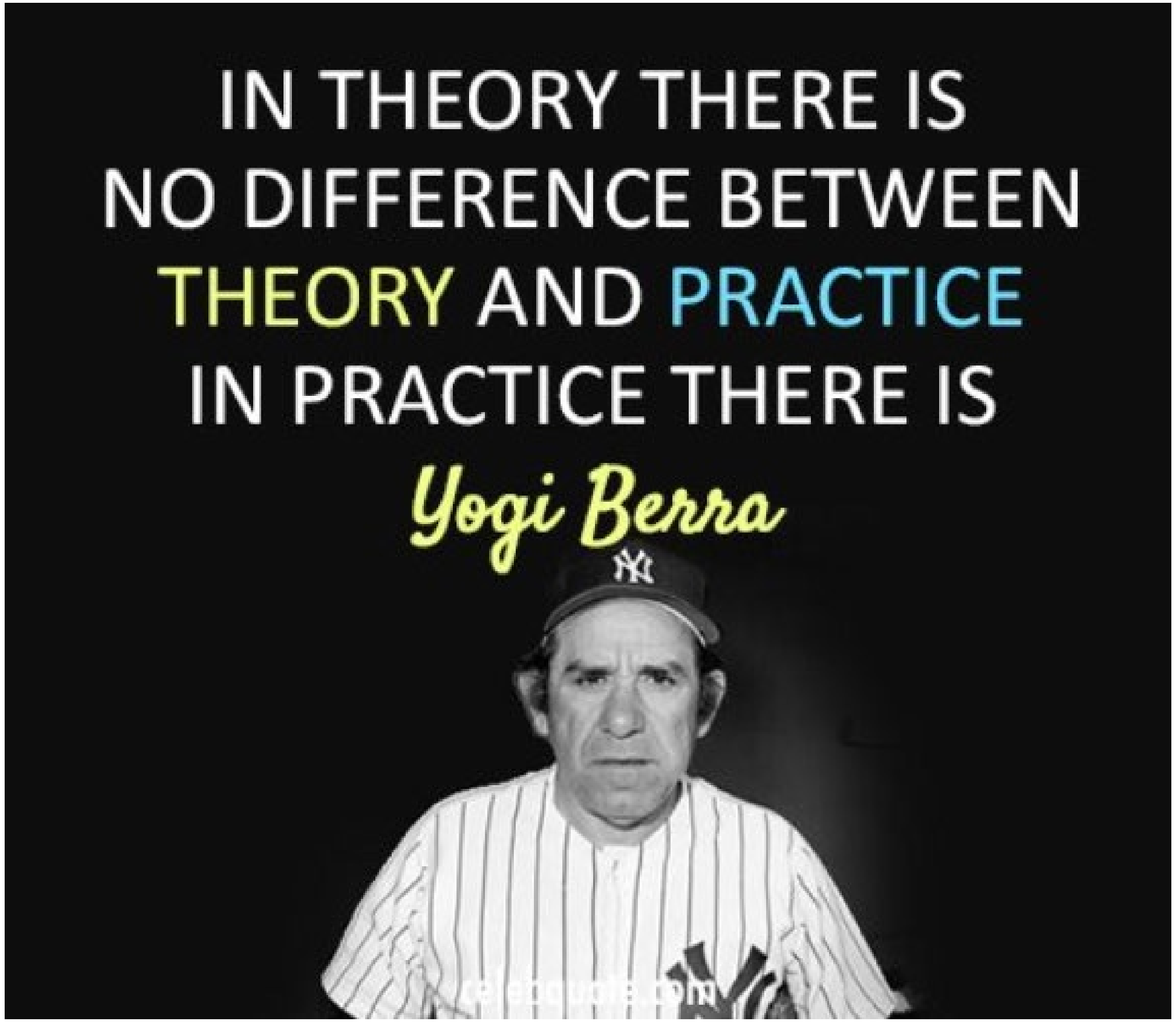
Membrane Testing Challenges, Standardization

Mike Yandrasits

2019 Alkaline Membrane Fuel Cell Workshop

DallasTexas, May 30th, 2019



I really didn't say everything I said

-*Yogi Berra*

ARPA-E AEM Performance Targets

ID	Metric	Value
3.1	Membrane chemical stability (at ≥80°C immersed in a pH≥14 solution)[A]	≥1000 hours with ≤2% loss in ion exchange capacity, ionic ASR, spectroscopic measures of membrane state, and mechanical properties
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3.6	Electronic ASR	≥1000 Ohm-cm2
3.7	Humidity Stability Factor[D]	>5
3.8	Swelling in liquid water at 25°C	<50%
3.9	Pressure differential (bar)	≥1
3.10	H_2 crossover and O_2 crossover	≤25 nmol/cm2-s
3.11	Cost for membrane that can be practically integrated in a device[E]	≤20 $/m2
3.12	Membrane break strength[F]	> 15 MPa at 50 C and 50% RH

[A] For a discussion of spectroscopic and mechanical tests that may be done to characterize degradation see [19] or [82]

[B] Component development and testing work may be done on areas smaller than that defined in metric 3.2, but a scientifically principled approach to scale-up must be developed and components with the area in metric 3.2 must be made and tested by the end of the project.

[C] The RH testing procedure is described in reference [83]. Membrane mechanical properties must be sufficiently retained during RH cycling; the most important metric for this is the membrane's ability to maintain low levels of gas crossover, as defined in metric 3.10.

[D] Definition: (Strain at breaking point at 25°C and 50% RH) / (Linear swelling at 100°C in liquid water). This metric is a rough check to ensure that a membrane can stretch more at 25°C than it naturally swells when fully hydrated at 100°C, and has been found to correlate with RH cycles to failure. See references [84] and [85] for further discussion.

[E] At a production capacity to supply 100,000 fuel cell vehicles per year. "Practically integrated" refers to the mechanical properties required for handling and device manufacturing.

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3M

A Few Words About PFSA Conductivity

Nafion Published Conductivity

- **3539 records from 310 original reports**
- **Red stars are the *maximum* value of proton conductivity reported in each report**

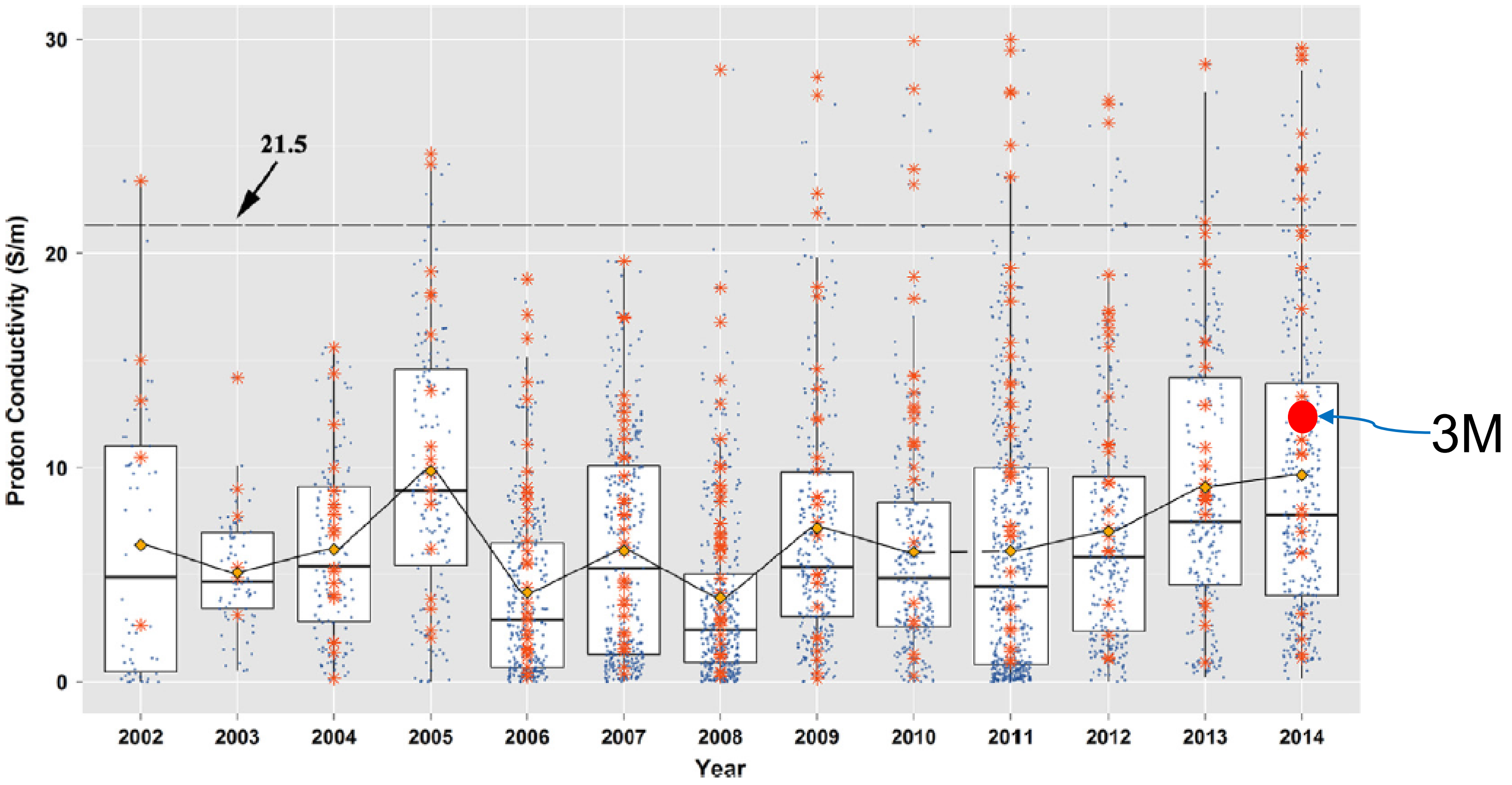
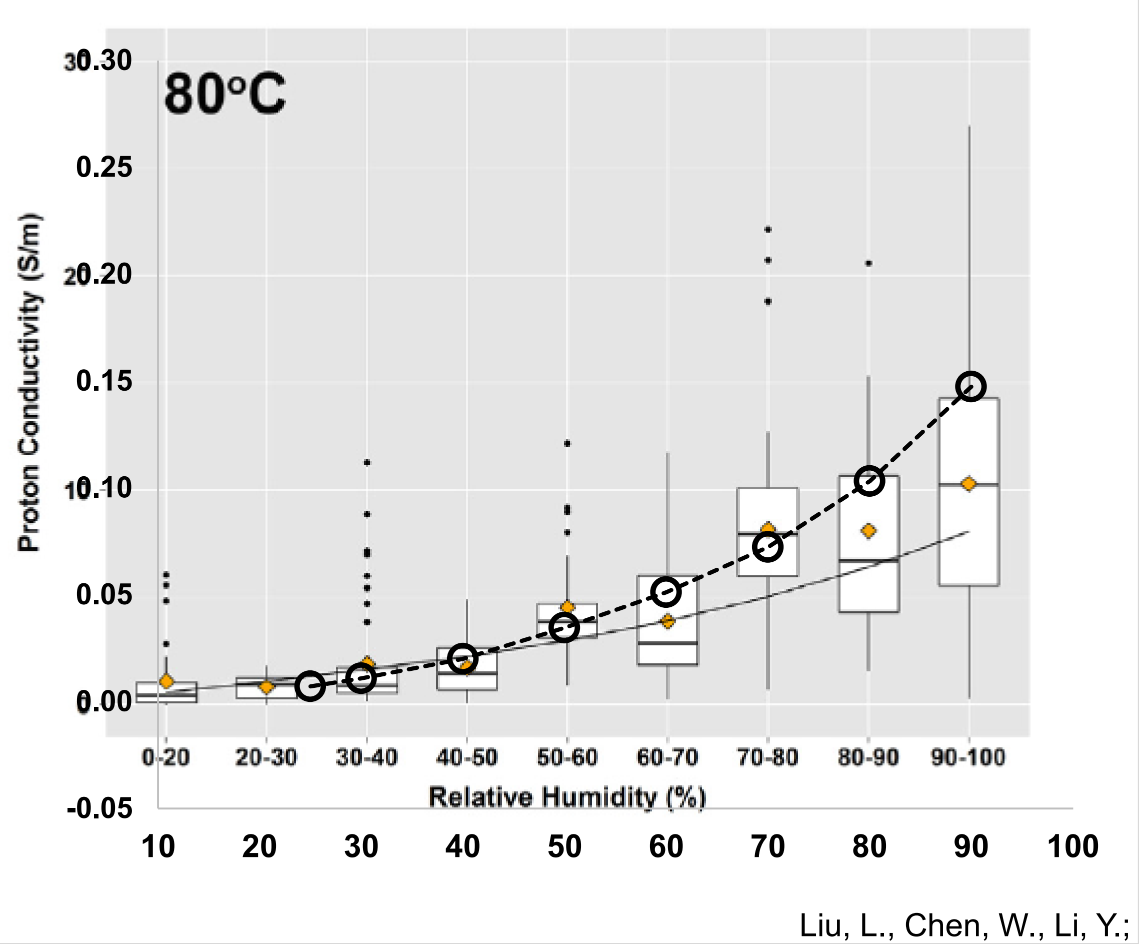


Fig. 5. The trend to improve the proton conductivity of Nafion membranes in recent 13 years. The line across years linked the mean of the proton conductivity over the records reported in the corresponding year. The red stars are the maximum value of proton conductivity reported in each report. The black dash line is the threshold of proton conductivity with 21.5 S/m. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

