BATTERY SEPARATORS

A Closer Look at Oxidation Mechanisms and O_2 Transport

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18TH ASIAN BATTERY CONFERENCE & EXHIBITION

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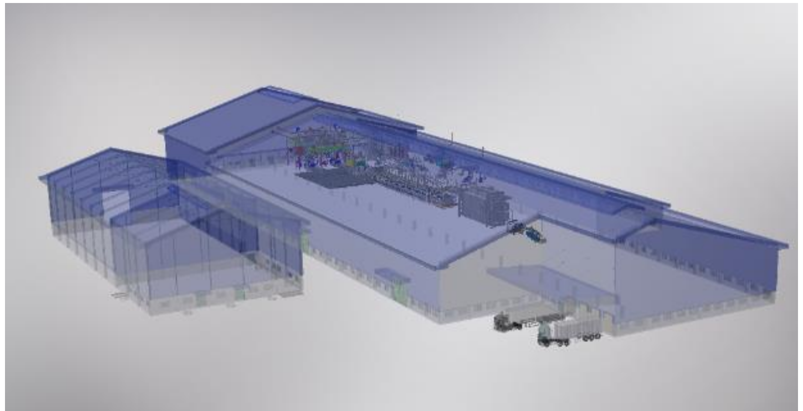
ENTEK NSG

SEPARATOR FORMULATIONS

- **ISY** - NSG special formulation for Japanese battery manufacturers
- **STD** - Traditional ENTEK formulation
- **LT (LTO)** - Low ER, excellent wettability,
  - high or low MD elongation depending upon customer
- **LR** - LR formulation, high MD elongation, excellent toughness
  - designed & approved for EFB
- **RUB** - Rubber containing formulation
  - e-Rickshaw batteries
- **IND** - Industrial with diagonal or straight ribs



Indonesia JV – capacity expansion

UHMWPE AND OXIDATION RESISTANCE

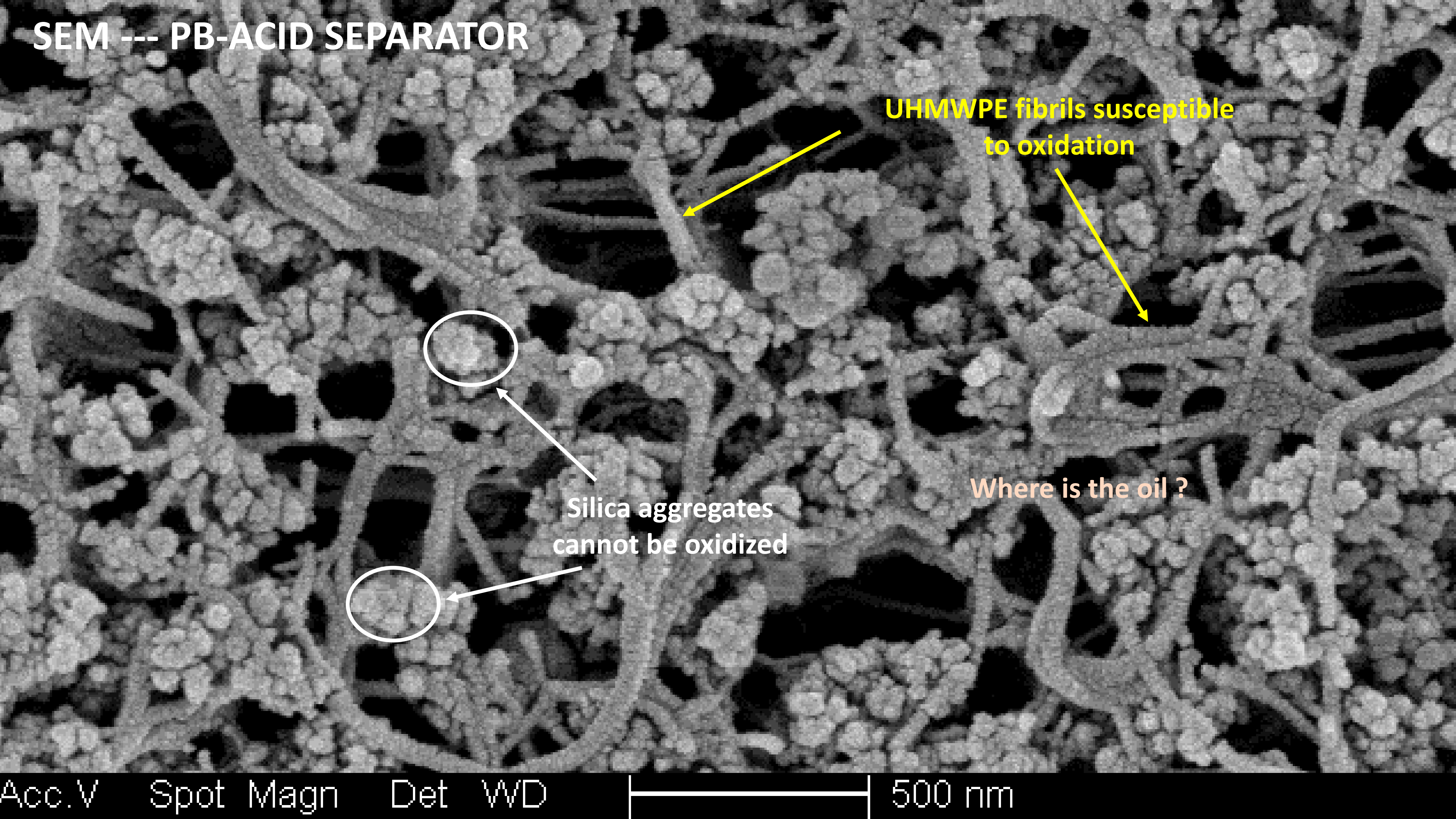
Component	Function
UHMWPE	mechanical properties
Silica	wettability & porosity
Residual oil	oxidation resistance
Additives	oxidation resistance, color, wettability
Pores / Voids	ion conduction

1. The ***UHMWPE polymer is responsible for the mechanical integrity*** of battery separators (i.e., puncture strength, flexural modulus, % elongation, tensile strength), but ironically, it is also susceptible to oxidation

2. If the ***UHMWPE undergoes chain scission or crosslinking when attacked by oxygen***, the elongation of the separator will be reduced.

3. As such, a small amount of ***process oil is purposefully left behind in separators so that it can be preferentially oxidized to protect the UHMWPE polymer***

4. The ***oxidized oil will often be solubilized into battery acid*** and subsequently converted to CO_2 and H_2O.


SEM --- PB-ACID SEPARATOR
UHMWPE fibrils susceptible to oxidation
Silica aggregates cannot be oxidized
Where is the oil ?
Acc.V Spot Magn Det WD
500 nm

LABORATORY TESTS --- OXIDATION RESISTANCE

- Test methods
  - **Hydrogen peroxide in sulfuric acid (Perox 80)**
  - **Potassium dichromate in sulfuric acid**
  - **Heated sulfuric acid**
  - **Simulated electrochemical oxidative condition in battery cell under charging**
  - Oxidation induction time
  - High temperature battery life test

- Material considerations
  - Polymer matrix
  - Residual oil
  - Oil / PE ratio

= Battery Council International (BCI) test method

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OXIDATION RESULTS --- MASS LOSS

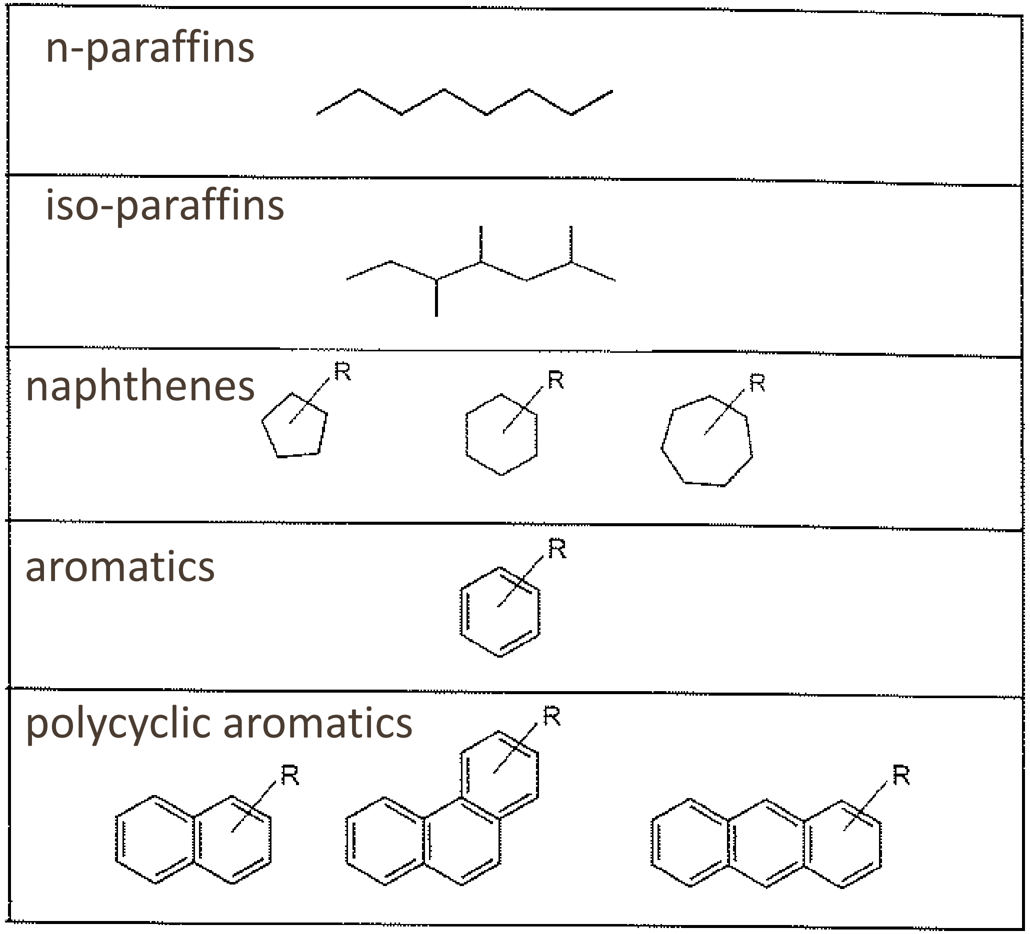
156-0.90-0.25 RN_RUB(Rubber containing)

