SEPARATOR DESIGN CONSIDERATIONS FOR EFB MICRO-HEV APPLICATIONS

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September 28, 2012

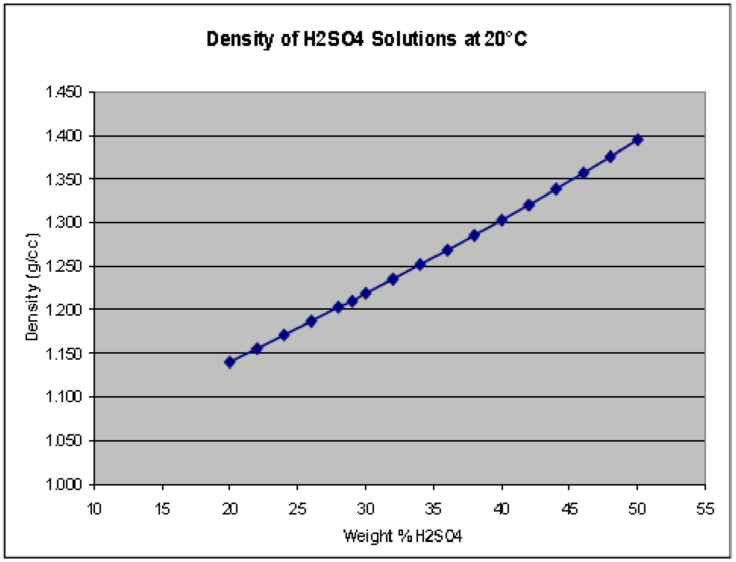
OUTLINE

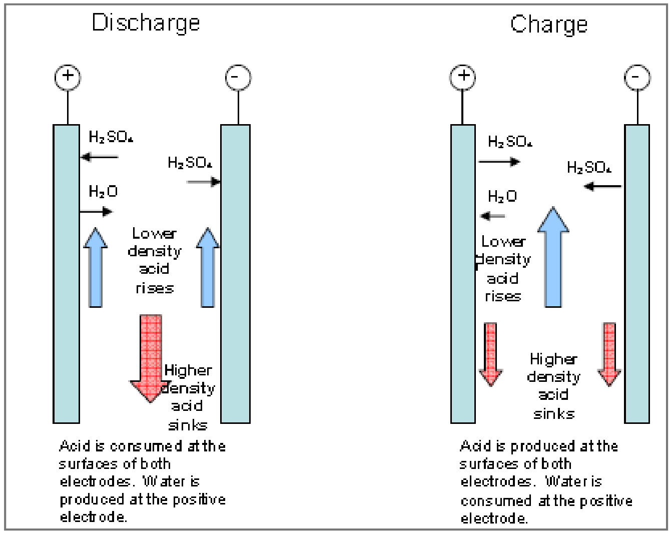
- Extended Flooded Batteries (EFB)
  - Acid Stratification
    - Mitigation Approaches
      - Current density
      - Rib design
      - Fiber mat
      - Mixing
  - Electrical resistance
    - Palico vs. CCA
    - Boiled vs. soak
    - Temperature
- Separator design considerations
  - Composition
  - Pore size distribution
  - Tortuosity
- Future approaches
  - Gels
  - Fibers
  - Foams

ACID STRATIFICATION

Positive electrode: $PbO_2 + H_2SO_4 + 2H+ + 2e- \leftrightarrow PbSO_4 + 2H_2O$

Negative electrode: $Pb + H_2SO_4 \leftrightarrow PbSO_4 + 2H+ + 2e-$





Acid is consumed at the surfaces of both electrodes. Water is produced at the positive electrode.

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On discharge:	Dilute, lower density acid produced at electrodes. Rises in laminar flow without mixing with bulk electrolyte.
On charge:	Concentrated, higher density acid produced at electrodes. Falls in laminar flow without mixing.

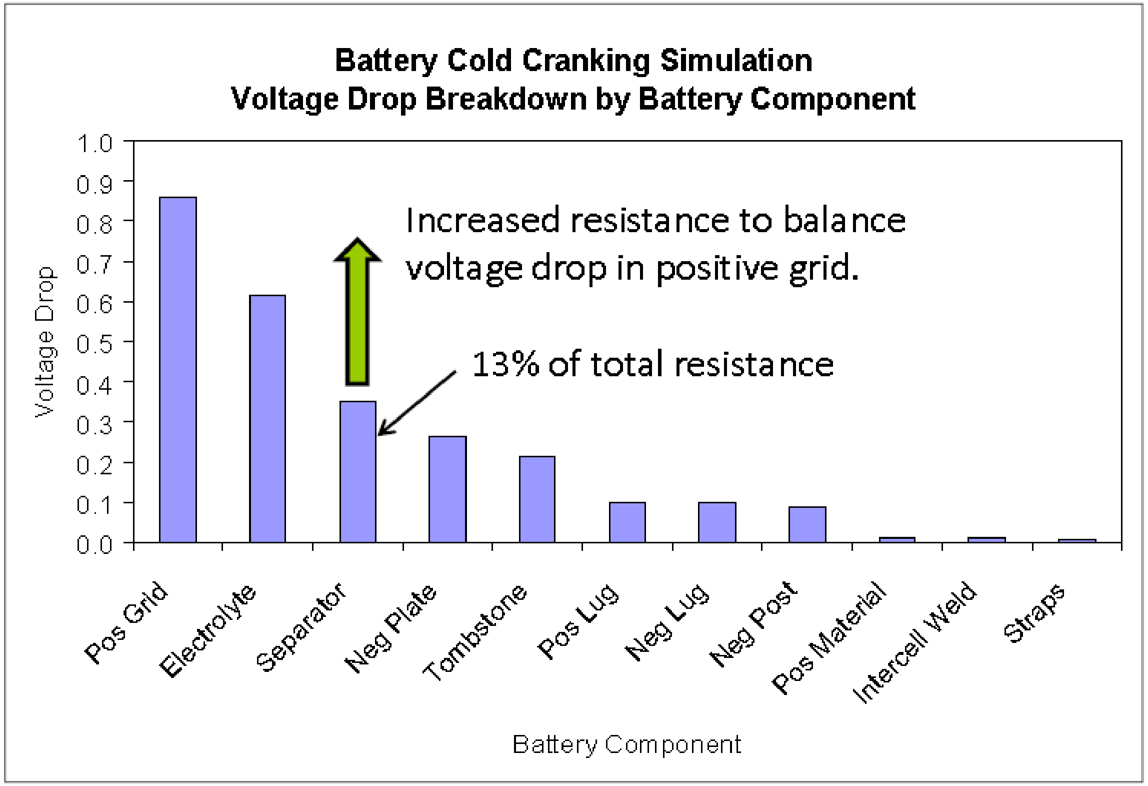
APPROACHES TO REDUCED STRATIFICATION

- Improve current density uniformity
  - Grid design: heavier, more grid strands at bottom.
  - Tab location and design: Reduce distance to tab.
  - Increased, or graduated, separator resistance.

- Disrupt convection
  - Glass mat on Positive electrode.
  - Rib design that disrupts laminar flow on electrode surface and encourage electrolyte mixing.
  - AGM

- Promote electrolyte mixing
  - Move electrolyte by pumping or gas lift

STRATIFICATION: SEPARATOR RESISTANCE



Increased separator resistance would result in more uniform current density, but at a cost of reduced efficiency and CCA performance.

