Membrane Performance and Durability Overview for Automotive Fuel Cell Applications

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Outline

- Fuel Cell Vehicle Commercialization
  – Automotive Competitive Fuel Cell Membrane Requirements
- Proton Exchange Membranes
  – Performance: Requirements & Status
  – Durability: Requirements & Status
- Closing

Vehicle Commercialization Requirements

H1 H_2-FC Vehicle (2000):

H3 H_2-FC Vehicle (2003):

GM/Opel Vehicle Prototypes

- **External humidified H_2/air**
- **Reduced passenger/trunk space**

- **Internal humidification**
- **Reduced range & peak power**

Commercialization Requirements:

- Performance – at least equal to internal combustion engine vehicles
- Durability – 6000 hours service, 10 years life
- Cost -- $5000 for power train including H_2 storage
  - About $50/kW for 100 kW system
  - Less than $10/kW target for membrane electrode assembly (supported catalyst, membrane, diffusion media, fabrication)

Automotive FC System Operating Conditions

Fuel cell materials and design that enable higher temperature operation will be preferred in vehicle applications.

- smaller radiator
- greater packaging / styling flexibility

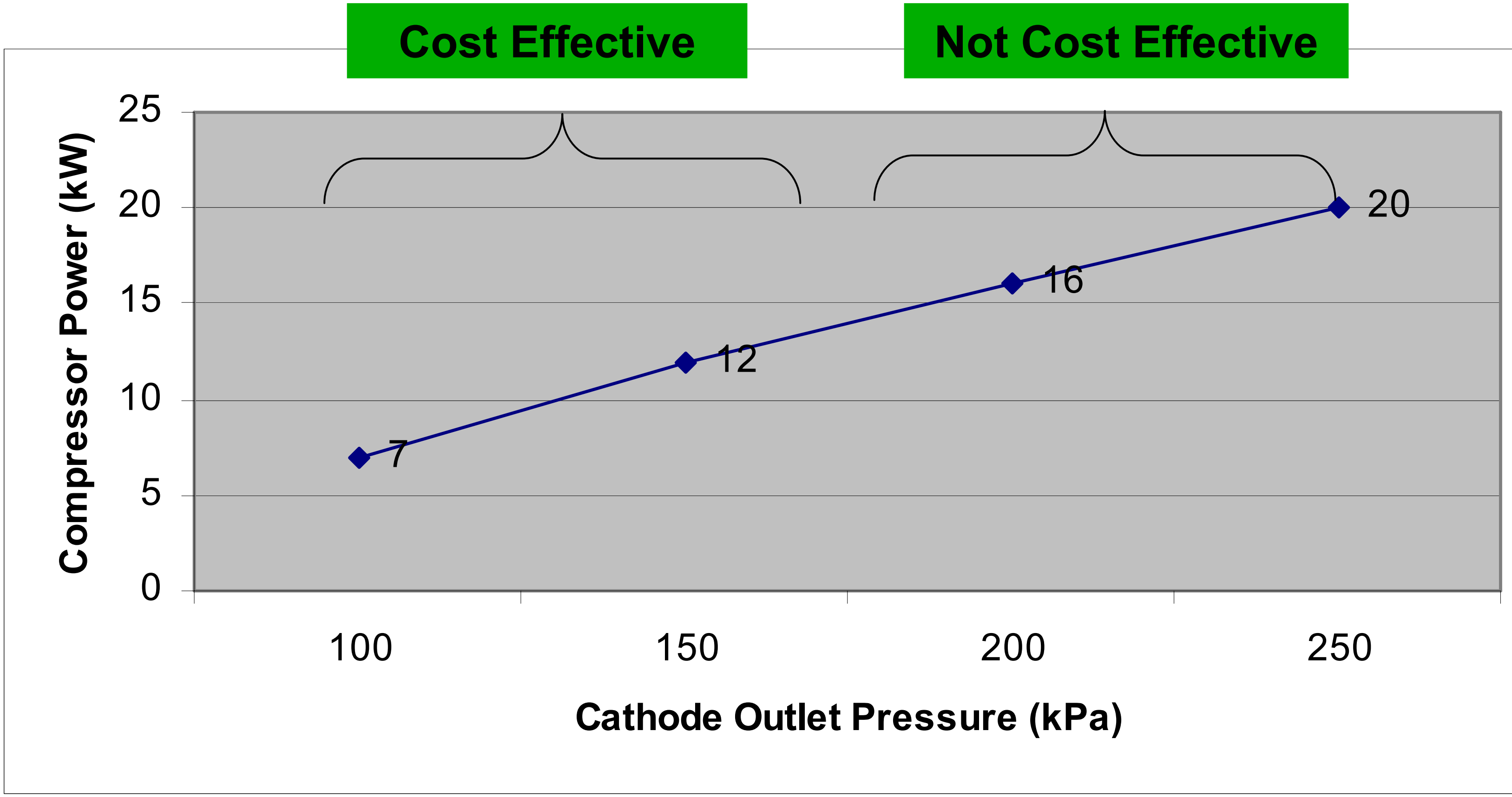
For a higher temperature system to be feasible, the membrane must have improved proton conductivity at low RH vs. current materials.