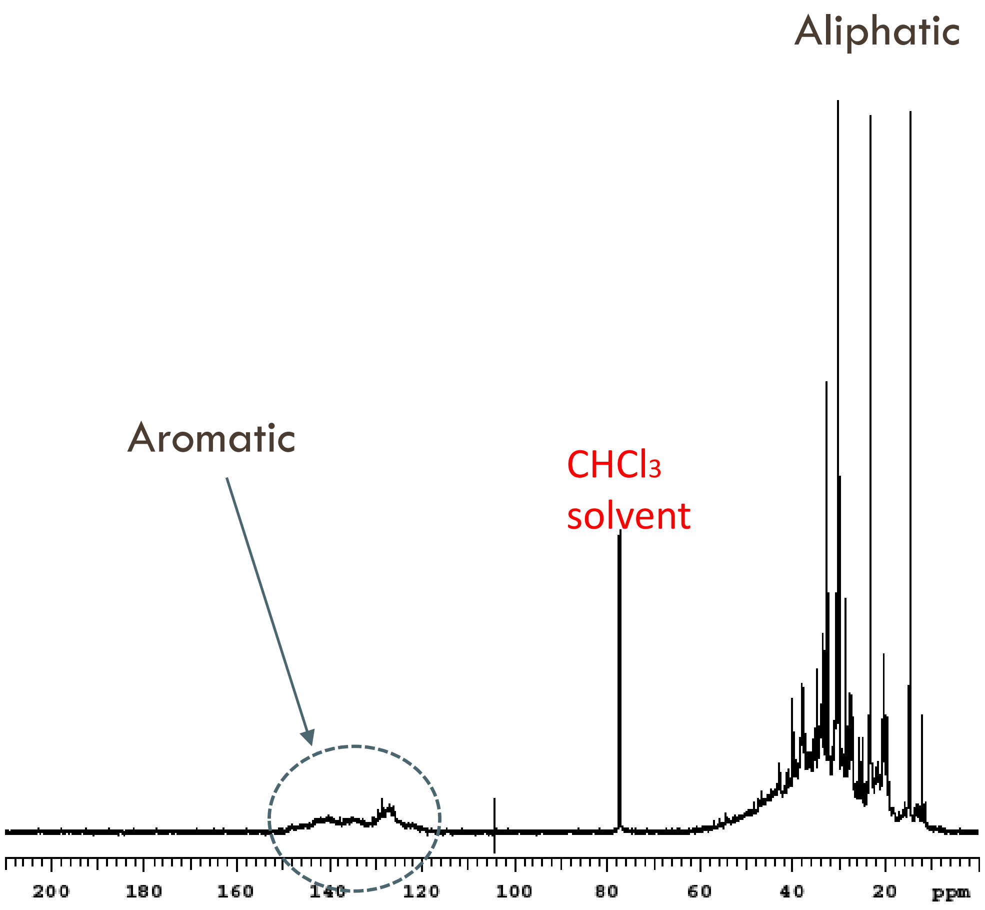
Roll No	Acid Weight loss, %				
	After oxidized 3 hrs		After oxidized 20 hrs		
	Chromic acid BCI std	Perox-80 BCI std	Chromic acid BCI + extended time	Perox-80 BCI + extended time	Hot Sulfuric acid ENTEK-US method
Average	*5.39*	*5.30*	*8.09*	*9.39*	*3.89*
Max	*6.71*	*6.25*	*11.24*	*10.29*	*4.50*
Min	*3.65*	*3.33*	*5.12*	*8.40*	*3.38*

Observations:

1. **Similar weight loss for separators exposed to Chromic acid or Perox 80 solutions after 3 hrs at 80 C**
2. **Greater weight loss is observed in each test after 20 hrs at 80 C**
3. **Hot sulfuric acid test, which is most representative of battery environment, shows ~1/2 the mass loss of the other tests after 20 hrs at 80 C**

PROCESS OILS ARE COMPLEX CHEMICAL MIXTURES





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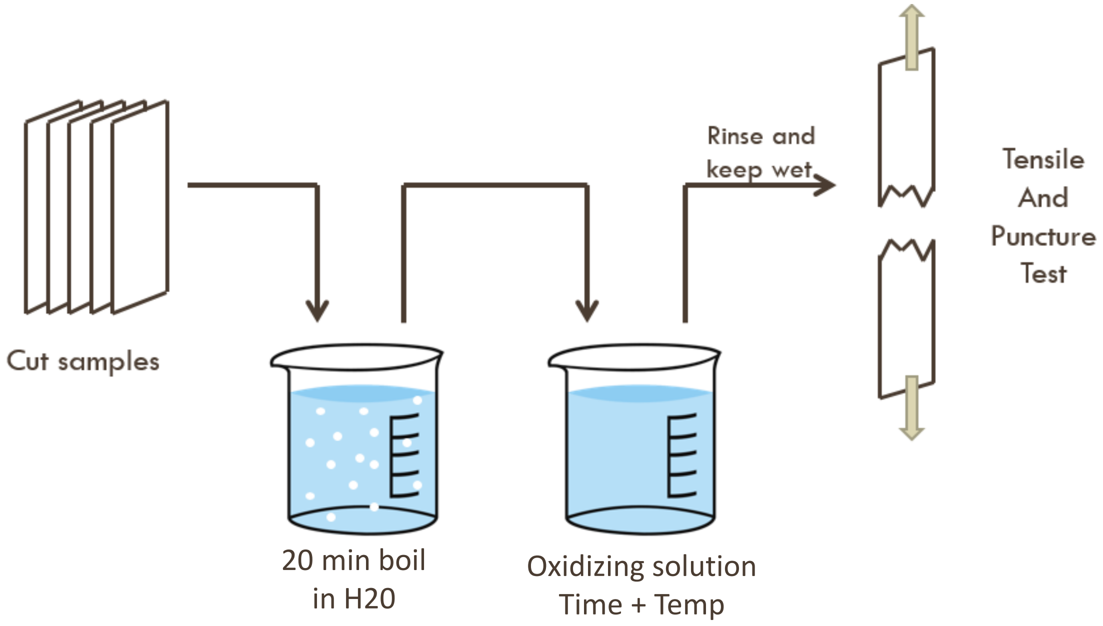
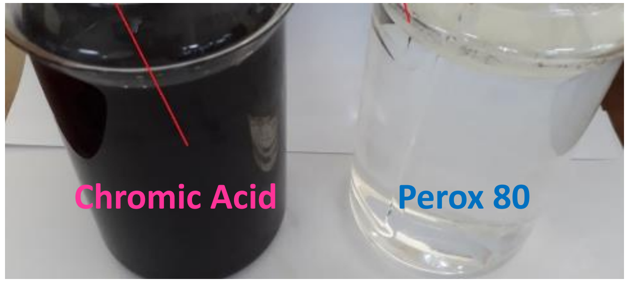
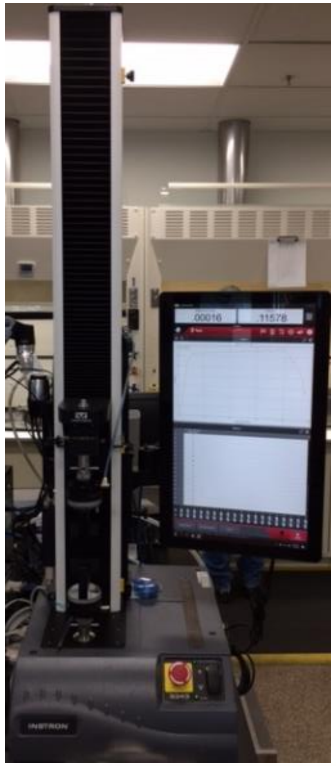
TEST PROCEDURE AND SET-UP







OXIDATION RESULTS --- MECHANICAL PROPERTIES

156-0.90-0.25 RN_RUB(Rubber containing)

Roll No	CMD Elongation, %					
	Chromic acid (20 hrs)			Perox-80 (20 hrs)		
	Before oxidizing (A)	aft. oxidizing (B)	% Retention (B / A) x 100	Before oxidizing (C)	aft. oxidizing (D)	% Retention (D / C) x 100
Average	421	377	89.84%	422	372	88.25%
Min	364	322	72.84%	366	310	74.60%
Max	496	442	100.00%	496	422	98.99%

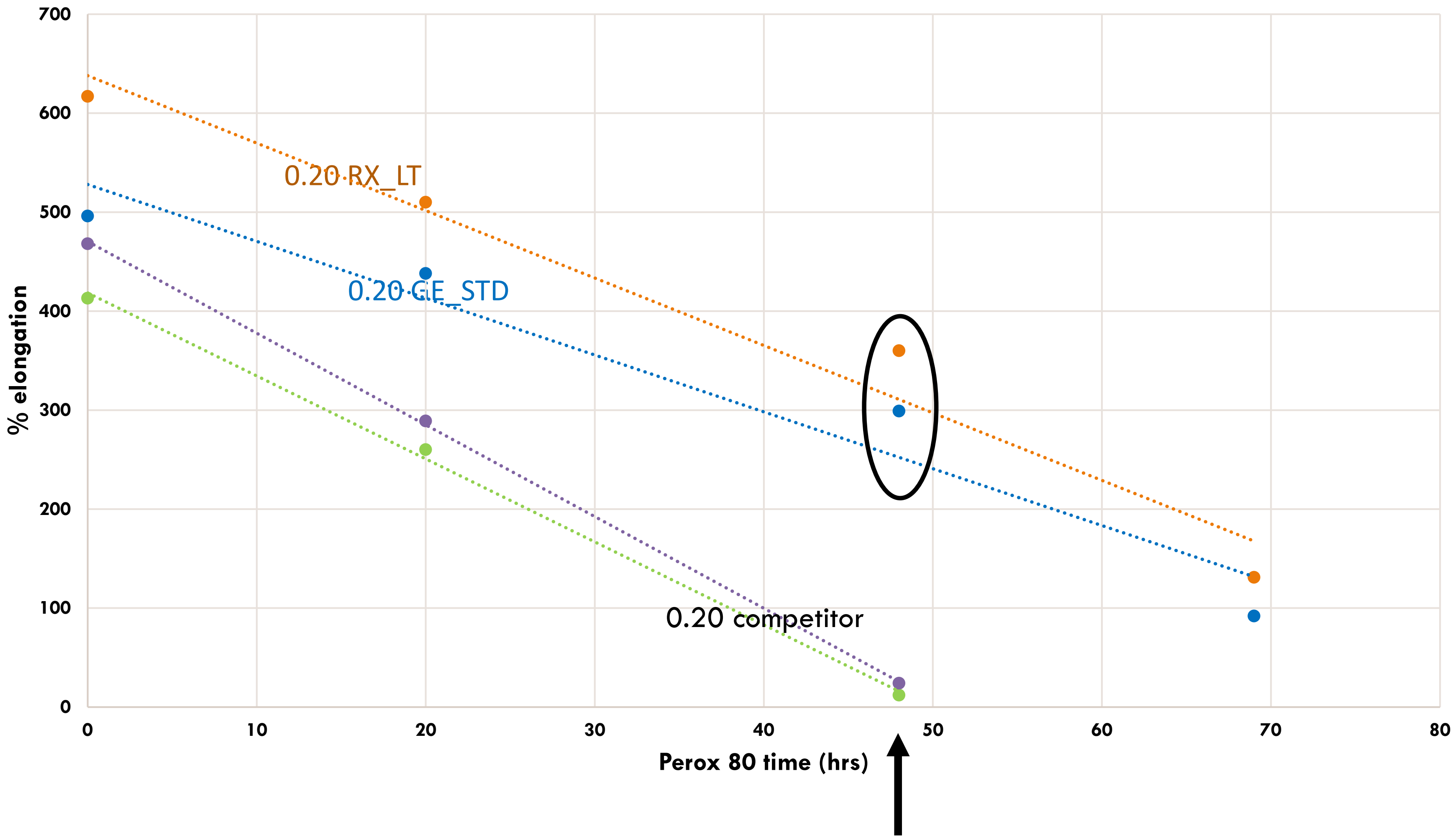
Roll No	BW Puncture (N)					
	Chromic acid (20 hrs)			Perox-80 (20 hrs)		
	Before oxidizing (A)	aft. oxidizing (B)	% Retention (B / A) x 100	Before oxidizing (C)	aft. oxidizing (D)	% Retention (D / C) x 100
Average	10.26	9.69	94.6%	10.26	9.39	91.5%
Min	9.76	8.41	79.1%	9.76	8.65	85.3%
Max	10.79	10.33	103.7%	10.79	9.98	99.9%

Observations:

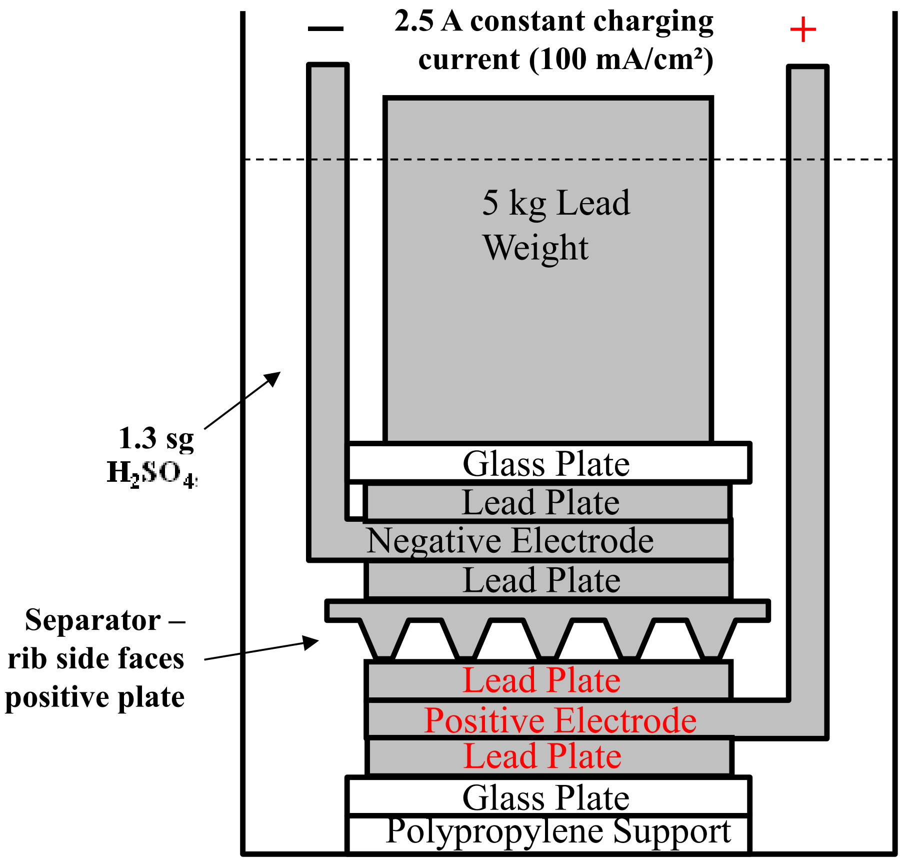
1. **Rubber containing separators retained > 88% of their original CMD elongation and > 90% of their original puncture strength after 20 hr at 80 C when exposed to either a chromic acid or Perox 80 solution**

2. **48- or 72-hour exposure times in an oxidizing solution at elevated temperature are required for substantial reductions in separator mechanical properties**

PEROX 80 --- EXTENDED TIME TEST RESULTS

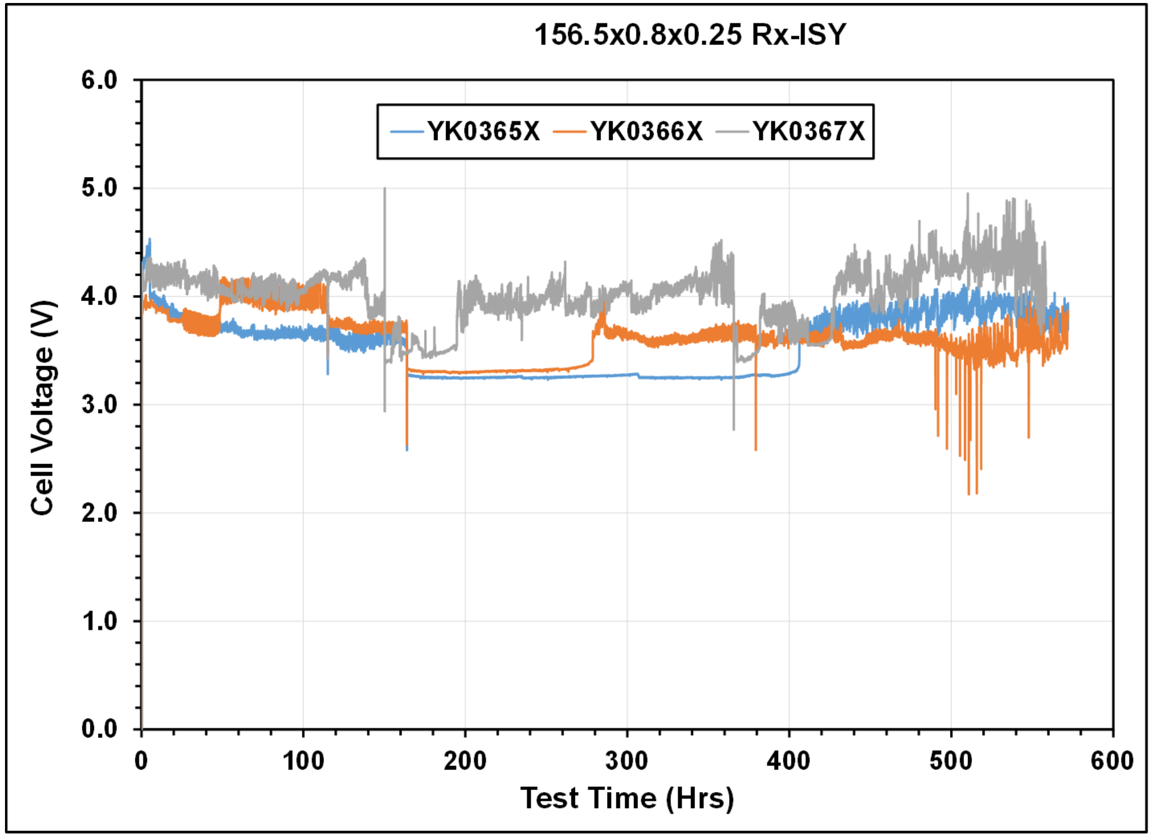


ELECTROCHEMICAL OXIDATION TEST PROCEDURE

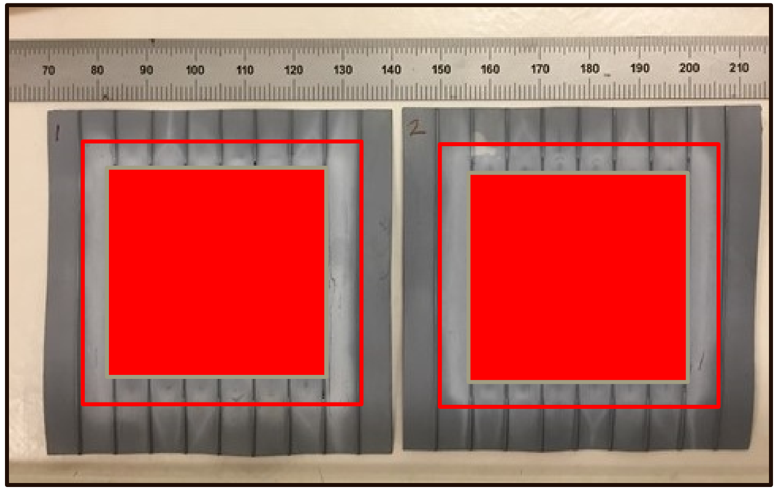


- Originated from Japanese National Railways; modified by Japanese battery manufacturer
- 7 x 7 cm² separator sample is placed with the rib side facing positive plate.
- The cell stack is assembled inside a 2000 mL glass beaker filled with 1.3 sg H_2SO_4, maintained at elevated temperature in a water bath:
  - 5kg lead weight is placed on top of the cell stack
- The cell is overcharged with a 2.5 A constant current (100 mA/cm²):
  - Test is terminated when $\frac{\Delta V}{\Delta t} > 0.2V/min$

ISY SEPARATOR --- 0.25 BW



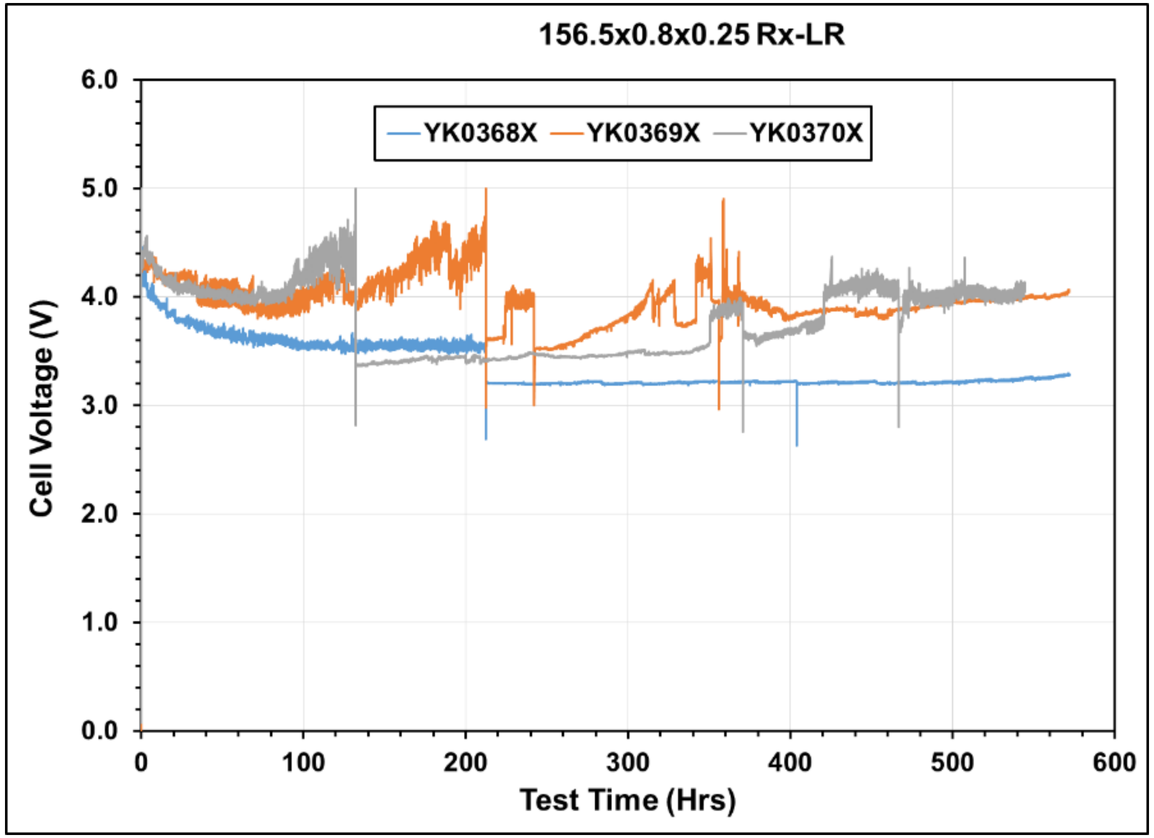
Test ID	Time to Failure (hrs)
YK0365X	423
YK0366X	490
YK0367X	353
Avg.	422



Separator samples after termination of the test

Test ID	Test ID	Pristine		Center of test area		Edges of test area		Edges of separator	
		BW Oil (%)	SiO2/PE	BW Oil (%)	SiO2/PE	BW Oil (%)	SiO2/PE	BW Oil (%)	SiO2/PE
ISY-1	YK0365X	16.7	2.03	3.2	2.28	4.2	2.48	9.9	2.24
ISY-2	YK0366X	16.7	2.03	3.8	2.32	3.4	2.31	8.5	2.24
ISY-3	YK0367X	16.7	2.03	3.2	2.43	2.3	2.71	5.3	2.28
Average	**Average**	**16.7**	**2.03**	**3.4**	**2.34**	**3.3**	**2.50**	**7.9**	**2.25**