ANTI-STRATIFICATION RIB DESIGNS

U.S. Patent Sep. 6, 1983 Sheet 1 of 2 4,403,024

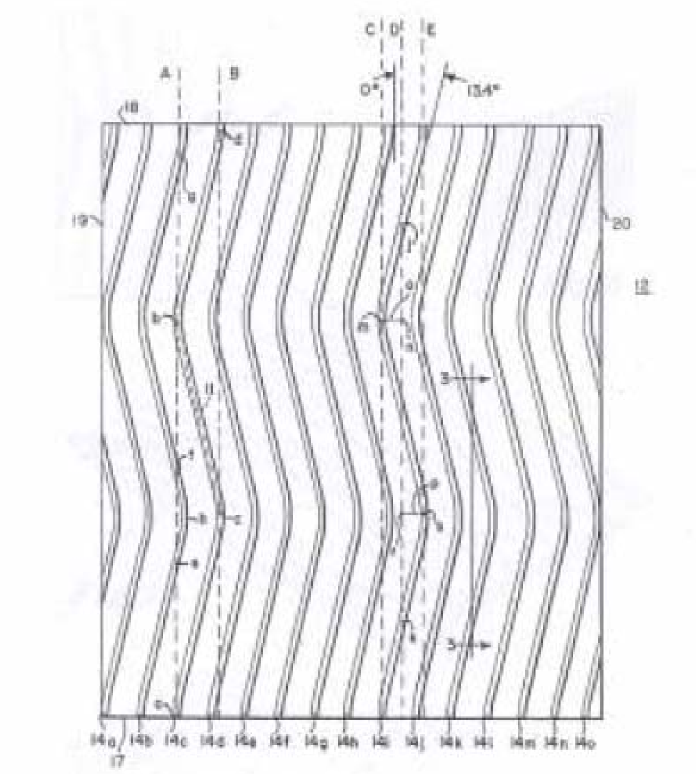


Fig.1

W.R. Grace

U.S. Patent Oct. 28, 1986 4,619,875

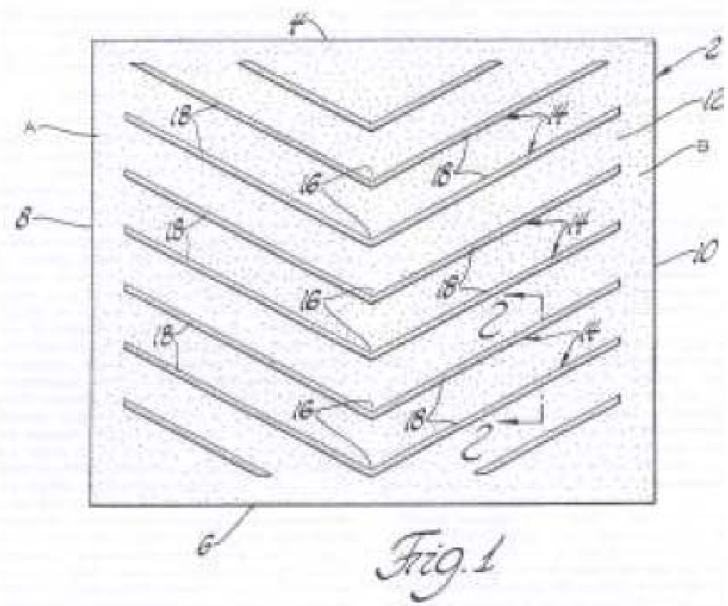
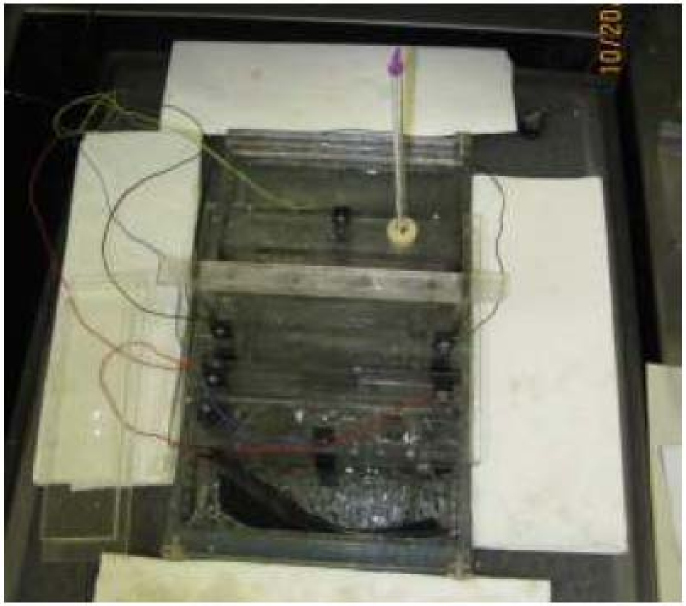


Fig.1

General Motors

THE PALICO SYSTEM

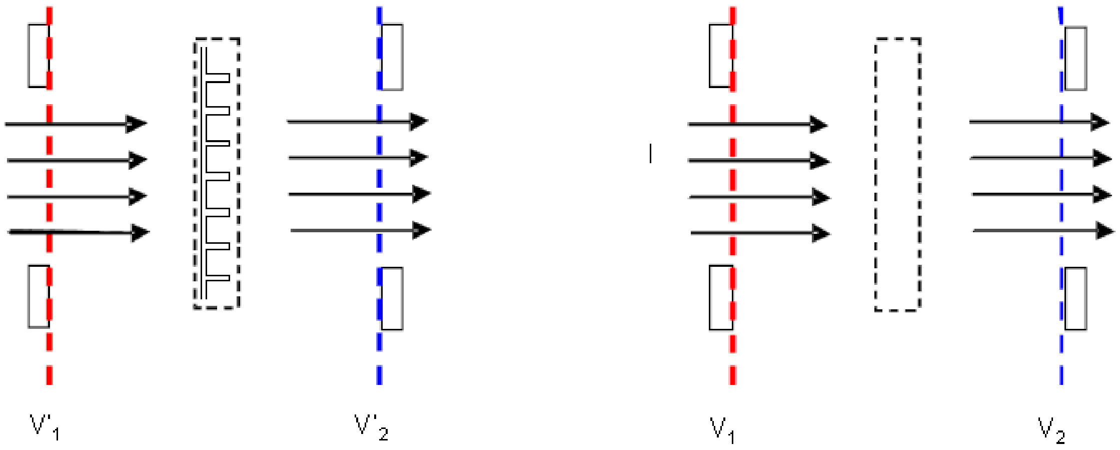


Palico Test Bath

Palico Low Resistance Measuring System

The Palico sends a 83 msec pulse of +100/-100 mA through the current delivery electrodes. It then senses the voltage response to the current at the voltage sensing electrodes.