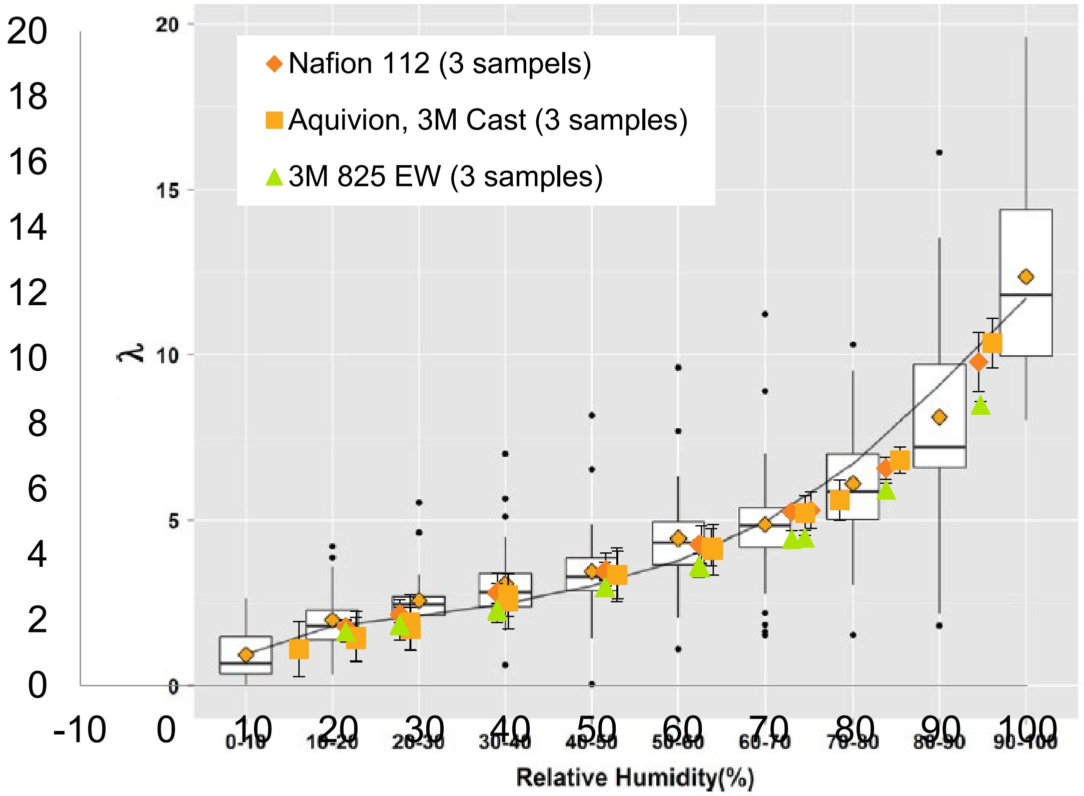
Liu, L., Chen, W., Li, Y.; *J. Membrane Sci*. **504** (2016) 1-9

80°C Conductivity and Water Uptake

80°C Conductivity



80°C Water Uptake



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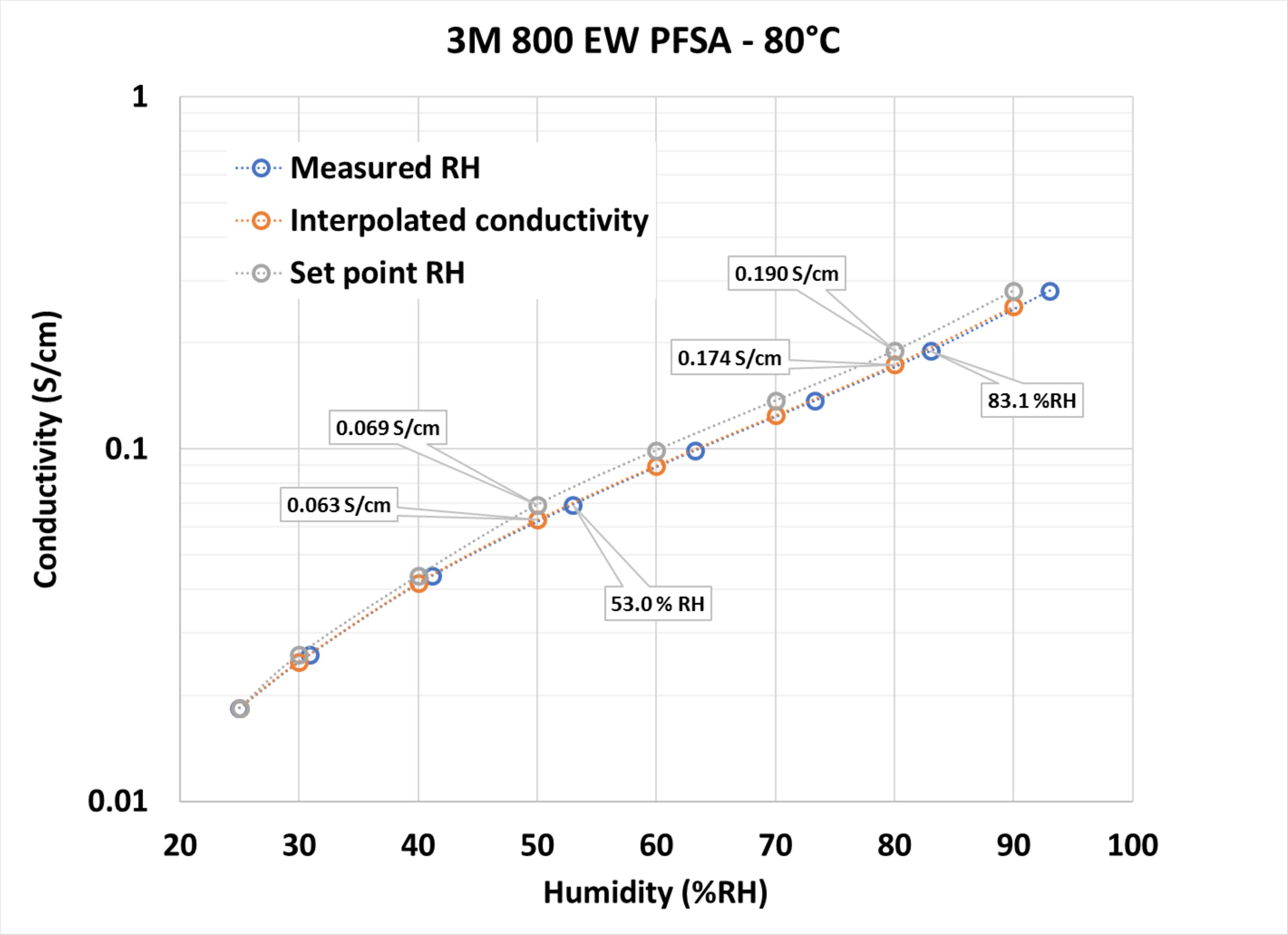
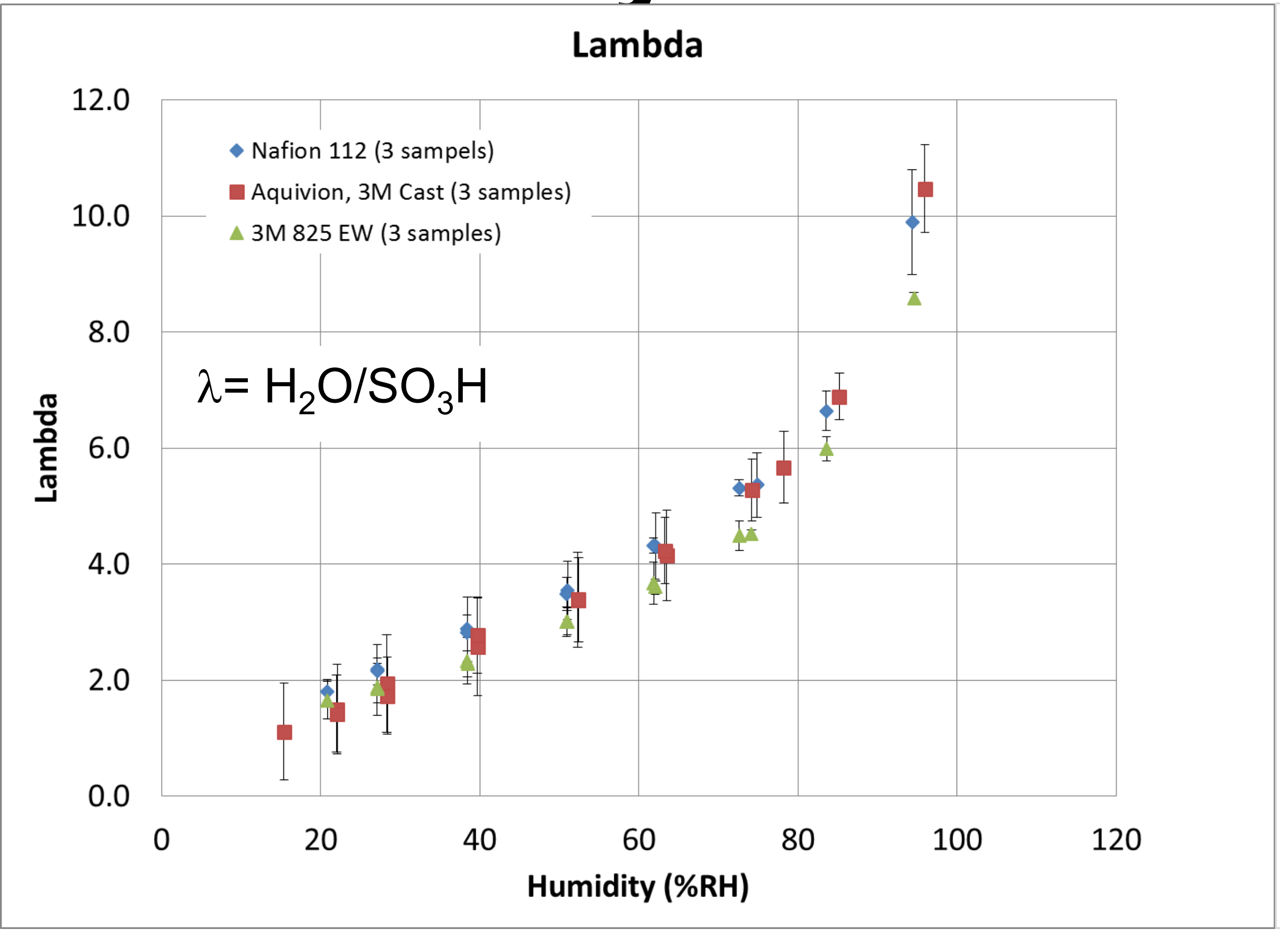
Conductivity and Humidity

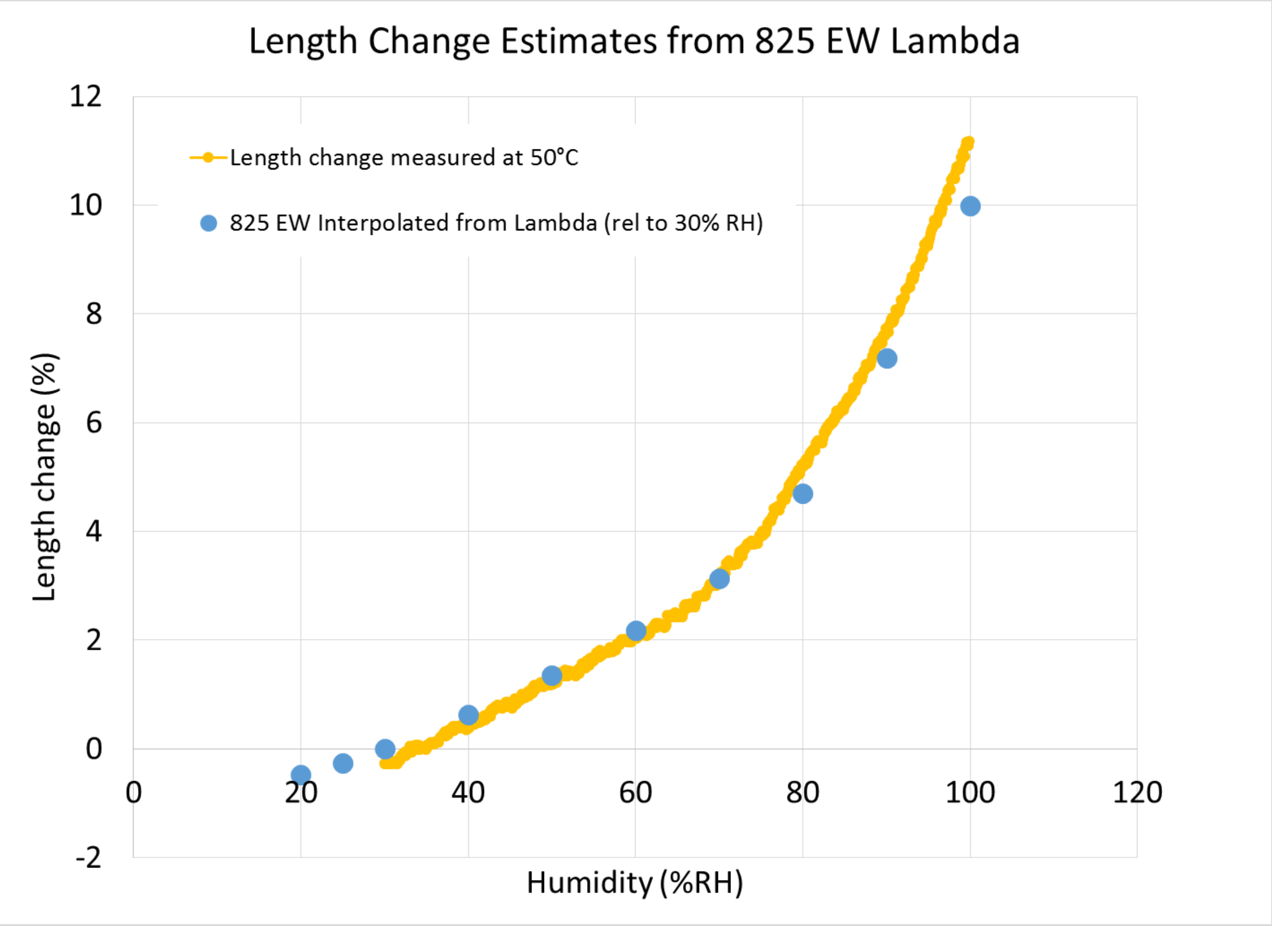


- “Gold Standard*” Vaisala gauge used to determine ‘true’ RH
- +/-3% RH can make 20-30% difference in reported conductivity