Comparison of Internal Combustion Engine (ICE) vs. Fuel Cell System (FCS)

	ICE	FCS
Power from system	80 kW	80 kW
Heat rejected (Q)	< 80 kW	100 kW (@0.6 v, including parasitics)
$T_{ambient}$	40°C	40°C
$T_{coolant}$	120°C	80 → 95 → 120°C
"Q/ITD" Proportional to radiator size	<1 kW / K	2.5 → 1.8 → 1.25 kW / K

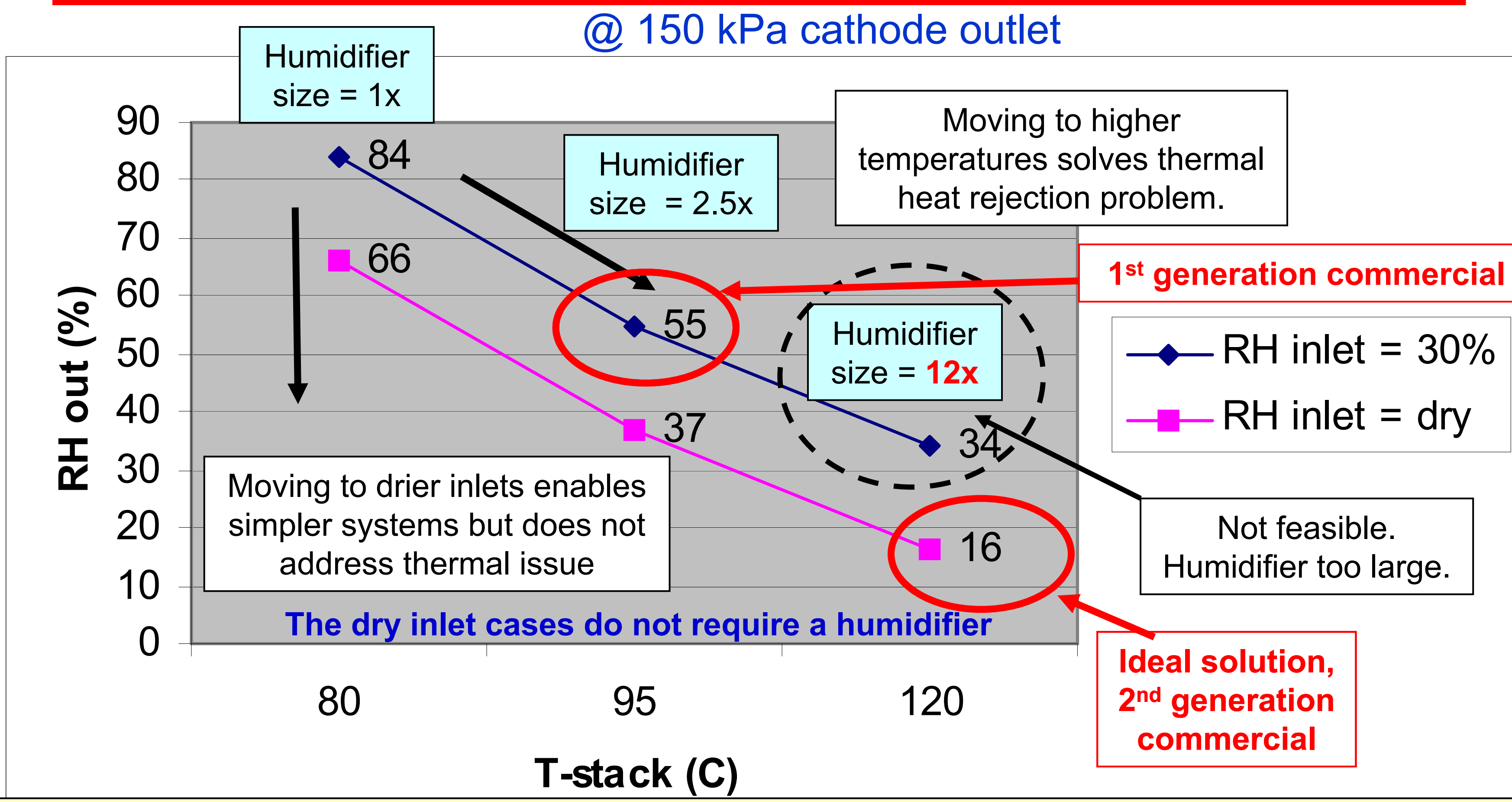
We ultimately want $T_{coolant}$ (FCS) as close as possible to $T_{coolant}$ (ICE), 120°C.

Effect of Cathode Outlet Pressure on Cost



- Maximum feasible operating pressure considered to be 150 kPa abs.
- Operating at higher cathode outlet pressures, to achieve higher RH, is not a cost effective or high efficiency option.

Effect of Temperature on Humidifier Size



- Higher temperature requires lower RH operating conditions to allow cost effective and packagable humidification system.
- Membrane operating at 95°C could enable a FC System that can compete with the ICE.

Automotive FC System Operating Requirements

150 kPa cathode outlet

T (°C)	RH in (%)	RH out (%)	Q/ITD Proportional to radiator size	Membrane Conductivity	Comment
80	30	84	2.5	0.1 S/cm at 80% RH Commercial PFSA	Not competitive with ICE
95	30	55	1.8	0.1 S/cm at 50% RH Demonstrated PFSA	May be competitive with ICE
120	0	<20	1.25	0.1 S/cm at <20% RH (non-existent)	Ultimate solution