SEPARATOR GEOMETRY – ER MODEL



$R'_T = (V'_1 - V'_2)/I$

With Separator

$R = (V_1 - V_2)/I$

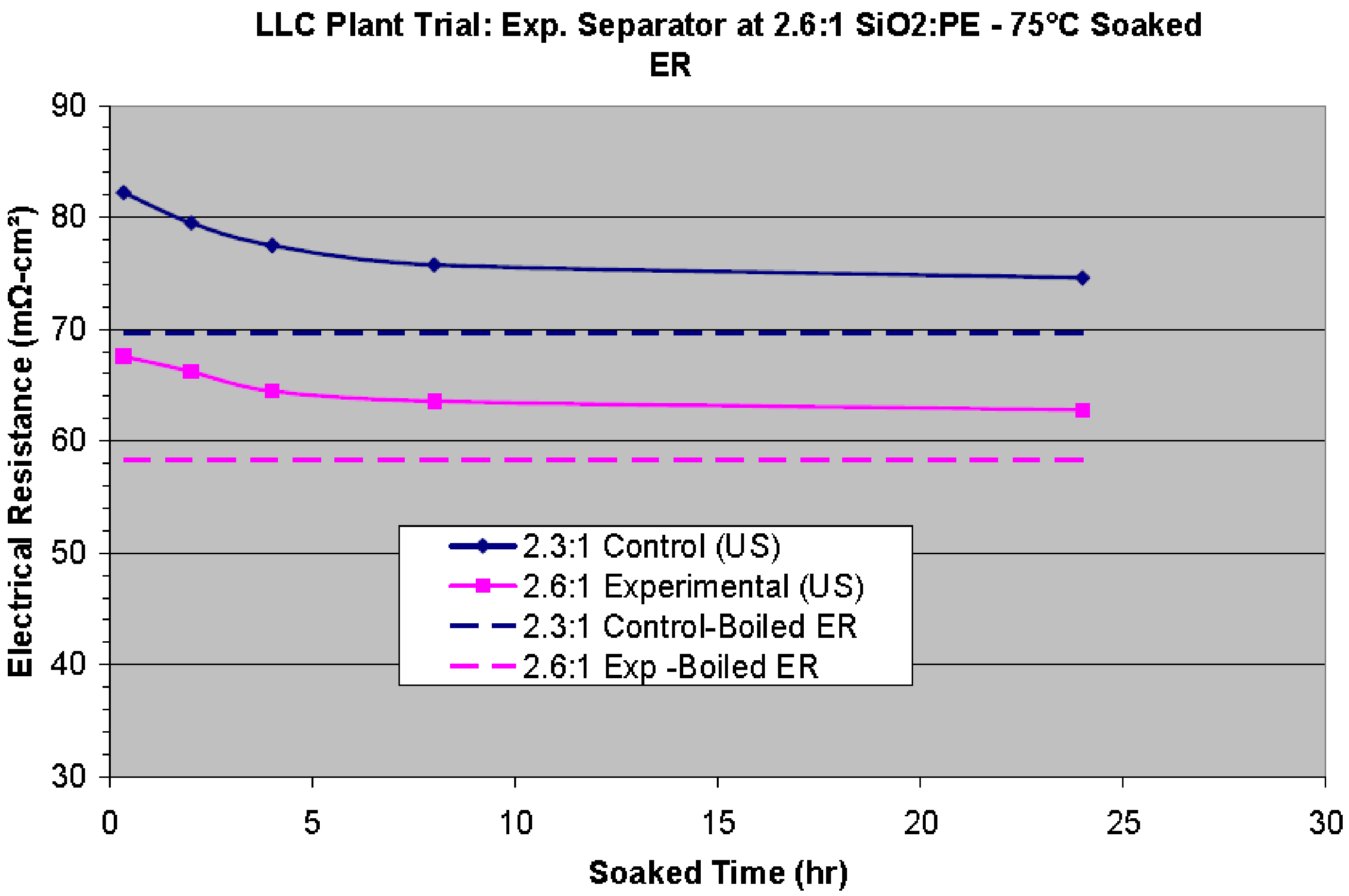
Without Separator

$$R_{sep} = R'_T - R$$

Schematic showing the approach used by Palico for measuring separator resistance. The separator resistance is the total resistance between the sets of voltage-sensing electrodes with, and without, the separator.

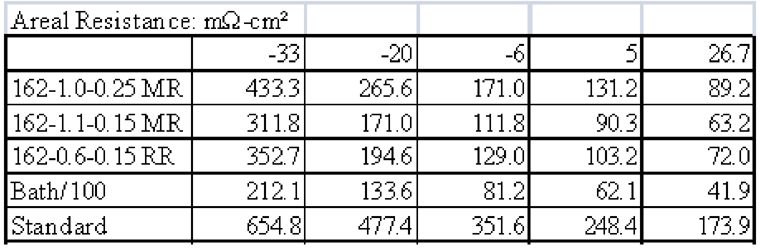
- A model was developed to relate separator profile/geometry to its electrical resistance as measured on the Palico system.
- Laboratory ER measurements are typically performed after boiling separator in DI water for 10 min. followed by a 20 min. acid soak

US SEPARATOR --- SIO_2/PE = 2.3 VS 2.6

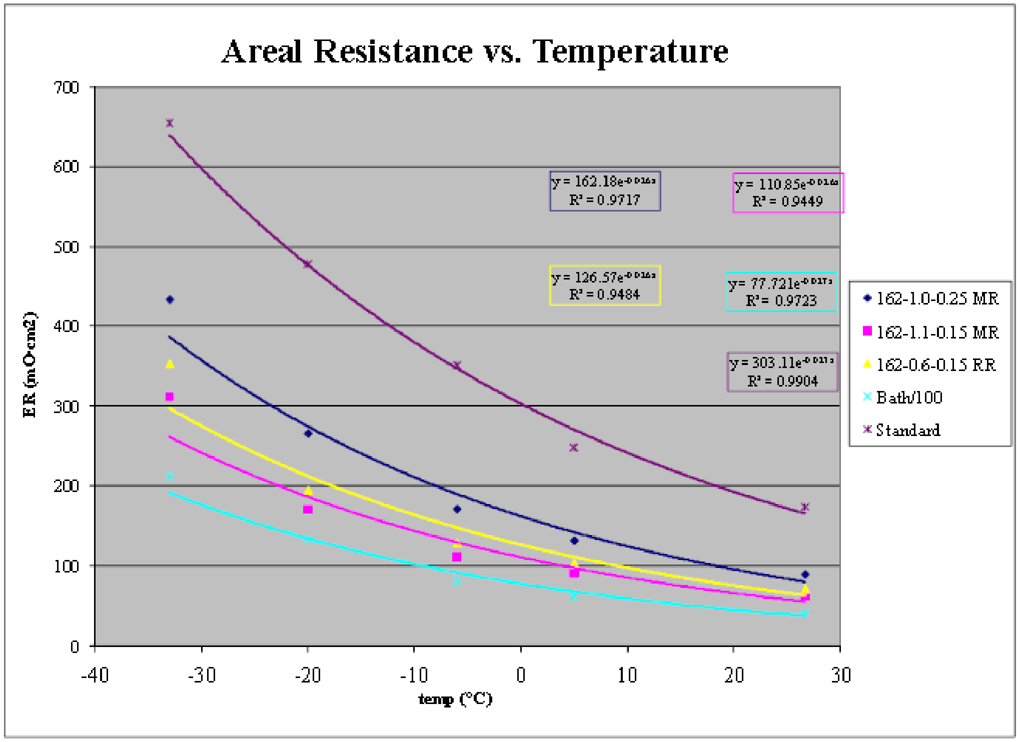


ER MEASUREMENT RESULTS

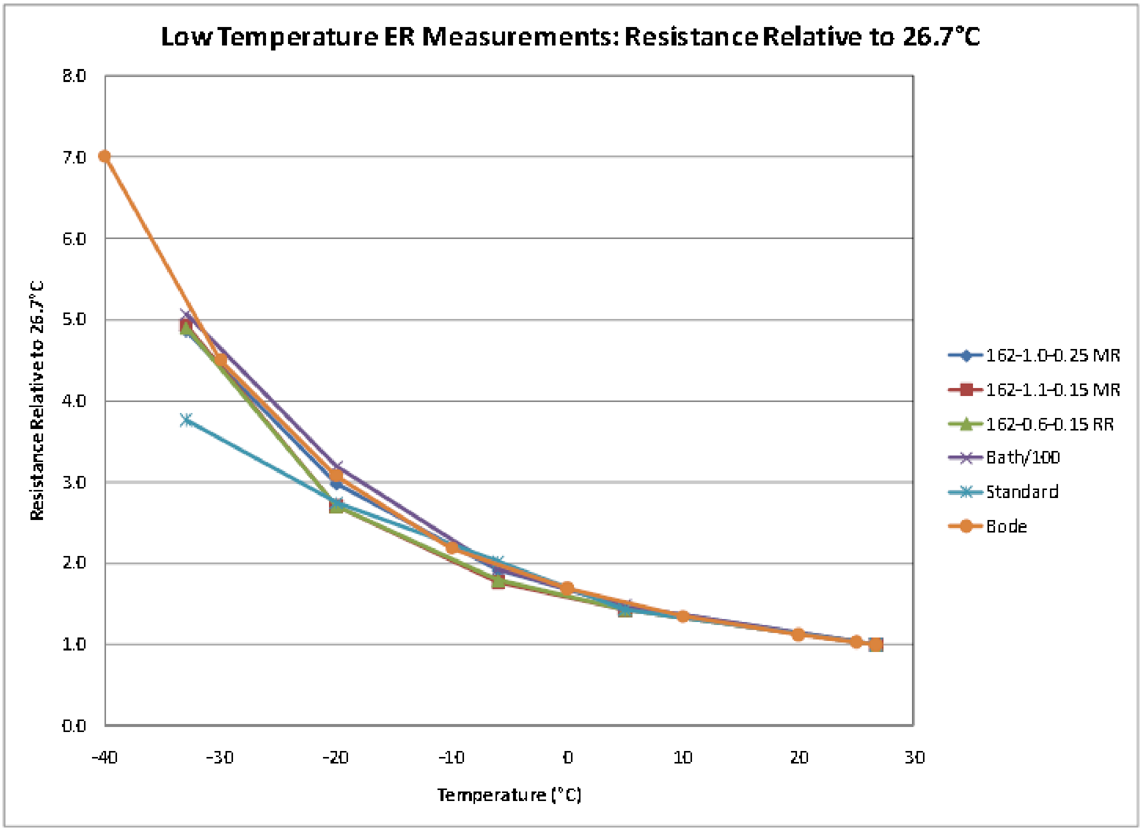
Resistance increased smoothly for all test articles as the bath resistance increased.