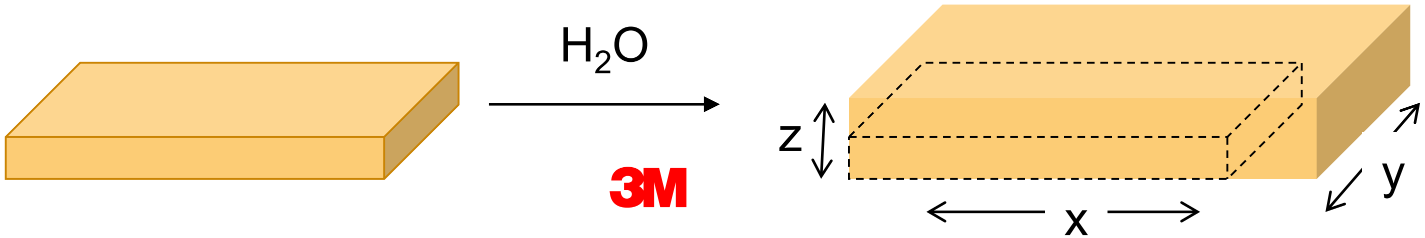
* Calibrated annually by 3M metrology

Swell Estimated from Lambda for Conductivity/Resistance Conversions



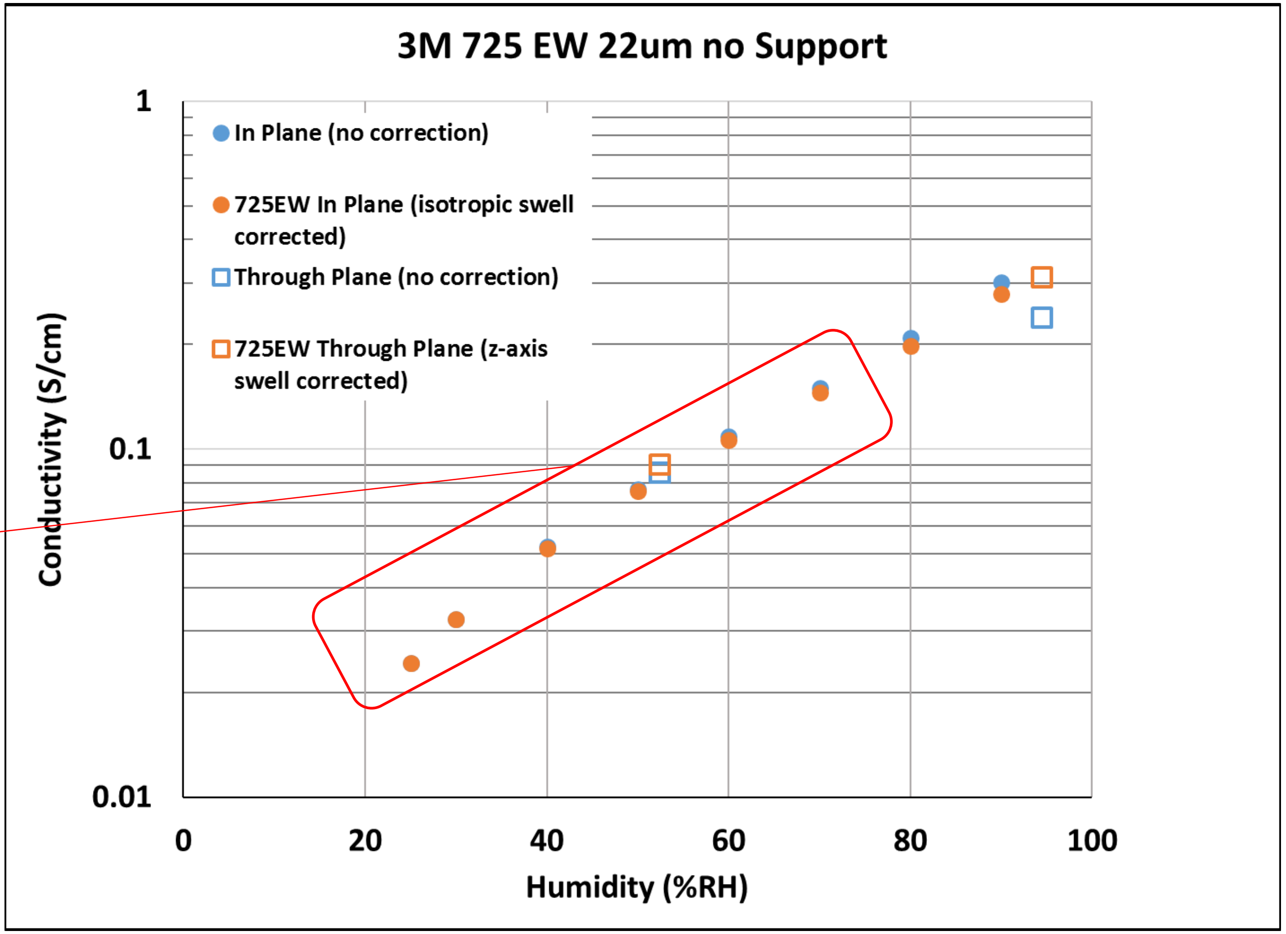


$$\sigma = \frac{l}{R \cdot w \cdot t}$$



In-Plane and Through Plane at 80°C

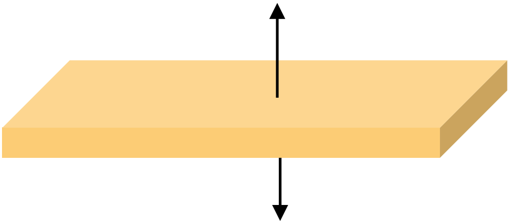
Region of interest for PEMs effectively insensitive to swell corrections



Conversion from σ to R most sensitive at high RH

4pt probe and in-cell data agree when swell corrected!

In-plane
(4 pt probe)



Through-plane
(in cell imp.)

What about AEMs?

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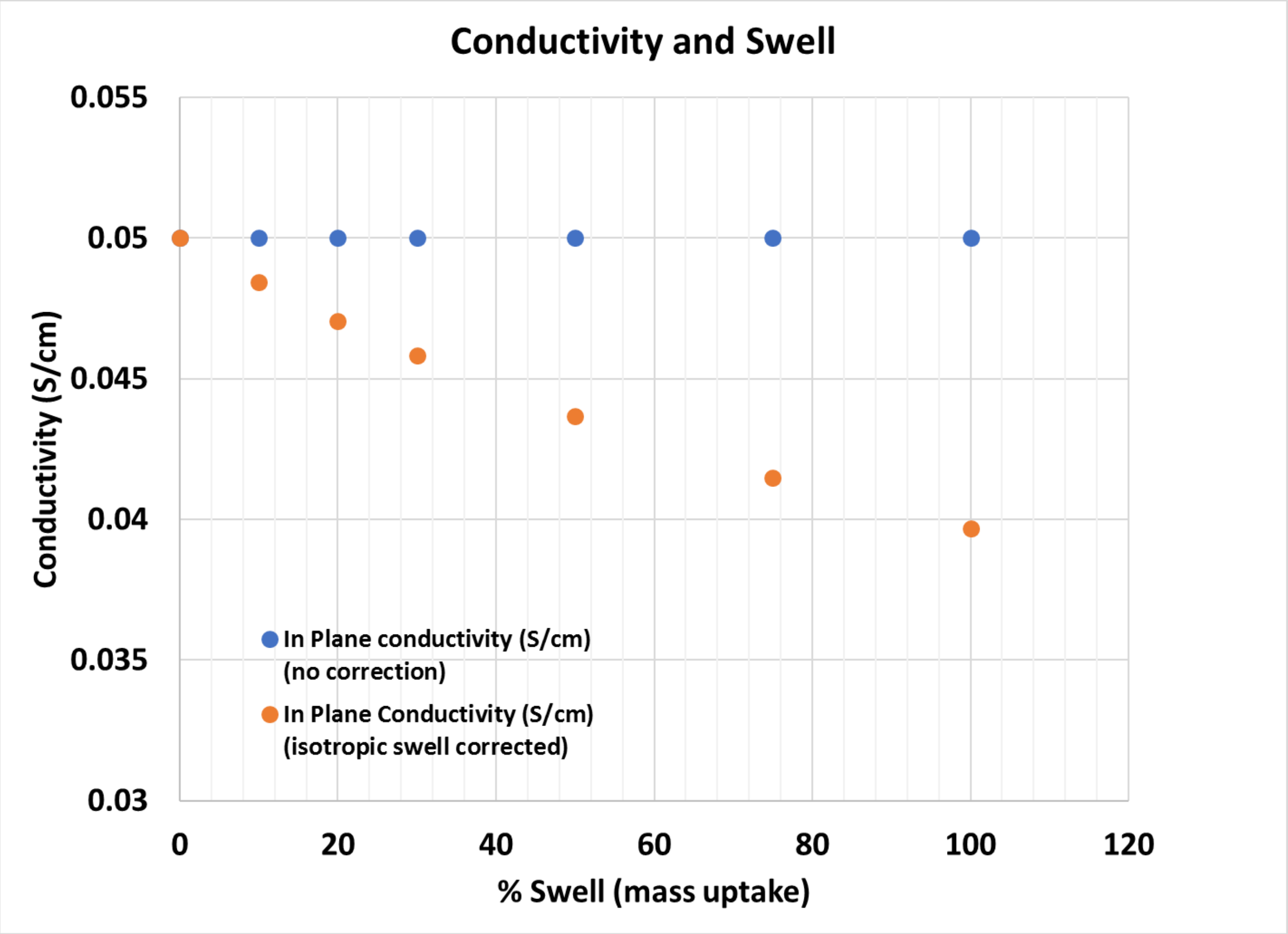
Effect of Dry vs Wet Dimensions

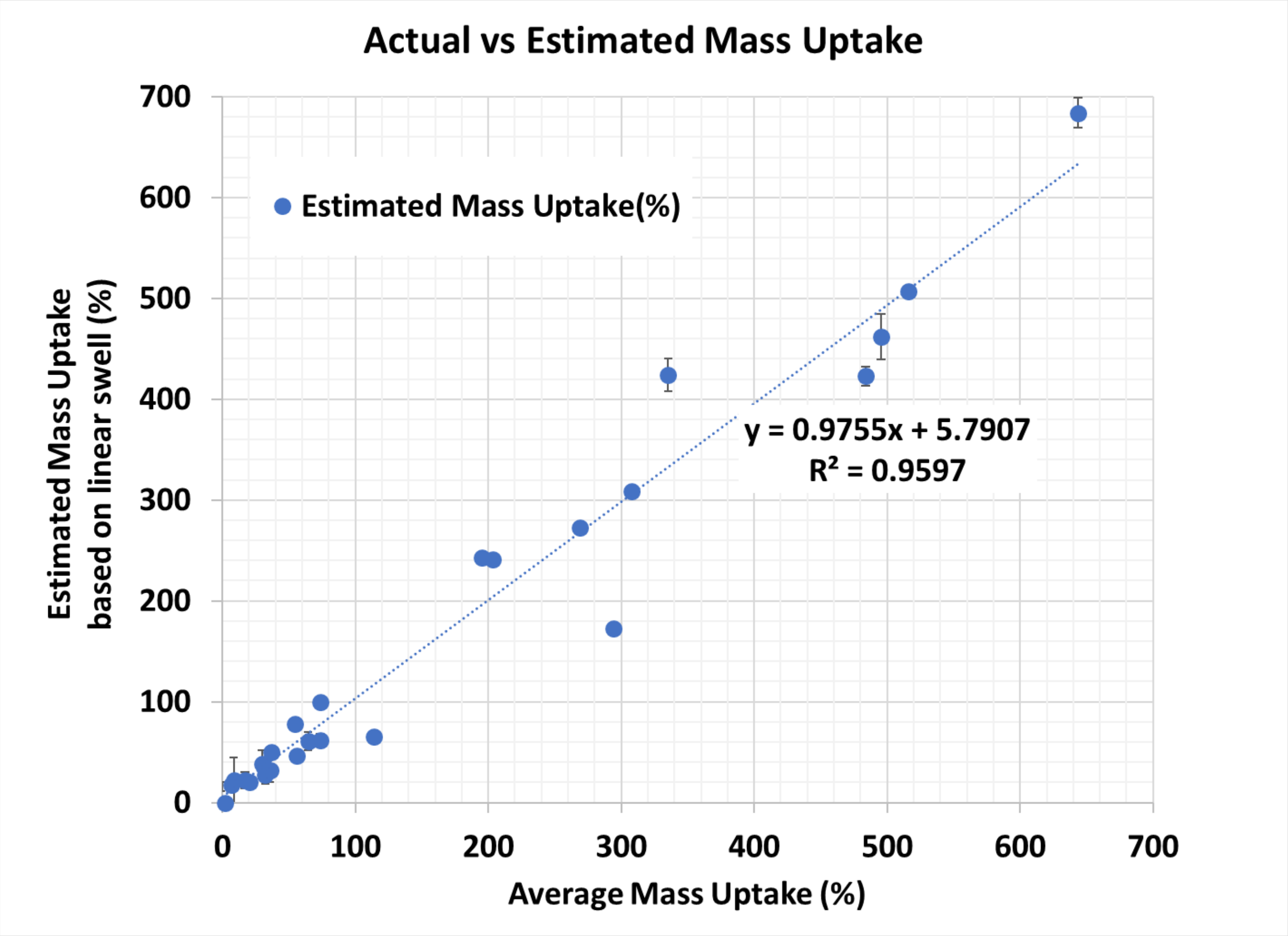
$$\sigma = \frac{l}{R \cdot w \cdot t}$$

