Automotive Perspective on PEM Evaluation

Craig Gittleman
Lab Group Manager – Membrane and Ionomer
General Motors Fuel Cell Research Lab
10 Carriage St., Honeoye Falls, NY 14472

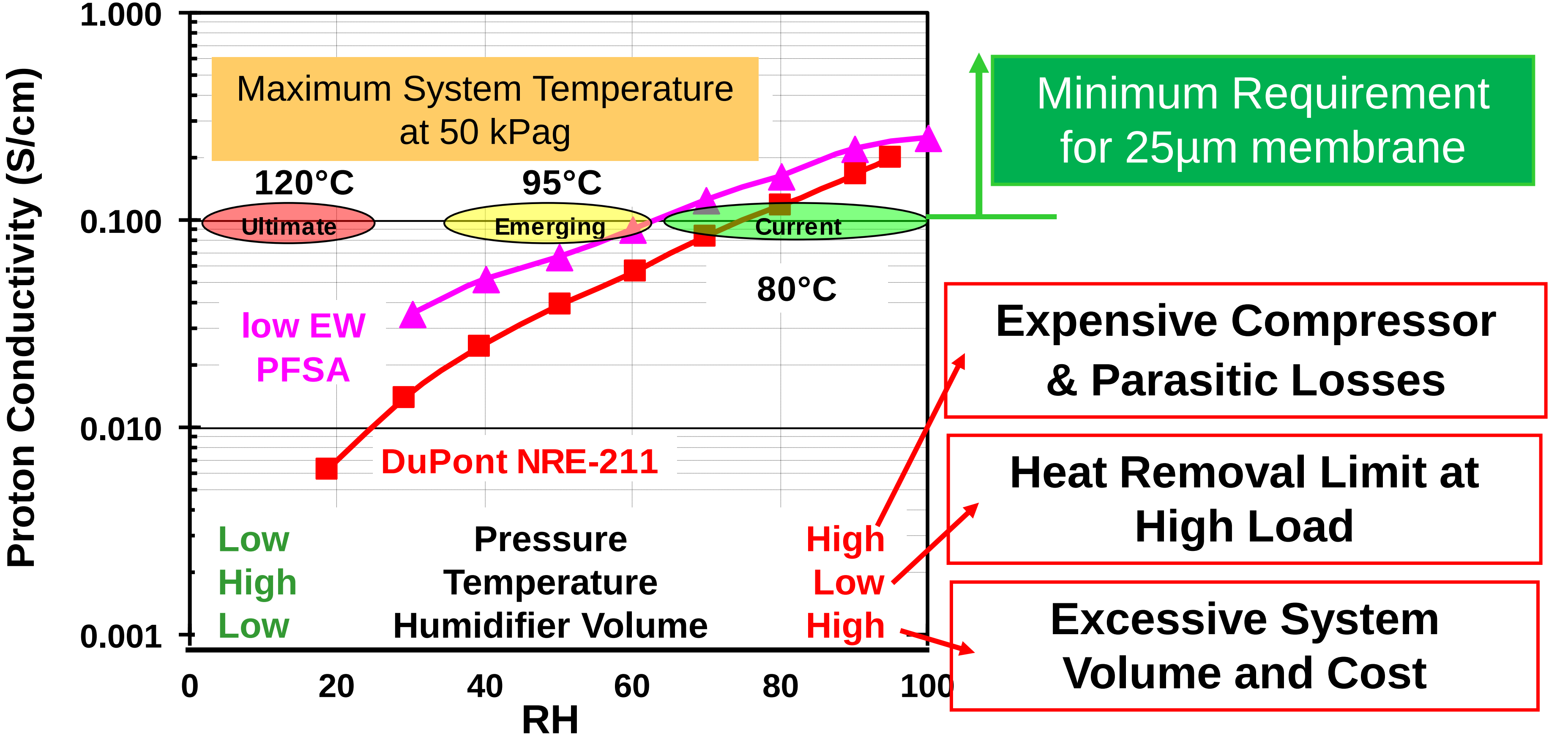
High Temperature Membrane Working Group Meeting
May 18, 2009

Outline

- Automotive PEM FC Operating Conditions
- Performance Durability Tradeoffs
- Automotive PEM Requirements
- Evaluation Test Methods
- Performance Considerations
  - Proton Transport Resistance
  - Fuel Cell Performance
  - Freeze Start
- Durability Considerations
  - Mechanical Durability
  - Chemical Durability
  - Shorting
- Summary
- Acknowledgements

Fuel Cell Membrane Needs

Membranes Need Water to Conduct Protons

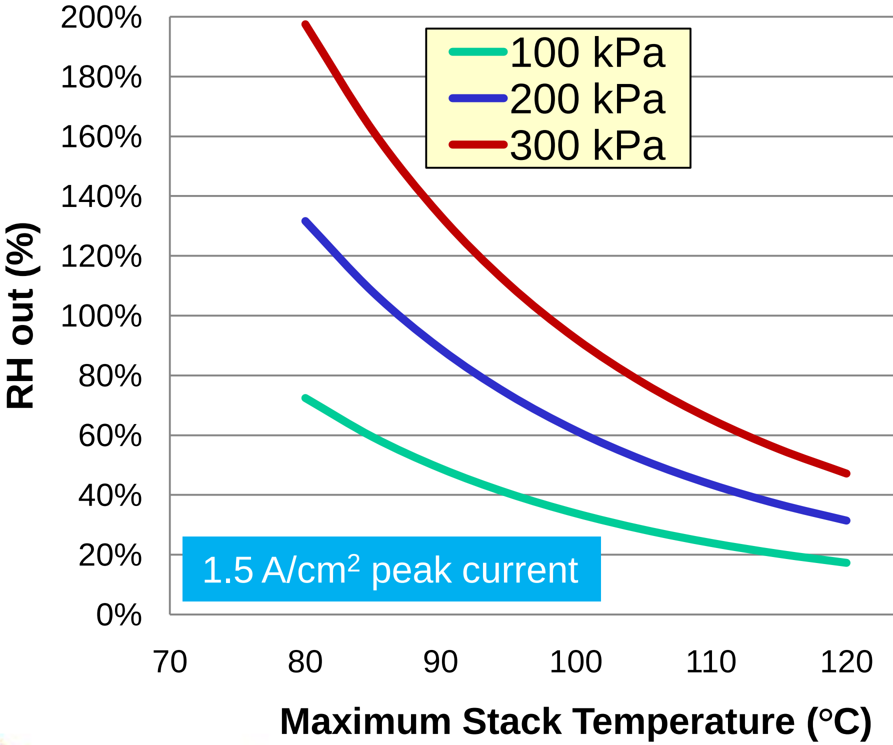


- Current membranes enable 80°C, low pressure system, but this limits maximum vehicle power due to heat removal capacity (radiator size)
- Minimum 95°C peak power operation needed for heat rejection

Automotive Operating Conditions

Automotive FC systems must be designed for their peak power operating point

- The hottest (& driest) conditions will exist at peak power
  - >90% of the time system will run colder &, thus, wetter
- Humidity will depend on system pressure
  - While there is no universal agreement among OEM's on automotive FC system pressure, systems are not expected to operate above 300 kPa-abs.
- The most desirable membranes will enable low pressure systems



Analysis done for most aggressive system including an effective cathode water recovery system and low cathode stoichs

- Current DOE target of 120°C requires >300 kPa-abs system to achieve 50% RH
- US OEMs currently focusing on 95°C peak power system, where RH could range from 40 - >100% RH depending on pressure