Areal Resistance: mΩ-cm²					
	-33	-20	-6	5	26.7
162-1.0-0.25 MR	433.3	265.6	171.0	131.2	89.2
162-1.1-0.15 MR	311.8	171.0	111.8	90.3	63.2
162-0.6-0.15 RR	352.7	194.6	129.0	103.2	72.0
Bath/100	212.1	133.6	81.2	62.1	41.9
Standard	654.8	477.4	351.6	248.4	173.9



RELATIVE RESISTANCE VS. TEMPERATURE



Except for the perforated plastic "standard", all separators and the bath follow the same relative resistance behavior as the literature values (*Bode, Lead Acid Batteries.*)

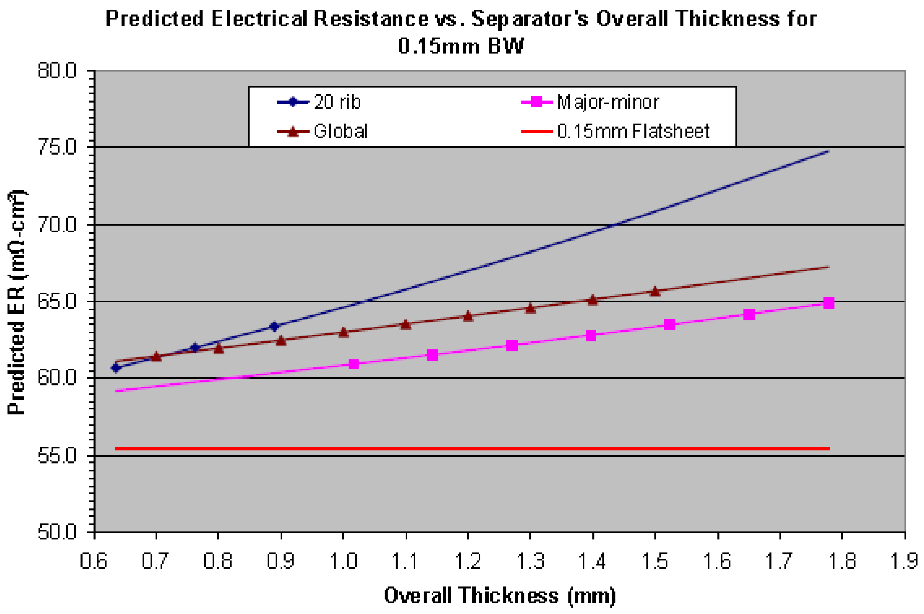
LIMITATIONS OF PALICO TEST MEASUREMENTS

- Current densities:
  - Palico separator ER test: (100ma)/(32.3cm^2) = 3.1 ma/cm^2
  - Battery Impedance Tester: (150ma)/(2200cm^2) = 0.068 ma/cm^2
  - Cold crank test: (680000ma)/(2200cm^2) = 309 ma/cm^2

- Test temperatures:
  - Palico separator ER test: 27°C
  - Battery Impedance Tester: room temperature (20-25°C)
  - Cold crank test: -18°C

COMPETING FACTORS IN PB-ACID SEPARATOR OPTIMIZATION

↑ polymer	↑ mech props	↑ ER
↑ silica	↓ mech props	↓ ER



SEPARATOR ER

- Separator resistance is a function of **pore structure** and **composition.**

- Resistance of electrolyte within a porous structure:

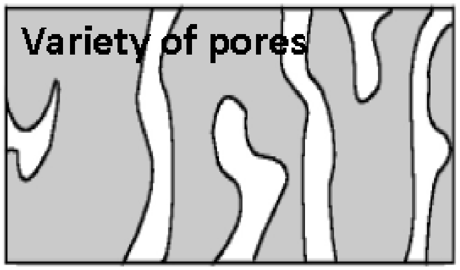
$$R = pLT^2 / P$$

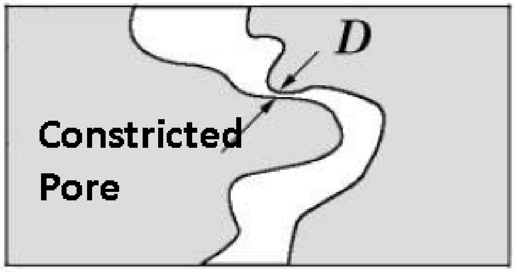
Where

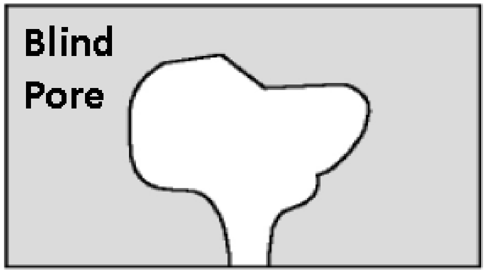
p = resistivity of the electrolyte, f ([C], T)
L = thickness of the separator
T = tortuosity of the pore path (i.e. structure)
P = porosity filled with acid (structure and composition)