Assume sample mounted dry and undergoes isotropic swell

Dry thickness convention no longer appropriate



Swell and Water Uptake



Estimated WU from linear swell

$$WU = 100 * [(s + 1)^3 - 1]$$

WU	Water Uptake (mass %)
s	linear swell (fraction)

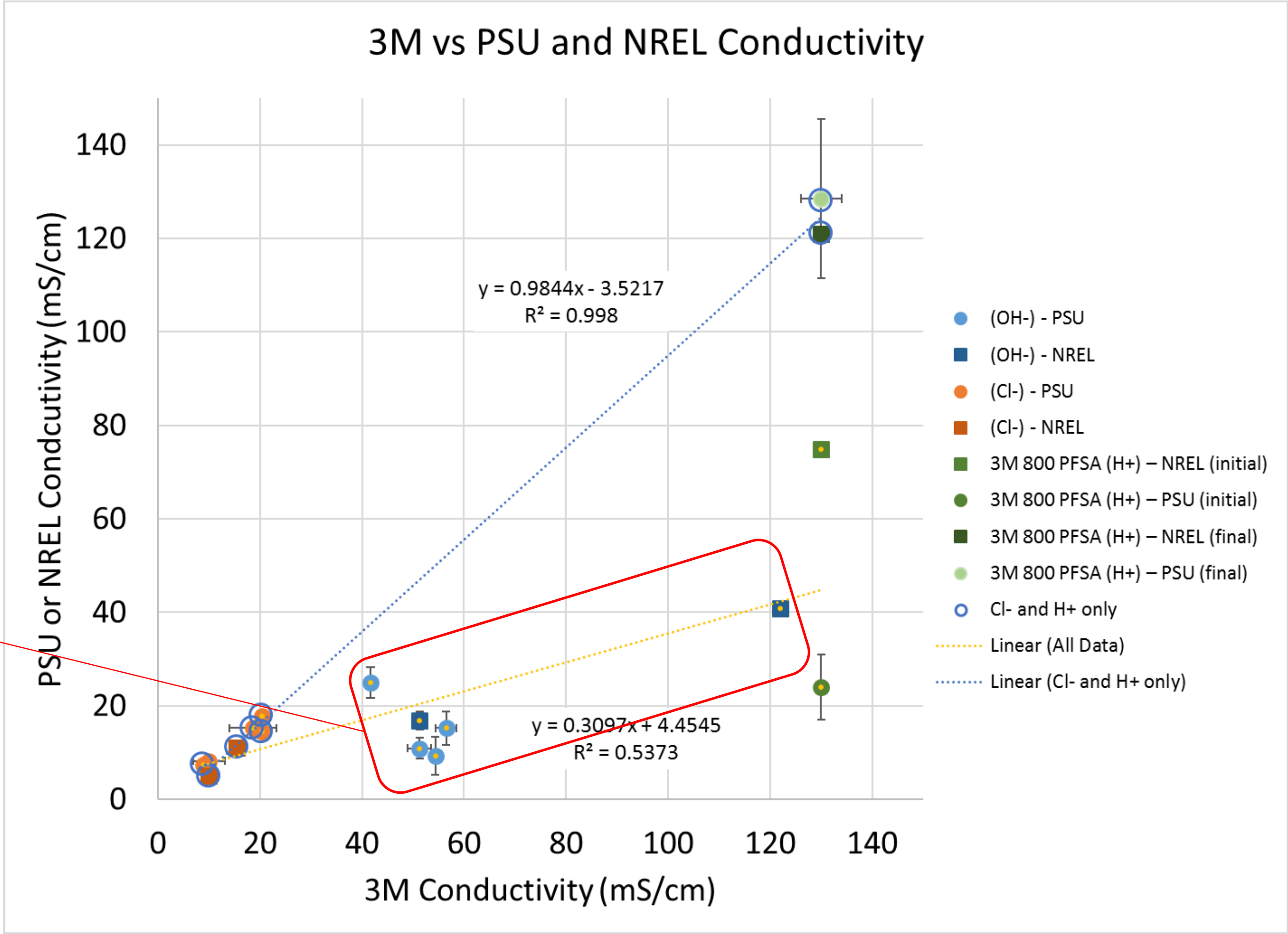
Assume ionomer density and water density are 1 g/cm^3

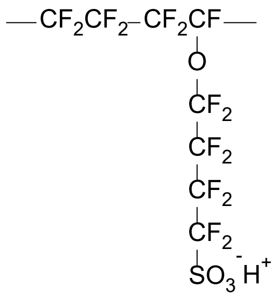
3M and PSU Conductivity Round Robin

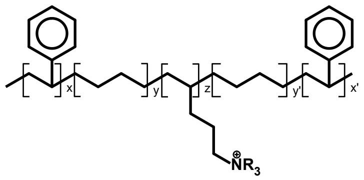
RT in liquid water

Cl$^-$ and H$^+$ (eventually) agree well

Could poor correlation with OH$^-$ be due to poor ion exchange?





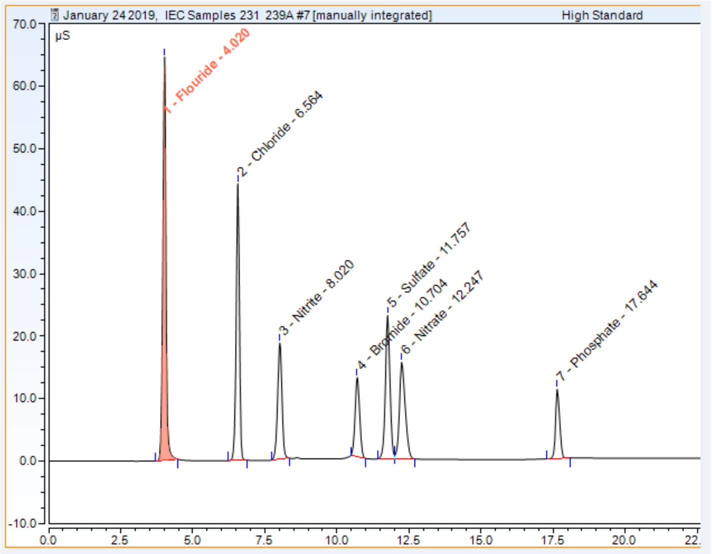


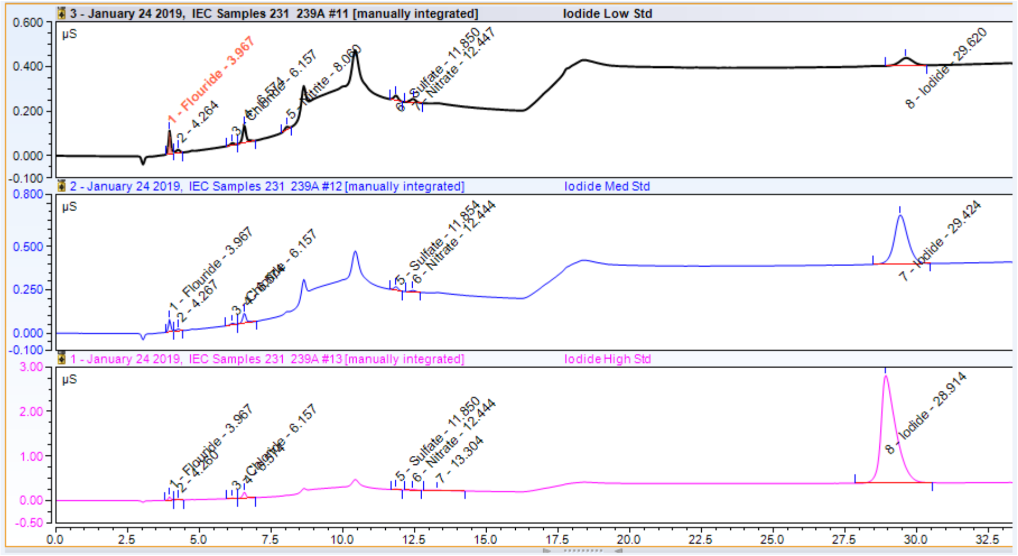
After round 1 000 Ω resistors were sent from 3M to NREL and PSU

3M

Cl^- and I^- by Ion Chromatography (IC)

Typical IC calibration data





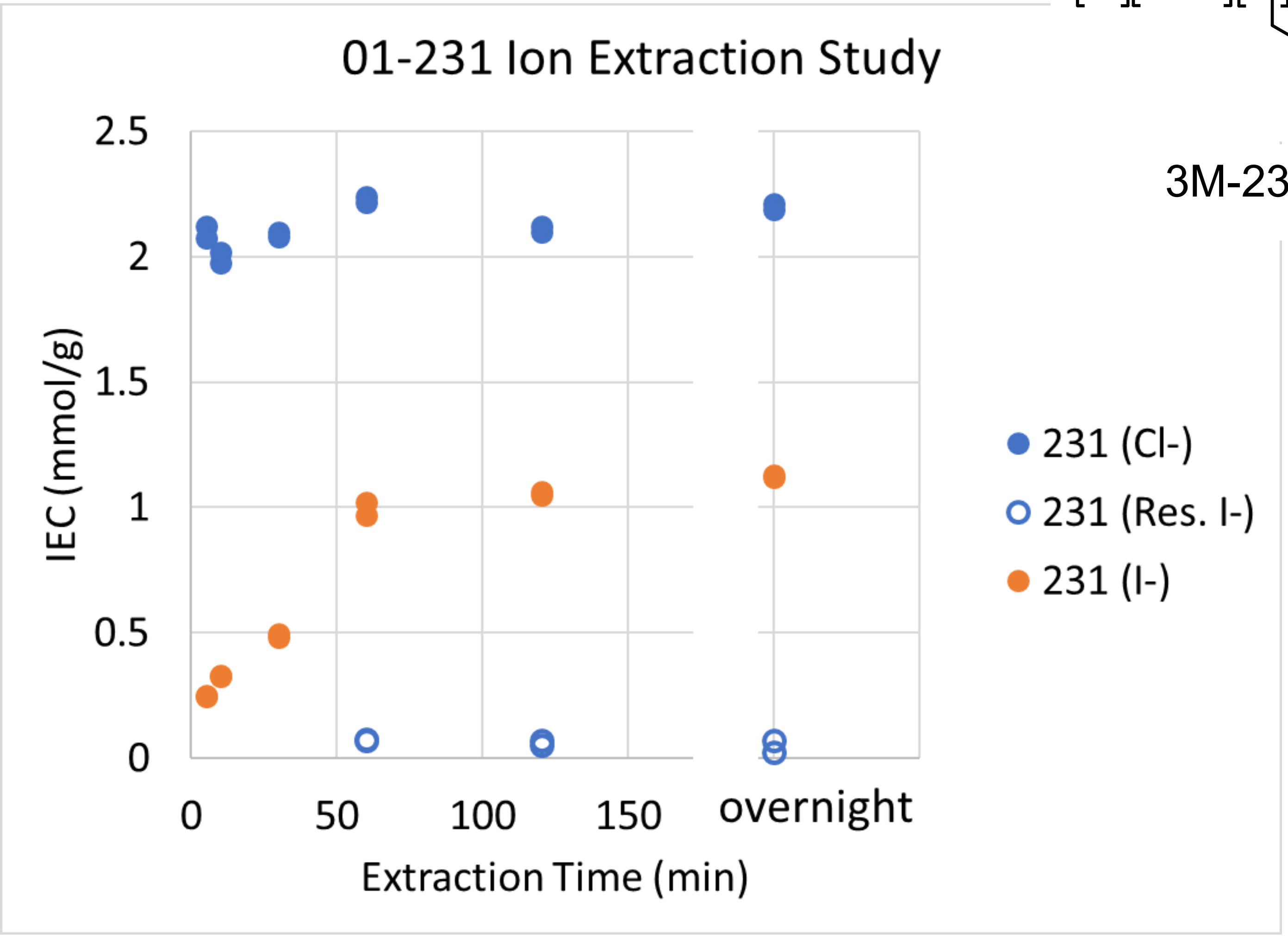
Mixed standards

(F^-, Cl^-, NO_2^-, Br^-, SO_4^{2-}, NO_3^-, PO_4^{3-})

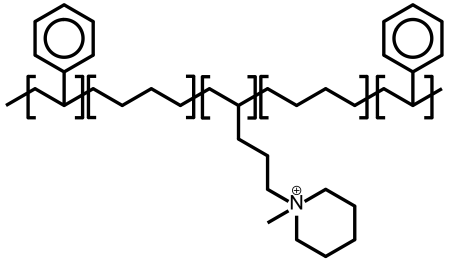
Iodide Std (homemade)

