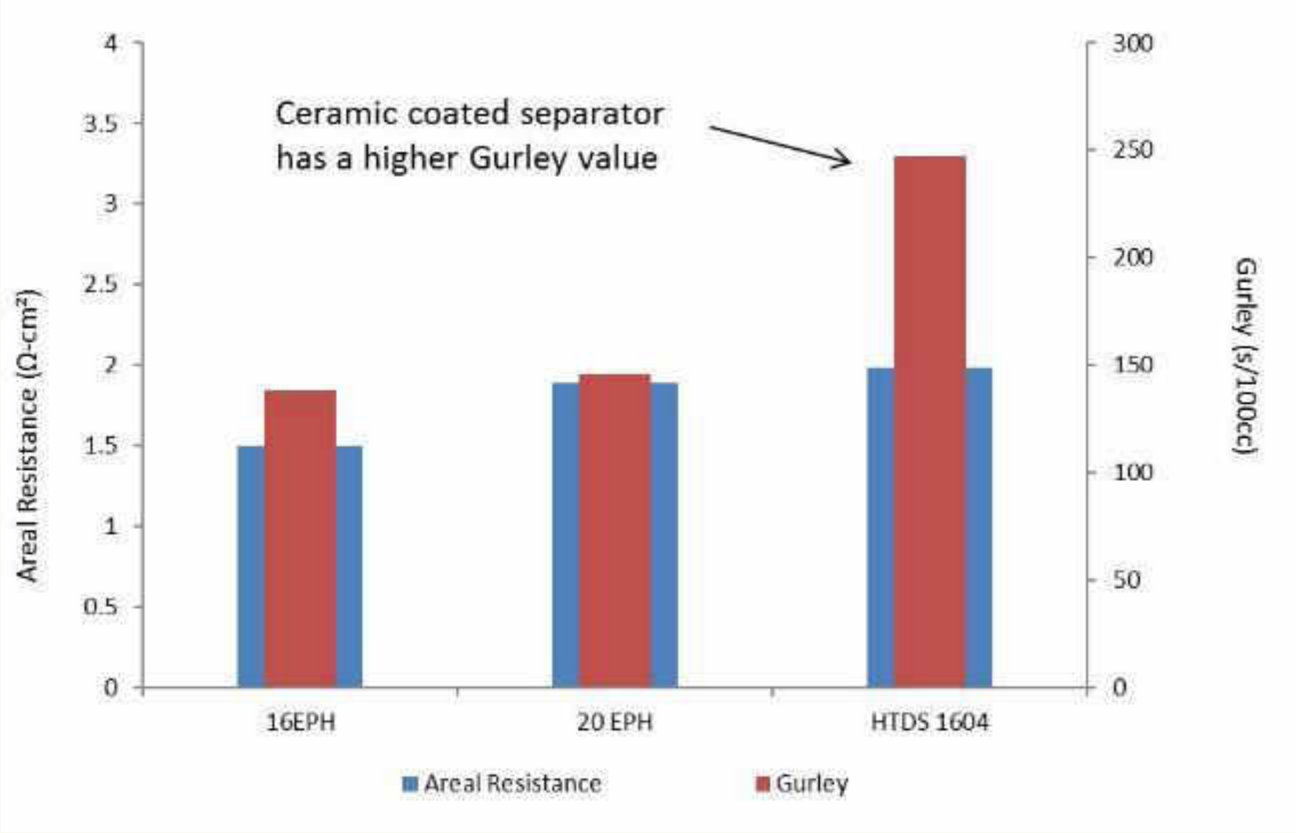
- Separator suspended in air to prevent solvent wicking on glass
- Droplet placed on separator by micro-pipette. Wetted area measured over 5 minutes.
- Solvent: propylene carbonate/tri(ethylene glycol) dimethyl ether = 1/1 (vol.)