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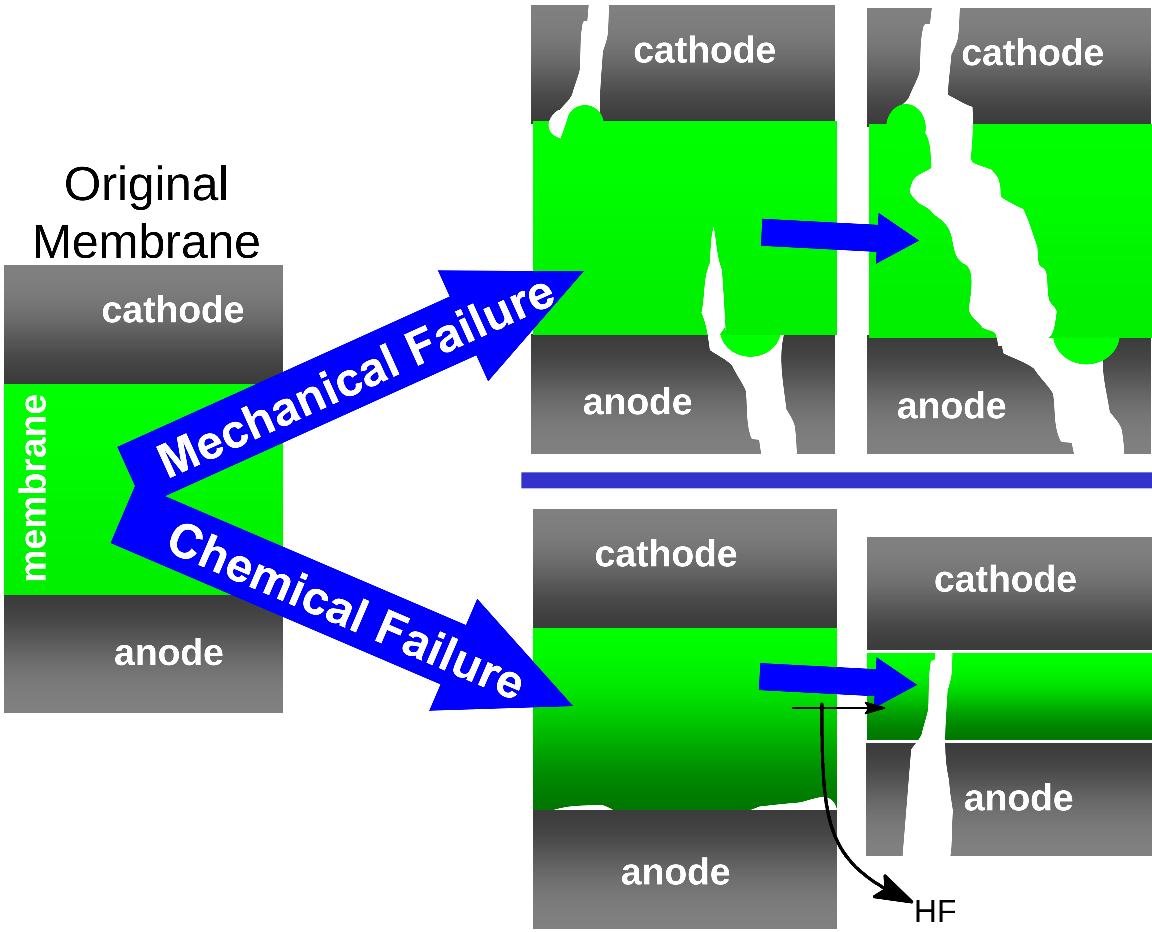
Membrane Durability



During humidity cycling

- Membrane swells/shrinks with changing relative humidity
- Repeated stressing of membrane leads to fatigue induced fracture

During fuel cell operation

- Chemical radicals generated at electrodes
- Radicals attack polymer structure of membrane
- Membrane thins, releasing HF

Membrane shorting – electronic current passes through membrane

- Caused by over-compression and/or high local potentials
- Can lead to extreme temperatures and thermal decomposition

Performance Durability Tradeoffs

Pathways to lower proton transport resistance

– More sulfonation - increased IEC (reduced EW)
  - Leads to high swelling – mechanical durability issues

– Thinner membranes
  - Higher gas crossover (efficiency penalty, accelerates failure)
  - Reduced shorting resistance

– Non-polymeric additives [Ceramics (SiO_2, ZrO, etc.), to increase water retention, Heteropolyacids for improved conductivity]
  - May embrittle membrane
  - May leach out and poison electrodes

– Improved membrane chemistry/morphology
  - Better pathways for proton & water transport
  - Potential to also improve durability

Performance Durability Tradeoffs

Pathways to Improved Durability

- Composite membranes [polymer supports, elastomer blends]
  - Non-conductive component increases proton transport resistance
- Chemical stabilizing additives [Ce^{3+}, Mn^{2+}]
  - Can bind to acid sites and lower conductivity
  - Can move to electrodes during operation and impact performance
- External Reinforcement
  - Can add additional electron and gas transport resistances to cell
- Lower compression (for shorting)
  - Increased contact resistance at material interfaces
- Improved membrane chemistry/morphology
  - Reduced swelling & improved strength
  - Potential to also improve performance

Proton Exchange Membrane Targets

Characteristic		Units	DOE 2010 target	DOE 2015 target	GM target
Maximum operating temperature		°C	120	120	95
Area specific proton transport resistance	Maximum operating temp and water partial pressures from 40 to 80 kPa	Ohm cm^2	0.02	0.02	.025
	80°C and water partial pressures from 25 - 45 kPa	Ohm cm^2	0.02	0.02	.025
	30°C and water partial pressures up to 4 kPa	Ohm cm^2	0.03	0.03	NA
	-20°C	Ohm cm^2	0.2	0.2	NA
Maximum Oxygen cross-over[b]		mA/cm^2	2	2	NA
Maximum Hydrogen cross-over[b]		mA/cm^2	2	2	5
Minimum Electrical resistance		$\Omega*cm^2$	1000	1000	1000
Cost (500K veh/yr)		$\$/m^2$	20	20	10[a]
Mechanical Durability		RH Cycles	20,000	20,000	20,000
Chemical Durability		hours	500	500	500
Unassisted start from	(MEA target w/ membrane impact)	°C	-40	-40	-40

[a] 1MM veh/yr
[b] Tested in MEA at 1 atm O_2 or H_2 at nominal stack operating temperature

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GM testing of PEMs

Ex-situ Membrane Tests

Test	Properties
Water Mass Uptake	Liquid Water Capacity
Water Isotherms	λ vs. RH
Dimensional Stability	Volumetric Swelling & Shrinking in Water
Tensile Tests	Elastic Modulus, Yield Strength, Tensile Strength, Elongation
Tear Tests	Fracture Toughness
Blister Test	Burst Strength, Biaxial Fatigue
Dynamic Mechanical Analysis	Storage/Loss E, T_g, Master Curve, Shift Factor
Shrink Tension	Residual Stress
Ion Exchange Capacity	Concentration of SO_3H (or other acid)
In-plane Conductivity	Conductivity vs T, RH (including freeze to -40°C)

GM testing of PEMs

In-situ Membrane Tests

Test	Properties
Gas Permeability Tests	H_2, N_2, O_2 permeability/crossover
Water Transport	Water permeability
Electrical Resistance	Membrane shorting
Electrical Impendence Spectroscopy (MEA)	Through-plane membrane resistance and electrode proton transport resistance
Fuel Cell tests (MEA) • Polarization curves • Temperature sensitivity • RH sesnsitivity • Pressure sensitivity	Fuel Cell performance
Fuel Cell durability (MEA) • RH cycling • OCV degradation • High Voltage – Pressure Ramp • Accelerated Durability	 • Membrane mechanical durability • Membrane chemical durability • Accelerated shorting resistance • All of the above
Charge Storage (MEA)	Water capacity during freeze start

Membrane Shorting and Crossover tests

Objective: Evaluate membrane for shorting and gas crossover

Method: 50 cm^2 fuel cell test

Standard electrodes, carbon fiber GDM with MPL

- Compress to 20% GDM strain
- Standard test: Fully humidified, room temperature, no back pressure
- Also test under range of FC operating conditions

Shorting: N_2/N_2, 0.5V DC

H_2 Cross-over: H_2/N_2, 0.5V DC

Targets

Shorting: $> 1000\ \Omega \cdot cm^2$

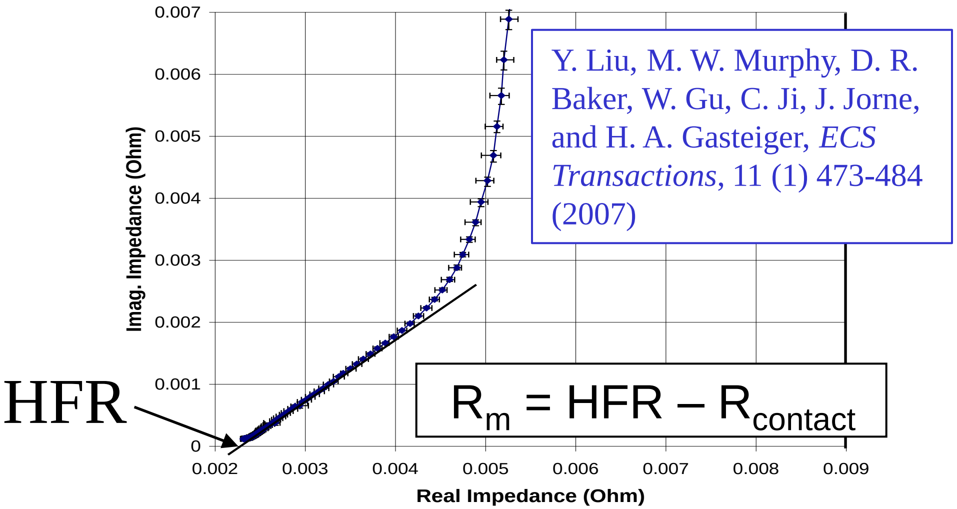
H_2 Cross-over: $< 5\ mA/cm^2 \cdot atm$

