PB-ACID SEPARATORS

The Impact of Raw Material Selection on Structure-Property Relationships

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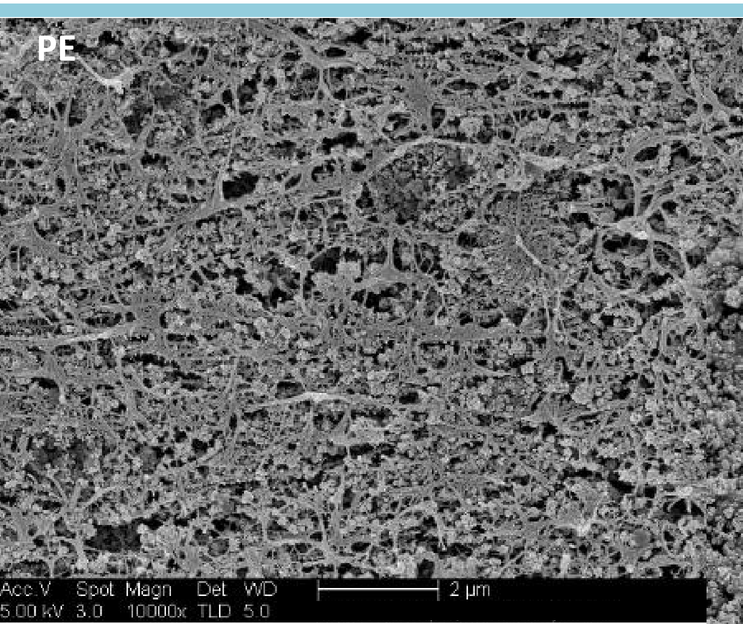
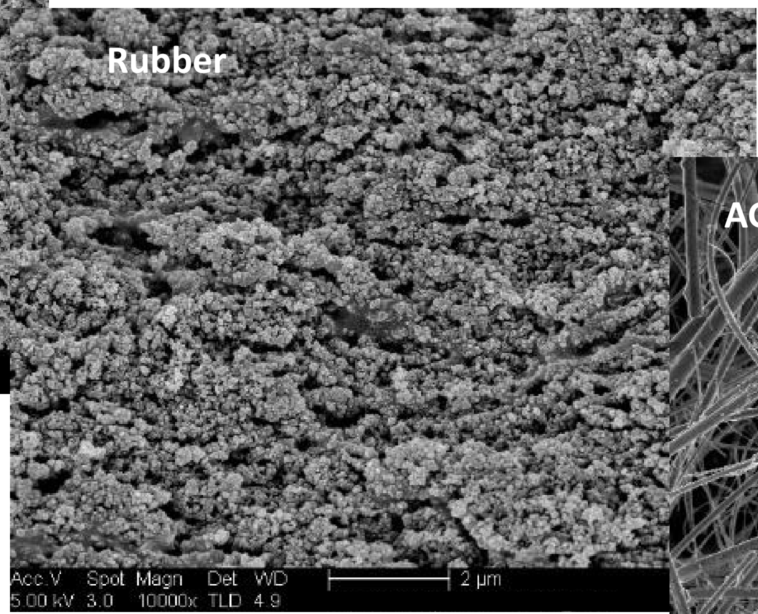
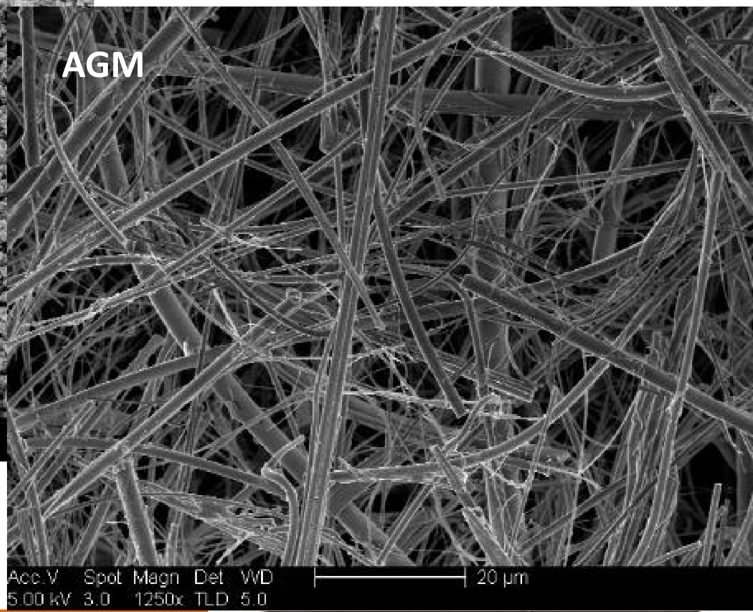
COMMON PB-ACID SEPARATORS







The terms -- “PE” and “Rubber” separators -- are misnomers since each contain large percentages of precipitated silica

MAJOR CONSTITUENTS --- PE/SILICA SEPARATORS

Component	Function
UHMWPE	mechanical properties
Silica	wettability & porosity
Residual oil	oxidation resistance
Additives	oxidation resistance, color, wettability
Pores / Voids	ion conduction

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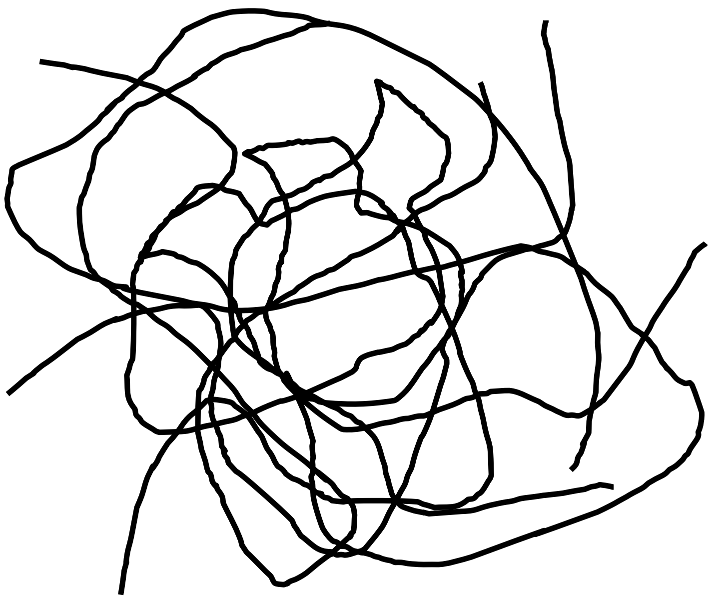
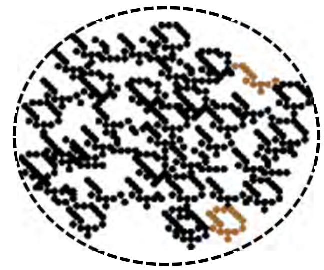
UHMWPE GEL PROCESSING