INCREASED WETTING RATE



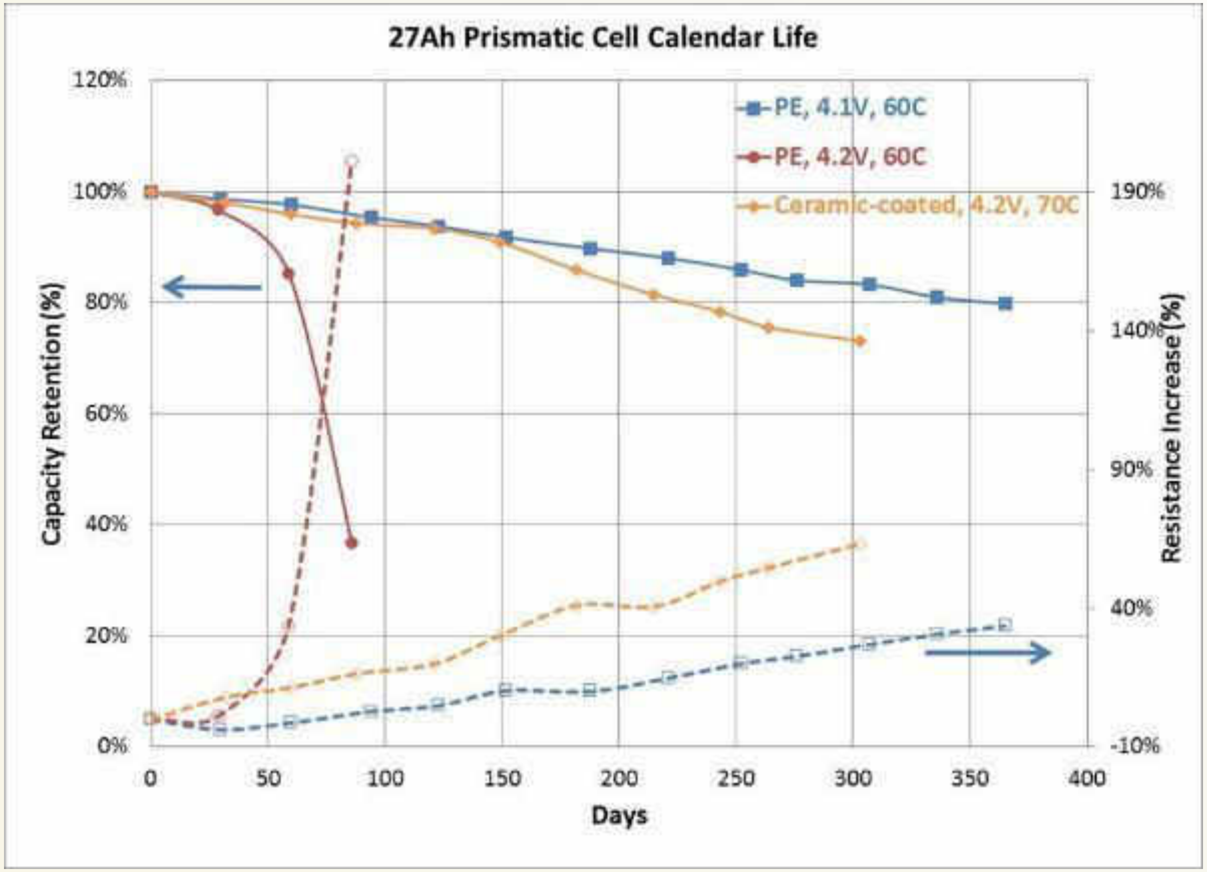
- Electrolyte filling is often a bottleneck in cell manufacturing
- Separator coated with high surface area, alumina nanoparticles shows excellent wetting

NO IMPACT ON IMPEDANCE



- Coating PE separator with alumina nanoparticles increases Gurley values **without** increasing ionic resistance