Targets should be met at beginning of life and after durability testing

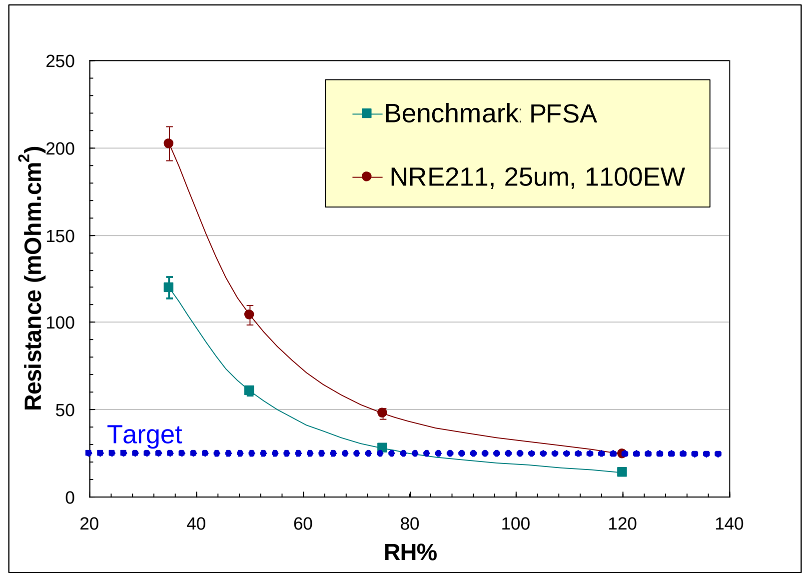
In-Situ Proton Transport Resistance using AC Impedance

Through plane membrane resistance is best indicator of membrane performance – accounts for membrane thickness & proton conductivity

- Principle: AC impedance spectrum to measure High Frequency Resistance (HFR) at real axis intercept in H_2/N_2 cell
- Run tests as a function of temperature and RH



$$R_m = HFR - R_{contact}$$

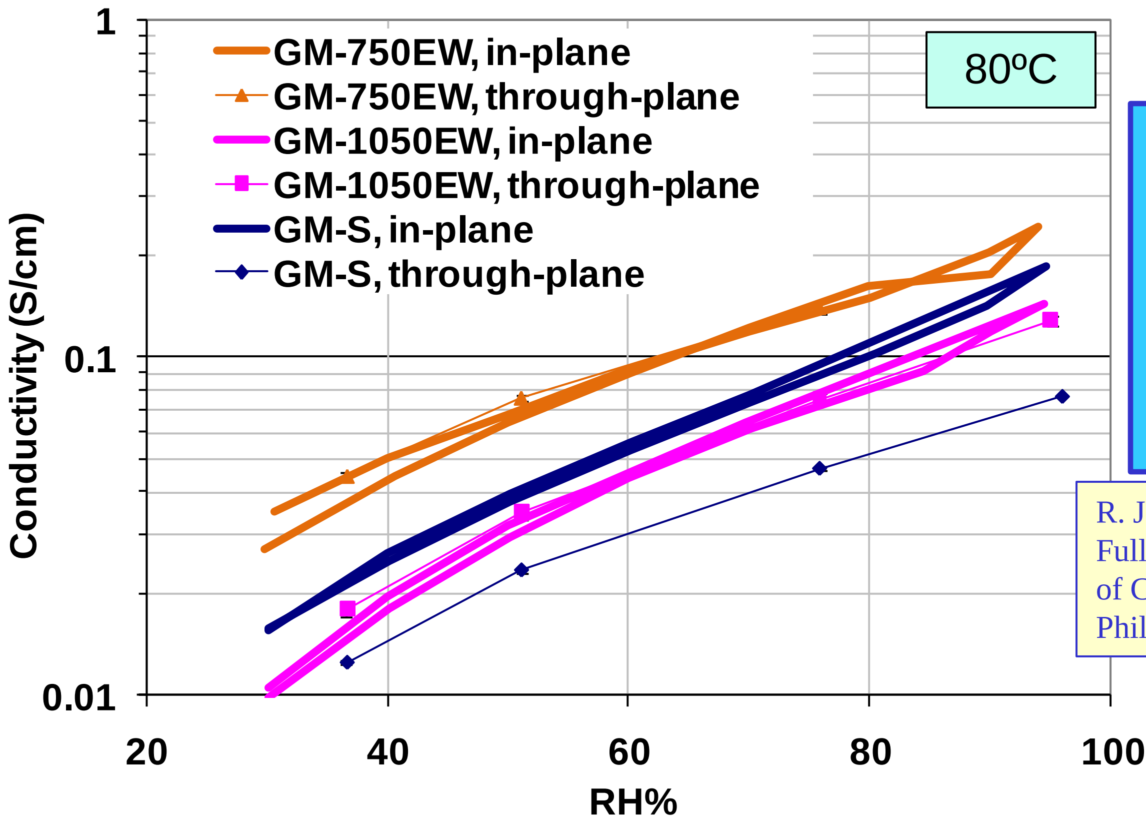


The measured HFR needs to be corrected for contact resistance

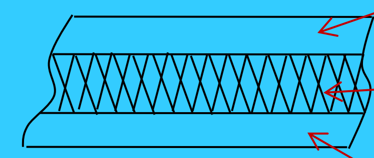
- Run “Blank” cells using gold foil instead of PEM
- Run membranes with various thickness and extrapolate to zero thickness

- In-situ resistance of Nafion NRE-211 meets target at >100% RH
- Benchmark PFSA meets target at 75% RH

Proton Conductivity: In-Plane *vs.* Through-Plane



GM-S: Supported PFSA



R. Jiang, M. Murphy, C. Mittelsteadt, T. Fuller, C. Gittleman, " American Institute of Chemical Engineering Annual Meeting, Philadelphia, PA, November 16 – 21, 2008

- Homogeneous membranes: GM-750 and GM-1050, through-plane conductivity agrees with the in-plane conductivity.
  - Indication of good determination of $R_{contact}$
- Non-homogeneous membrane GM-S with support layer: in-plane conductivity is about twice (50%RH) the though-plane conductivity.
  - Due to high resistance of support layer and swelling anisotropy

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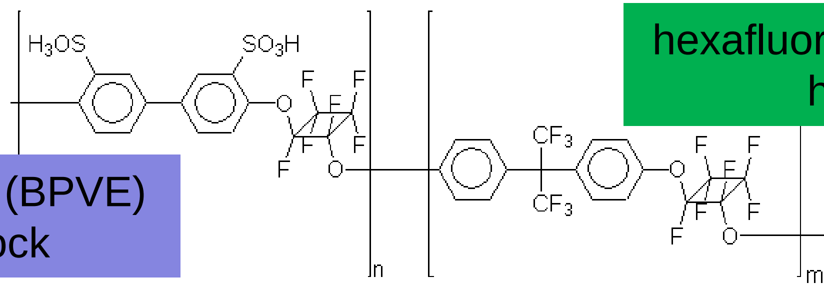
Beware of Focusing Solely on Conductivity

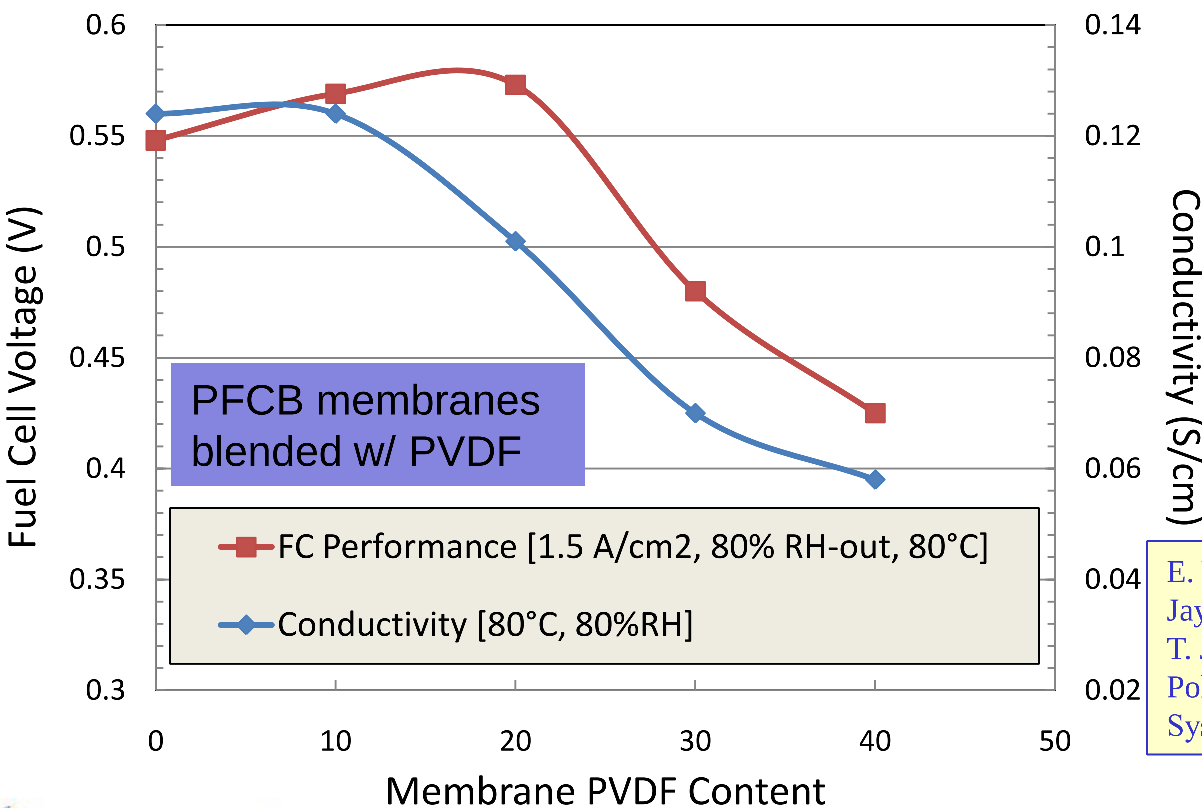
Sulfonated Perfluorocyclobutane (PFCB) Block Coploymers