Humidification system would be too large

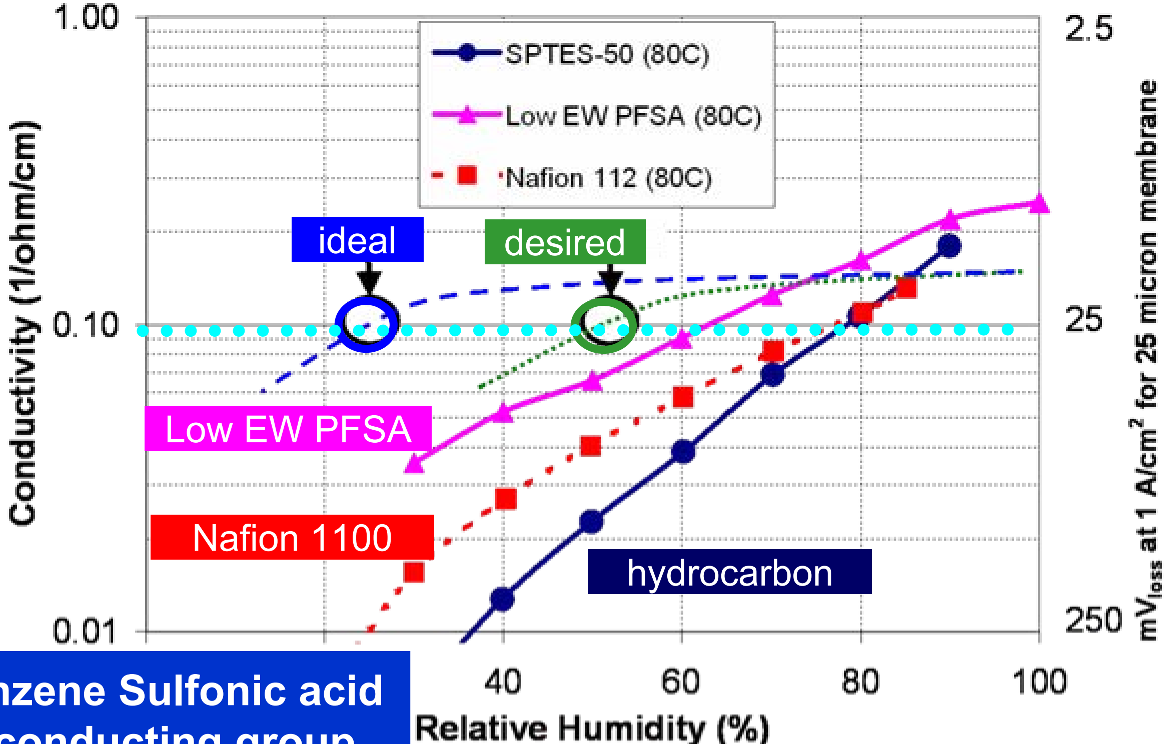
Radiator size 2-4 times ICE

E

able

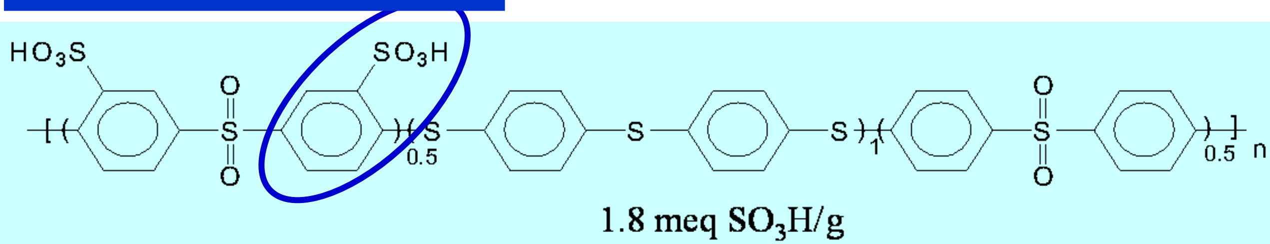
- 0.1 S/cm at 50% RH operating at 95°C could enable a FCS that could be an "Automotive Competitive System"
  - although it would still require a large humidifier and thermal system developments
- 0.1 S/cm at <20% RH operating at 120°C remain long term goal
  - GM does not believe materials exist which meet initial market launch timing