STORAGE TESTING AT 70°C

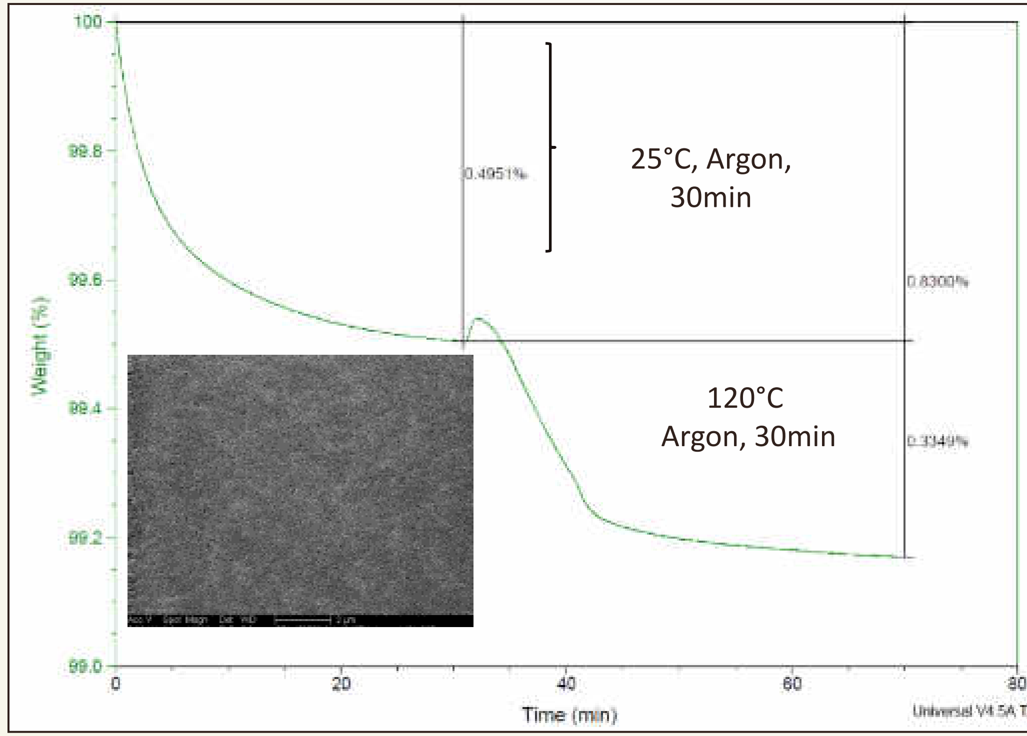


- ENTEK alumina coated separator has been successfully used in large prismatic cells tested under demanding calendar life conditions (70 C; 4.2 V)

MOISTURE EVALUATION

- Alumina coated separator was Tested for Karl Fischer moisture and TGA weight loss
- TGA Isotherms:
  - 25°C isotherm, 30 minutes under argon
  - 120°C isotherm, 30 minutes under argon
  - ***No special drying prior to testing***

Coated with **high** surface area alumina nanoparticles

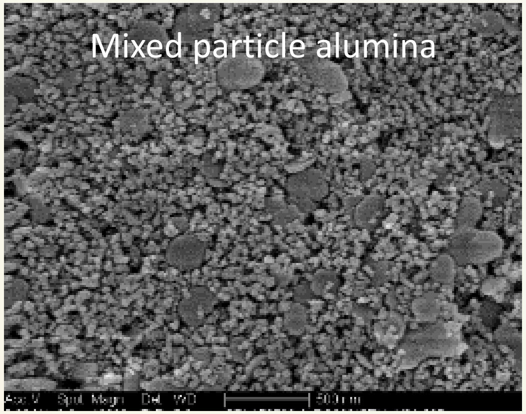


	Coating Weight g/m2	Weight Loss (ppm)			KF moisture (ppm)
Sample		**25°C, Argon**	**120°C, Argon**	**Total Weight Loss**	
Higher surface area coating	5.9	4951	3349	8300	8190