3M

Ion Exchange Studies

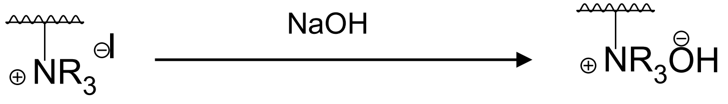


Each time point represents a one-time soak in 1M NaOH

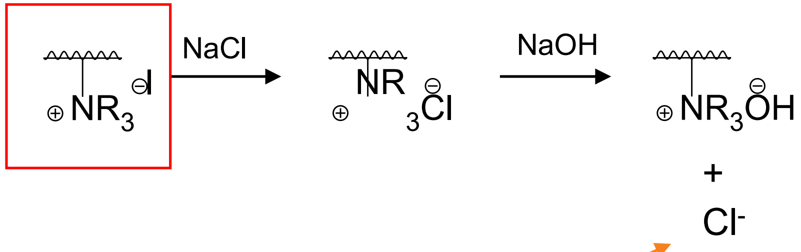


3M-231

Initial Exchange

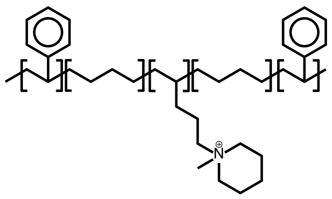


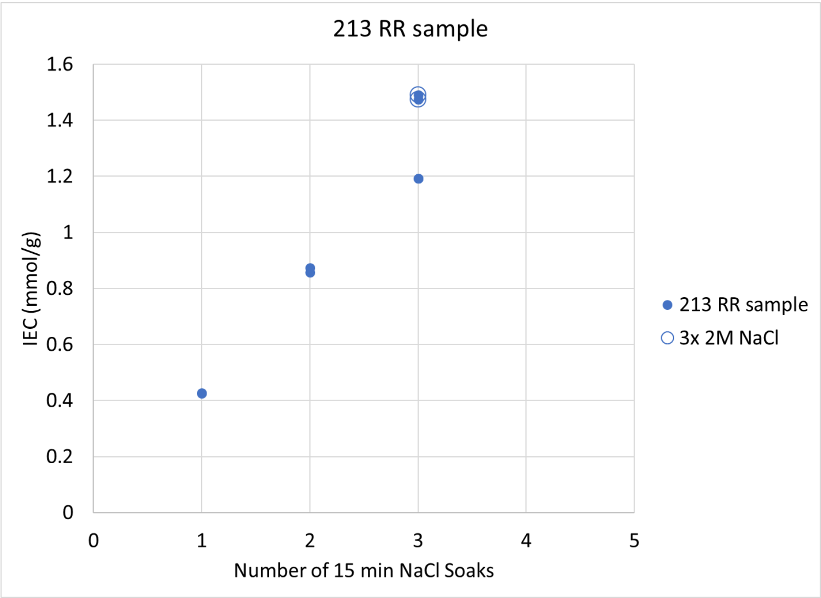
Exchange for IEC

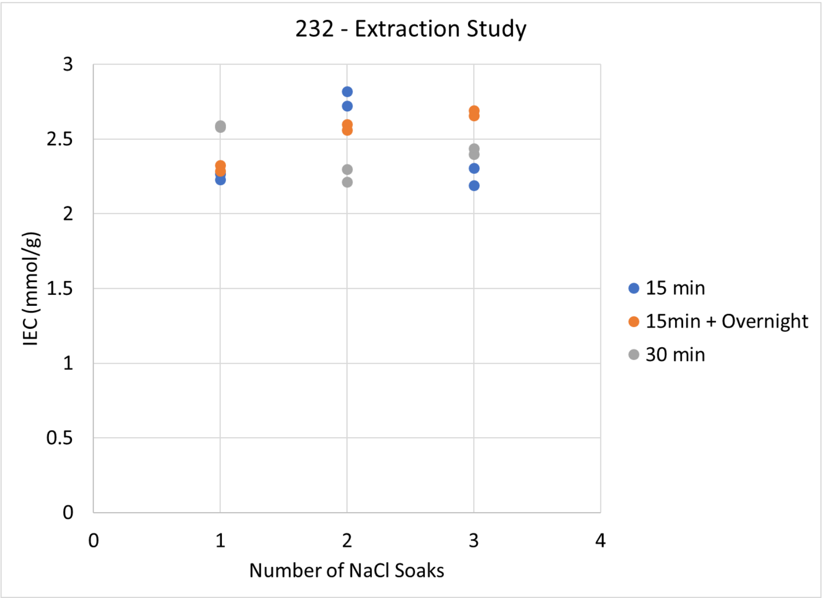


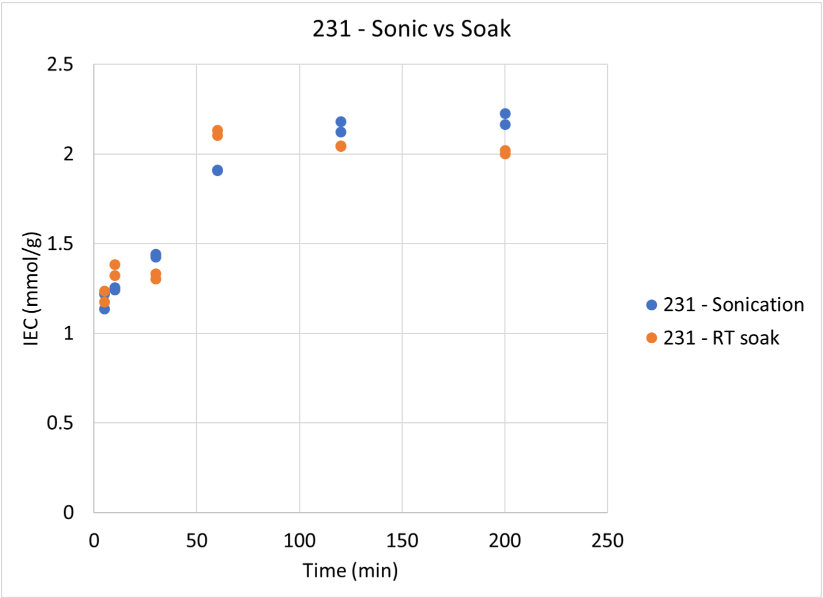
Quantify by ion Chromatography

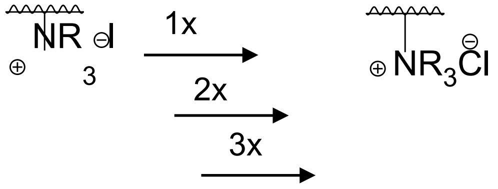
Ion Exchange Issues

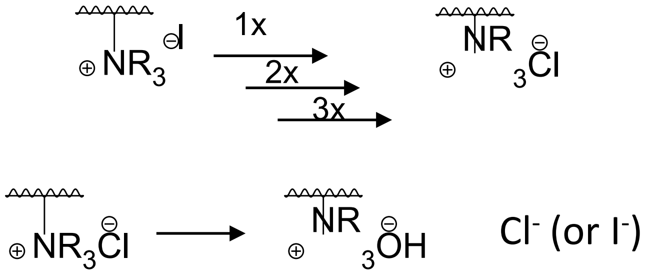


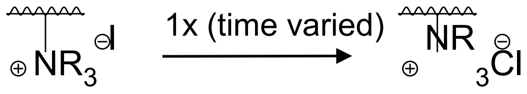












Ion Selectivity

Relative affinities of various anions (compared with the hydroxide ion) on polystyrenic strongly basic anion exchange resins, both Type 1 and Type 2.

Ion	Type 1	Type 2
OH^-	1.0	1.0
Benzene sulfonate	500	75
Salicylate	450	65
Citrate	220	23
I^-	175	17
Phenate	110	27
HSO_4^-	85	15
ClO_3^-	74	12
NO_3^-	65	8
Br^-	50	6
CN^-	28	3
HSO_3^-	27	3
BrO_3^-	27	3
NO_2^-	24	3
Cl^-	22	2.3
HCO_3^-	6.0	1.2
IO_3^-	5.5	0.5
Formate	4.6	0.5
Acetate	3.2	0.5
Propionate	2.6	0.3
F^-	1.6	0.3
$HSiO_3^-$	< 1.0	< 1.0
$H_2PO_4^-$	5.0	0.5

http://msdssearch.dow.com/PublishedLiteratureDOWCOM/dh_0988/0901b803809885be.pdf?filepath=liquidseps/pdfs/noreg/177-01755.pdf&fromPage=GetDoc

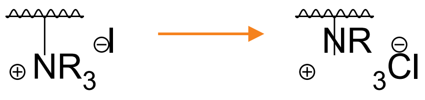
Originally pointed out by Yushan Yan

Assumptions:

IEC	2mmol/g
Mass	0.5g
NaX	1M
Vol	50 ml

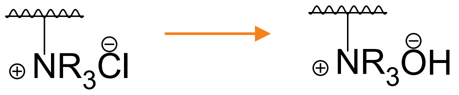
$$"app\ excess" = \frac{ion\ excess * S_{OH-}}{S_{X-}}$$

Ion	Selectivity	"Apparent Excess"
OH-	1	100
I-	175	0.6
Cl-	22	4.5
Br-	50	2.0
HSO3-	27	3.7
IO3-	5.5	18.2

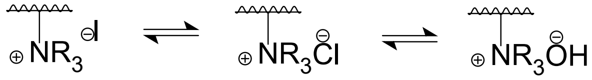


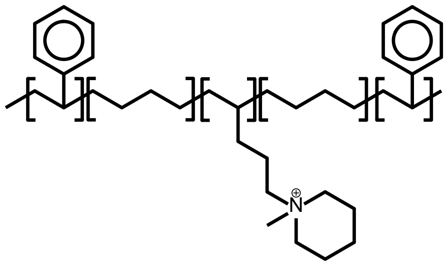
$$"app\ excess" = \frac{ion\ excess * S_{Cl-}}{S_{X-}}$$

Ion	Selectivity	"Apparent Excess"
OH-	1	1100
I-	175	6
Br-	50	22
Cl-	22	50
HSO3-	27	41