Conductivity of Polymer Electrolyte Membranes



Target: 0.1 S/cm

Benzene Sulfonic acid
H^+-conducting group



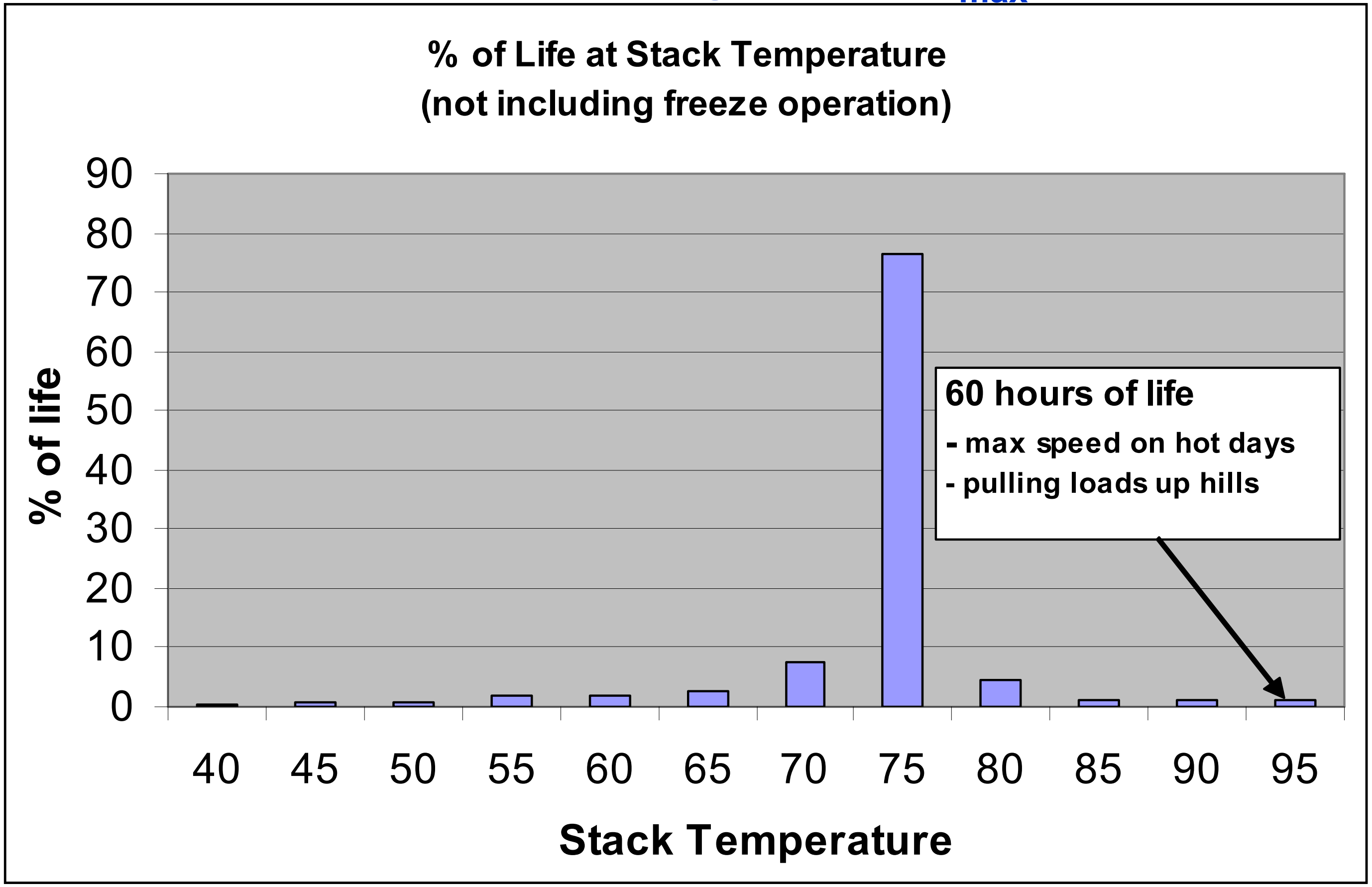
Sulfonated polyarylenethioethersulfone (SPTES)

Bai, Z.; Williams, L. D.; Durstock, M. F.; Dang, T. D.; *Polym. Prepr.*, **2004**, *45(1)*, 60.

- Sulfonated aromatic membranes are more conductive than Nafion® 1100EW at high RH, but are inferior at low RH.
- Nafion® 1100EW is not a good benchmark. Higher conductivity (lower EW PFSAs) are available.

Expected Stack Temperature-Life Profile

Assumed designed for T_{max} = 95°C



- The vast majority of stack life will be at 60-80°C stack temperature.
- Only 60 hours (~1%) of 5500 hr life are anticipated at 95°C.

Automotive-Competitive Membrane Summary

- PFSA membranes with evolutionary improvements should meet needs of 1st generation Fuel Cell Systems
  - Conductivity at 95°C & 50% RH in order to demonstrate an "Automotive Competitive System"
- Membrane needs to survive 60 hours at 95°C
  - Durability tests must properly assess membrane's ability to do this
- Revolutionary new materials (non-PFSA membranes) are desired for 2nd-generation automotive. These materials will relieve constraints (system complexity, operating conditions, cost) imposed by current materials.

Membrane Performance Screening

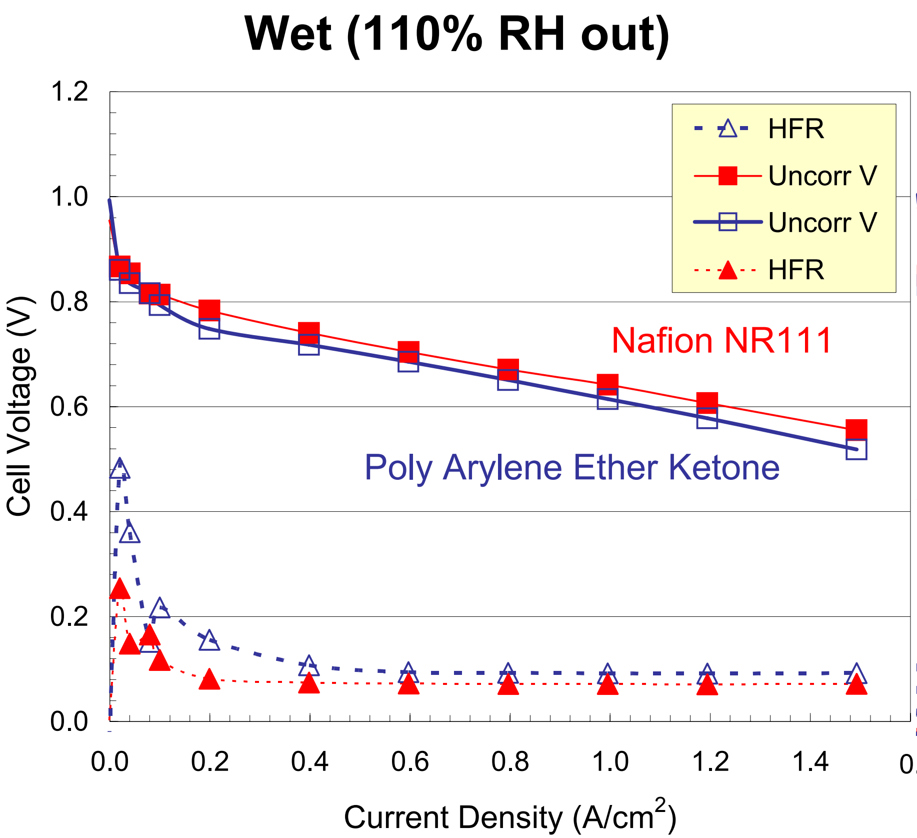
Objective: Evaluate membrane performance in a fuel cell over entire range of automotive operating conditions