LR SEPARATOR --- 0.25 BW



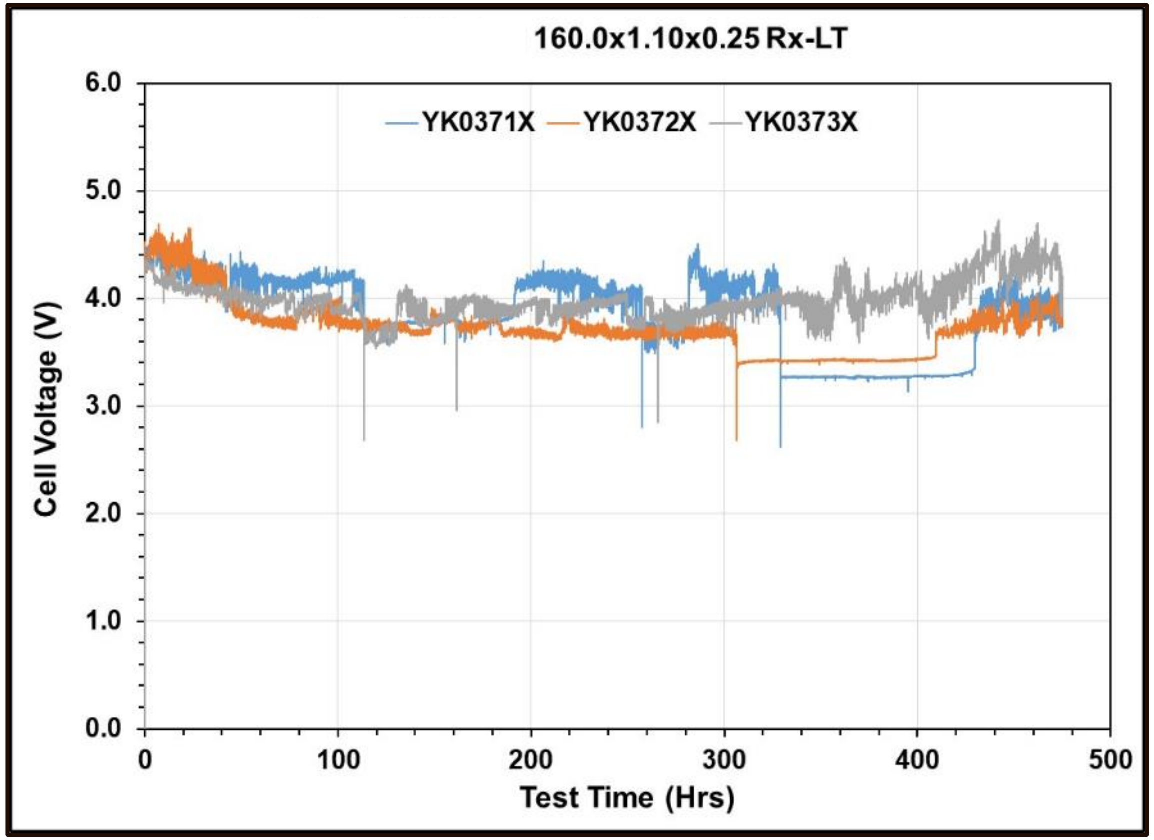
Test ID	Time to Failure (hrs)
YK0368X	572
YK0369X	315
YK0370X	425
Avg.	437

YK0368X: After test termination

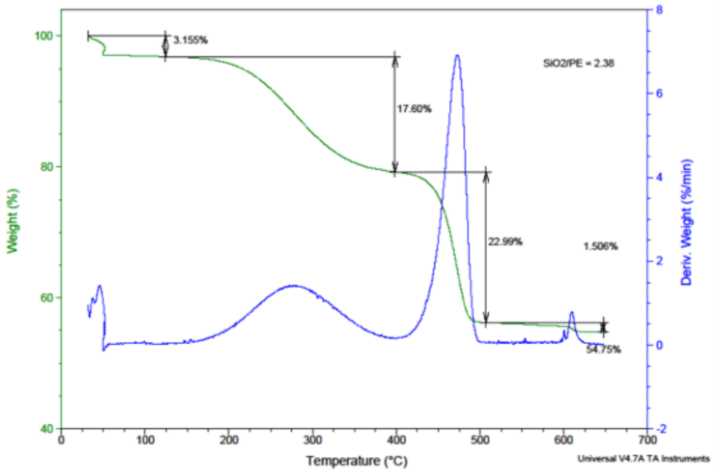
YK0369X: After test termination

Test ID	Test ID	Pristine		Center of test area		Edges of test area		Edges of separator	
		BW Oil (%)	SiO2/PE	BW Oil (%)	SiO2/PE	BW Oil (%)	SiO2/PE	BW Oil (%)	SiO2/PE
LR-1	YK0368X	18.4	2.09	4.9	2.04	3.2	2.12	5.8	1.98
LR-2	YK0369X	18.4	2.09	3.9	2.07	1.7	2.35	4.7	2.01
LR-3	YK0370X	18.4	2.09	4.6	2.05	2.5	2.34	4.7	2.04
Average	**Average**	**18.4**	**2.09**	**4.5**	**2.05**	**2.5**	**2.27**	**5.1**	**2.01**

LT SEPARATOR--- 0.25 BW

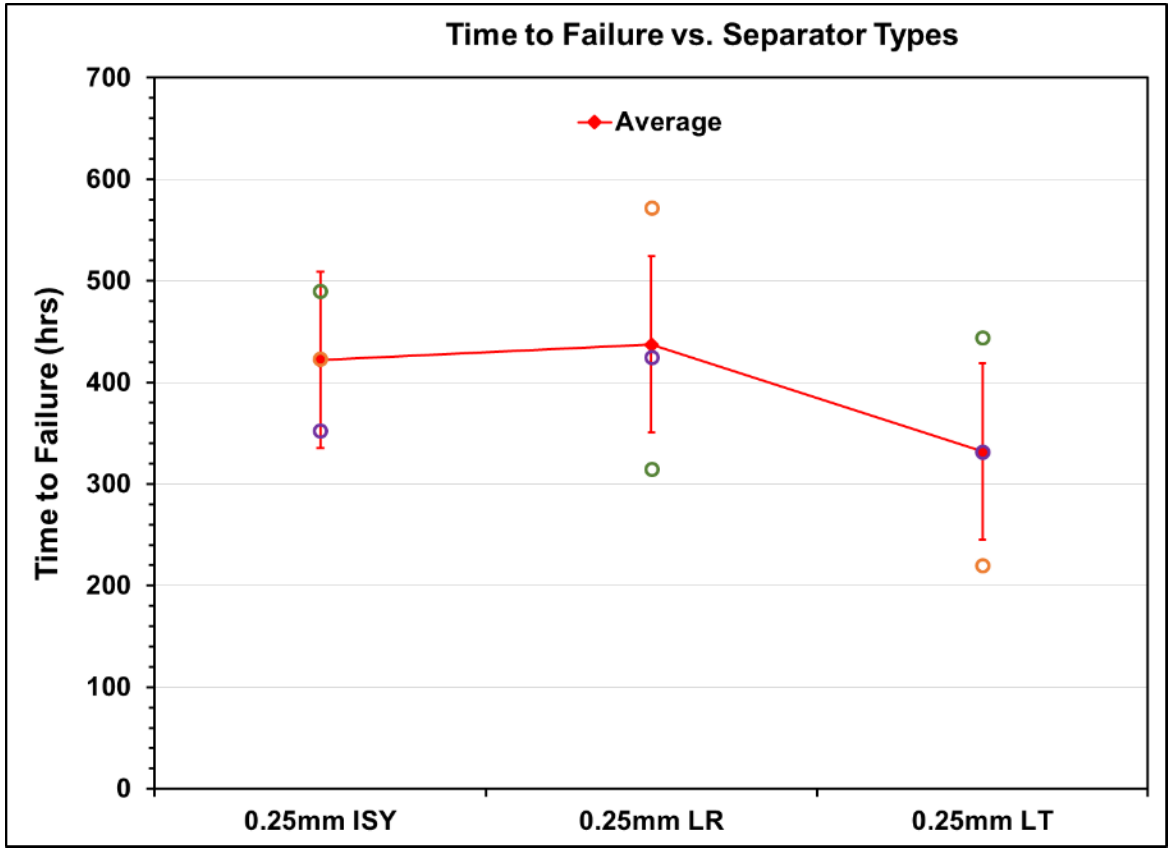


Test ID	Time to Failure (hrs)
YK0371X	220
YK0372X	444
YK0373X	332
Avg.	332



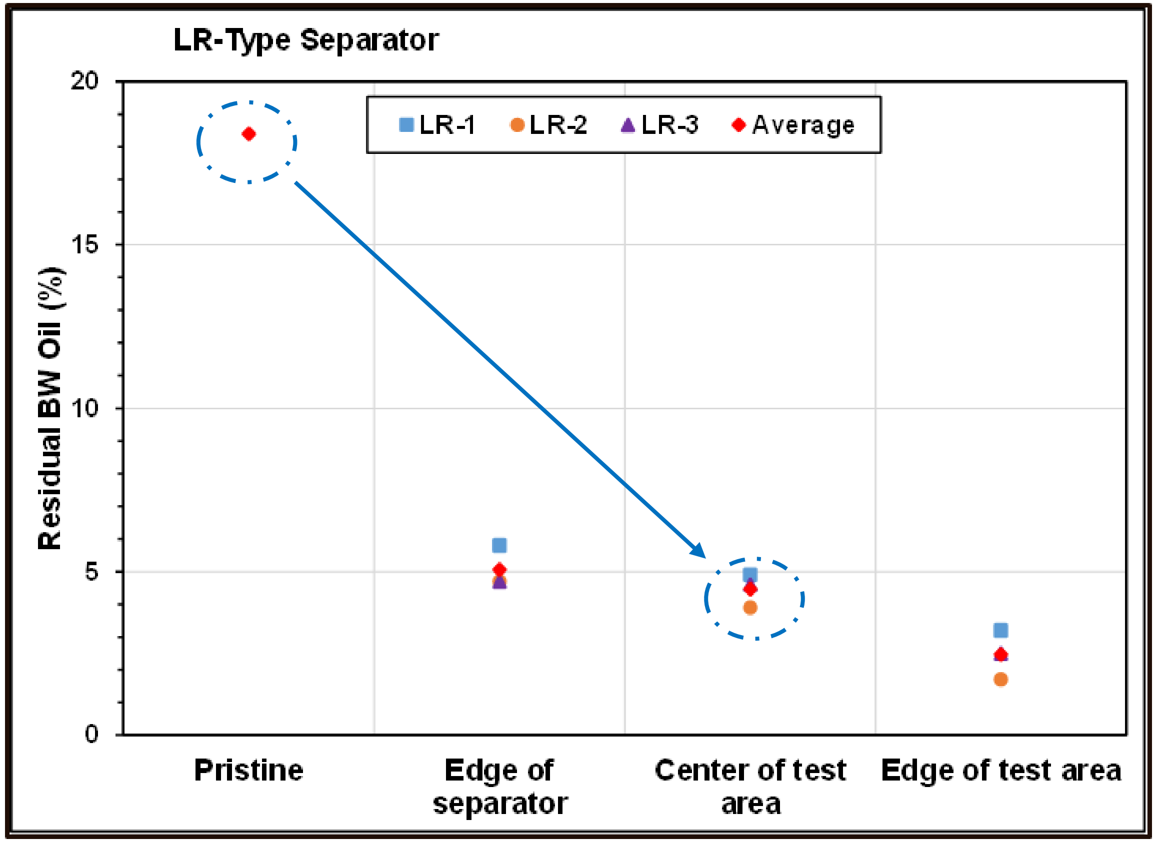
Test ID	Test ID	Pristine		Edge of separator		Center of test area		Edge of test area	
		BW Oil (%)	SiO2/PE	BW Oil (%)	SiO2/PE	BW Oil (%)	SiO2/PE	BW Oil (%)	SiO2/PE
LT-1	YK0371X	19.6	2.23	17.4	2.14	6.4	2.23	4.5	2.27
LT-2	YK0372X	19.6	2.23	14.6	2.09	5.7	2.30	3.8	2.34
LT-3	YK0373X	19.6	2.23	14.2	2.07	4.9	2.32	3.5	2.29
Average	**Average**	**19.6**	**2.23**	**15.4**	**2.10**	**5.7**	**2.28**	**3.9**	**2.30**