hexafluorobiphenyl vinyl ether (6F) hydrophobic block

biphenyl vinyl ether (BPVE) hydrophilic block

In collaboration with Tetramer Technologies



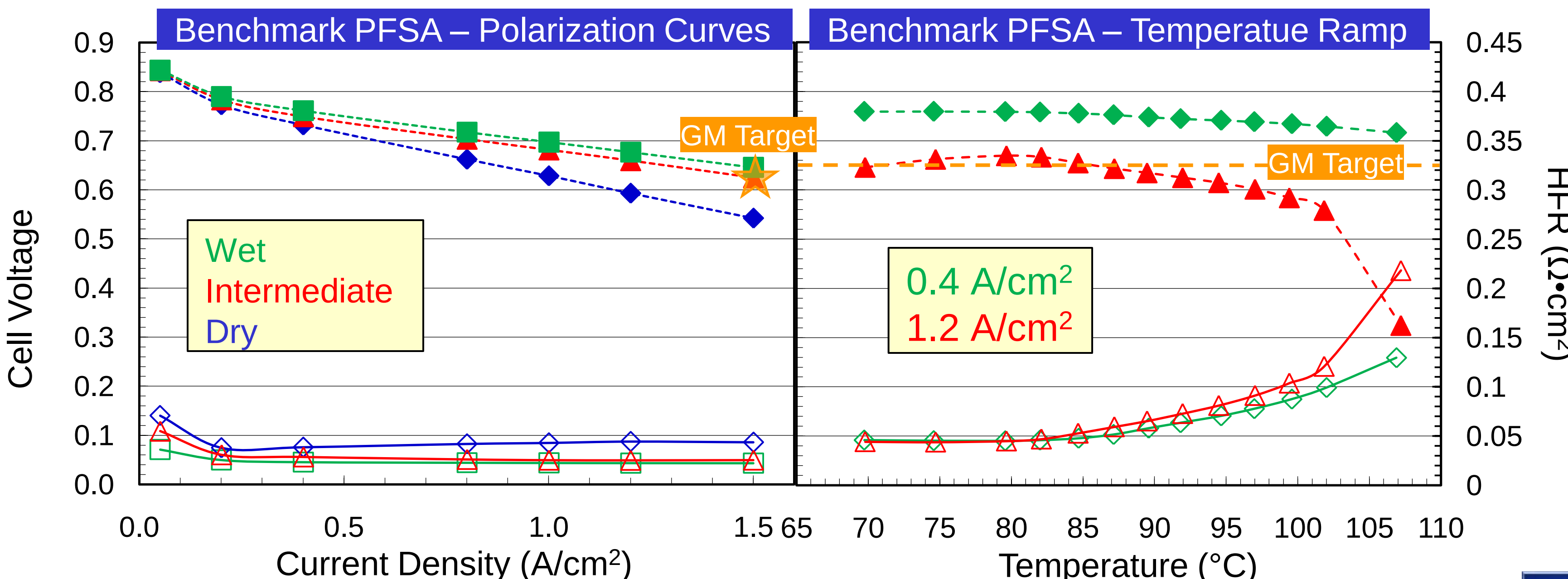
- Fuel Cell testing is the best indicator of membrane performance
- Actual membrane RH is extremely sensitive to in cell water transport

E. Wagener, D. Smith Jr., C. Topping, R. Jayasinghe, J. Jin, A Singh, S M. MacKinnon, T. J. Fuller, and C. S. Gittleman “Advances in Polymer Electrolyte Membrane Fuel Cell Systems 2009”, Pacific Grove, Ca.

Membrane Performance Screening

50 cm² H_2-Air fuel cell test (Standard GM flowfields, electrodes & GDM, counterflow)

1. Polarization Curves (V vs. i) over range of RH & temperature (50 kPag)
   - Wet (110% RH out, 80°C)
   - Intermediate (85% RH out 80°C)
   - Dry (55% RH out, 95°C)
2. Humidity Sweep at fixed temperature & current (50 kPag)
   - 1.5 A/cm² – 80°C, 95°C
3. Temperature Ramp with fixed inlet humidification (62°C dew pt., 50 kPag)
   - 0.4 A/cm², 1.2 A/cm² & 1.5 A/cm²



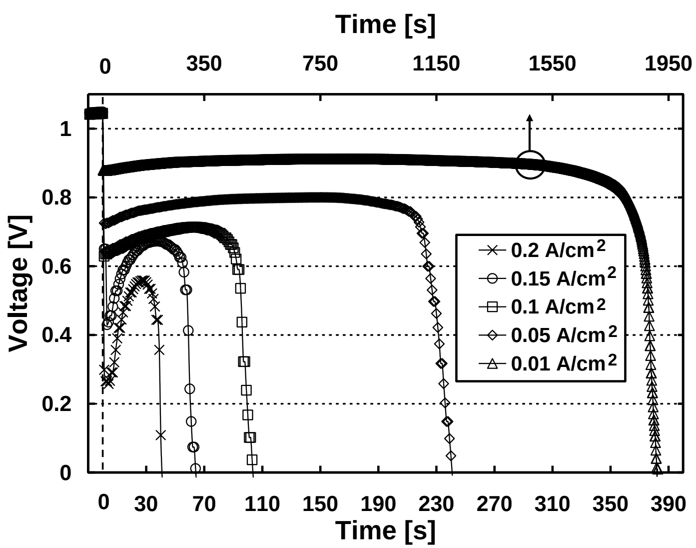
Freeze Start Considerations

- Membrane must conduct protons at low temperatures (to -40°C) to enable freeze start – but proton transport resistance is not limiting
- Membrane must have significant capacity for water so the water generated by ORR does not freeze in electrode pores & GDL during freeze start (thus cutting off O_2 transport) before cell gets hotter than 0°C.

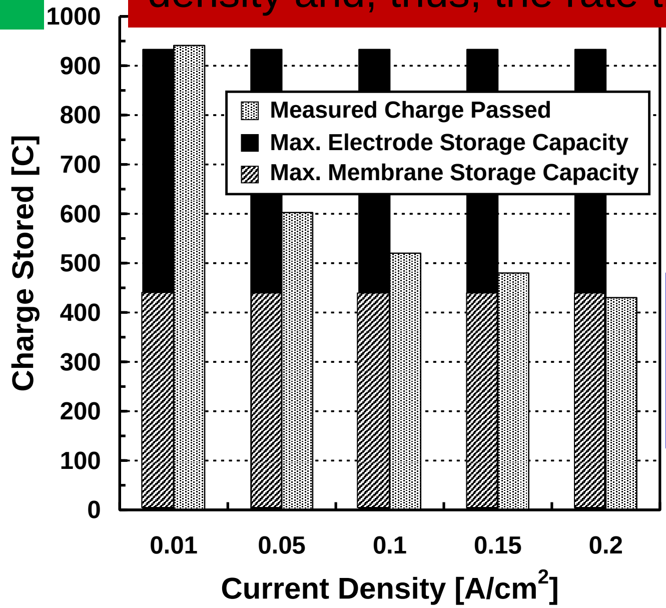
➢ Both considerations are strongly dependent of hydration state of membrane at shutdown and startup strategy (especially current density).