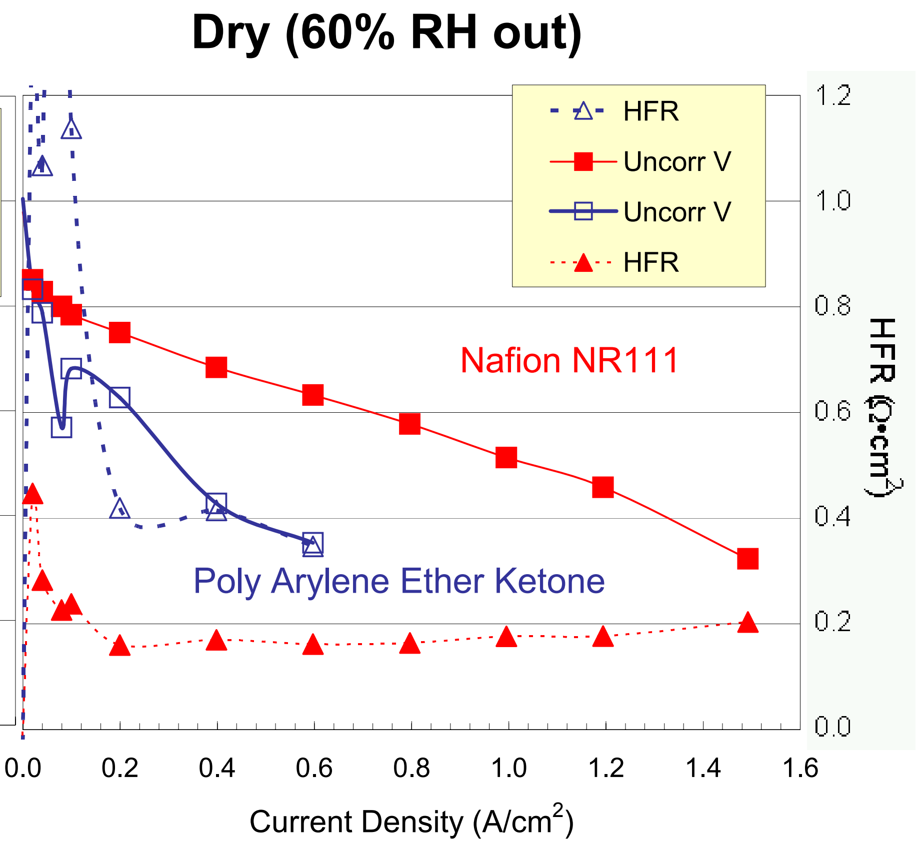
Method: 50 cm^2 H_2-Air fuel cell test

1. Polarization Curves over range of RH (80°C, 50 kPag, 2-3 Stoichs)
    a) Wet (110% RH out)
    b) Intermediate (80% RH out)
    c) Dry (60% RH out)
2. Humidity Sweep over operating window (50 kPag, 2/2 Stoichs)
    a) 0.4 A/cm^2 – 80°C
    b) 0.4 A/cm^2 – 95°C
    c) 1.2 A/cm^2 – 80°C
    d) 1.2 A/cm^2 – 95°C