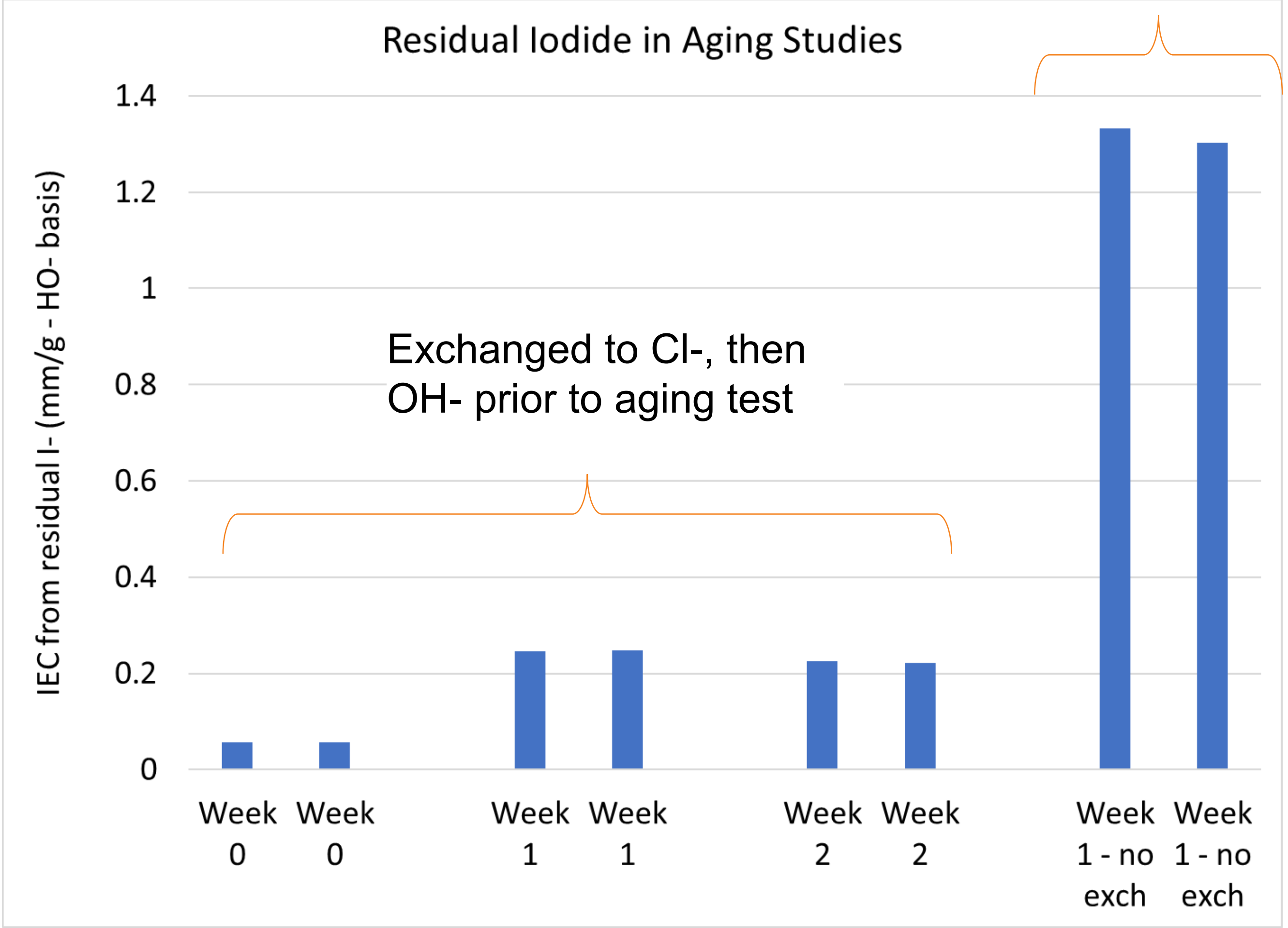
Residual I^- in Aging Study





Original IEC 1.9 mmol/g

Aging started from I- form



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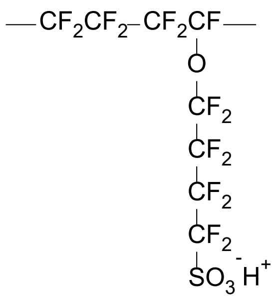
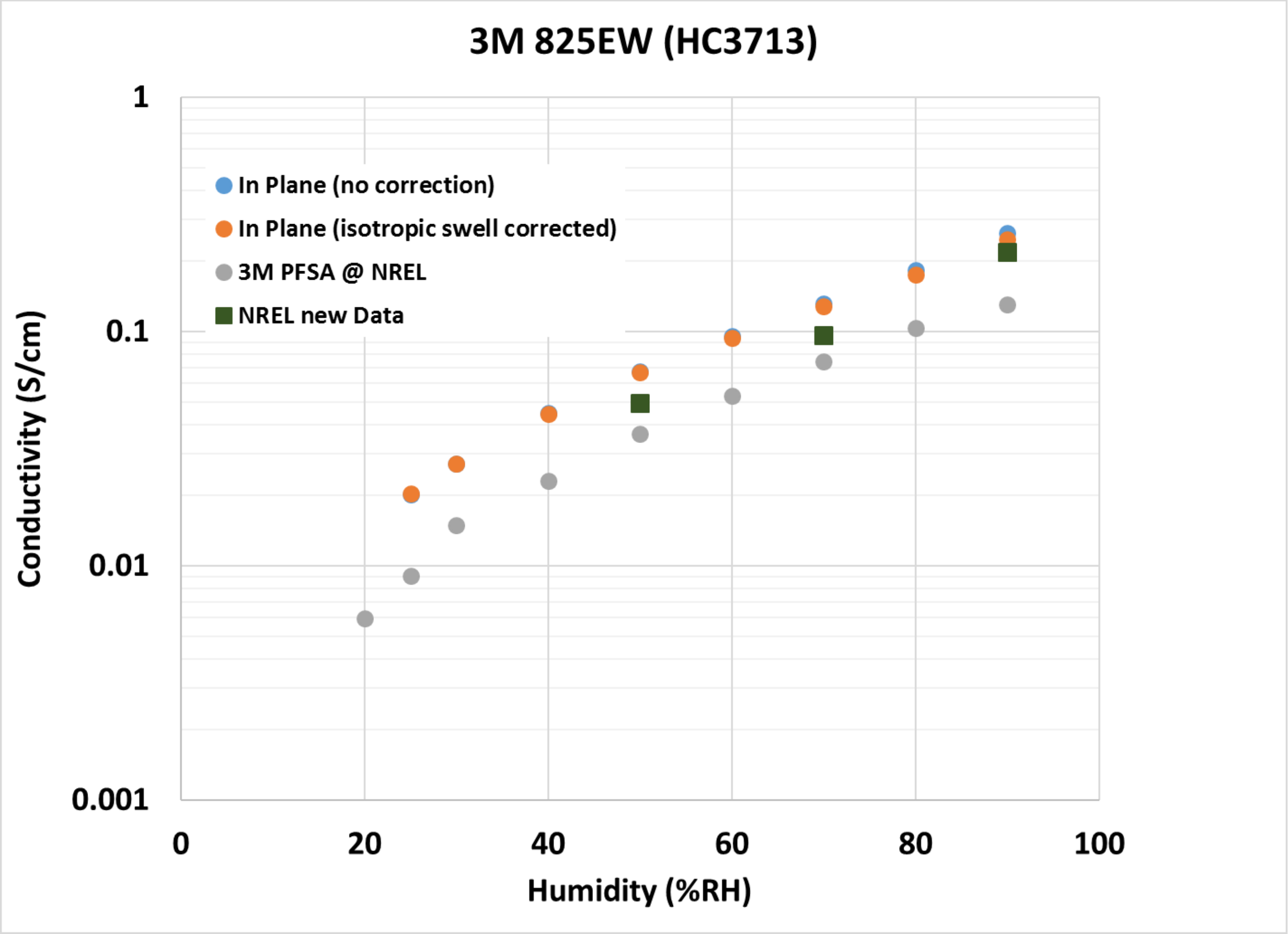
More Round Robin 3M and NREL

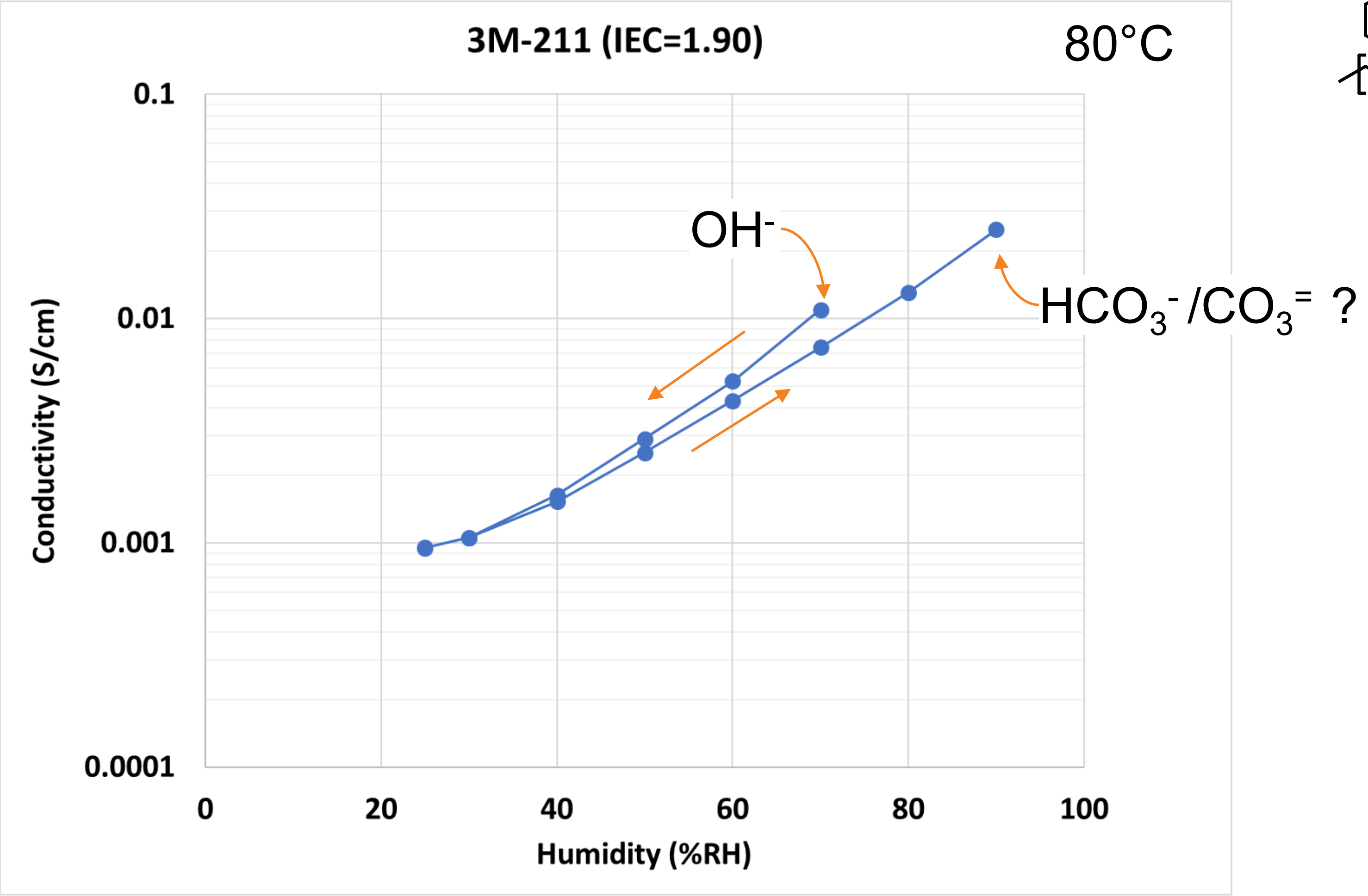


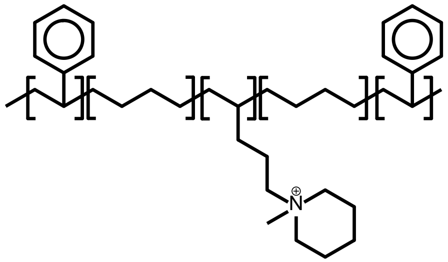


Humidity control/recording issues identified at NREL

Better but still a discrepancy

CO_2 and Carbonate





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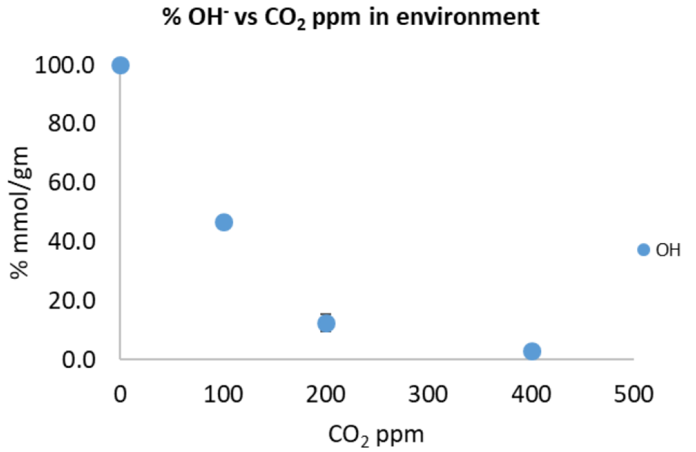
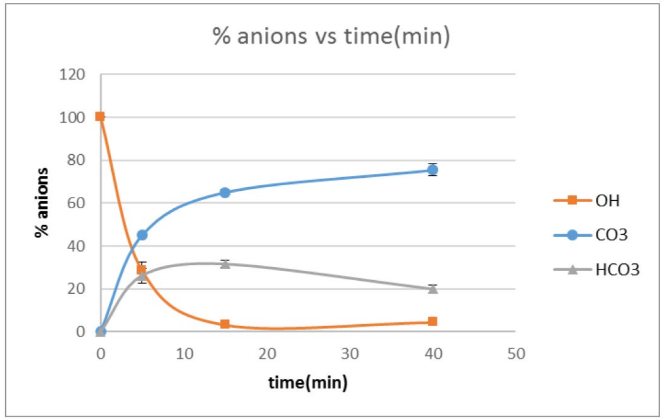
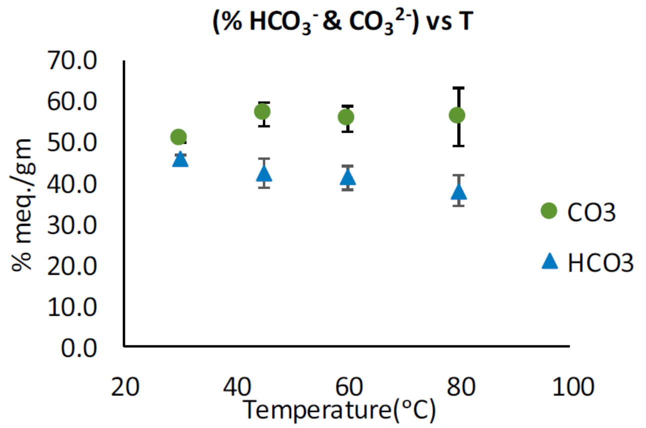
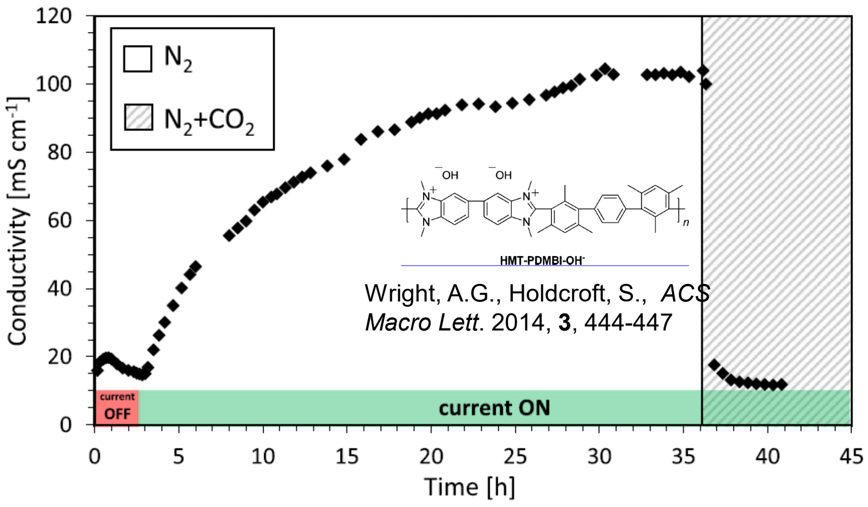




Divekar, A.G., Park, A.M., Owczarcyk, Z. R., Seifert, S., Pivovar, B.S., Herring, A.M., *ECS Trans*. **80 (8)** 1005-1011 (2017)