Charge storage test

- Precondition cell at membrane λ~ 3.5
- Run at -20°C until voltage drops



Membrane water uptake rate at low temperature limits start-up current density and, thus, the rate that cell heats



E. L. Thompson, W. Gu, J. Jorne, and H. A. Gasteiger, *J. Electrochem. Soc.*, **155(6),** (2008).

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Membrane Mechanical Durability

Table 4 Membrane Mechanical Cycle and Metrics (Test using a MEA)		
Cycle	**Cycle 0% RH (2 min) to 90°C dewpoint (2 min), single cell 25-50 cm^2**	
Total time	Until crossover >2 mA/cm^2 or 20,000 cycles	
Temperature	80°C	
Relative Humidity	Cycle from 0% RH (2 min) to 90°C dew point (2 min)	
Fuel/Oxidant	Air/Air at 2 SLPM on both sides	
Pressure	Ambient or no back-pressure	
Metric	**Frequency**	**Target**
Crossover*	Every 24 h	$\leq$2 mA/cm^2
Shorting resistance	Every 24 h	>1,000 ohm cm^2

* Crossover current per USFCC "Single Cell Test Protocol" Section A3-2, electrochemical hydrogen crossover method

- Results very sensitive to cell design and specific operation
  - Flow field geometry, compression, GDL, MEA processing, wetting & drying rates
- Recommend to benchmark against NRE-211 with specific set-up
  - NRE-211 should fail at ~5000 cycles

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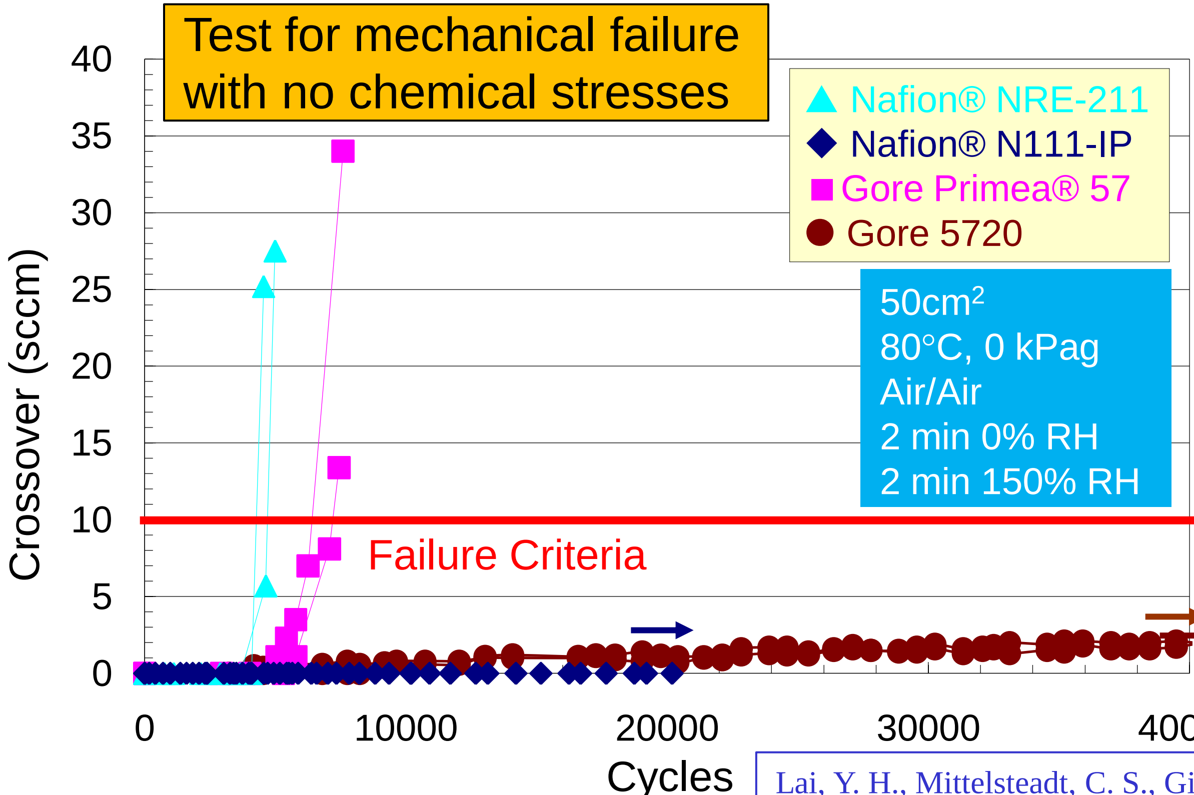
Humidity Cycling of PFSA Membranes



Lai, Y. H., Mittelsteadt, C. S., Gittleman, C. S., and Dillard, D. A., *ASME J. Fuel Cell Sci. Tech.*, **6** (2009) 21002.

<u>Homogeneous Membranes</u>

- DuPont™ NRE-211
  - 25µm, 1100EW cast Nafion®
- Ion Power™ N111-IP
  - 25µm, 1100EW extruded Nafion®

<u>Composite Membranes</u>

- Gore™ Primea® Series 57 (Expanded PTFE filled Reinforcement)
- Gore™ Primea® 5720 (Improved Reinforcement)

- Humidity cycling accelerates mechanical failures in the absence of electrochemical degradation
- Different processing methods for same polymer dramatically effects humidity cycling durability
- Mechanical reinforcement can help prevent humidity cycling induced crossover leak, but is not required

Tensile Properties of PFSA Membranes

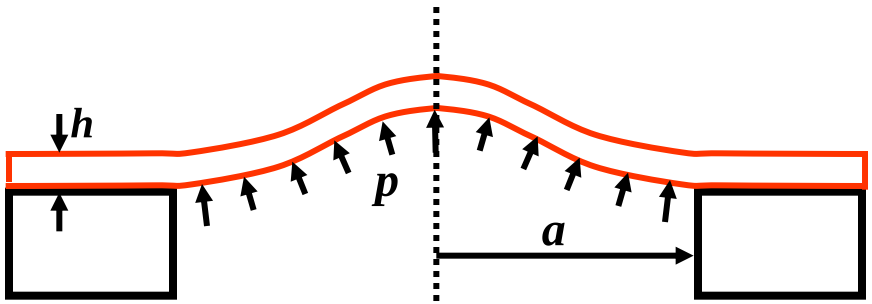
- ASTM method D882

Gittleman, C.S., Lai, Y.H., and Miller D., *Proceedings from the 2005 AIChE Annual meeting*, Cincinnatti, OH (2005)

Membrane		**NRE-211**		**N111-IP**		**Gore Primea® 57**	
	units	MD	TD	MD	TD	MD	TD
50% RH, 23°C							
Tensile Strength	MPa	**30.5**	**28.0**	**32.6**	**37.5**	**35.0**	**32.3**
Yield Strength (2% offset)	MPa	**14.4**	**14.0**	**14.1**	**14.9**	**18.0**	**15.6**
Elongation	%	**253**	**235**	**176**	**141**	**196**	**147**
Young's Modulus	MPa	**272**	**253**	**304**	**319**	**324**	**340**
submerged, 80°C							
Tensile Strength	MPa	**8.9**	**9.5**	**17.2**	**16.1**	**18.4**	**15.1**
Yield Strength (2% offset)	MPa	**4.4**	**4.6**	**5.0**	**5.3**	**5.2**	**4.1**
Elongation	%	**159**	**188**	**193**	**127**	**153**	**157**
Young's Modulus	MPa	**23.9**	**25.1**	**45.0**	**51.5**	**58.0**	**28.3**

- Tensile properties of N111-IP not superior to other PFSA membranes
- Cannot use tensile tests as predictor for mechanical durability