Target: Robust Operation over range of Temperature and Humidity levels

Membrane Performance Screening: Wet vs Dry

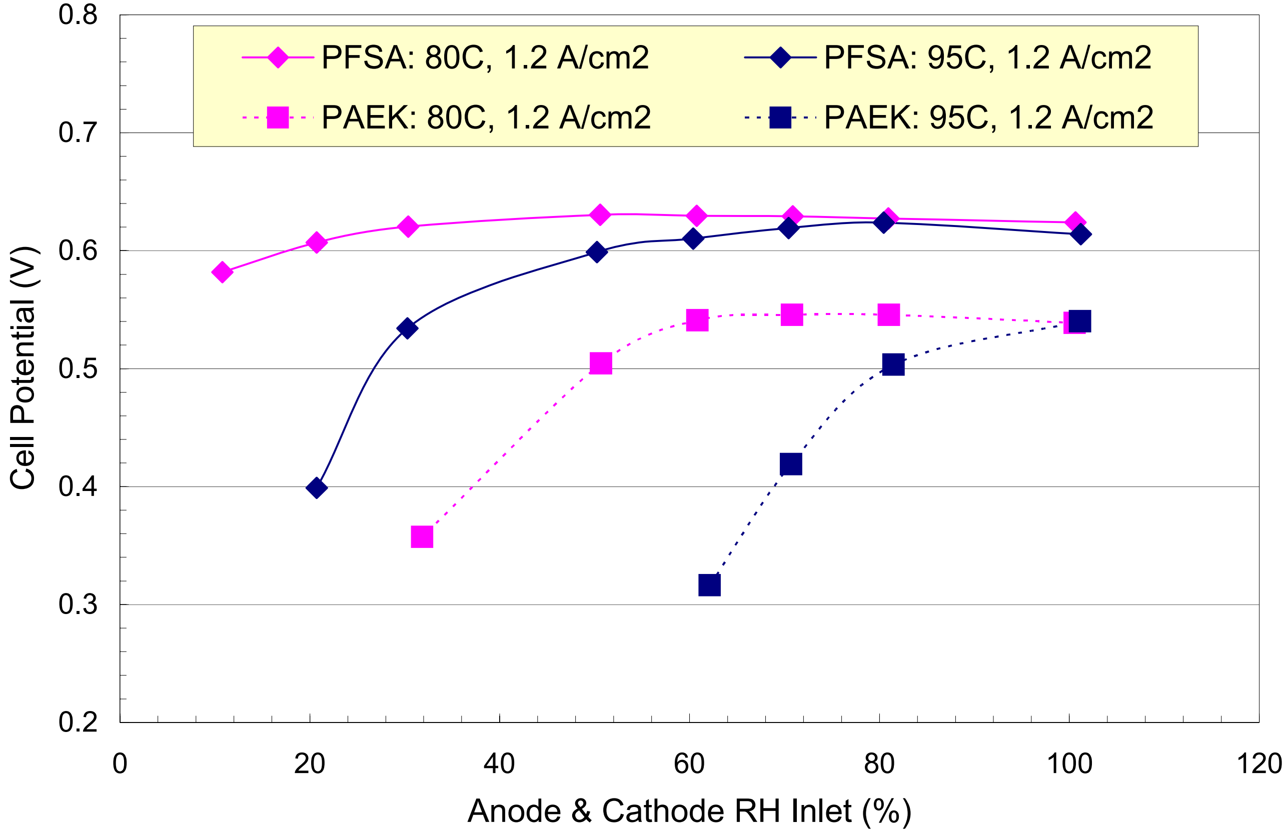




At wet conditions some HC membranes perform comparably to PFSA

At dry conditions most HC membranes cannot run stably to 1.5 A/cm²

Membrane Performance: RH Sensitivity



- 80°C @ 1.2 A/cm^2: PFSA performance stable down to 30% RH
  HC performance dropping below 50% RH.
- 95°C @ 1.2 A/cm^2 : PFSA performance dropping below 50% RH
  HC performance dropping below 100% RH.

Exchange Capacity vs. Water Uptake

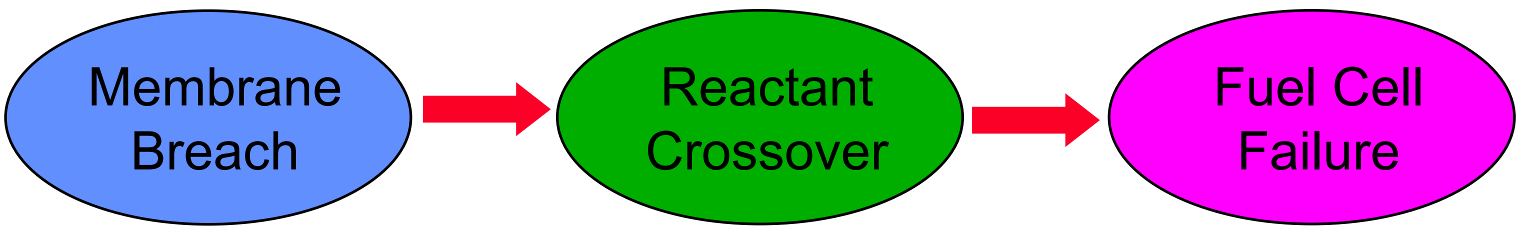
Higher IECs increase conductivity, but also increase swelling

Membrane	**IEC**	**Dry Density**	**Wt% Uptake**	**Swelling**
Data at 100°C	mEq/cm^3	gm/cm^3	100 + mass H2O/ mass dry polymer	wet volume/ dry volume
Nafion 112	1.8 (1100 EW)	1.9	40	1.8
Low EW PFSA	2.9 (700 EW)	1.9	60	2.2
SPTES-50	2.2 (1.8 mEq/gm)	1.2	450	6.3

- Membrane should not swell excessively in liquid water at 100°C.
  - Volumetric exchange capacity more relevant than gravimetric
  - Volume swell in fuel cell stack can cause excessive mechanical force
  - Durability issues (e.g. fatigue) in wet-dry cycling
  - **Swelling of 2 suggested as screening limit**
- Important that water taken up by membrane contribute efficiently to proton conductivity!