STRATEGIES FOR REMOVING MOISTURE

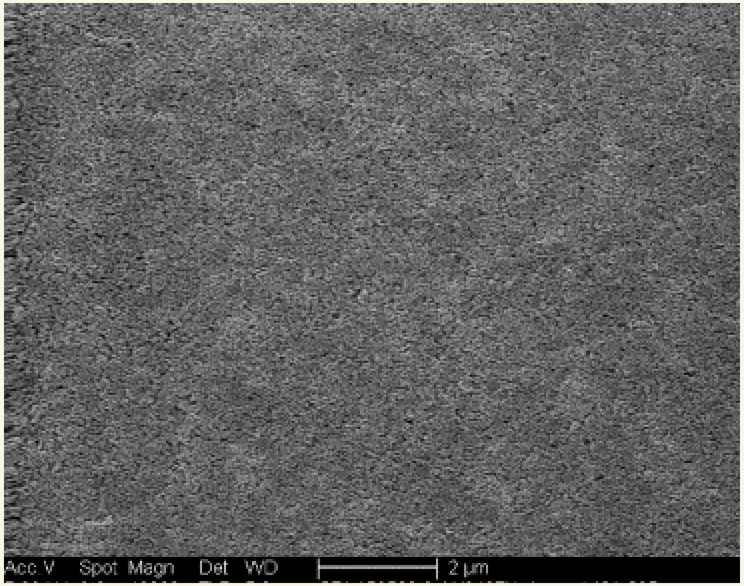
- Pre-dry coated separator and package with moisture-barrier films

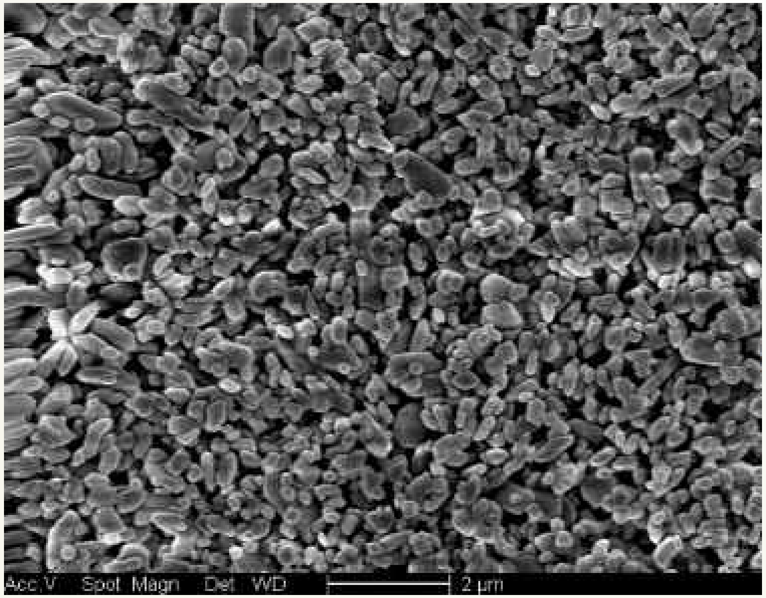
- Dry wound jelly roll prior to electrolyte filling