Blister Membrane Strength Test



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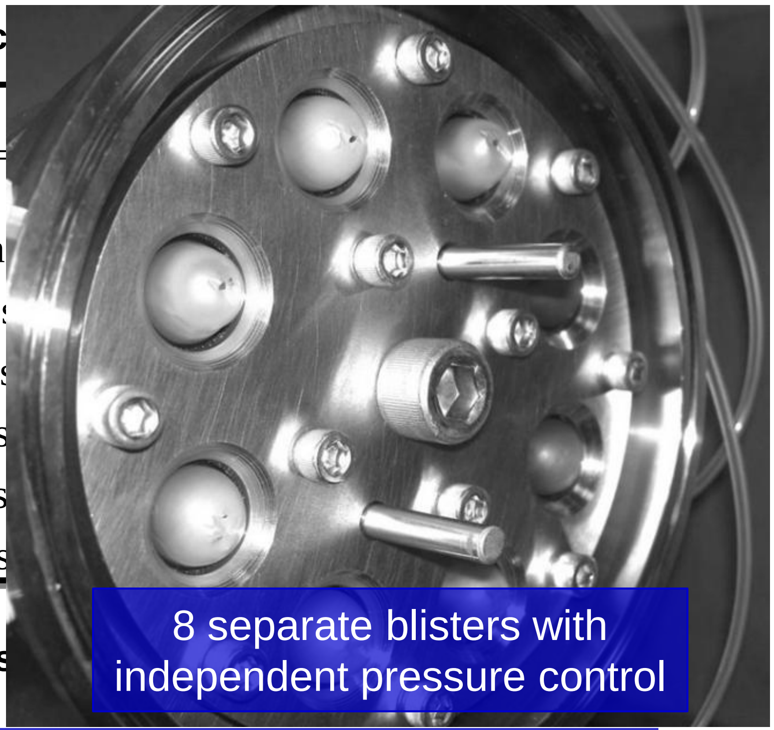
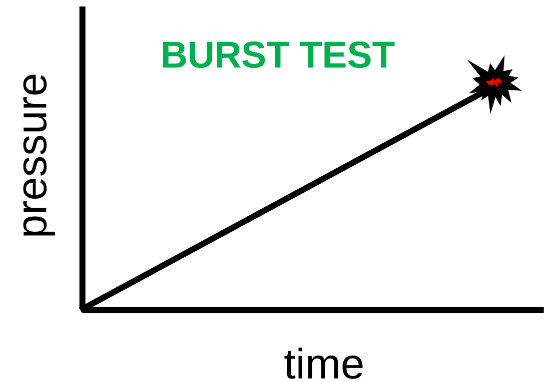
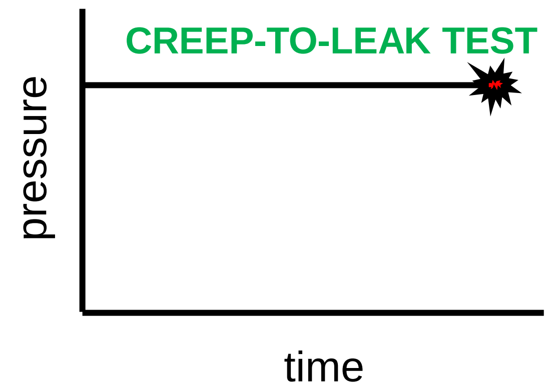
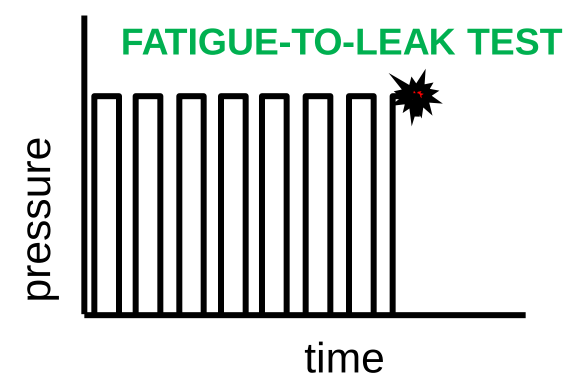


Quasielas
Hencky's

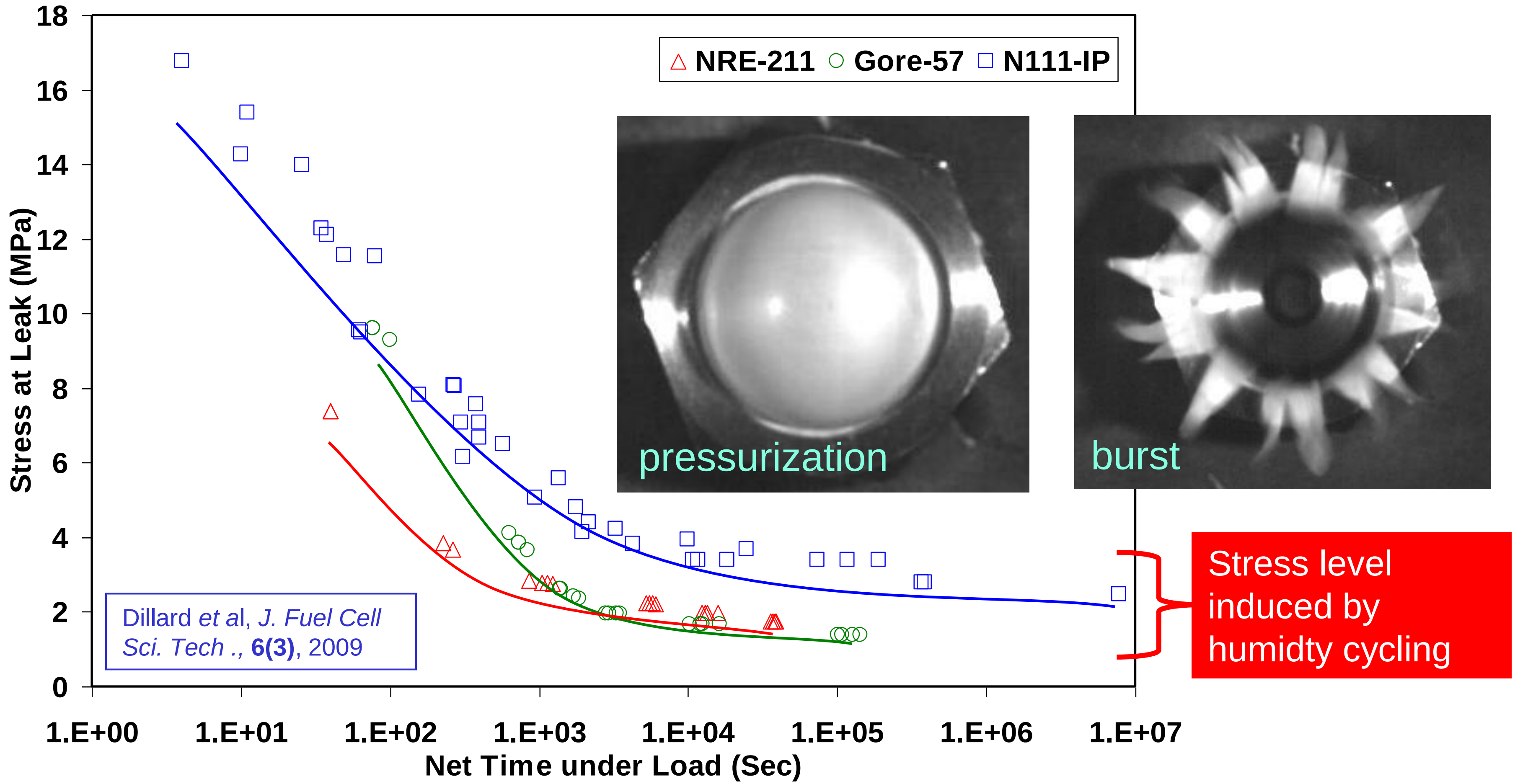






Dillard, D. A., Li, Y., Grohs, J., Case, S. W., Ellis, M. W., Lai, Y. H., Budinski, M. K., and Gittleman, C. S., *J. Fuel Cell Sci. Tech.*, **6(3)**, 2009

Creep Blister Strength of PFSA Membranes



- At stress levels expected during automotive operation extruded Nafion 111-IP oulasts Gore-Select 57 & Nafion NRE-211 by 10-100X
- This ranking agrees with the ranking from humidity cycling tests.

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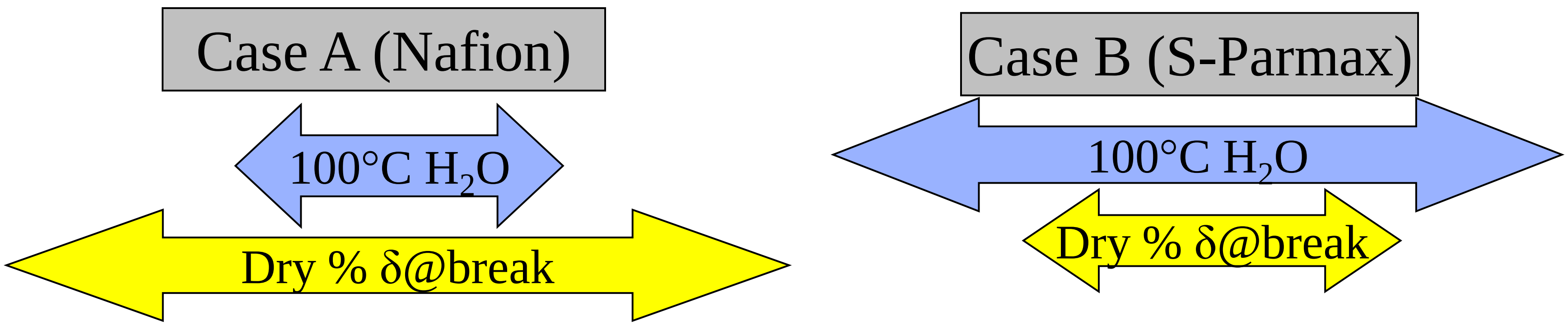
Simple Mechanical Durability Screening