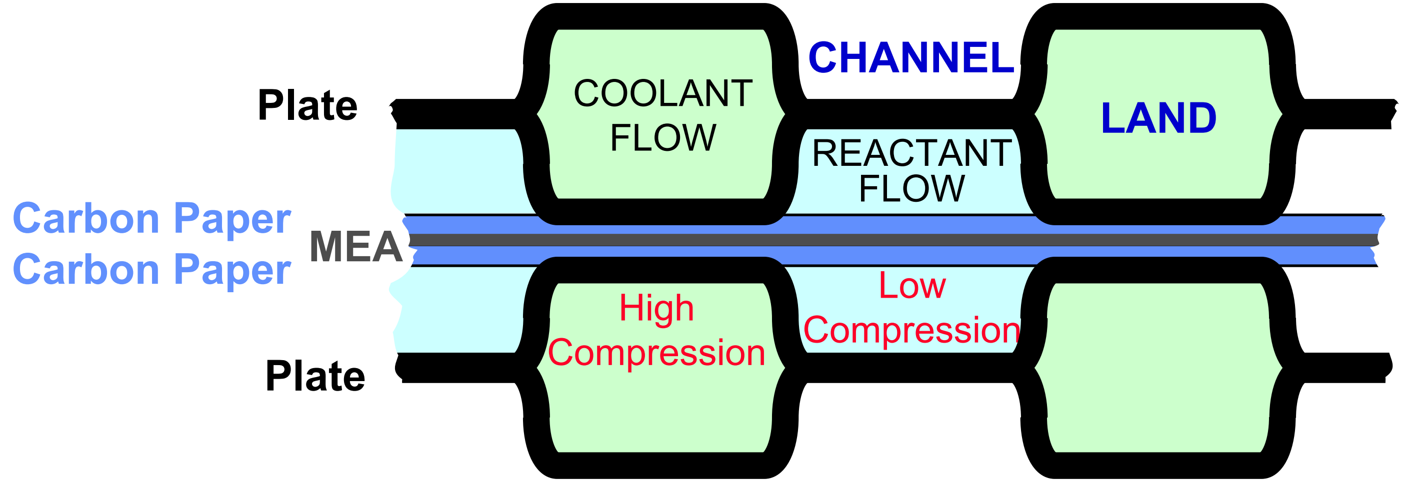
Proton Exchange Membrane Durability

- Automotive Fuel Cells must survive 10 years and 6000h operation.
  - Electrochemically active environment
  - Transient operation
  - Start-Stop & Freeze-Thaw cycling



- We need to determine the conditions that lead to membrane failure.
- Promote development of materials that can withstand these conditions.

Why Do Membranes Fail?



Mechanical Degradation

- Stresses caused by Membrane Shrinking/Expansion with Fluctuations in Temperature or Humidity
- Stresses caused by Stack Compression & Compression Variation
- Creep/Stress Rupture

Chemical Degradation

- Polymer chain attack by radicals or other active species

Thermal Degradation

- Weakening of Membrane by Overheating (higher than operating temp)

Combined Effects of Mechanical & Chemical Degradation

Hypothesis for Membrane Mechanical Failure

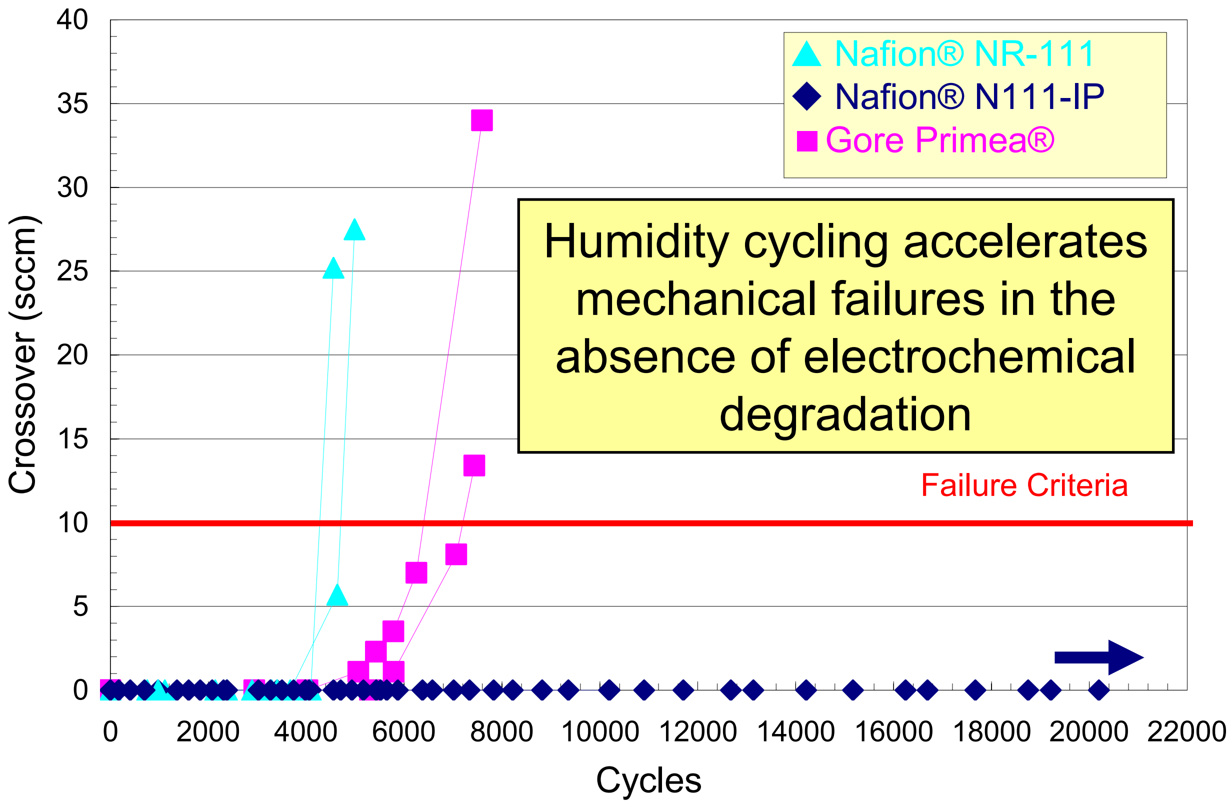
- Membranes & MEAs swell after soaking in water and subsequently shrink upon drying
- In plane: tension & compression are caused as membrane constrained from shrinking & swelling cycles between wet & dry
- Fatigue from humidity cycling induced stresses causes pinholes