- Modify formulation to tailor thermal shrinkage and moisture properties

PARTICLE SIZE – COATING IMPLICATIONS



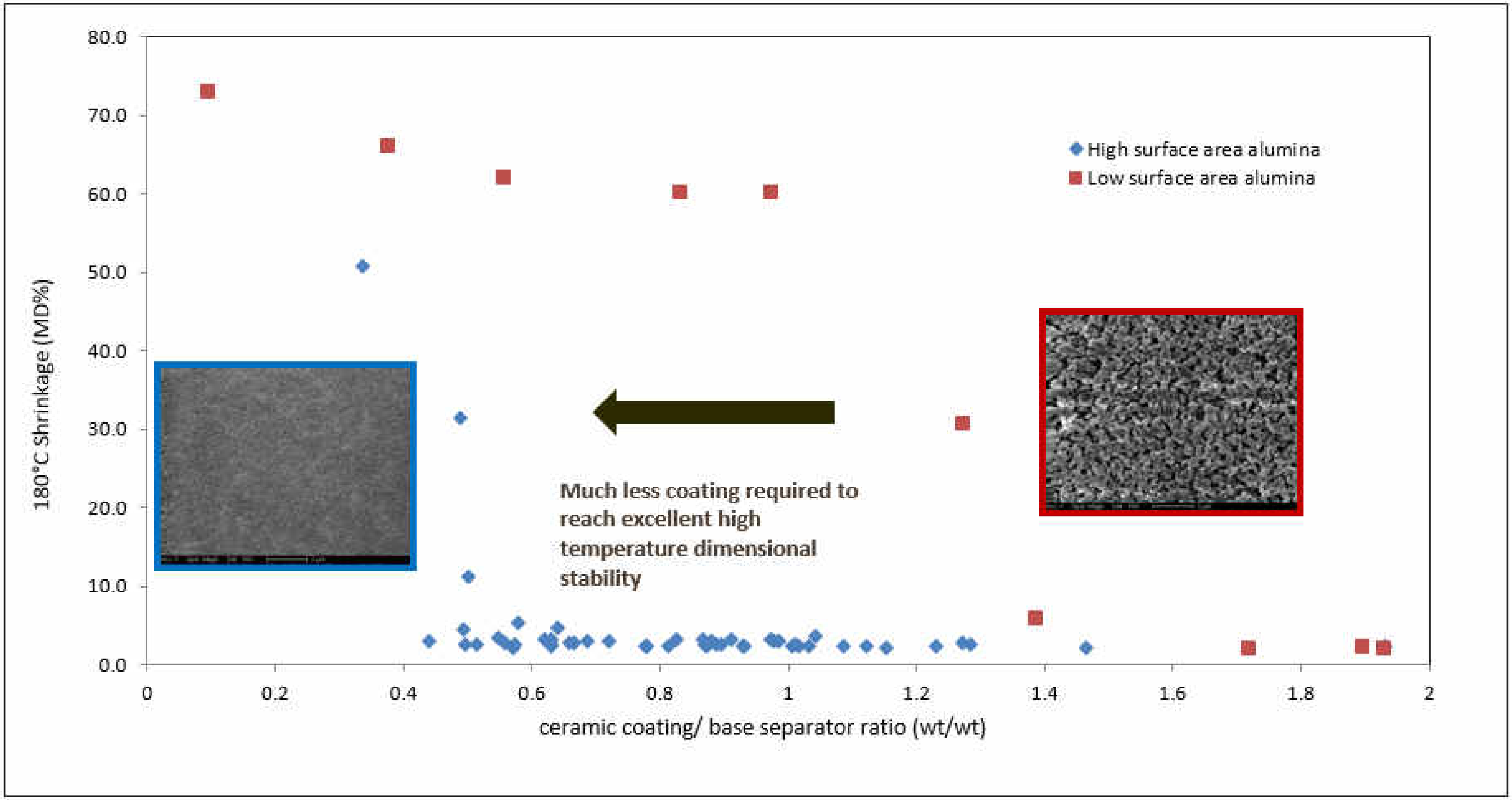


- **High surface area alumina**
  - Very thin, uniform coatings can be applied
    - Improved energy density
    - Reduced cost
  - Excellent dimensional stability, improved safety
  - Higher moisture content

- **Low surface area alumina**
  - Thicker coatings required for low shrinkage
  - Low moisture content