If facilities are not available for RH cycling or blister testing, at the very least , measure swelling and elongation to break

Tests Required

- Tensile Elongation to break at ambient conditions
- Linear Swelling in boiling water

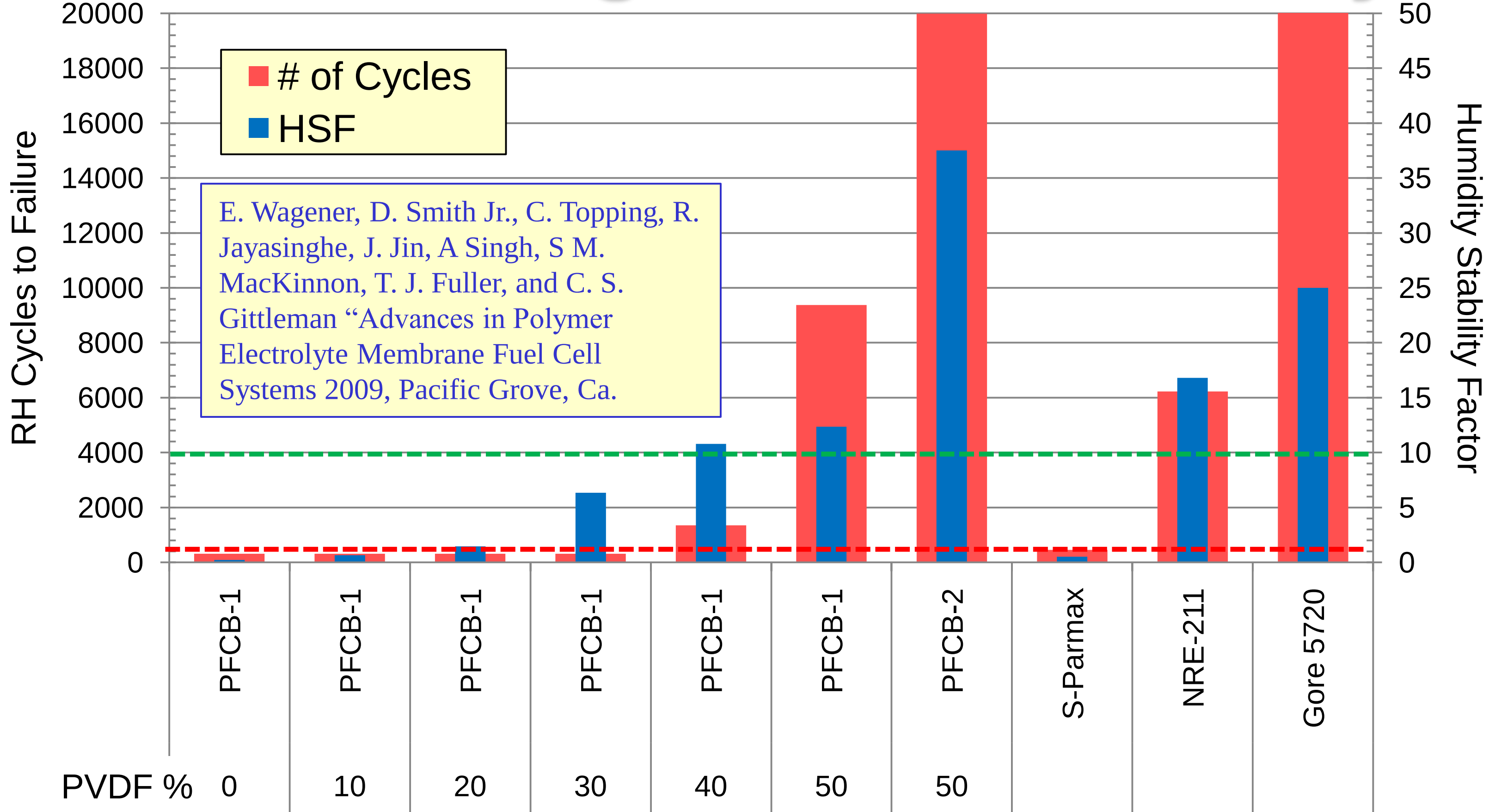
Sanity Check: Does the membrane stretch more when dry then it swells when wet?



$$\text{Humidity Stability Factor (HSF)} = \frac{\text{strain @ break (25°C ,50\%RH)}}{\text{linear swelling (100°C } H_2O)}$$

MacKinnon, S. M., T. J. Fuller, F. D. Coms, M. R. Schoeneweiss, C. S. Gittleman, Y-H Lai, R. Jiang and A. Brenner, *Encyclopedia of Electrochemical Power Sources, Edited by Juergen Garche, Elsevier,* (2009) in press

Correlating HSF w/ Durability



General guidelines

- If HSF<1: find a way to reduce swelling and improve elasticity ASAP
- If 1<HSF<10: I'd still focus on reducing swelling and improving elasticity, but at least it's worth running FC tests
- If HSF>10: material may be durable enough with MEA optimization

Screening for PEM Chemical Stability

Ex-situ Fenton's ageing tests are not representative of *in-situ* fuel cell degradation

- Initial H_2O_2 concentration much higher than observed in operating fuel cells
- H_2O_2 concentration decreases rapidly with time
- Absence of H_2
- Presence of liquid water

Consequences of depending on Fenton's tests

- False positives
  - End group stabilized PFSA membranes are stable in Fenton's solutions, but degrade rapidly in *in-situ* accelerated fuel cell tests [N. Cipollini, *ECS Transactions.* **11 (1),** 1071 (2007); F. D. Coms, H. Liu, J. E. Owejan, *ECS Transactions*, **16 (2)**, 1735-1747 (2008).]
- False negatives
  - BPSH membranes degrade rapidly in Fenton's solutions, but are relatively stable in *in-situ* accelerated fuel cell tests [Sethuraman *et al*, *JECS,* **155 (2),** B119-B124 2008]

Membrane Chemical Durability

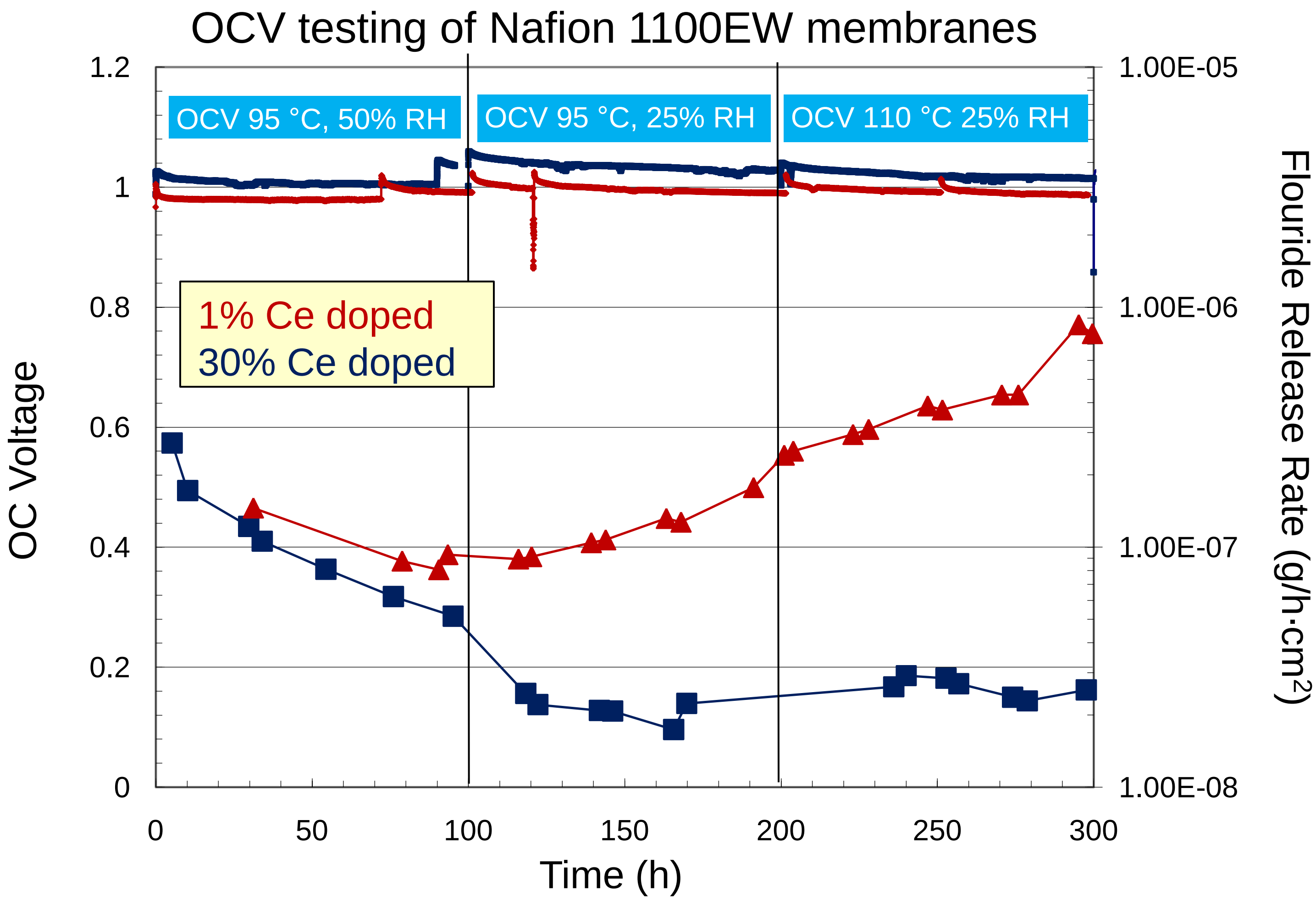
Table 3 MEA Chemical Stability and Metrics		
Test Condition	**Steady state OCV, single cell 25-50 cm^2**	
Total time	500 h	
Temperature	90ºC	
Relative Humidity	Anode/Cathode 30/30%	
Fuel/Oxidant	Hydrogen/Air at stoics of 10/10 at 0.2 A/cm^2 equivalent flow	
Pressure, inlet kPa abs (bara)	Anode 150 (1.5), Cathode 150 (1.5)	
Metric	**Frequency**	**Target**
F$^-$ release or equivalent for non-fluorine membranes	At least every 24 h	No target – for monitoring
Hydrogen Crossover (mA/cm^2)*	Every 24 h	$\leq$2 mA/cm^2
OCV	Continuous	$\leq$20% loss in OCV
High-frequency resistance	Every 24 h at 0.2 A/cm^2	No target – for monitoring
Shorting resistance	Every 24 h	>1,000 ohm cm^2