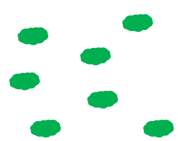


UHMWPE

$(-CH_2-CH_2-)_x$



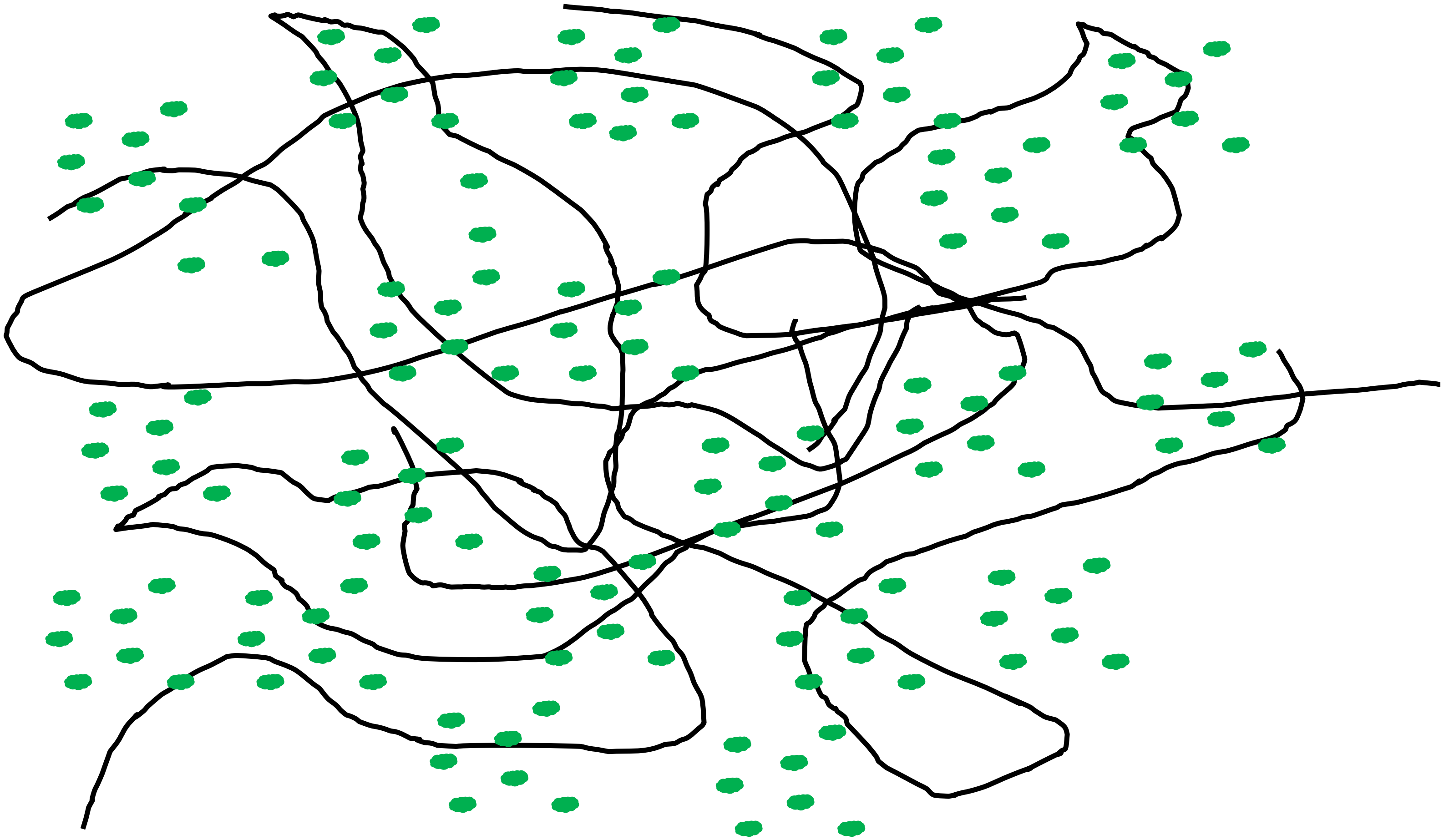
Silica



Oil

Twin Screw
Extrusion

UHMWPE + OIL + SHEAR → CHAIN DISENTANGLEMENT



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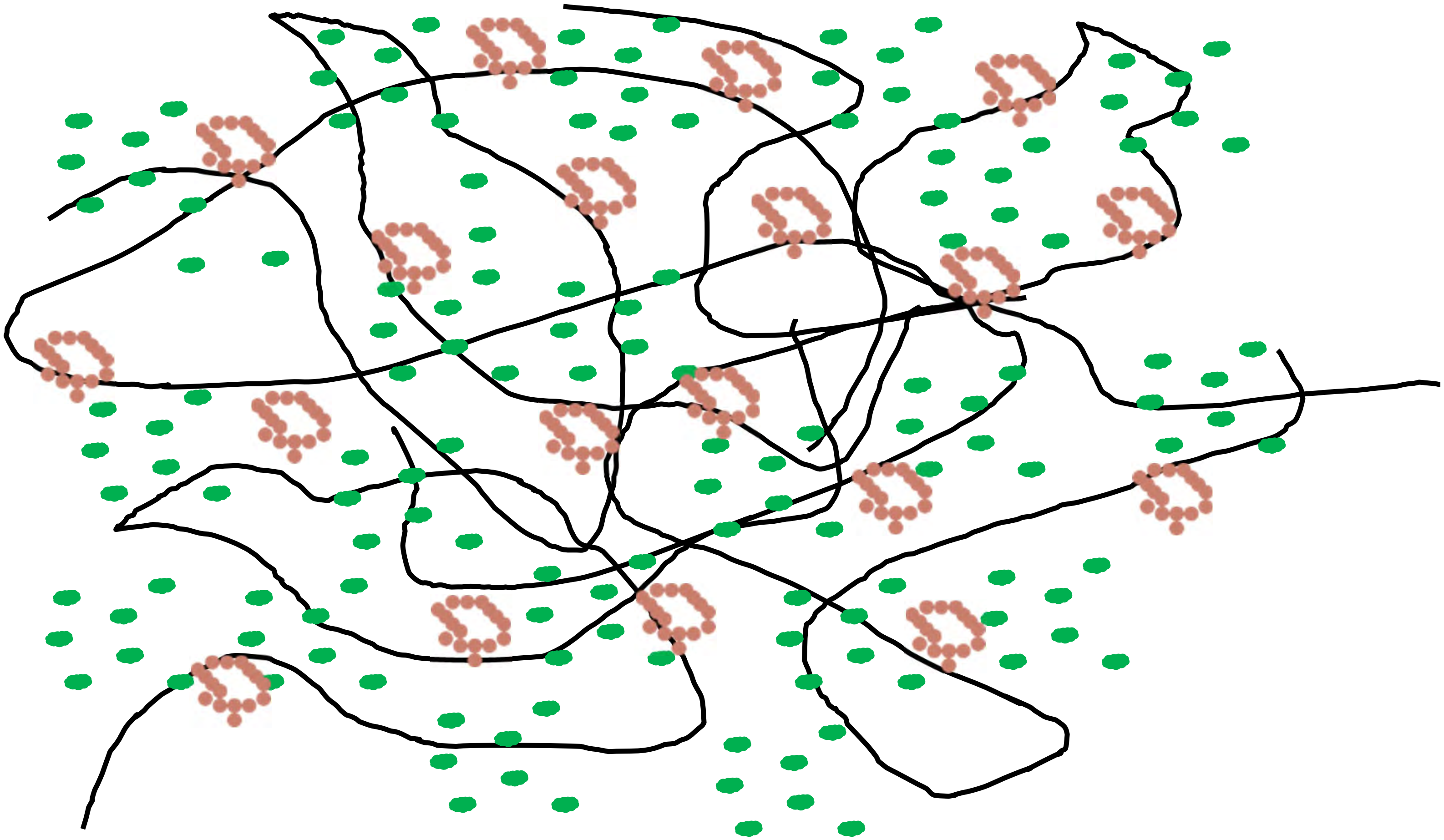
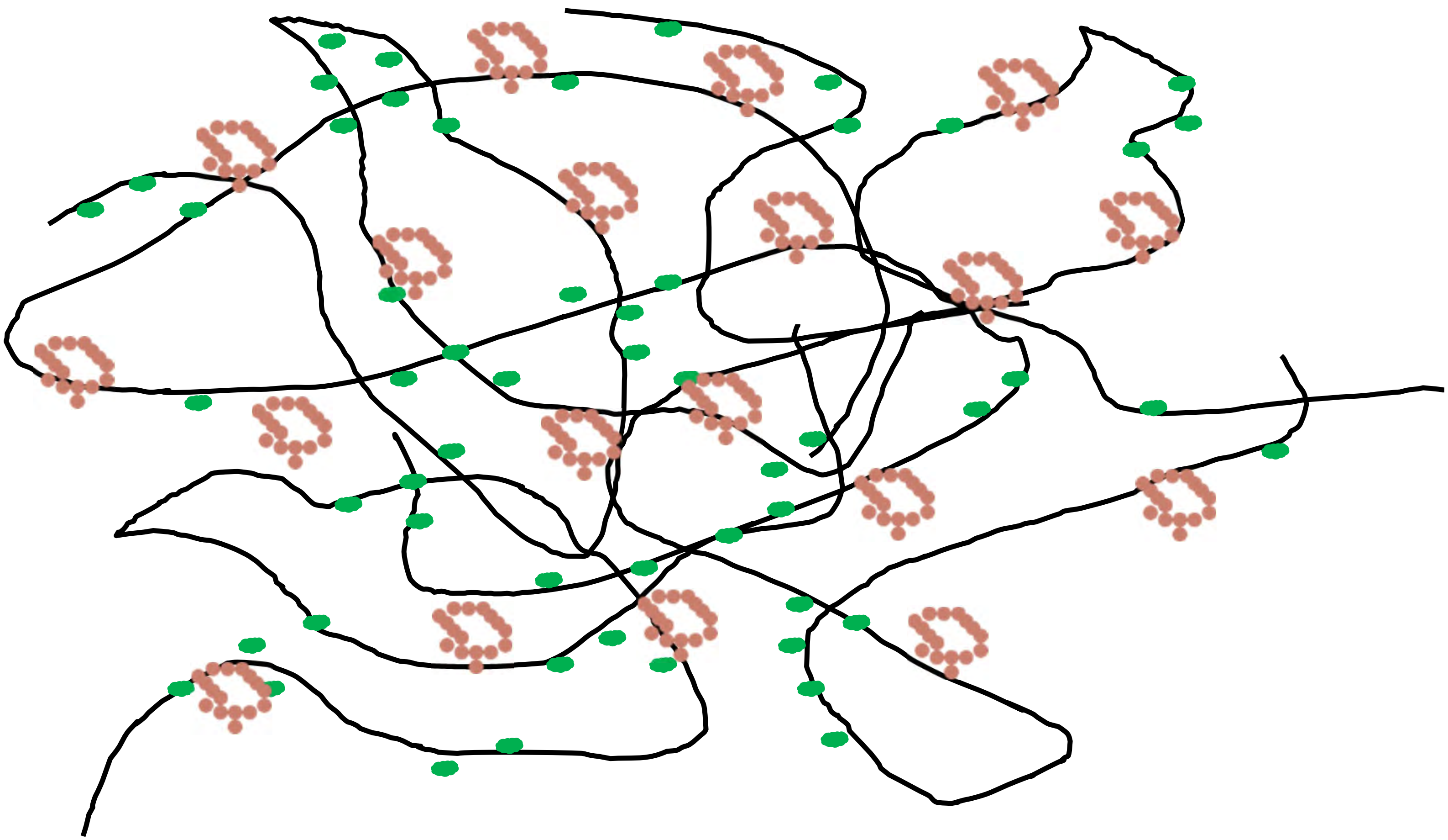
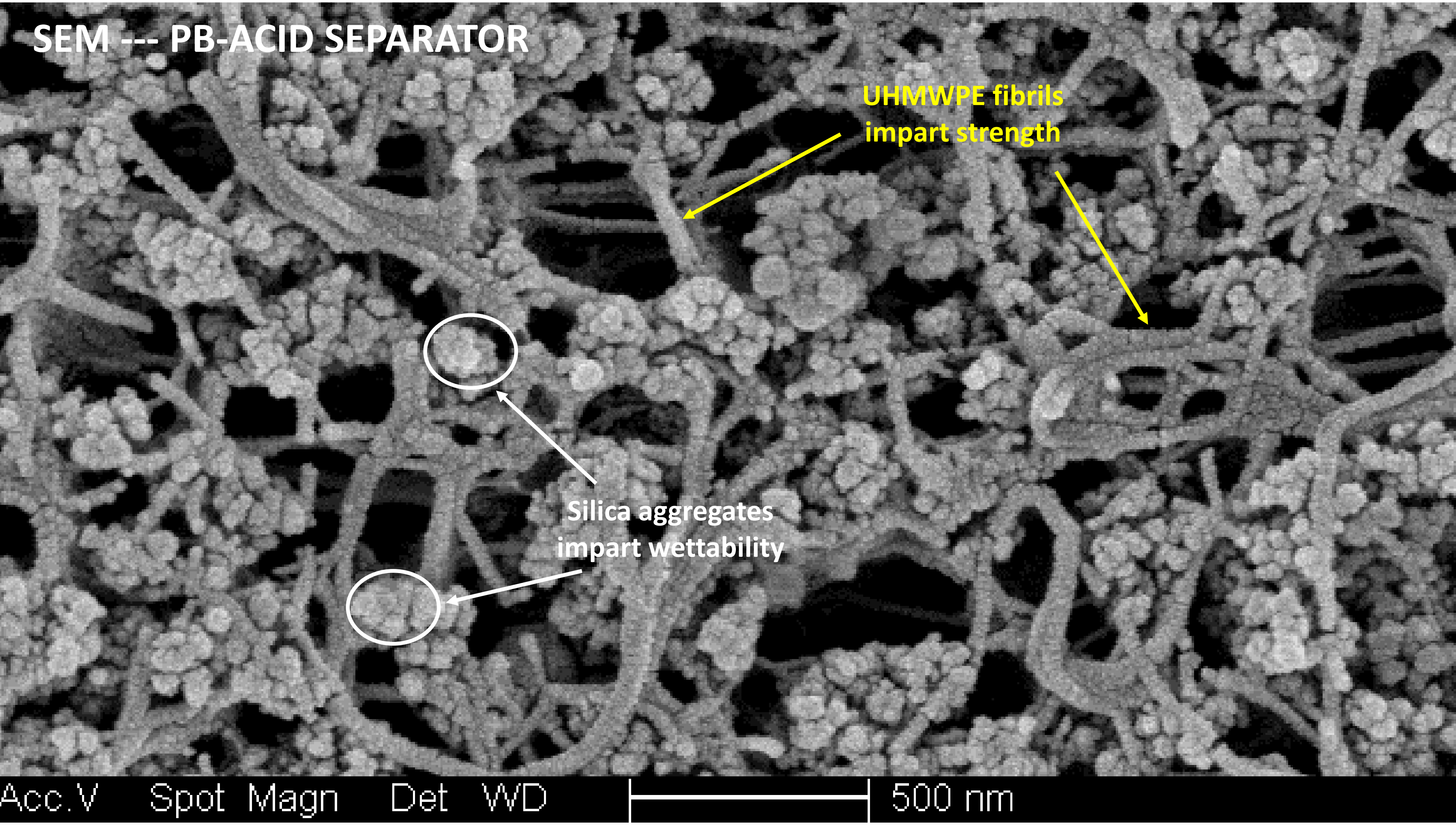
SILICA AGGREGATES DISPERSED THROUGHOUT THE POLYMER MATRIX