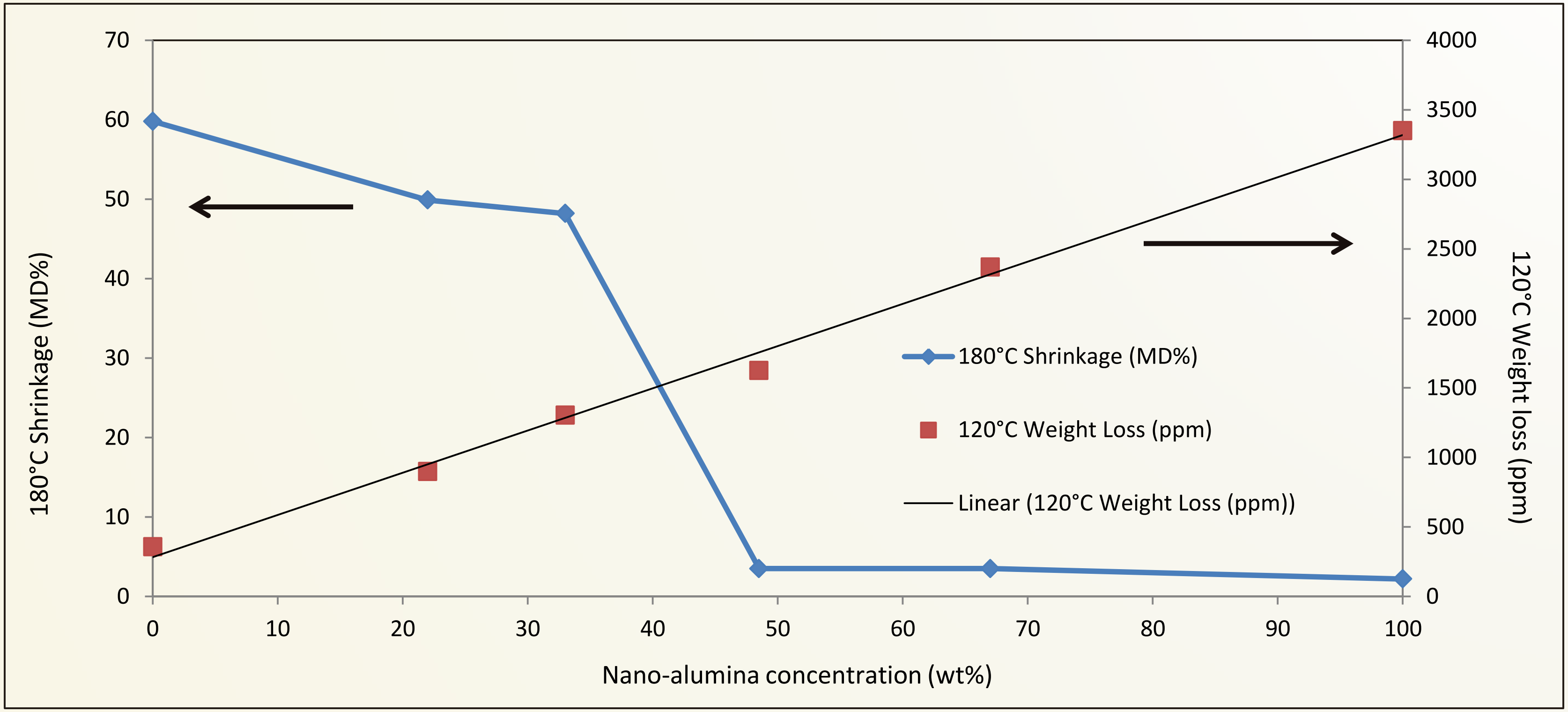
=> More expensive

THERMAL SHRINKAGE: HIGH VS. LOW SURFACE AREA



Alumina coated separators with higher surface area, nanoparticles require much lower loading levels in order to achieve <5% shrinkage @180°C

"MIXED" ALUMINA - THERMAL SHRINKAGE VS. MOISTURE



Nominally 7g/m² coating onto 16um base material

Combining high surface area and low surface area particles allows a compromise in critical coat weight and moisture content while maintaining excellent high temperature dimensional stability

SUMMARY

- Continued growth of xEVs and portable electronics will increase demand for thinner separators with good oxidation resistance and excellent safety, i.e. thermal stability at high temperatures.

- Nanoparticle coatings offer excellent high temperature dimensional stability at the lowest coat weights, thereby allowing battery manufacturers to achieve higher energy densities at lower cost.

- While nanoparticle coatings have very high surface areas and high moisture content, cycle life data at extreme conditions (70°C, 4.2V) indicate that moisture is sequestered in nanopores and inaccessible to the electrolyte.

- Further benefits of nanoparticle coatings include rapid cell-fill times and minimal impact on impedance.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