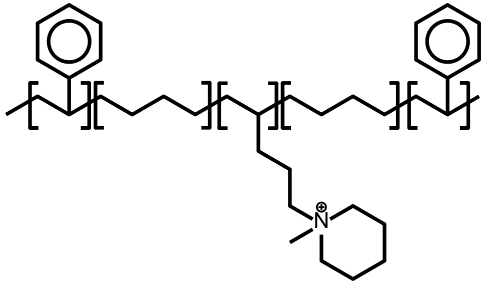


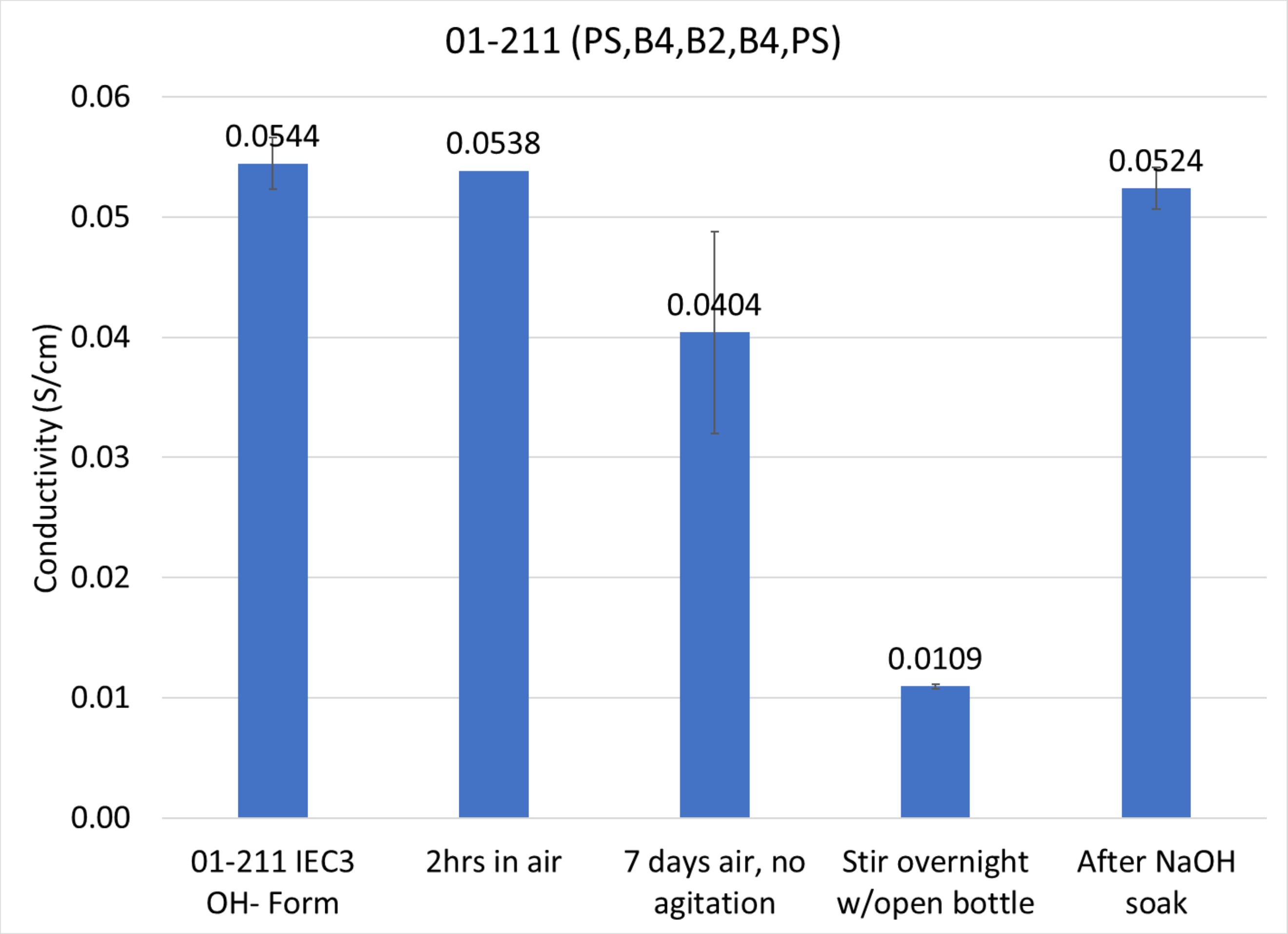
Divekar, A.G., Pivovar, B.S., Herring, A.M., *ECS Trans*. **86 (13)** 643-648 (2018)



Ziv, N., Dekel, D. R., *Electrochemistry Com*. **88** (2018) 109-113

More CO_2 and Carbonate





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3.4	Ionic ASR (80°C, ≤50% RH, under air exposure, *i.e.*, in presence of 400 ppm CO_2)	≤0.08 Ohm-cm^2
3.5	Mechanical durability during humidity cycling[C]	≥20,000 RH cycles
3.6	Electronic ASR	≥1000 Ohm-cm^2
3.7	Humidity Stability Factor[D]	>5
3.8	Swelling in liquid water at 25°C	<50%
3.9	Pressure differential (bar)	≥1
3.10	H_2 crossover and O_2 crossover	≤25 nmol/cm^2-s
3.11	Cost for membrane that can be practically integrated in a device[E]	≤20 $/$m^2$
3.12	Membrane break strength[F]	> 15 MPa at 50 C and 50% RH

[A] For a discussion of spectroscopic and mechanical tests that may be done to characterize degradation see [19] or [82]

[B] Component development and testing work may be done on areas smaller than that defined in metric 3.2, but a scientifically principled approach to scale-up must be developed and components with the area in metric 3.2 must be made and tested by the end of the project.

[C] The RH testing procedure is described in reference [83]. Membrane mechanical properties must be sufficiently retained during RH cycling; the most important metric for this is the membrane's ability to maintain low levels of gas crossover, as defined in metric 3.10.

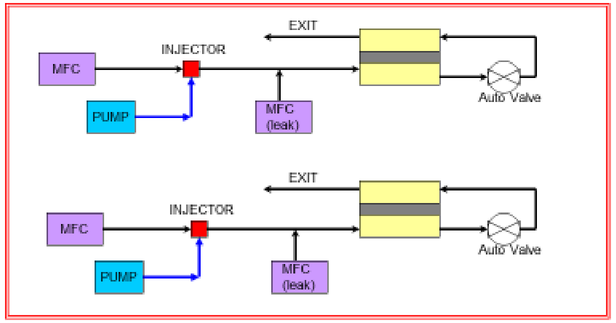
[D] Definition: (Strain at breaking point at 25°C and 50% RH) / (Linear swelling at 100°C in liquid water). This metric is a rough check to ensure that a membrane can stretch more at 25°C than it naturally swells when fully hydrated at 100°C, and has been found to correlate with RH cycles to failure. See references [84] and [85] for further discussion.

[E] At a production capacity to supply 100,000 fuel cell vehicles per year. "Practically integrated" refers to the mechanical properties required for handling and device manufacturing.

[F] Not in original FOA

RH Cycle Cell Design

Mechanical Membrane Cycling-Configuration

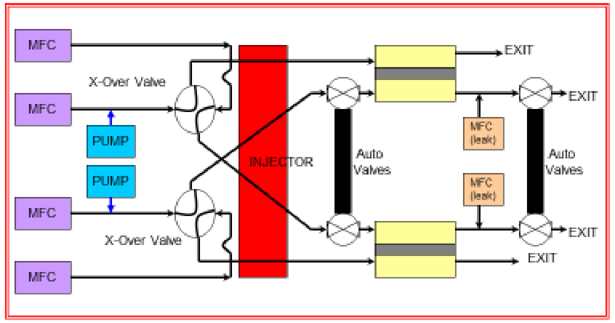


Configuration 1

- Single Flow (2 slm Air) wrap around
- Automated off-valve and leak measurement MFC
- Pumps turn on/off for wet cycle to dry cycle

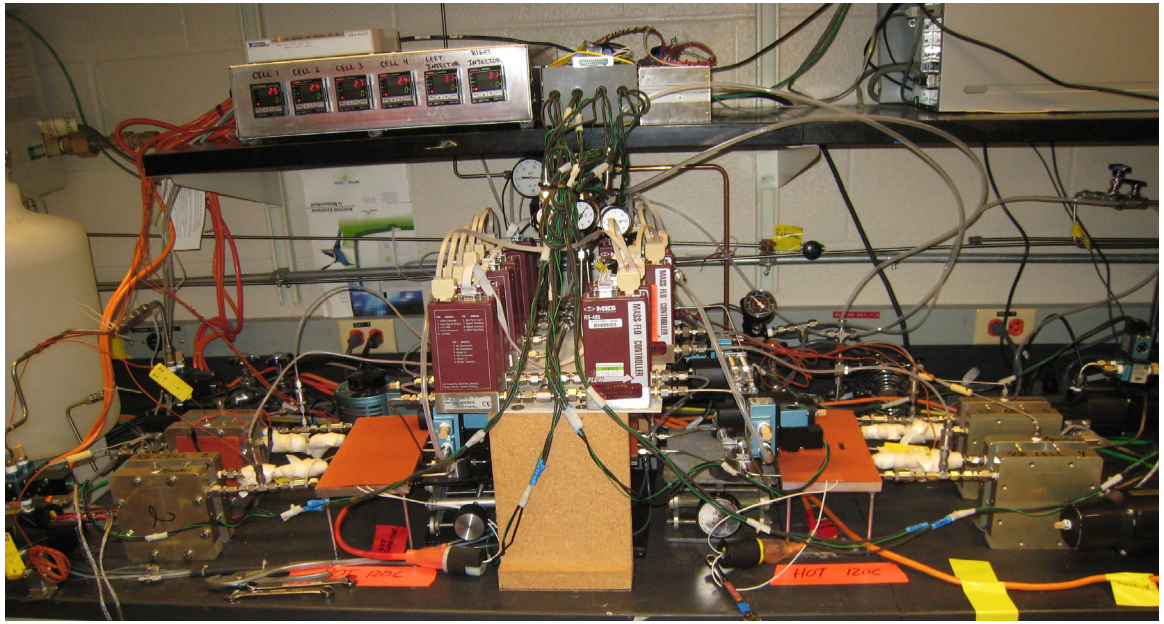
Configuration 2

- Double Flow (2 slm Air)
- Automated off-valve and leak measurement MFC
- Crossover Valves (while one cell is wet the other is dry)