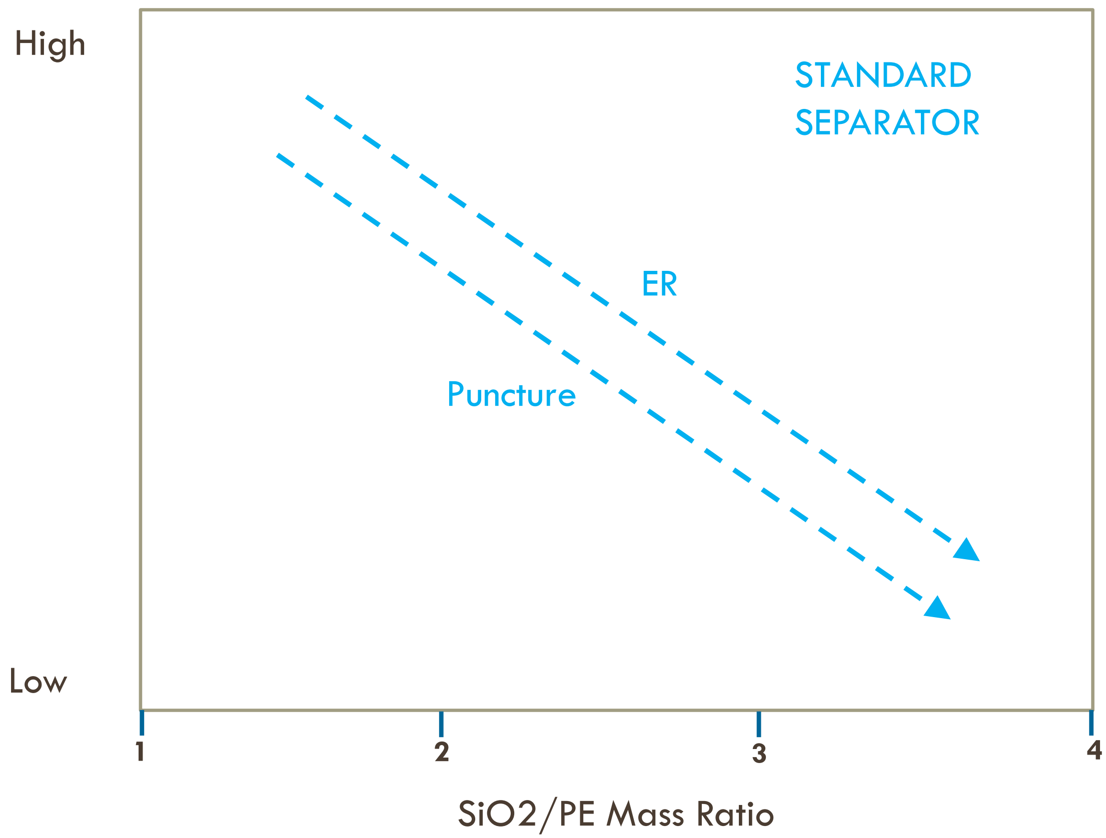


OIL EXTRACTION + SOLVENT DRYING → POROUS SEPARATOR




SEM --- PB-ACID SEPARATOR
UHMWPE fibrils impart strength
Silica aggregates impart wettability
Acc.V Spot Magn Det WD
500 nm