PORE STRUCTURE

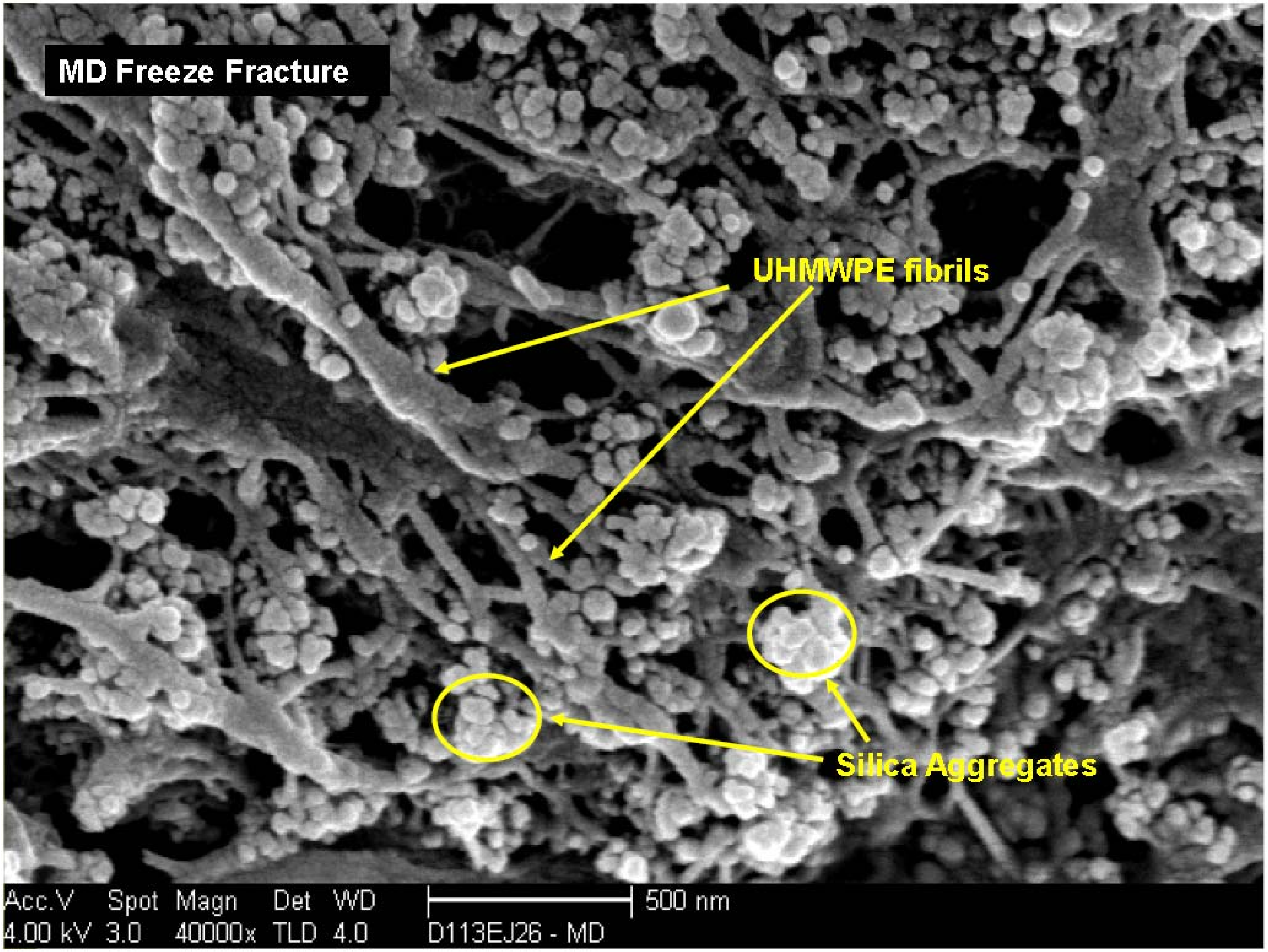
- The pore structure of PE/silica separator is characterized by its heterogeneity:
  - Hydrophilic silica aggregates of different sizes
  - Hydrophobic polyethylene fibrils
  - Differences in structure between surface (polymer-rich) and bulk (silica-rich)
  - Not all pore volume is filled with electrolyte
    - Total pore volume:
    - Water accessible pore volume:



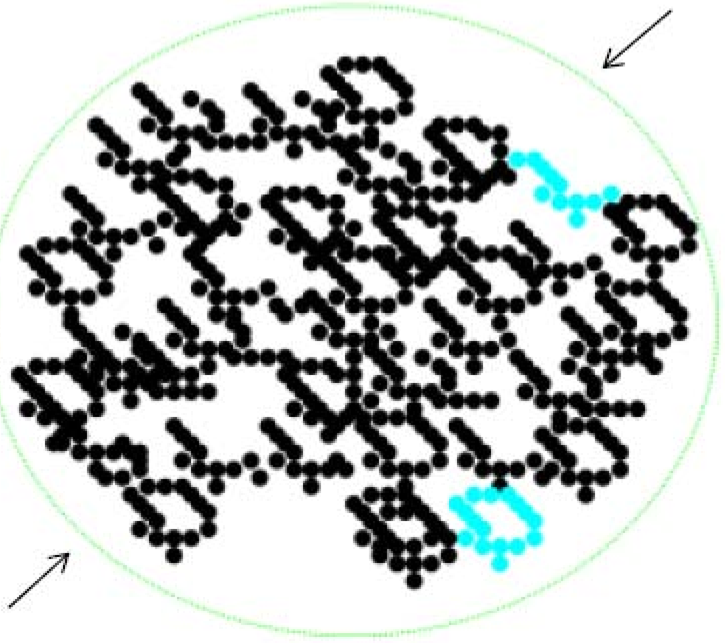




FREEZE FRACTURE



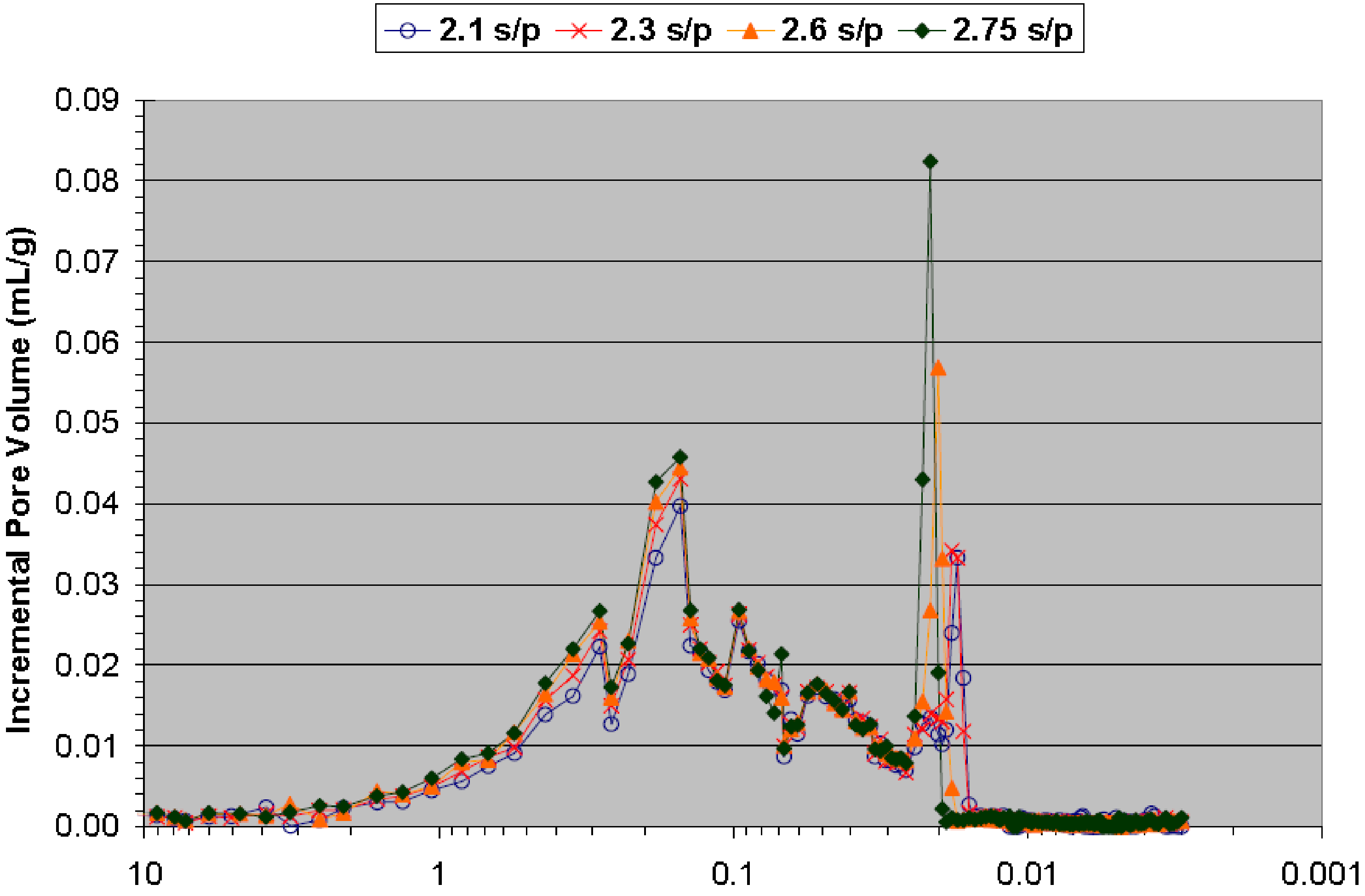
HOW CAN WE POTENTIALLY IMPACT PORE STRUCTURE AND WETTABILITY ?