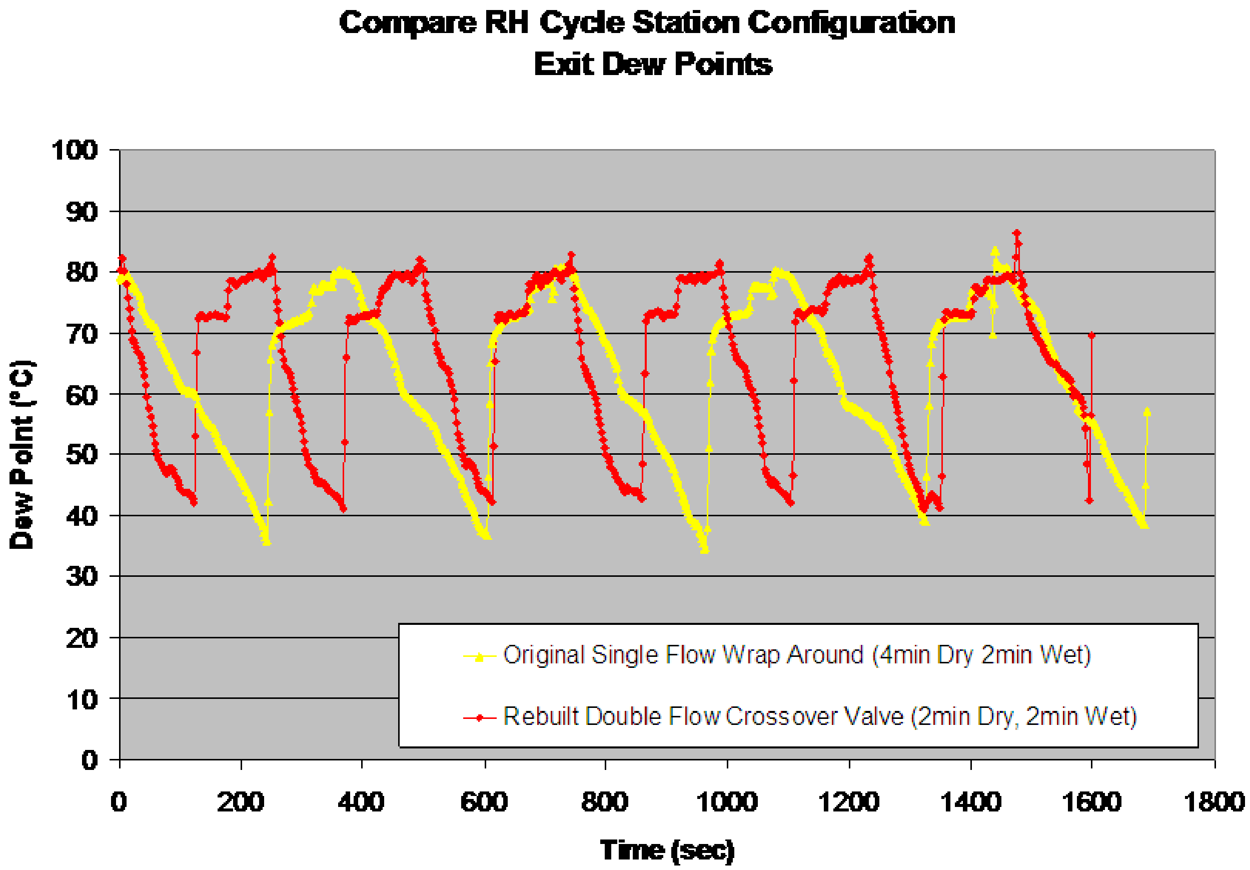


Membrane Durability Testing and Electrode Development 3

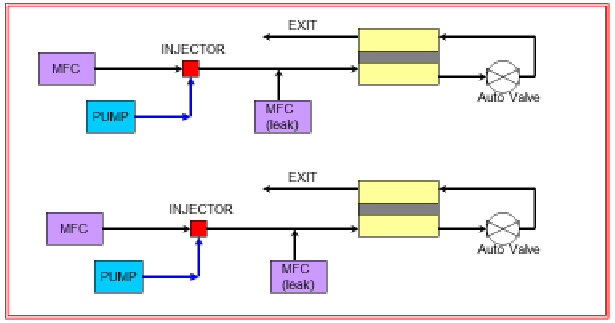
3 Fuel Cell Components



RH Cycle



Mechanical Membrane Cycling-Configuration



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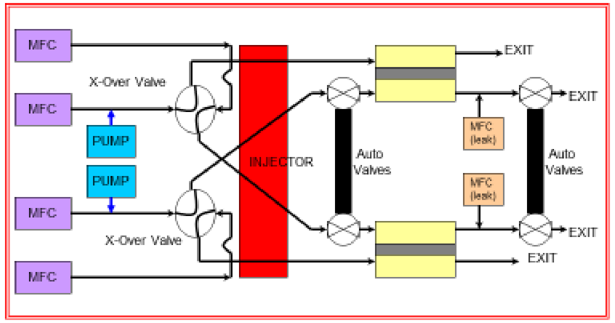
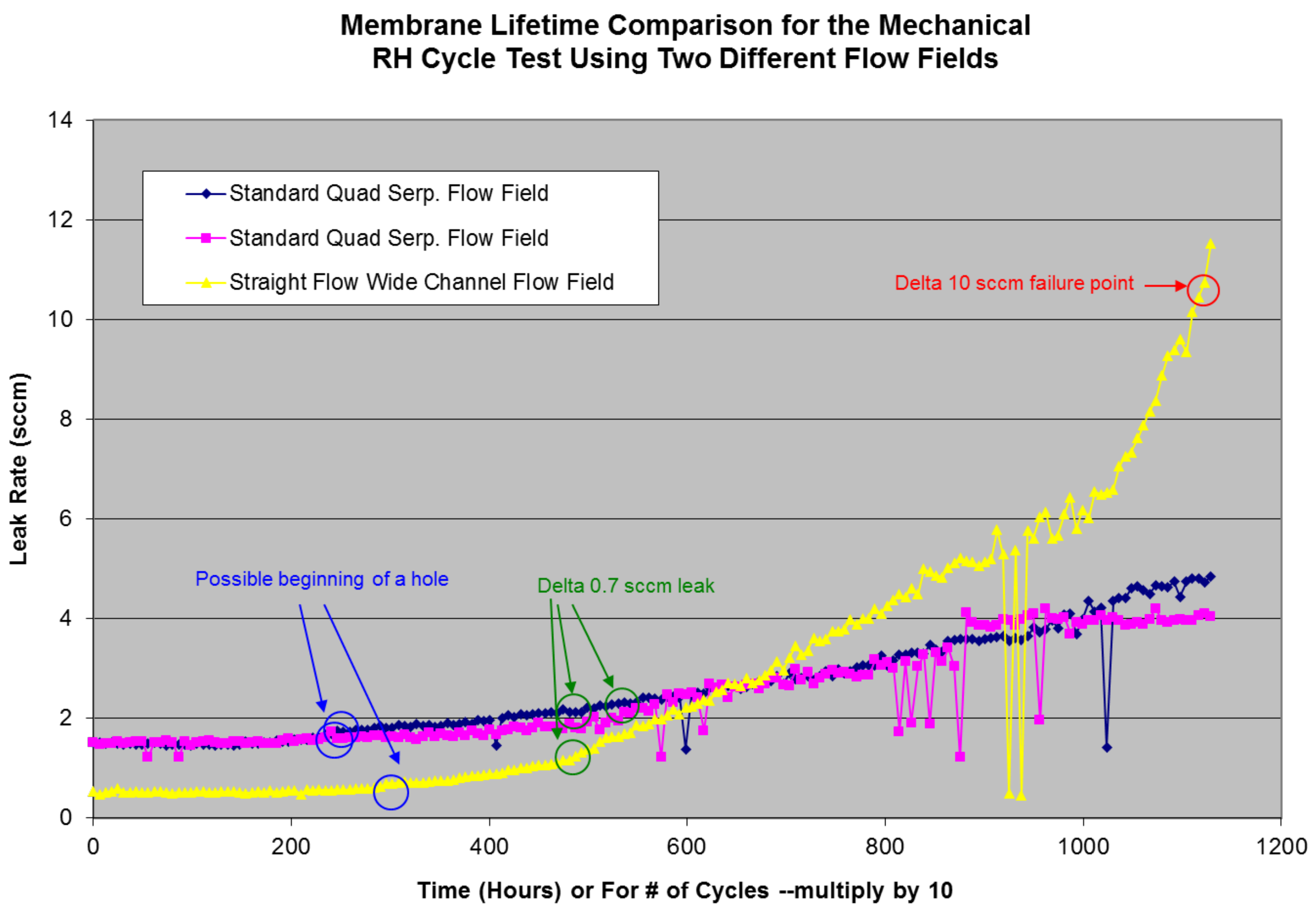


Membrane Durability Testing and Electrode Development 3   3 Fuel Cell Components

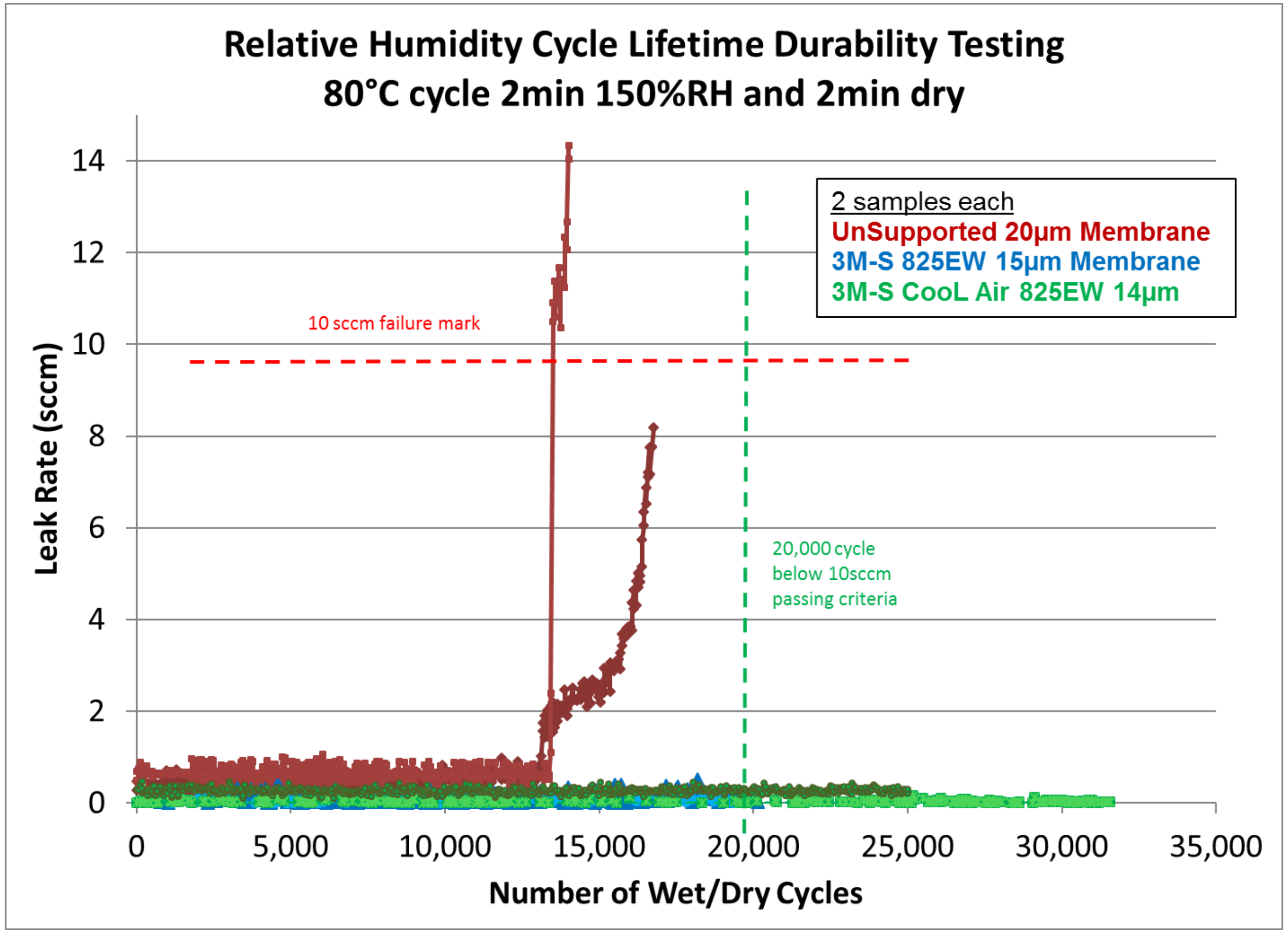
RH Cycle



Membrane Lifetime Comparison for the Mechanical
RH Cycle Test Using Two Different Flow Fields
Standard Quad Serp. Flow Field
Standard Quad Serp. Flow Field
Straight Flow Wide Channel Flow Field
Delta 10 sccm failure point
Possible beginning of a hole
Delta 0.7 sccm leak
Leak Rate (sccm)
Time (Hours) or For # of Cycles --multiply by 10
0
2
4
6
8
10
12
14
0
200
400
600
800
1000
1200

3M

Unsupported and Supported PFSA

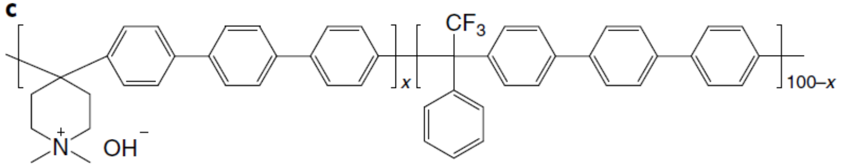


3M

RH Cycle on AEM membrane

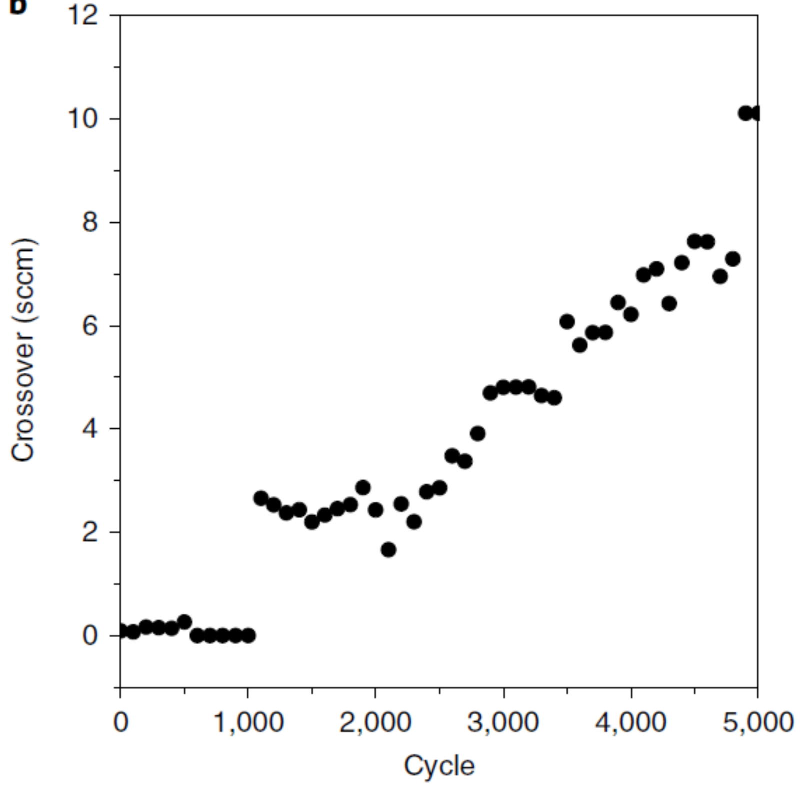
Relative humidity cycling test. PAP-TP-85 membrane (25 µm, bicarbonate form) was assembled in 5 cm² fuel cell test hardware using SGL 39BC gas diffusion layers and polytetrafluoroethylene (PTFE)-coated fibre glass gaskets. Air at 1 l min⁻¹ was passed through both flow fields and the cell was held at 80 °C. The gas streams were cycled between dry (humidifier bypass) and 90 °C dewpoint with 2 min at each step. Crossover was measured every 100 wet/dry cycles by applying a 20 kPa pressure differential, closing the cathode inlet, and measuring the flow at the cathode outlet by mass flow meter.

c



PAP-TP-x

b



Wang, J., Zhao, Y., Setzler, B., Rojas-Carbonell, S., Yehuda, C., Amel, A., Page, M., Wang, L., Hu, K., Shi, L., Gottesfeld, S., Xu, B., Yan, Y. Nature Energy doi 10.1038/s41560-019-0372-8

Summary/Recommendations

- Relevant tests and methods for AEMs are likely to be different than PEMs
- Many routine measurements are harder to do well than they appear.
- Accurate relative humidity measurements are critical for RH dependent conductivity
- Conductivity measurements should specify conditions used for dimensional measurements (wet, dry, etc)
- Ion exchange methods especially important for iodide or other high affinity cations
- RH Cycle testing is both empirical and highly dependent on system design

- Even competent, conscientious, labs are prone to measurement errors…

Thank you