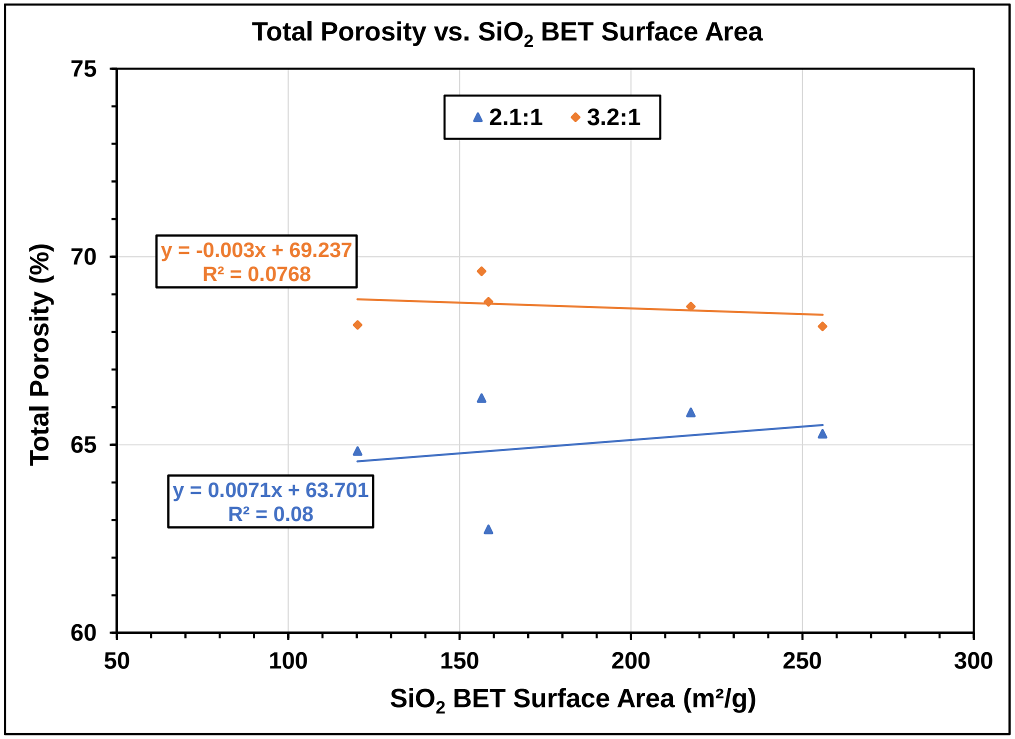
KEY SEPARATOR CHARACTERISTICS VS COMPOSITION

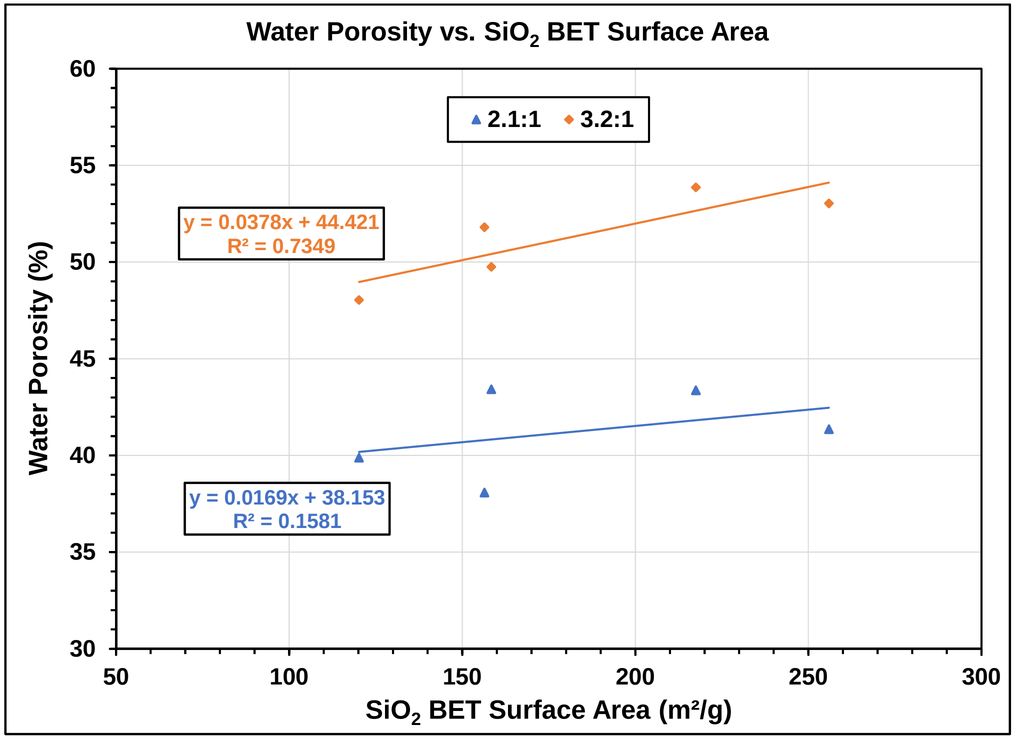


Material Parameters
- Silica Dispersibility
- Polymer Molecular Weight

Process Parameters
- Throughput
- Cooling rate
- Orientation

LAB EXTRUSION TRIAL WITH SILICAS HAVING DIFFERENT SURFACE AREAS





Water porosity results indicate that not all available pores are wetted out, but a higher percentage are at SiO2/PE = 3.2

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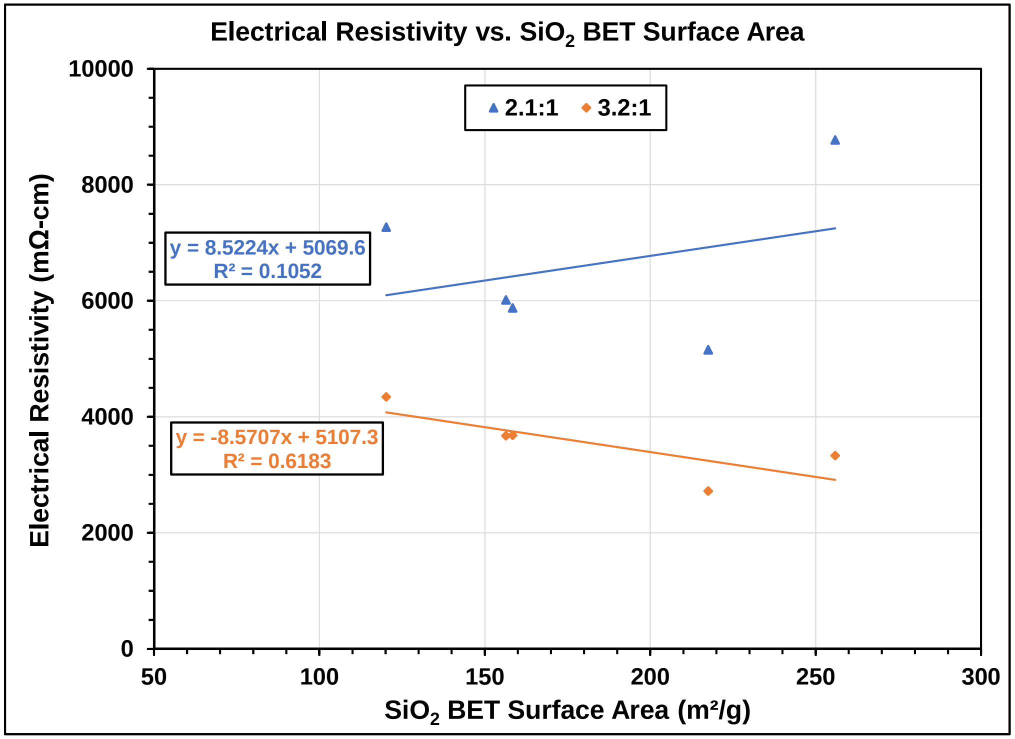
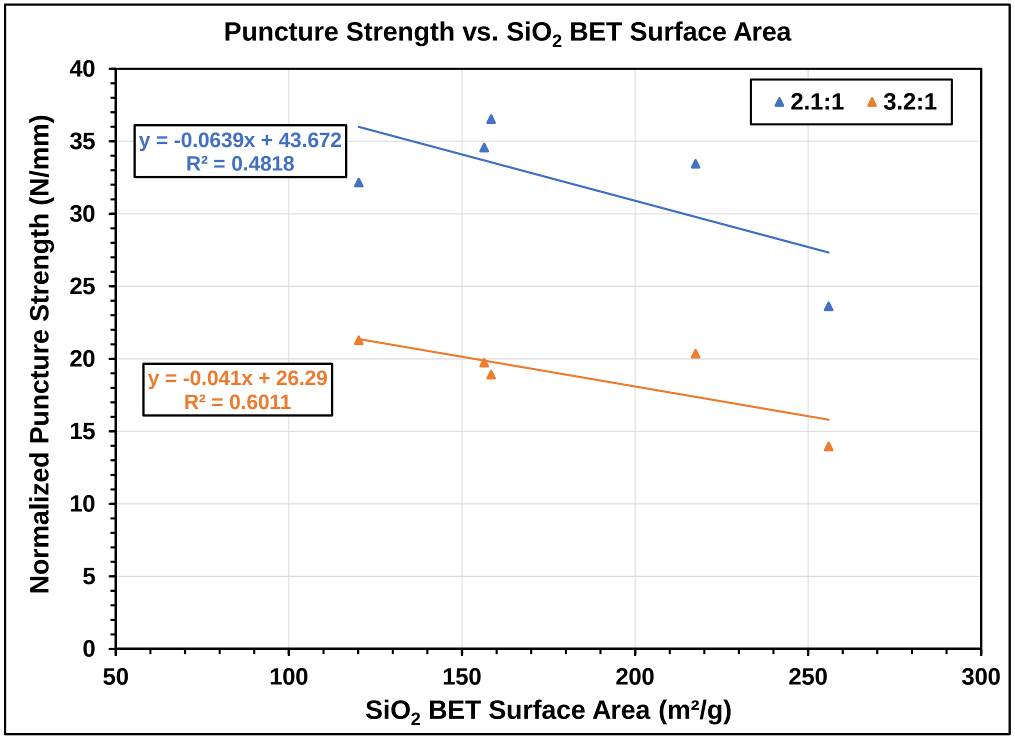
ELECTRICAL RESISTIVITY + PUNCTURE STRENGTH TRENDS





Expected trends observed for ER and puncture vs. SiO2/PE ratio; however, large differences in absolute values dependent upon silica surface area

UK PRODUCTION TRIAL

- 161 x 0.8 x 0.25 GE profile
- Similar process conditions utilized
  - Throughput
  - Cooling rate
  - Drying conditions
- Same precipitated silica was used in all formulations
- Polymer phase modified to promote wettability
- SiO2/PE mass ratio
  - XLR < LR ~ NS < HSL
- NS separator contains sodium sulfate which can be subsequently extracted with water or acid