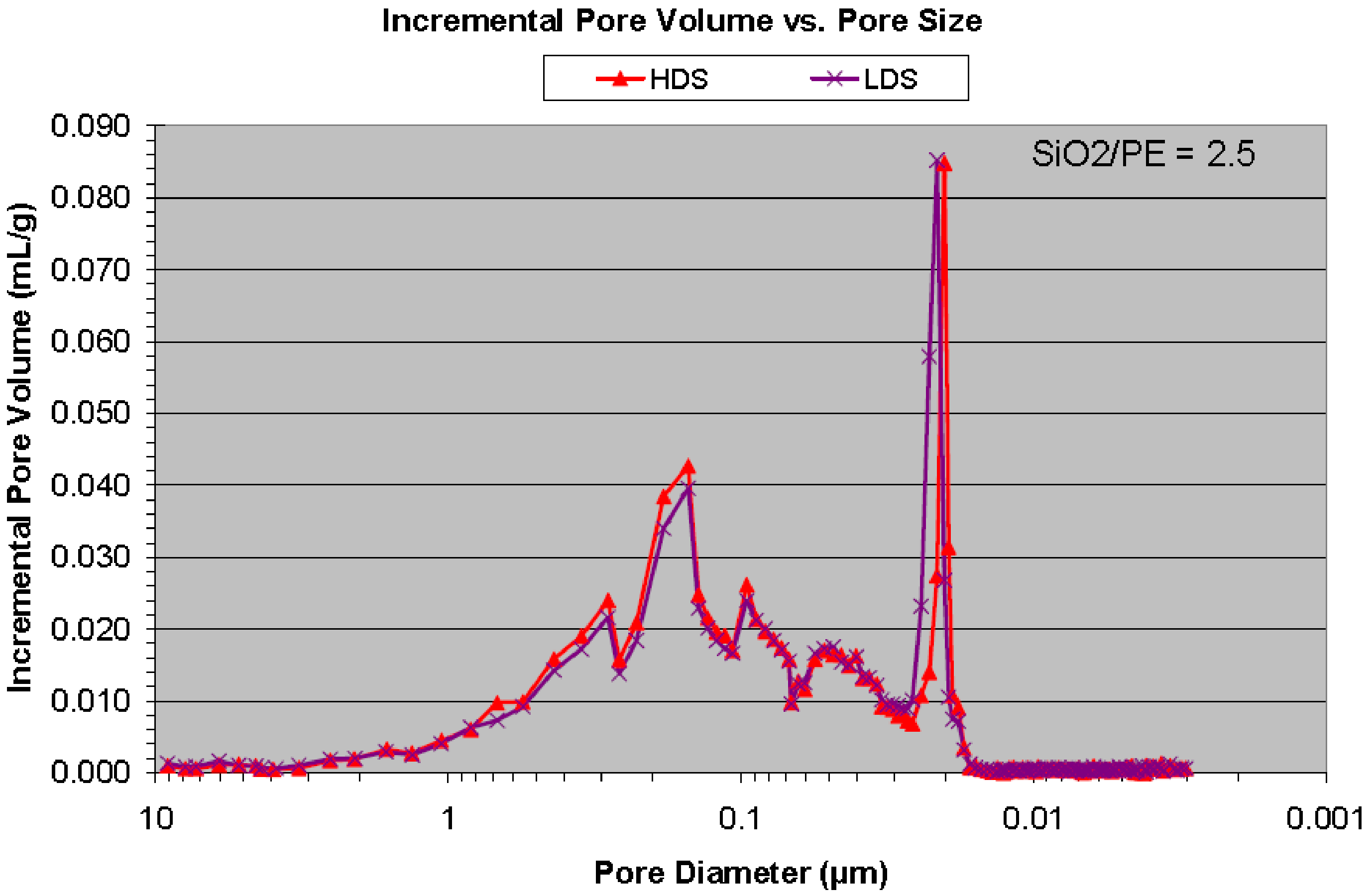
- Separator Composition
  - Oil Content
  - Silica/polymer ratio
    - $SiO_2/PE = 2.1 – 2.9$
  - Highly Dispersing vs. Conventional silica
    - Primary particle size
    - Aggregate particle size
    - Inter-aggregate bond strength
  - Sacrificial pore formers
  - Surfactants

- Process parameters
  - Cooling rate
  - Orientation
  - Solvent selection
  - Drying conditions