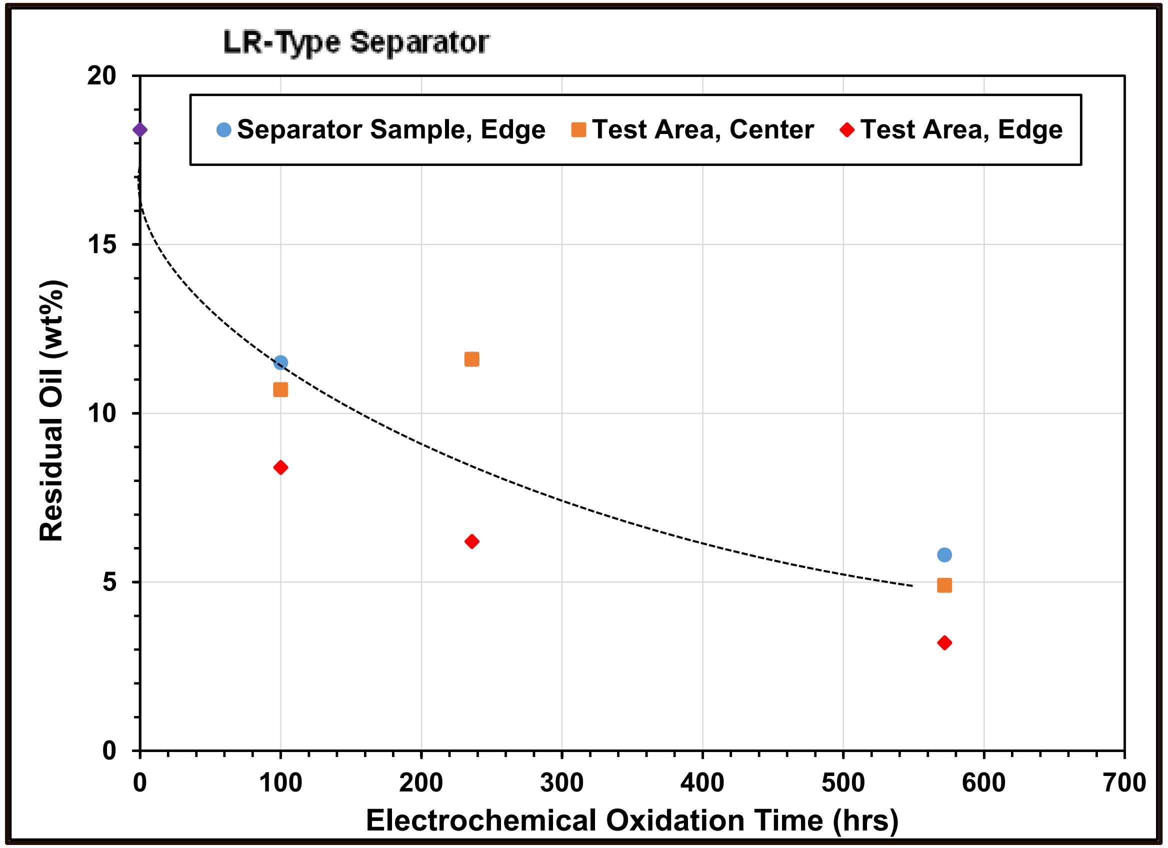
TIME TO FAILURE VS. SEPARATOR TYPE



- The LT separator contains less polymer and tends to fail earlier, but statistically, there is no difference in oxidation resistance between the 3 separators

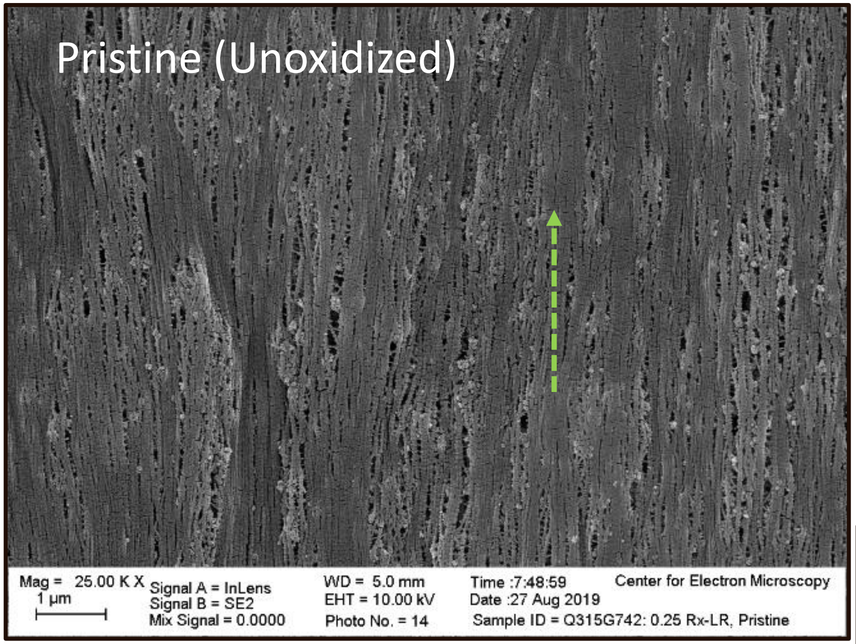
ELECTROCHEMICAL OXIDATION TEST --- OIL REACTIVITY & CONSUMPTION

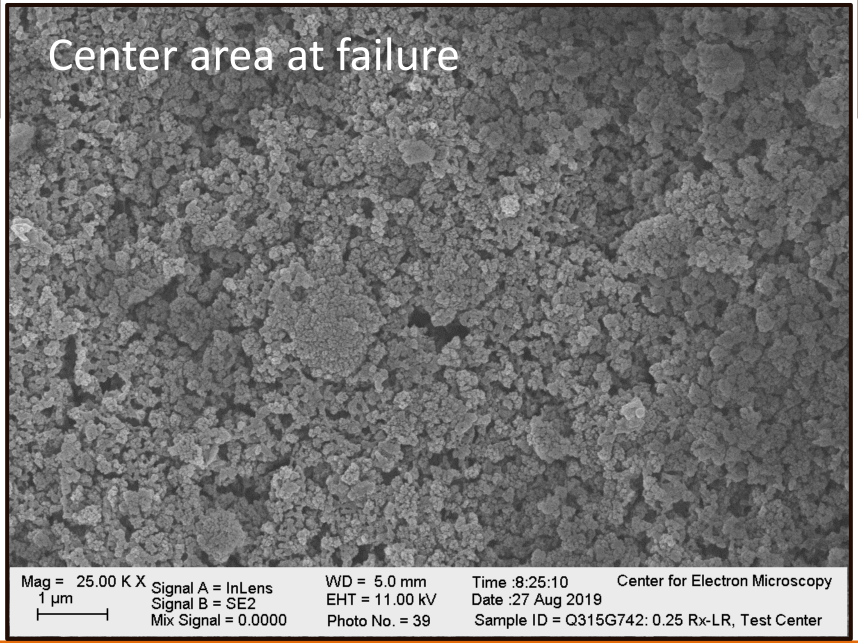


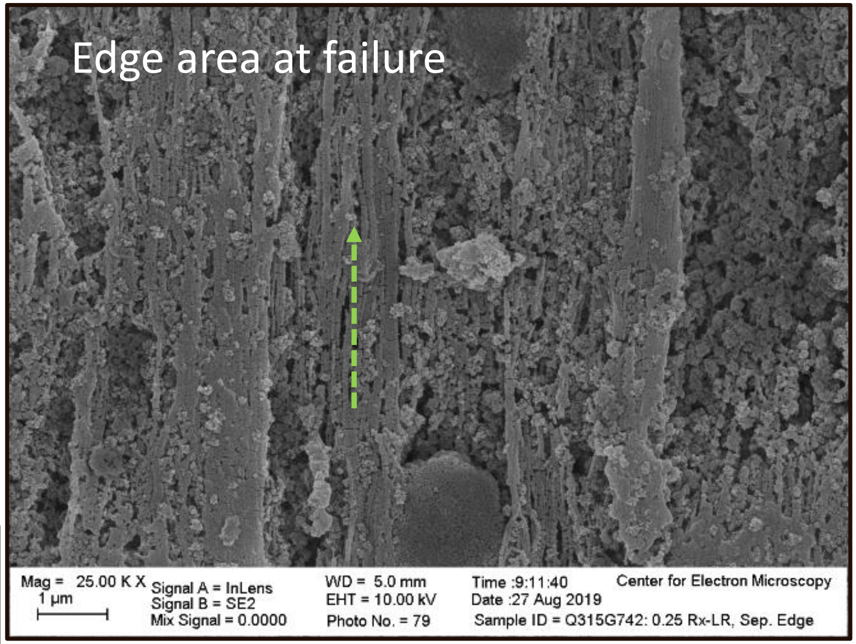


- All separator types show a significant reduction in oil content in the electrochemical test area
- Key considerations for improving oxidation resistance
  - Oil composition
  - Oil / UHMWPE ratio

SURFACE SEM --- LR SEPARATOR







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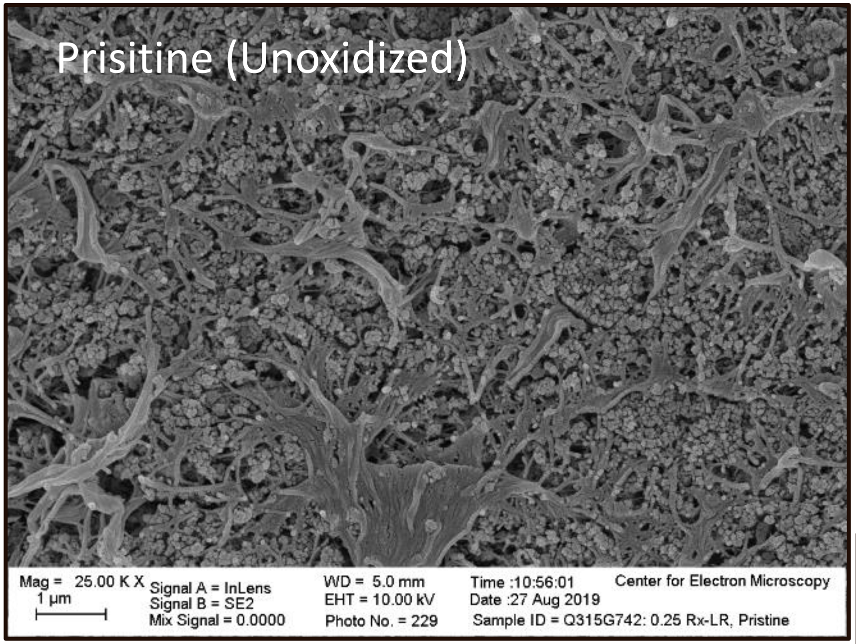
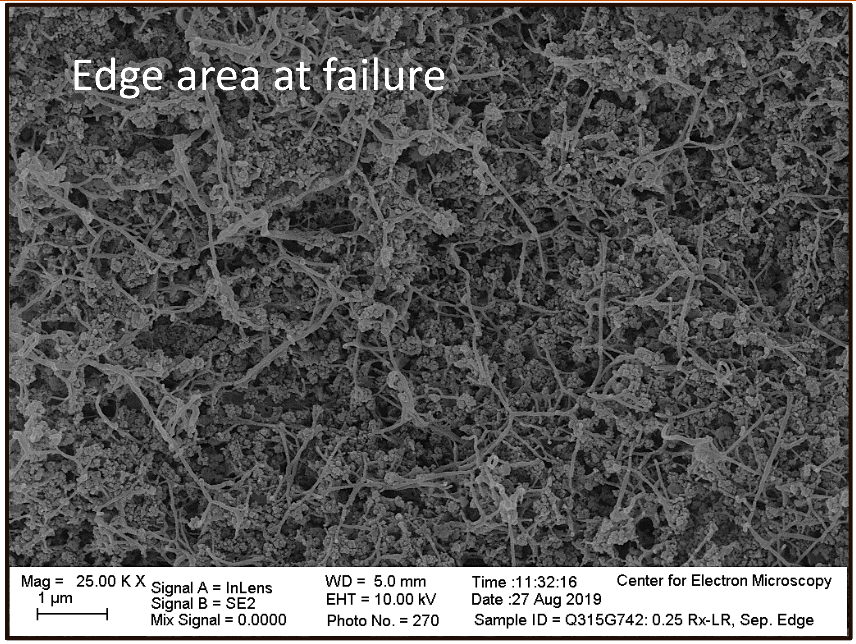
FRACTURE SEM --- LR SEPARATOR