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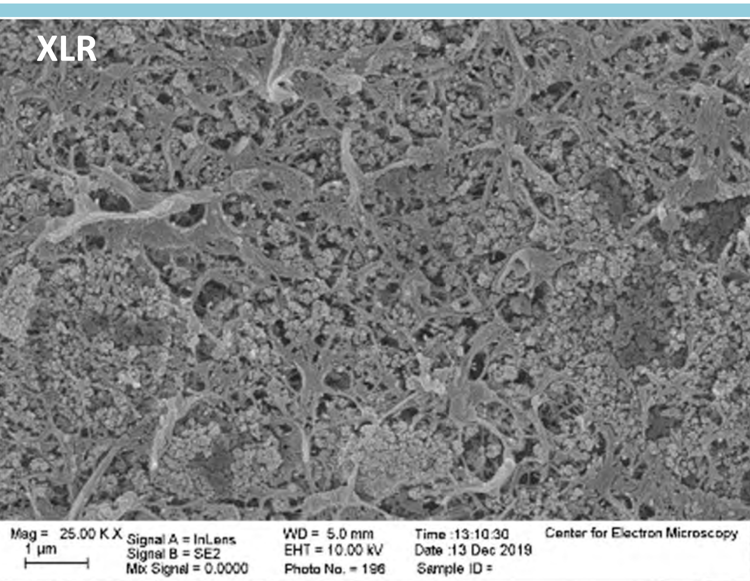
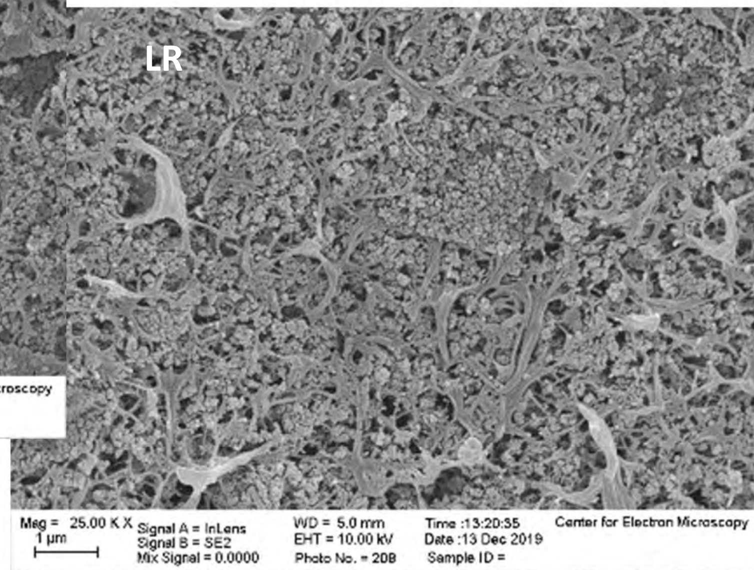
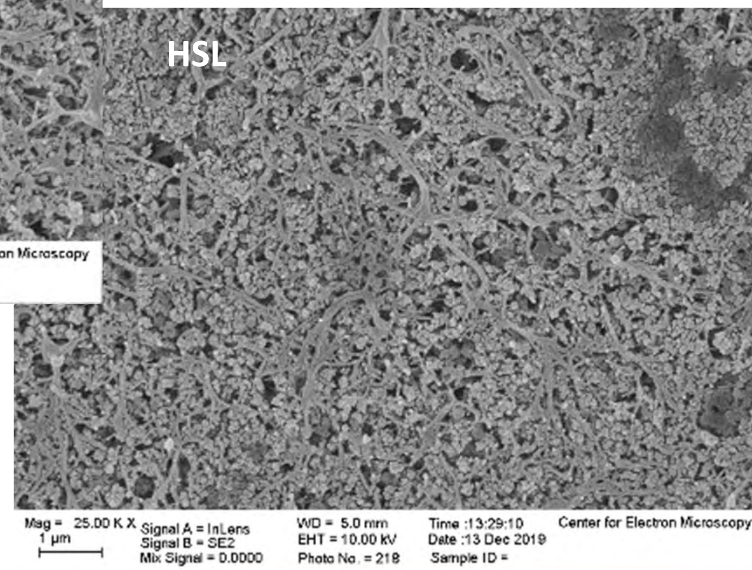
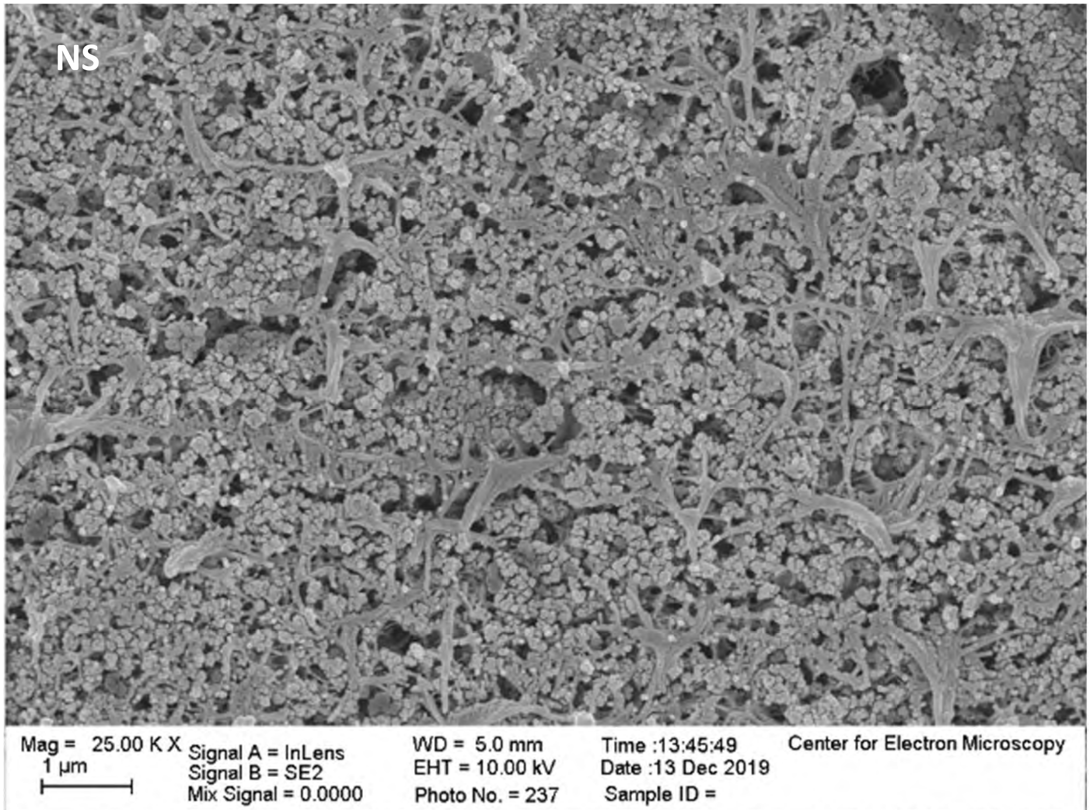
SEM – MD FRACTURE