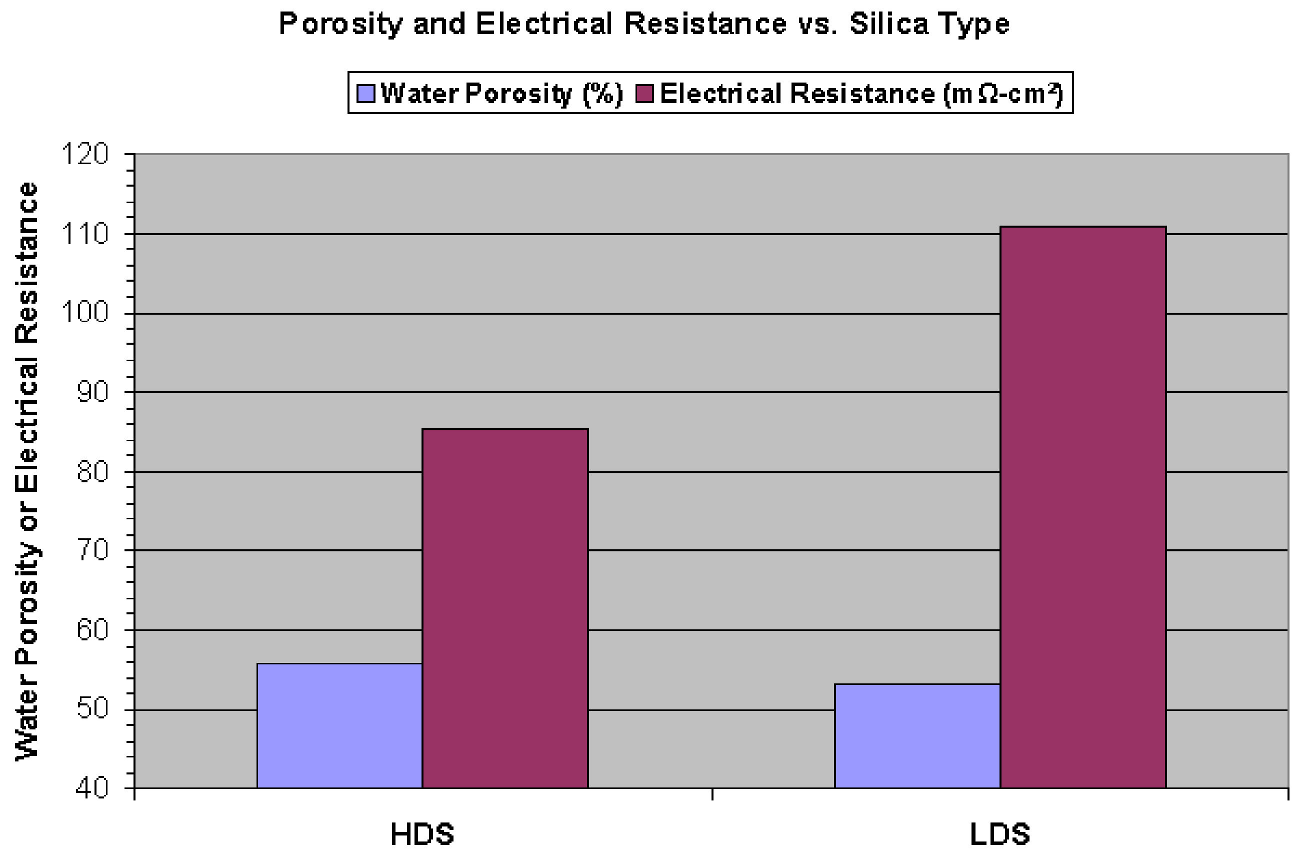
HG POROSIMETRY DATA AS A FUNCTION OF SIO_2/PE RATIO



HG POROSIMETRY DATA – DIFFERENT SILICA TYPES

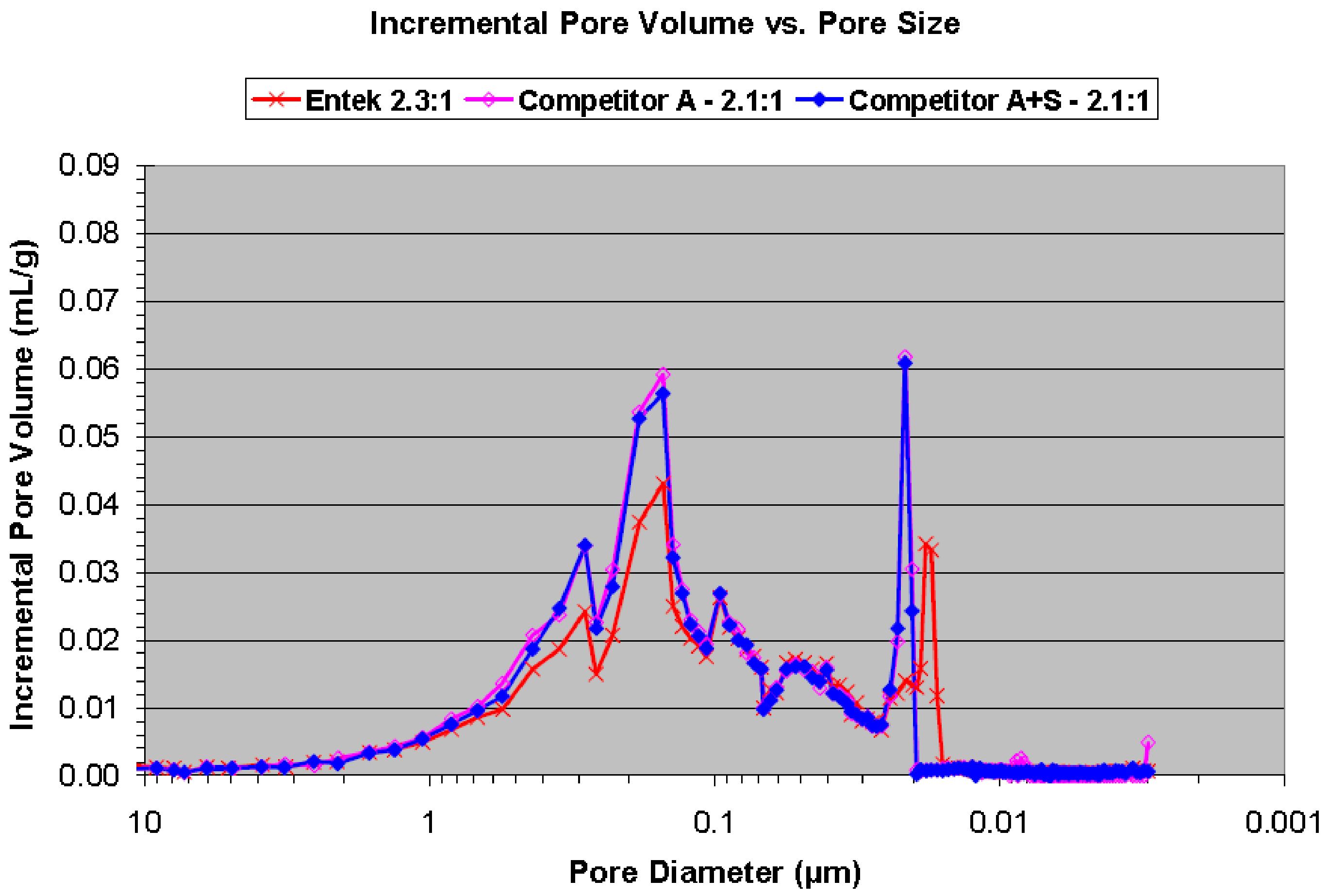


CHARACTERIZATION – WATER POROSITY & BOILED ER

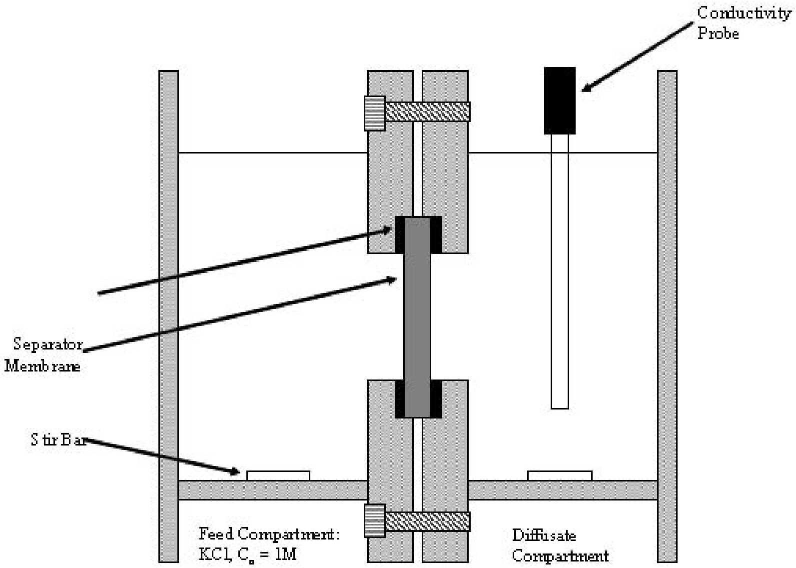


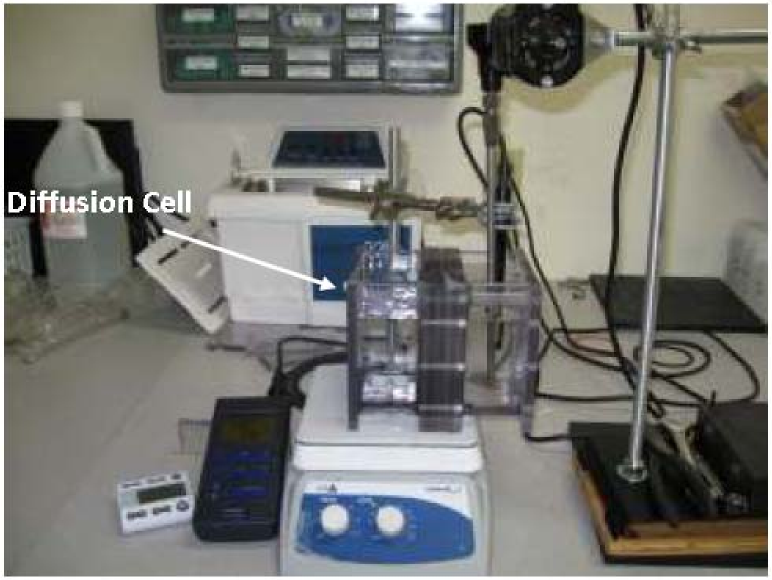
- At the same SiO_2:PE ratio, the LDS separator shows slightly lower water porosity compared to the HDS separator.
- The electrical resistance for the LDS separator is about 27% higher than the HDS separator at the same SiO_2:PE ratio.