Test ID	Test ID	Pristine		Center of test area	
		BW Oil (%)	SiO2/PE	BW Oil (%)	SiO2/PE
LR-1	YK0368X	18.4	2.09	4.9	2.04
LR-2	YK0369X	18.4	2.09	3.9	2.07
LR-3	YK0370X	18.4	2.09	4.6	2.05
Average	**Average**	**18.4**	**2.09**	0.00	2.21



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THE OXYGEN CYCLE

- Valve Regulated Lead Acid (VRLA) batteries rely on crossover of oxygen generated at the positive electrode during charge to be reduced at the negative electrode. This is sometimes referred to as "Recombination" or the "Oxygen Cycle"

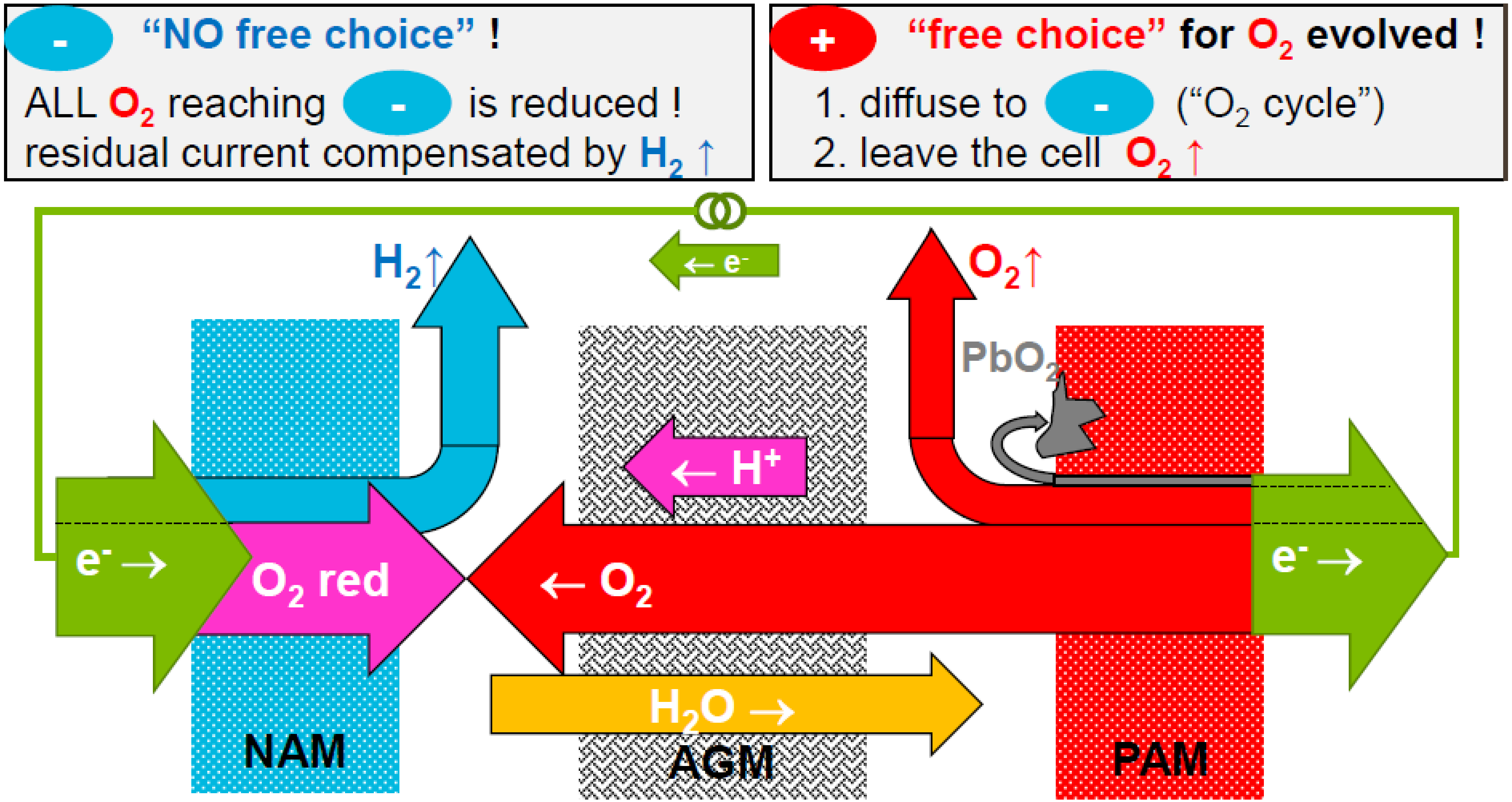
- An oxygen cycle may also play a role in reducing water loss in flooded lead acid batteries
  - Testing by OEMs and battery manufacturers shows that actual water loss is less than the total current passed during trickle charging would suggest
  - Eberhard Meissner suggests[1] that 40% of the trickle charge current on an EFB may be consumed in an oxygen cycle

- Depolarization of the negative electrode has been observed in ENTEK's voltammetry cell using commercial lead acid battery electrodes and supports the concept of significant oxygen transfer in flooded cells

- The current work is intended to demonstrate the oxygen cycle in flooded lead acid batteries and measure the rate of oxygen diffusion through different separators

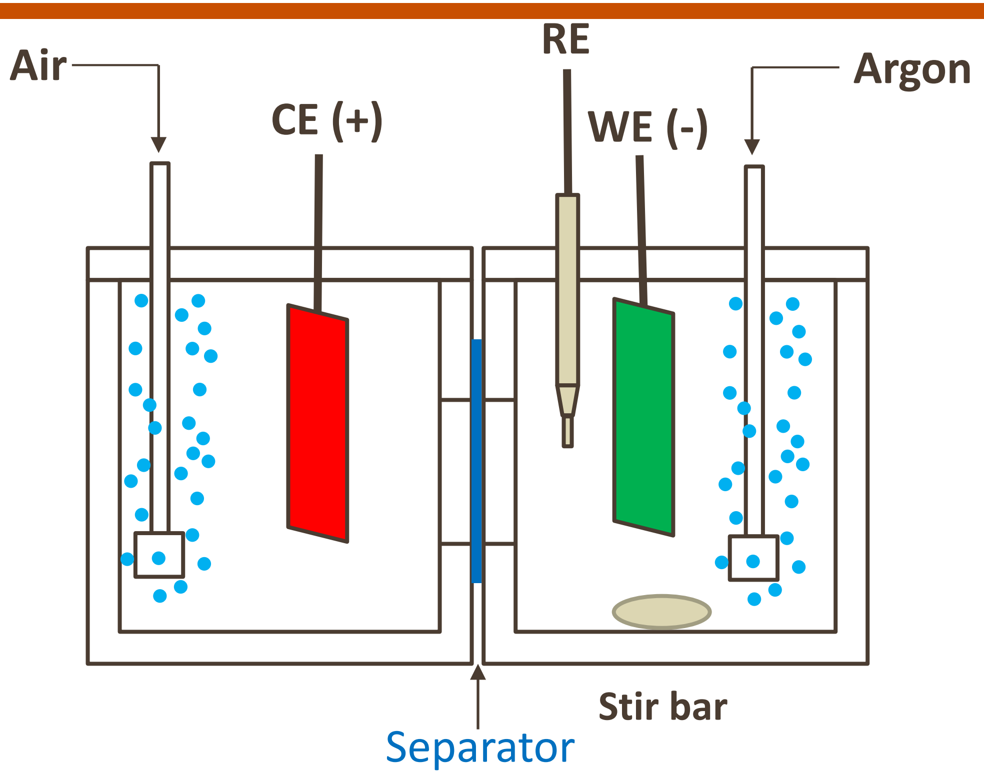
1. E. Meissner, Scientific Workshop: High-Temperature Durability Tests for Advanced Lead 12-V Batteries, 22-23 May 2019, Bruges, Belgium

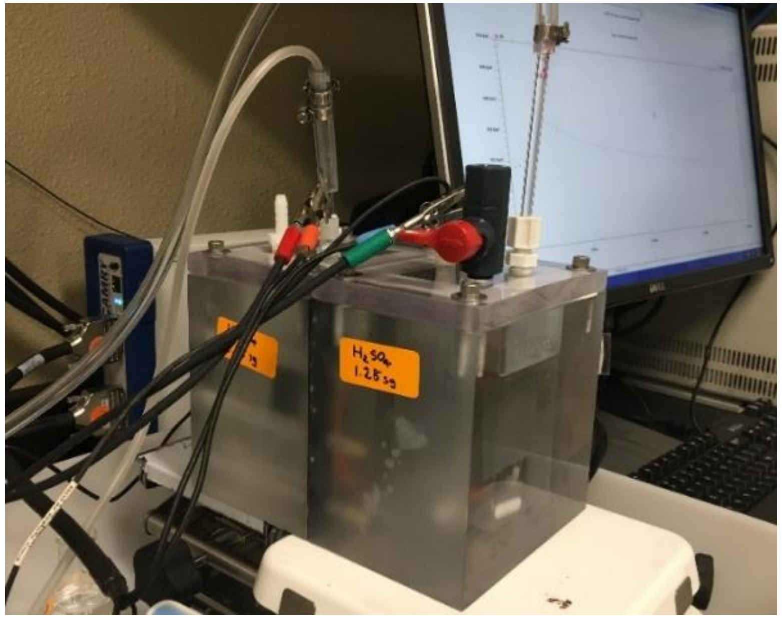
HOW DOES THE SEPARATOR INFLUENCE O_2 TRANSPORT ?



Reference: D. Berndt, Maintenance-Free Batteries; 2nd edition; Wiley, New York, 1997

OXYGEN DIFFUSION CELL





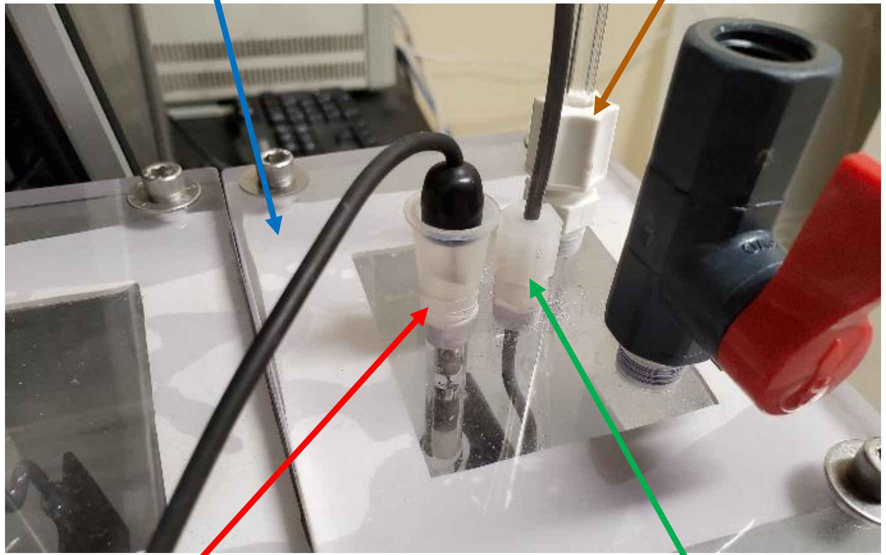
- The negative side of the cell is sealed from the atmosphere and purged with argon after conditioning cycles but before testing
- Air is bubbled into the positive side of the cell during testing to provide a constant concentration (assumed saturated) source of oxygen
- Measurements were made with different separators, for different lengths of time, to determine the effect of separator on the rate of oxygen transport