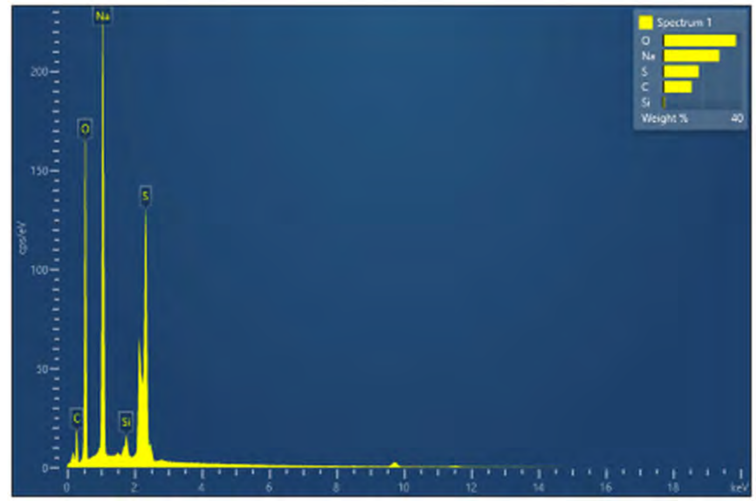




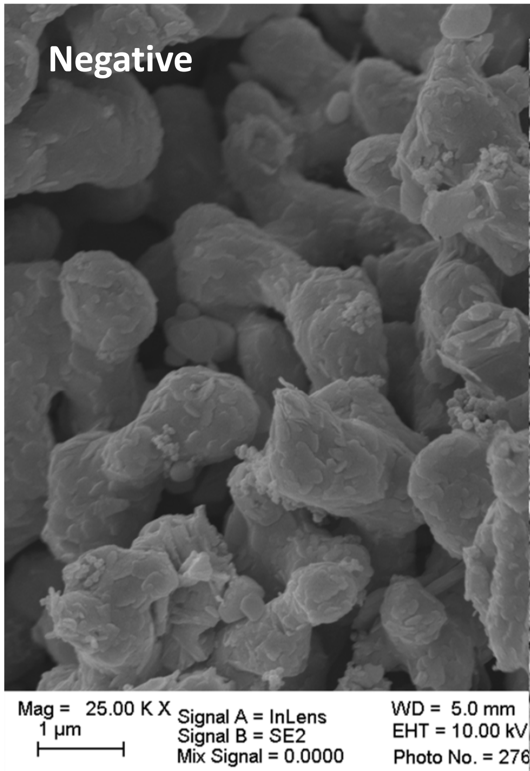


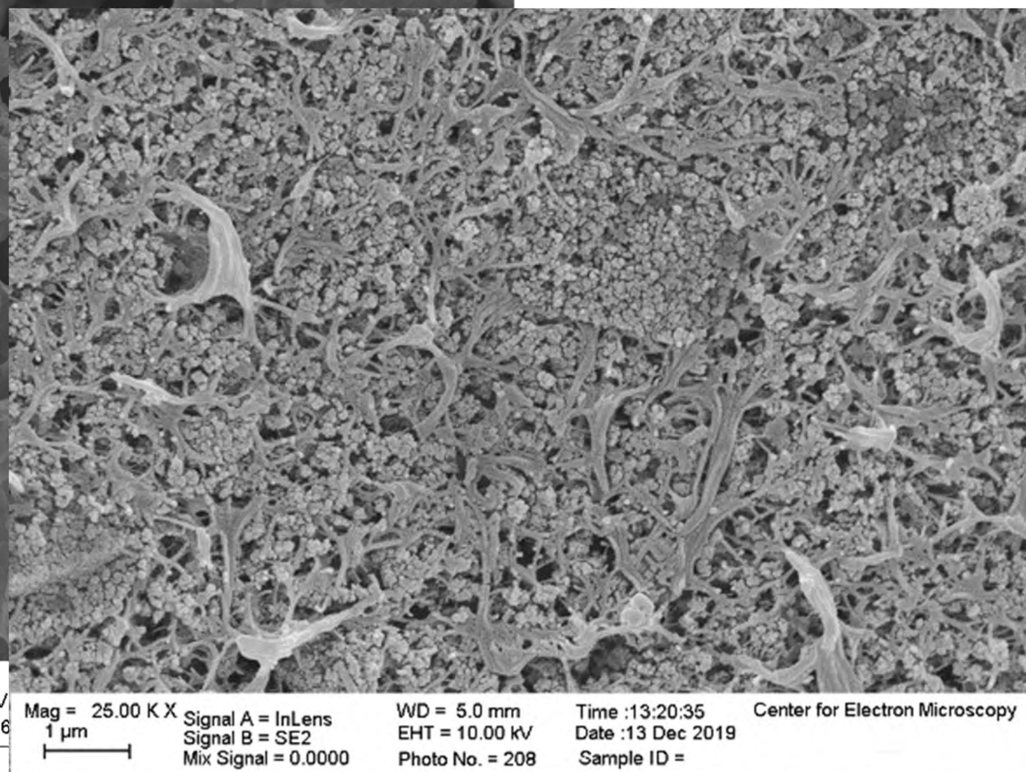
SEM – MD FRACTURE

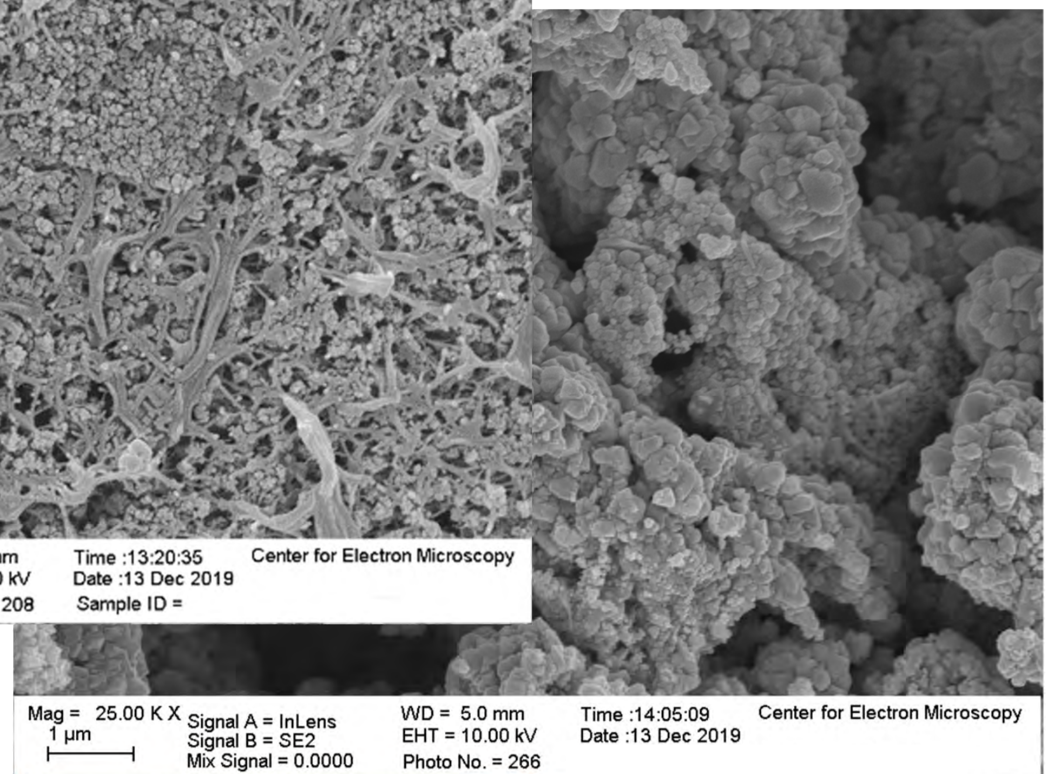




SEM – DRY CHARGE ELECTRODES







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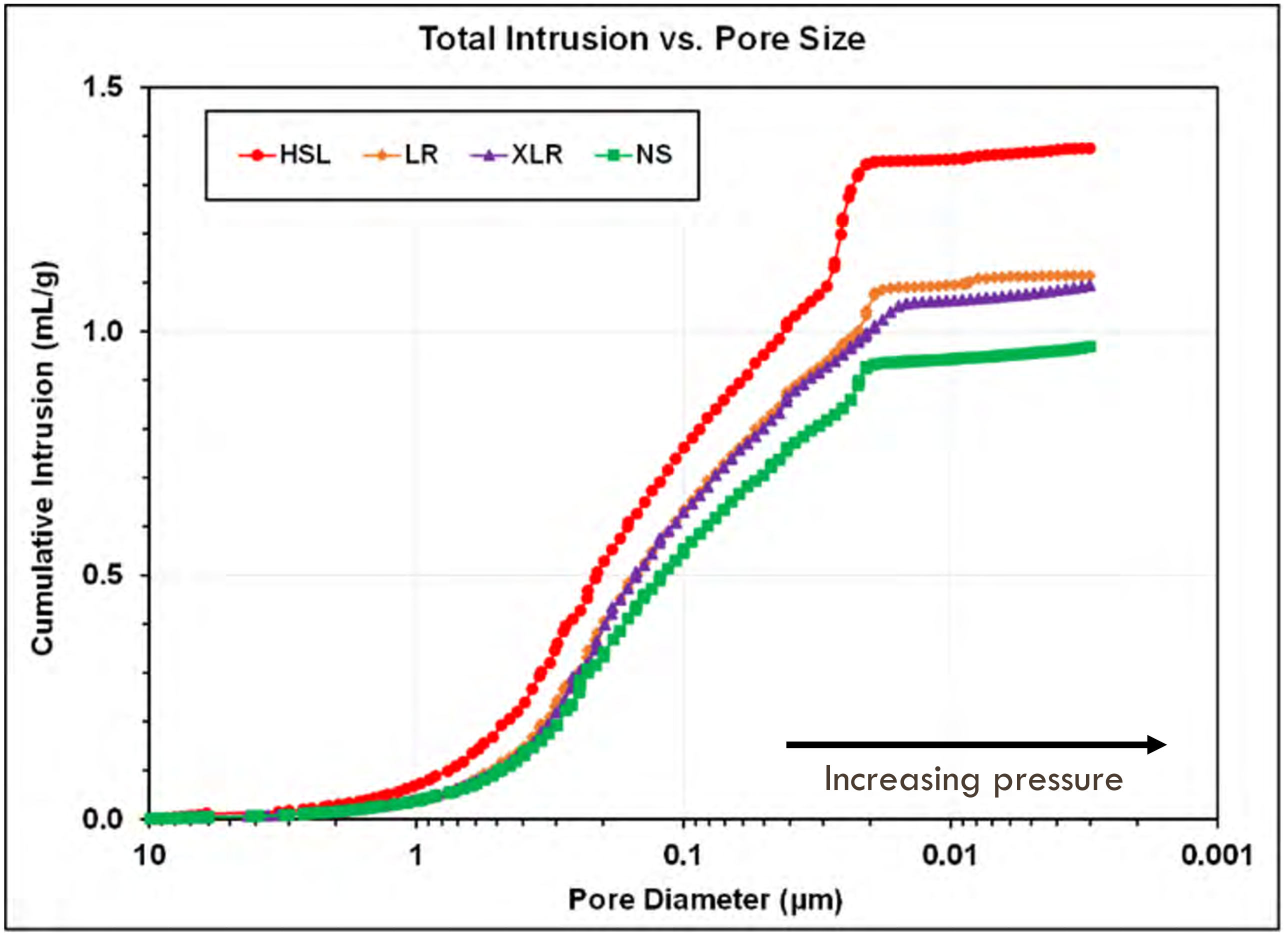
Hg POROSIMETRY – TOTAL INTRUSION



- Lower silica loading gives lower total intrusion volume: XLR < LR < HSL
- NS has the lowest total intrusion volume before extraction, but it also has a higher bulk density

Sample		XLR	LR	HSL	NS
Total Intrusion Volume =	mL/g	1.09	1.11	1.37	0.97
Total Pore Area =	m^2/g	87	74	96	74
Median Pore Diameter (Volume) =	µm	0.130	0.127	0.124	0.125
Median Pore Diameter (Area) =	µm	0.021	0.027	0.027	0.023
Average Pore Diameter (4V/A) =	µm	0.050	0.060	0.057	0.052