HG POROSIMETRY DATA --- ENTEK VS. COMPETITOR



PREDICTING SEPARATOR ELECTRICAL RESISTANCE FROM DIFFUSIONAL RESISTANCE





- Membrane electrical resistance can be calculated from the knowledge of tortuosity (τ) and porosity (ε):

$$Re = (R_{elyte} * t * \tau^2 / \varepsilon)/A$$

- Tortuosity can be independently evaluated from diffusional resistance measurement:

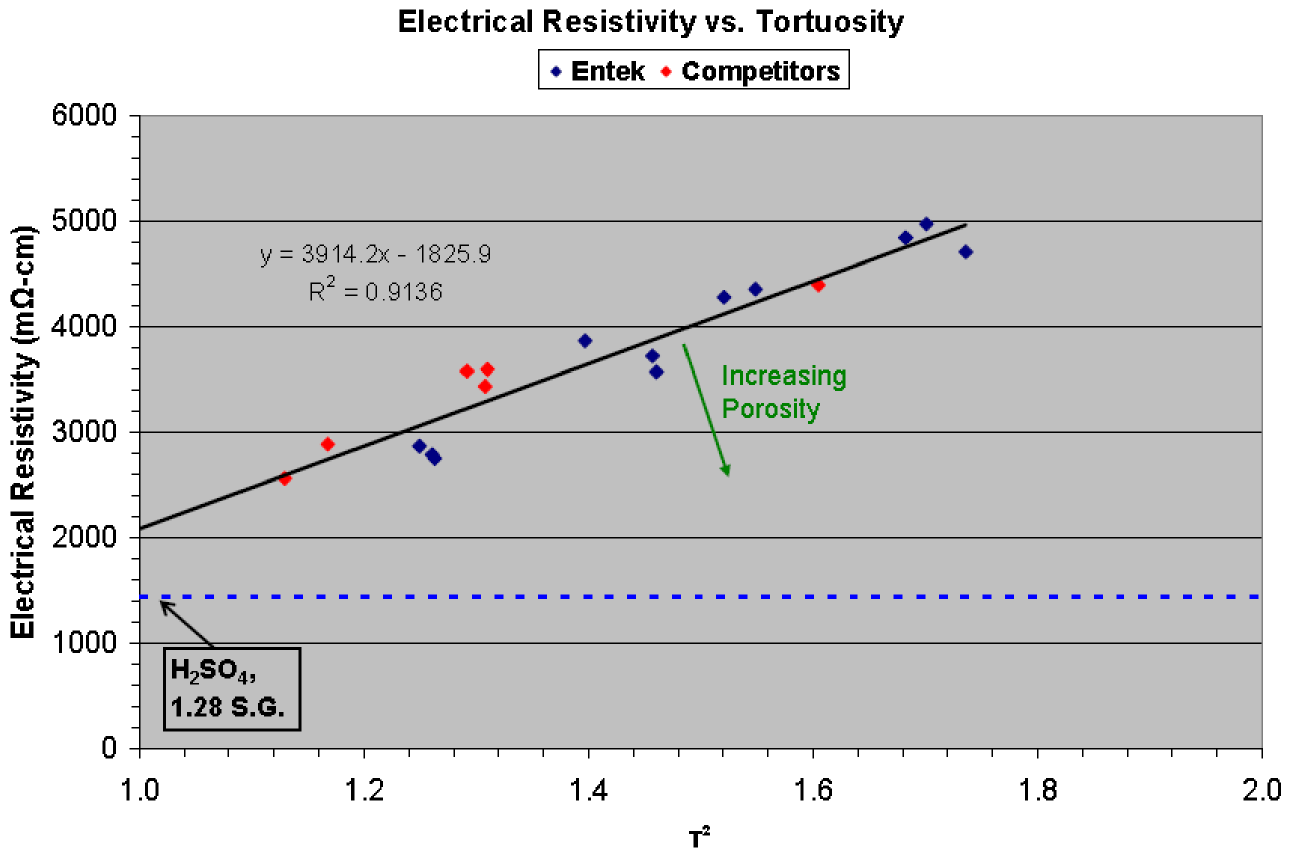
$$\frac{dn}{dt} = \frac{A \times D \times \varepsilon}{t \times \tau^2} \times \left[C_f(t) - C_d(t)\right]$$

PREDICTING SEPARATOR ELECTRICAL RESISTANCE FROM DIFFUSIONAL RESISTANCE

	Entek - 2.1:1	Entek - 2.3:1	Entek - 2.6:1	Entek - 2.75:1	Competitor A - 2.1:1	Competitor A+S - 2.1:1
Diffusional resistance R_d (cm^{-1}xsec)	2640	2407	2115	2054	2665	2024
Water porosity (%)	54.3	55.8	57.1	57.6	53.1	55.2
Tortuosity	1.30	1.24	1.18	1.21	1.27	1.14
Calculated Electrical Resistivity (mΩ-cm)	4585	4112	3621	3743	4471	3511
Measured Electrical Resistivity (mΩ-cm)	4849	4361	3869	3727	4401	3599

- ❑ Resistance to electrolyte diffusion through membranes decreases as more silica is added to the formula.
- ❑ Tortuosity decreases as more silica is loaded in the separator.
- ❑ The predicted electrical resistivity values agree fairly well with the measured boiled electrical resistivity values (difference is 6% or less).

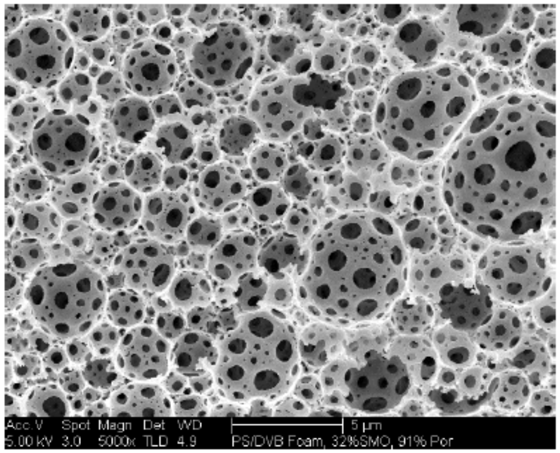
SEPARATOR RESISTIVITY VS. TORTUOSITY



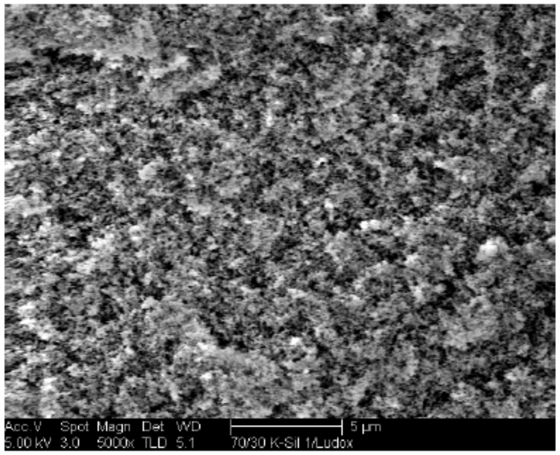
- ❑ Separator electrical resistivity can be reduced by reducing tortuosity and/or increasing porosity

ALTERNATIVE APPROACHES

- Microcellular Foam
  - Polystyrene
  - Unique structure that can withstand capillary forces associated with drying
  - High porosity (> 90%)
  - Electrical resistivity ~ 1500 mohm-cm, only slightly higher than 1.28 sp. gr. acid



- Silica/Fiber Gels
  - Gel structure can withstand capillary forces associated with drying
  - High porosity (> 88%)



SUMMARY

- The principal need for separators in EFB applications is for lower ER.
  - Cold crank
  - Warm crank at partial state of charge

- Separator ER is determined by pore structure
  - Wetted porosity
  - Tortuosity

- Pore structure is the result of
  - Composition
  - Manufacturing process

- New pore structures may be required for EFB
  - Microcellular foams
  - Filler/fiber composites

ENTEK

RAISING EXPECTATIONS.
KEEPING THEM THERE.