A CLOSER LOOK

Dry charge electrodes from Yuasa YTX-5L AGM motor sports battery

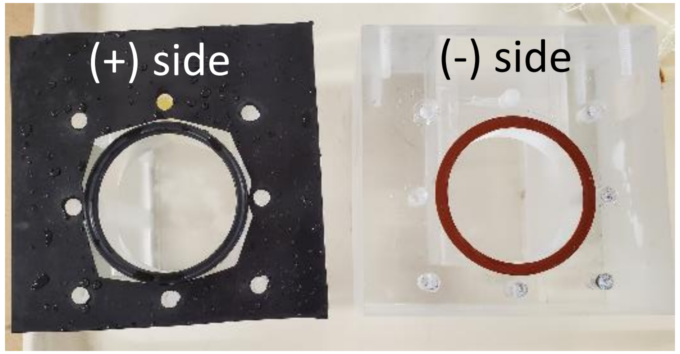
Gasket for sealing the top of the cell

Compression fitting for argon inlet

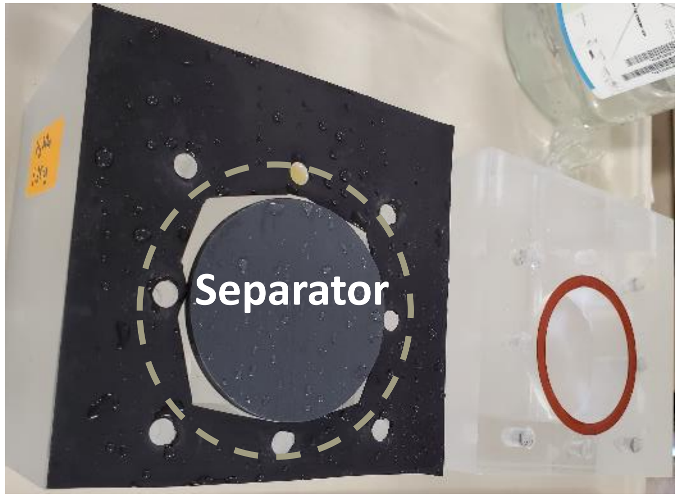


Reference electrode sealed with Teflon tape and spacer

Compression fitting on negative electrode lead

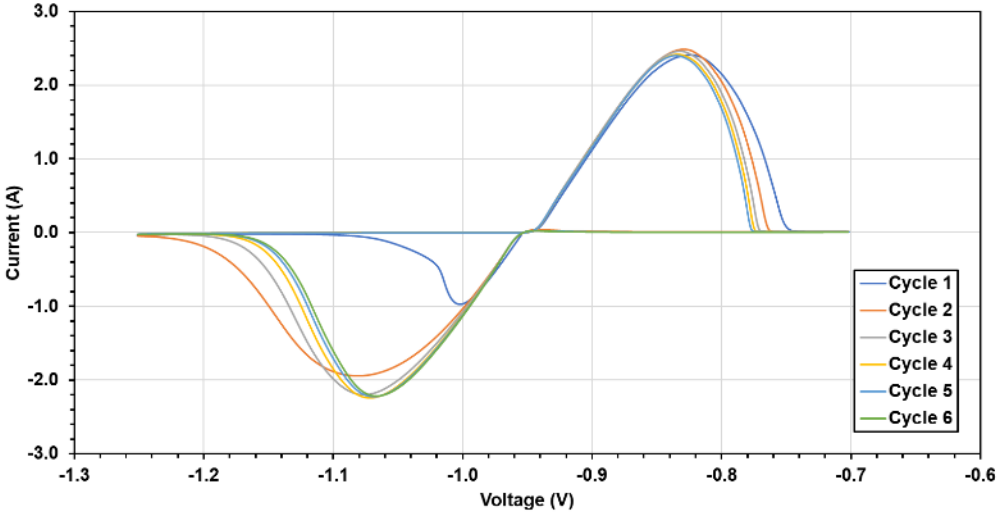


Thick rubber gasket on the left and thin gasket on the right



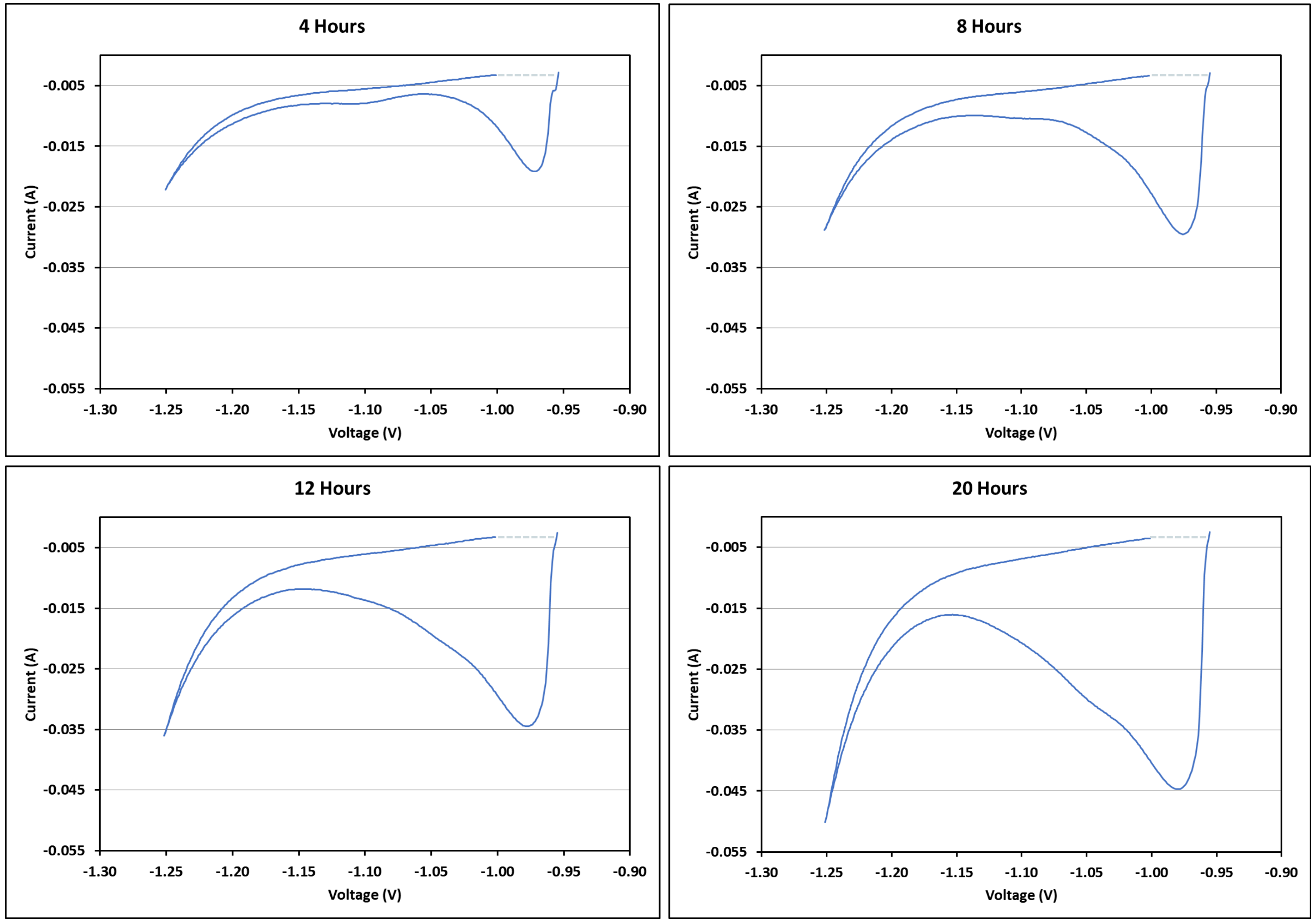
APPROACH

- Separator --- 10 min boil + > 30 min soak in 1.28 SG H_2SO_4
- Cell --- cycled 5x to condition electrodes and determine initial capacity of negative electrode
  - Potentiometric cycles at a constant sweep rate (0.05 mV/sec) from OCV to -1.25V to -0.80 V to -1.25 V negative electrode potential vs. $Hg/HgSO_4$ reference, ending at -1.25 V negative electrode potential
- After conditioning cycles, ***negative side was purged with argon gas for 30 minutes and then sealed***
- ***Air was bubbled through the positive side*** using a Mylivell Air Pump (300 mL/min ± 10%), while the cell rested at open circuit voltage (OCV) for 4, 8, 12, and 20 hours



Cycle	Charge Capacity (coulombs)	Discharge Capacity (coulombs)
1	-1131	5827
2	-5966	5596
3	-5706	5305
4	-5413	5095
5	-5203	4977
6	-5085	

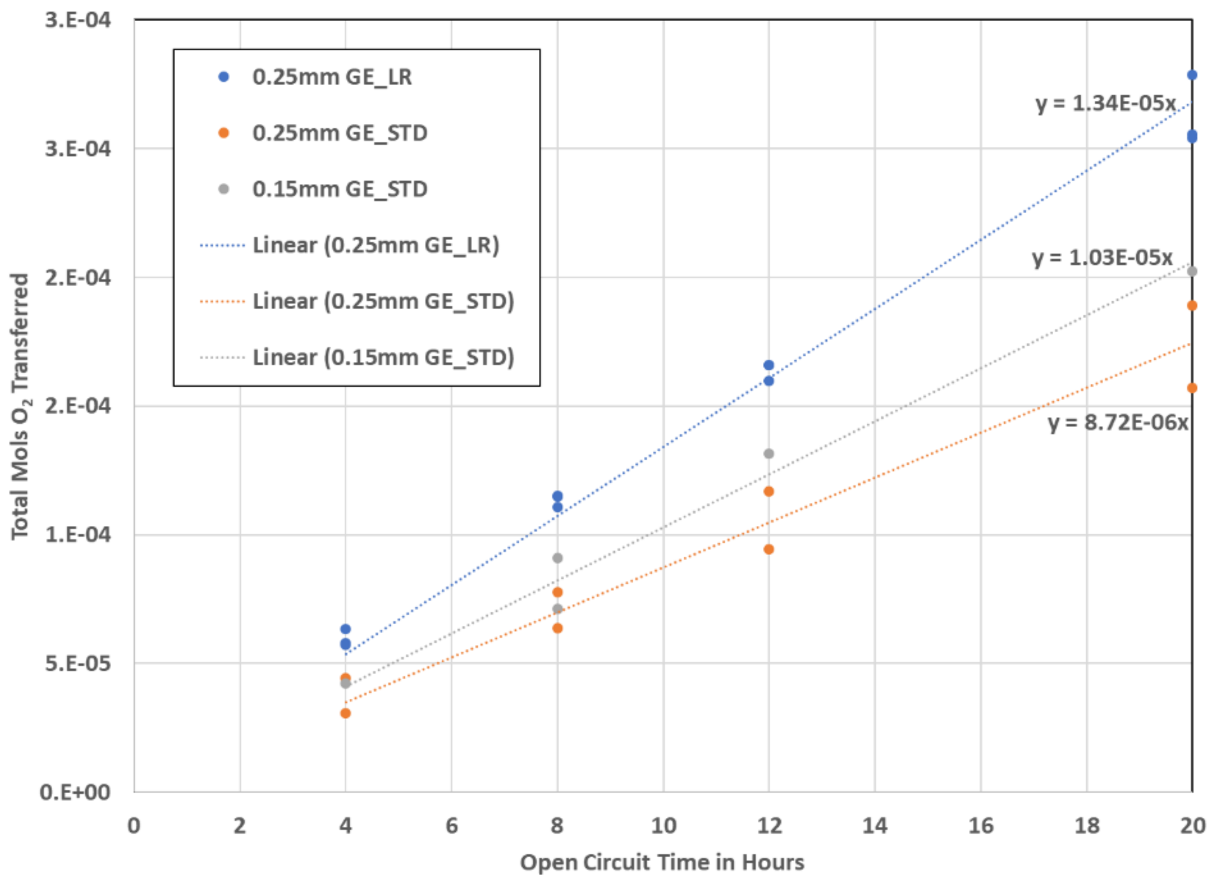
DEPOLARIZATION OF NEGATIVE ELECTRODE DUE TO OXYGEN DIFFUSION



- The depolarization of the negative electrode was measured after each rest period
  - Test scan: at 0.05 mV/sec, sweep from OCV to -1.25 V to -1.00 V to -1.25 V
  - The depolarization charge was determined by integrating the amount of charge current during the outward (negative) sweep using the return as a baseline