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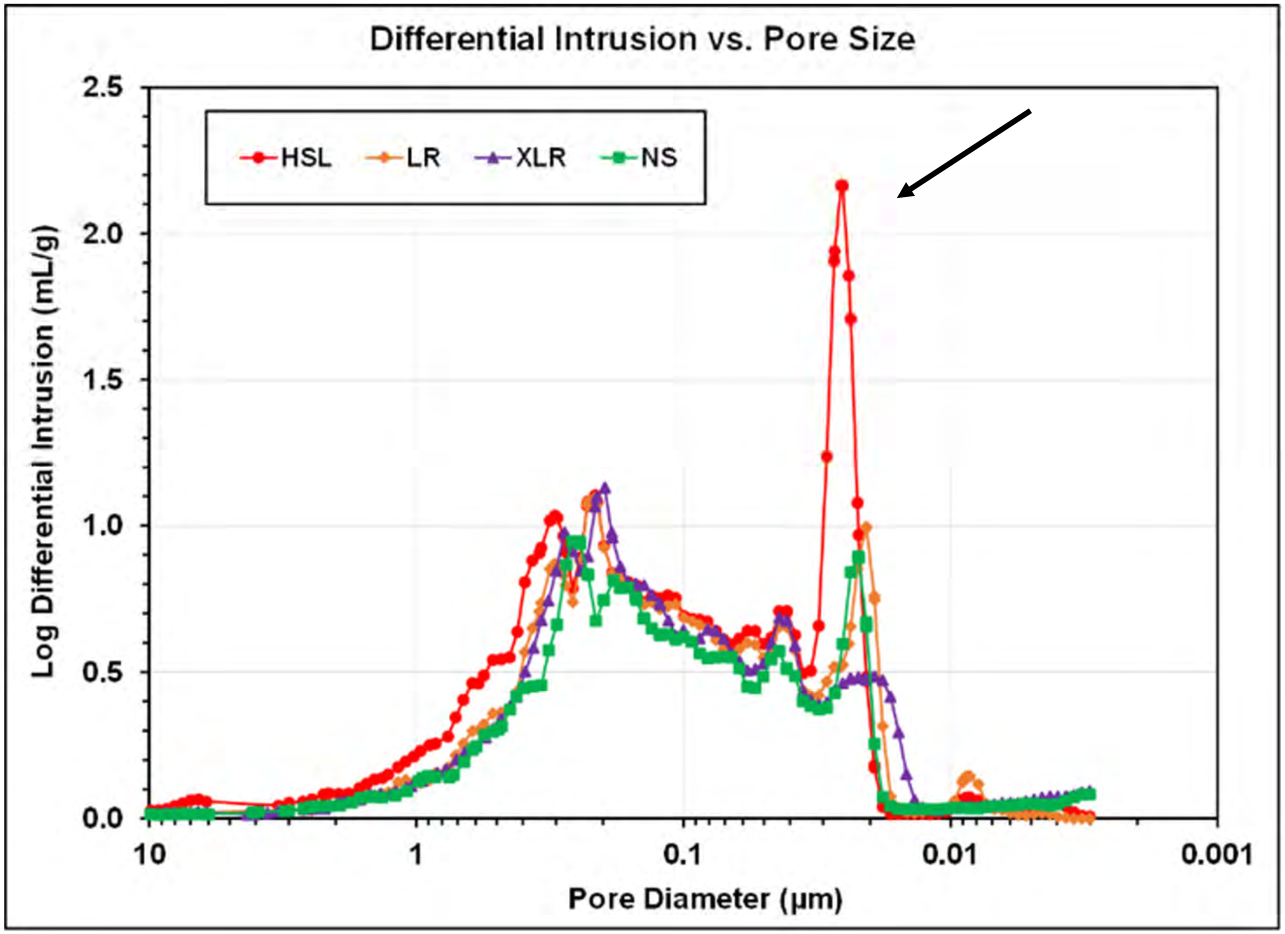
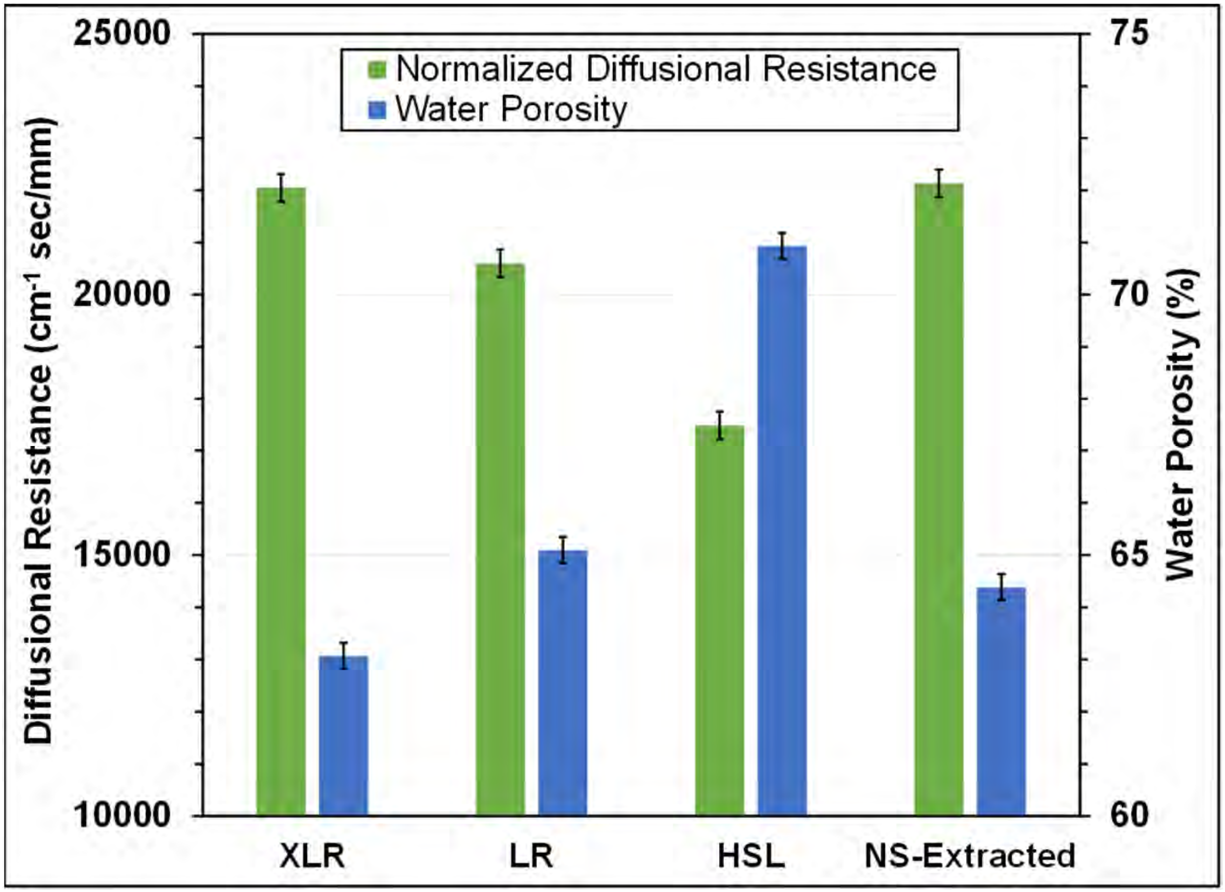
Hg POROSIMETRY – DIFFERENTIAL INTRUSION



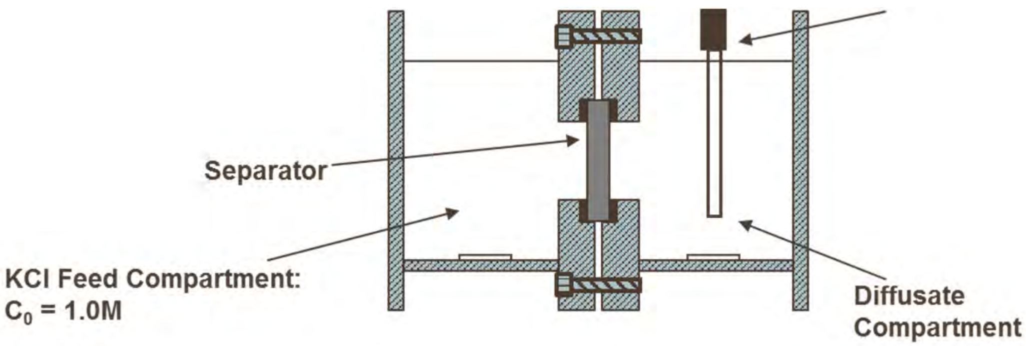
- HSL shows large intra-aggregate silica peak

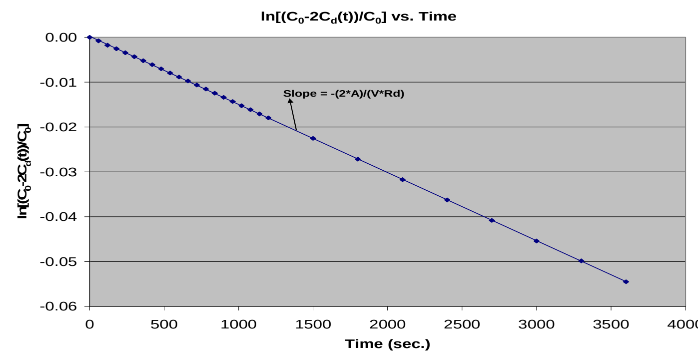
DIFFUSIONAL RESISTANCE AND WATER POROSITY



NS sample was boiled in DI water for 2 hrs, washed extensively, and kept wet prior to experiment