*Crossover current per USFCC "Single Cell Test Protocol" Section A3-2, electrochemical H2 crossover method

- Incorporation of chemical stabilizers has enabled excellent chemical stability
  - GM has developed a new OCV test that stepwise increases stress

Step	duration	temperature	RH	
1	100 h	95°C	50%	All steps run at OCV in H_2/Air with stoics of 5/5 at 0.2 A/cm^2 equivalent flow and 150 kPa-abs
2	100 h	95°C	25%	
3	100 h	110°C	25%	

Accelerated Membrane Chemical Durability

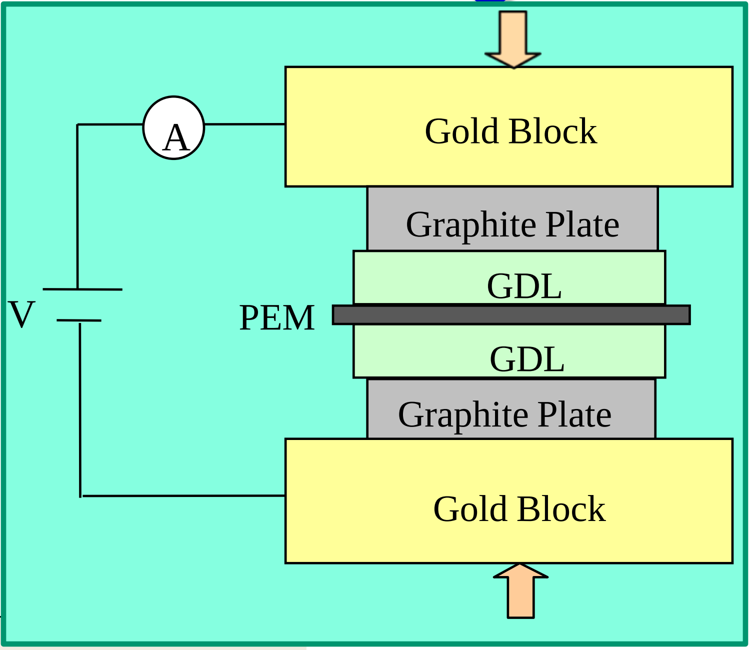


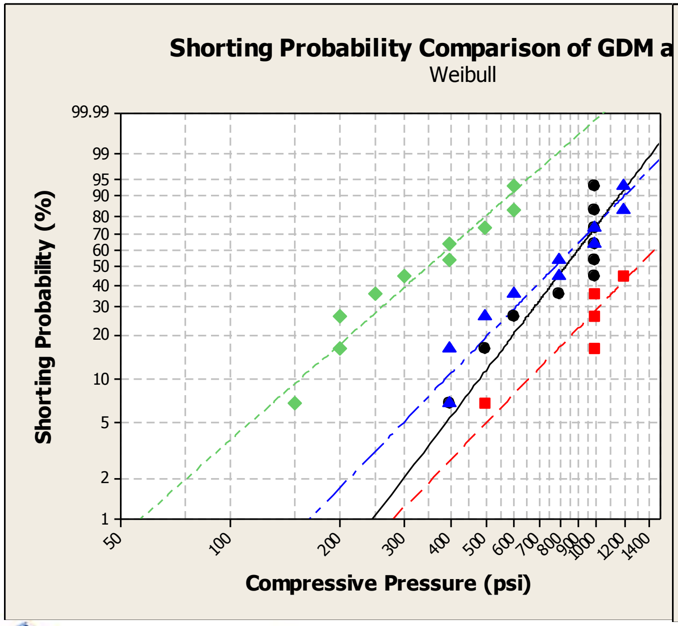
- At short times (< 100h) & standard conditions – no separation between low & high stabilization levels
- At longer times and hotter/dryer conditions, separation is observed

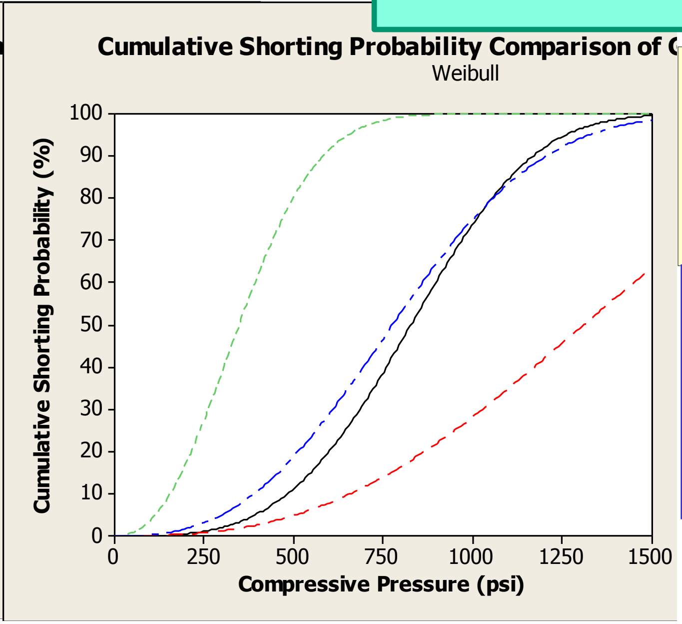
Accelerated Membrane Shorting

<u>Test Procedure</u>

- Bare membrane or non-platinized MEA
- Sandwiched between GDL and flat graphite plates
- Conditions can be controlled – standard test is in air, ambient temp & RH (also test dry at 95ºC)
- Ramp potential from 0-5V (0.5V/s) - monitor current
- Record whether or not membrane shorts (indicated by current spike)
- Increase compression stepwise from 100 - 1200psi
- ~10 samples to get Weibull plot







GDL -A, 20µm PEM
GDL -B, 20µm PEM
GDL -A, 12µm PEM
GDL -B, 12µm PEM

Membrane & GDL type & compression all impact membrane shorting

Summary

- Performance, durability and cost must all be considered when developing materials for automotive fuel cell systems.
- Measurements must be conducted at relevant operating conditions.
  - US OEMs focusing on temperatures up to 95ºC and humidities between 40-100% RH.
- A proper set of *ex-situ* tests can be used for initial screening of novel PEM materials.
  - eg, Humidity Stability Factor and/or blister tests for mechanical durability
- *In-situ* performance and durability testing is essential for novel PEM evaluation – but results are very sensitive to MEA & cell design.
  - Appropriate benchmarking is necessary.
  - Collaborations for MEA preparation & evaluation are needed.
- At sub-freezing temperatures, membrane rate and amount of water uptake is just as important as membrane conductivity.
- Critical membrane failure modes of mechanical degradation, chemical degradation & shorting must be all be considered.
- Please call or write your congressmen and representatives to urge their support for continued government funding for Hydrogen Fuel Cell development.

Acknowledgements

<u>General Motors Fuel Cell Research Labs</u>

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Eric Thompson

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Cortney Mittelsteadt

<u>Virginia Tech</u>

David Dillard
Scott Case
Michael Ellis