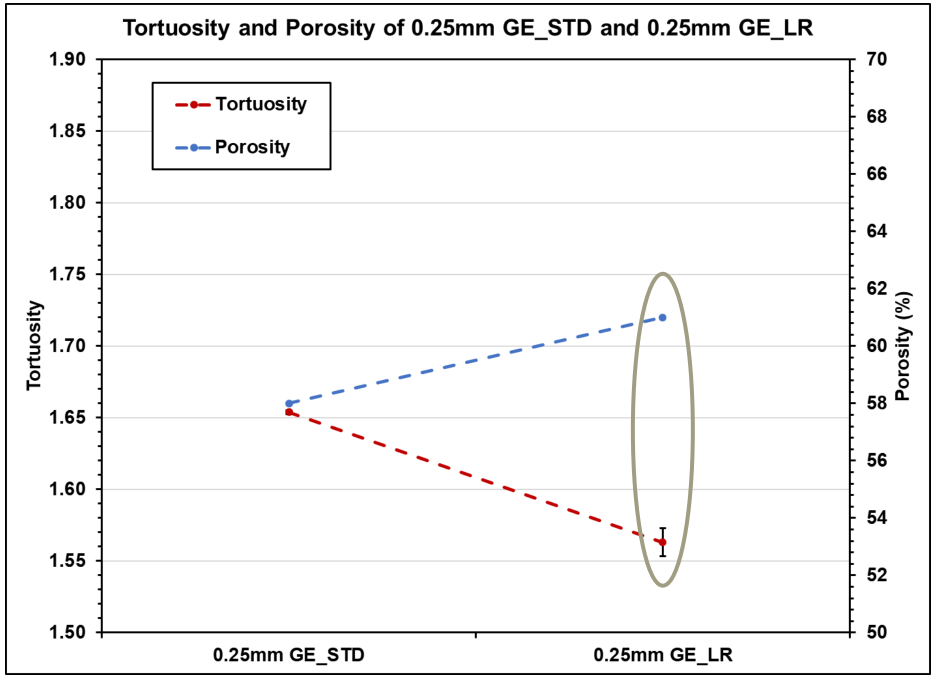
The depolarization charge increases as a function of the oxygen transported from the positive side of the cell through the separator.

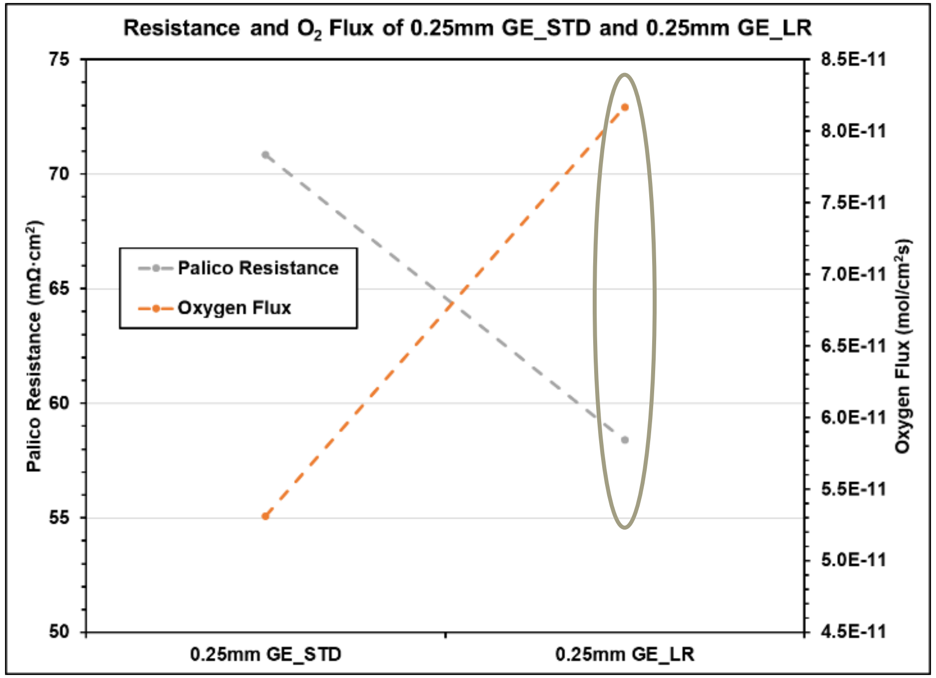
DEPOLARIZATION VS. TIME



- ENTEK 0.25mm GE_LR separator has the highest rate of oxygen transport of the three separators tested
  - ***The rate of oxygen transport is expected to be related to thickness, porosity, pore size distribution, and tortuosity of the separator***
- ENTEK 0.15mm GE_STD separator has a higher rate of oxygen transport than the ENTEK 0.25mm GE_STD separator
  - Oxygen transport through a thicker separator is slower

SEPARATOR COMPARISON_ STD VS LR FORMULATION

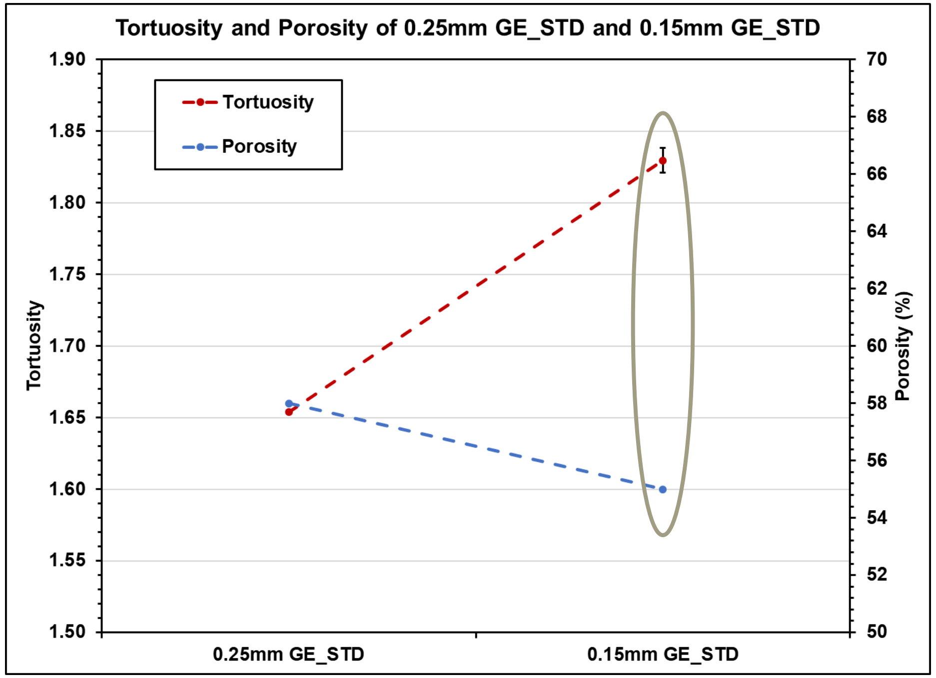


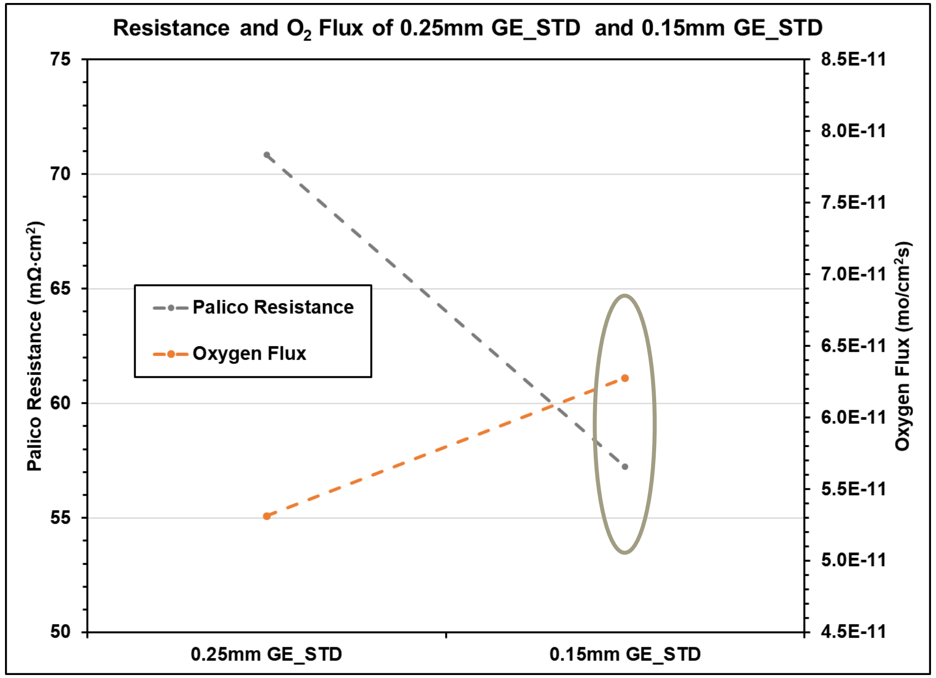


	Rate mol/Hr	Flux mol/(cm²s)	Diff Coef (cm²/s)	Metric ER mΩ·cm²	Resistivity mΩ·cm	Hg Porosity %	Ave Pore Diameter µm	Tortuosity
0.25 GE_LR	1.34E-05	8.17E-11	3.18E-06	58.39	2311	61	0.118	1.56
0.25 GE_STD	8.72E-06	5.31E-11	2.03E-06	70.84	2855	58	0.065	1.65

- The diffusion coefficient and flux were greater when using ENTEK LR separator than when using ENTEK Standard separator.
- The difference in flux and diffusion coefficient is expected due to the lower SES resistance, higher porosity, larger pore size and lower tortuosity of ENTEK LR separator.

SEPARATOR COMPARISON_ BACKWEB THICKNESS





	Rate mol/Hr	Flux mol/(cm²s)	Diff Coef (cm²/s)	Metric ER mΩ·cm²	Resistivity mΩ·cm	Hg Porosity %	Ave Pore Diameter µm	Tortuosity
0.25 GE_STD	8.72E-06	5.31E-11	2.03E-06	70.84	2855	58	0.065	1.65
0.15 GE_STD	1.03E-05	6.28E-11	1.37E-06	57.23	4047	55	0.064	1.83

- The diffusion coefficient was higher when using ENTEK 0.25 GE_STD separator than when using ENTEK 0.15 GE_STD separator, while the flux was greater with ENTEK 0.15 GE_STD separator.
- The difference in diffusion coefficient is expected to be due to lower SES resistivity, higher porosity, and lower tortuosity of ENTEK 0.25 GE_STD separator, while the difference in flux is expected to be due more to separator thickness
- This result may indicate that there is some skinning or surface effect that is more dominate in the thinner separator.

SUMMARY

- PE/SiO_2 separators will always be susceptible to oxidation in a Pb-acid battery
- Mass loss from separators exposed to oxidizing solutions gives an incomplete picture of separator degradation since residual oil is reacted or consumed as part of the mechanism for protecting the mechanical integrity of a separator
- Controlling the ***amount*** and ***type*** of residual process oil helps to mitigate chain scission or crosslinking of polyethylene
- Depolarization experiments support the existence of an oxygen cycle in flooded Pb-acid batteries with transport occurring through the separator, rather than over the top of the cell
- Oxygen transport through the separator is linked to several key characteristics including thickness, porosity, pore size distribution, and tortuosity.