TORTUOSITY WAS DERIVED FROM DIFFUSIONAL RESISTANCE MEASUREMENTS





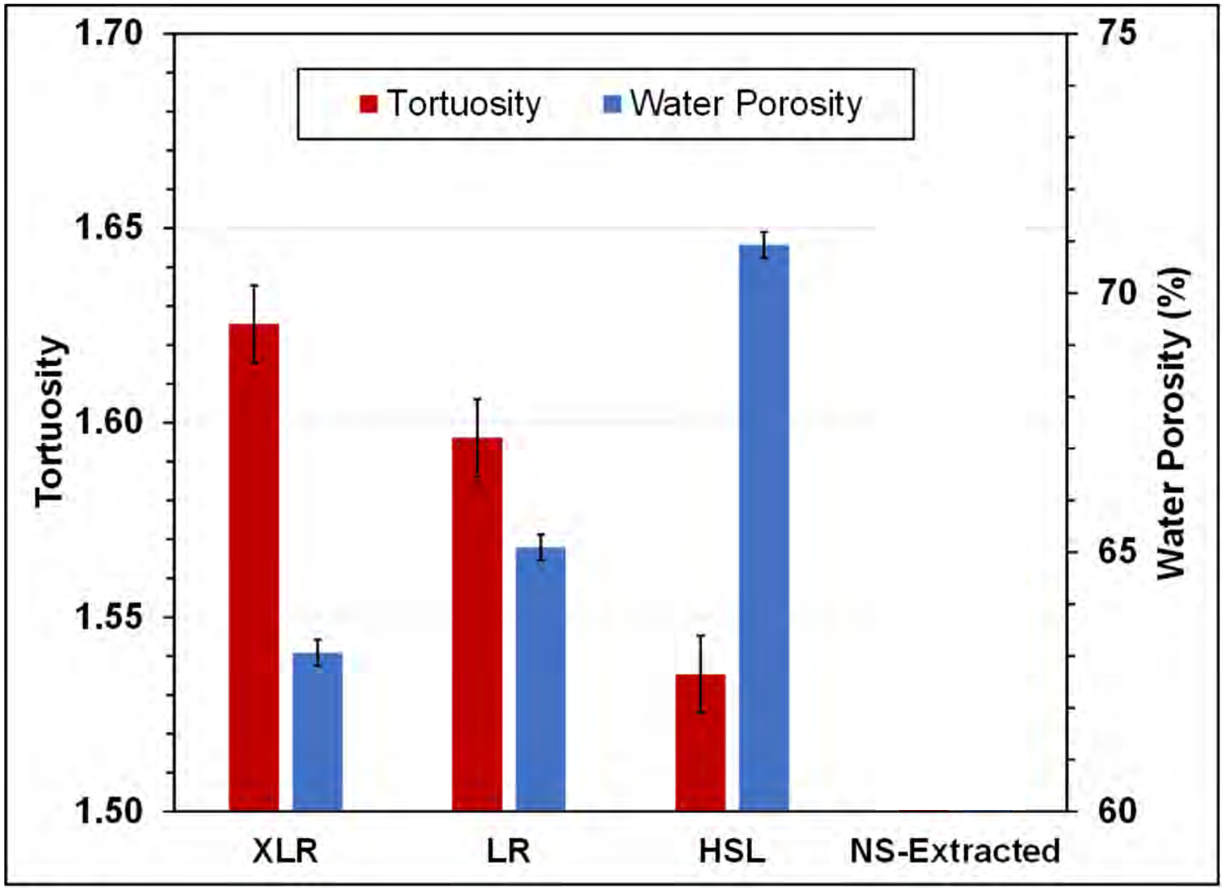
- Diffusion through a membrane separating two compartment:

$$\ln\left[\frac{C_0 - 2C_d(t)}{C_0}\right] = -\frac{2A}{VR_d} \times t$$

  - Slope of the left-hand-side vs. time can be used to calculate the diffusional resistance
    - C_0: initial concentration in the feed compartment
    - $C_d(t)$: concentration of KCl in the diffusate compartment at time t
    - A: Separator area exposed to the solutions
    - V: volume of solution in one compartment
    - R_d: Diffusional resistance of separator

$$R_d = \frac{t \times \tau^2}{D \times \varepsilon}$$

DIFFUSION CELL TORTUOSITY AND WATER POROSITY



SEPARATOR RESISTANCE

- Separator resistance is a function of the resistivity of the electrolyte (acid) plus the **design, pore structure, and composition** of the separator.

- Resistance of electrolyte within a porous structure (Ω):

$$R = \rho L \tau^2 / P\,A$$

where ρ = resistivity of the electrolyte, f (wt%, temperature)

L = thickness of the separator (**design**)

τ = tortuosity of the pore path (**structure**)

P = porosity filled with acid (**structure** and **composition**)

A = area of the separator through which ions flow

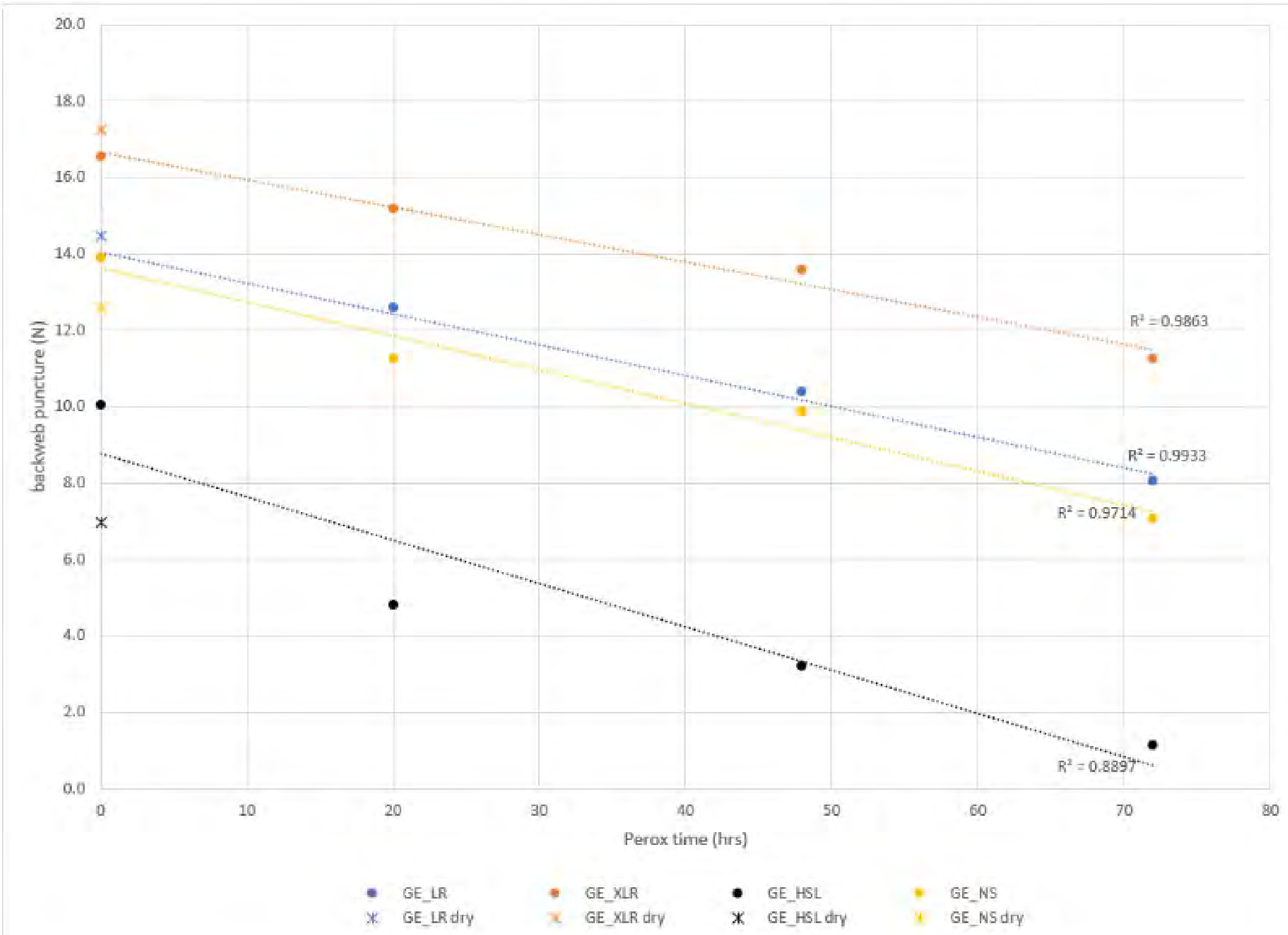
DATA SUMMARY

	Backweb Thickness (mm)	Overall (mm)	Electrical Resistance* (mΩ-cm²)	Electrical Resistivity (mΩ-cm)	Water Porosity (%)	τ-H2O	Backweb Puncture Strength (N)	Shoulder Puncture Strength (N)
XLR	0.259	0.778	56.3	2178.1	63.1	1.63	17.0	19.9
LR	0.255	0.784	54.1	2122.3	65.1	1.60	13.4	16.4
HSL	0.252	0.779	41.4	1646.0	70.9	1.54	7.5	9.1
NS	0.253	0.771	---	---	---	---	12.2	15.0
Extracted NS	0.253	0.771	38.3	1517.0	64.4	1.65		

* Measured in Palico instrument with barrier resistance > 15 ohms, indicating little leakage current

BACKWEB PUNCTURE RESISTANCE AFTER CHEMICAL OXIDATION

Increasing polymer content



Wetted separator exposed to H_2O_2/H_2SO_4 at 80 C for various time periods

Puncture resistance correlates with polymer content

Decay rates are similar for all formulations

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SUMMARY

- PE/SiO2 separators are complex, multicomponent membranes whose properties depend upon both ***composition*** and ***process conditions***
- Separators are homogeneous at a size scale that is much finer than that of Pb-acid electrodes.
- While thickness, porosity, pore size distribution, and tortuosity impact electrical resistance, these same parameters are expected to influence other transport processes (e.g., oxygen recombination)
- A more fundamental understanding of transport properties in separators and electrodes will help the industry to better design EFB batteries for start-stop applications
- ENTEK looks forward to working with manufacturers to further optimize the value proposition of Pb-acid batteries.