Accelerated Testing: *In-Situ* Humidity Cycling

- Test membranes for mechanical failure in the absence of reactive gases and electric potential
- Impose mechanical stresses on MEAs that would be experienced during fuel cell operation due to humidity fluctuations

Materials:	MEA (Pt/C electrodes) & Carbon Fiber Paper GDM
Cell Build:	50 cm^2 cell w/ single pass 2mm lands & channels
Cycle:	**2 min 150% RH air; 2 min 0% RH air flow**
Conditions:	**80°C, 0 kPa, 2 SLPM dry anode & cathode flow**
Diagnostics:	Physical crossover leak (failure = 10 sccm)

Humidity Cycling of PFSA Membranes



Homogeneous Membranes

- DupPont™ NR-111
  - 25μm, 1100EW Nafion®
- Ion Power™ N111-IP
  - 25μm, 1100EW Nafion®

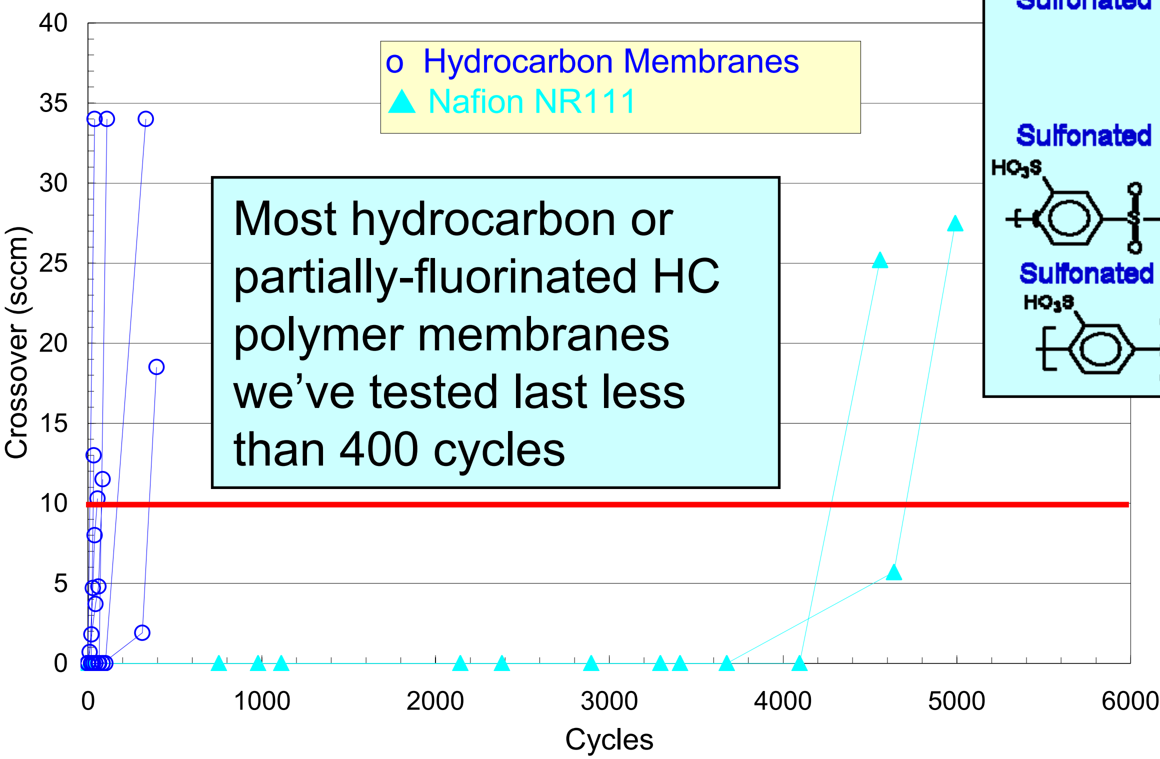
Composite Membranes

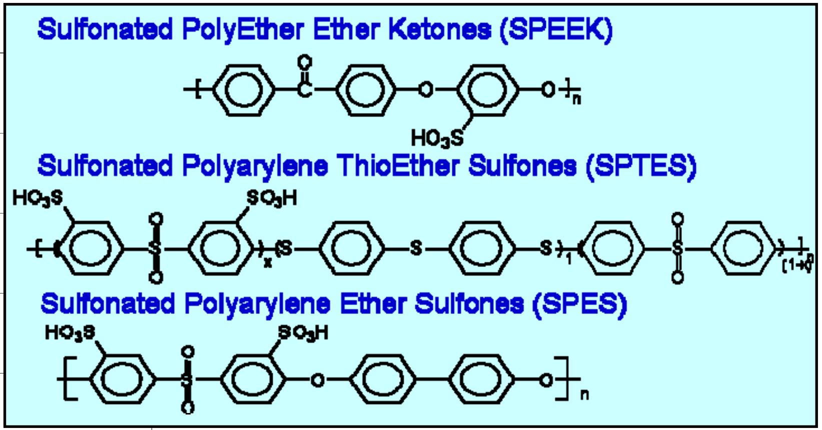
- Gore™ Primea® Series 57 (Expanded PTFE Filled Reinforcement)

- Different processing methods for same polymer dramatically effects humidity cycling durability
- Mechanical reinforcement insufficient to prevent humidity cycling induced crossover leak

Humidity Cycling of Alternative Membranes

- Most research on Hydrocarbon membranes focused on performance at high temperatures and low RH
- What About Durability?





- Humidity cycling durability is critical when developing FC membranes
- Concepts like block copolymers & cross-linking show promise

Chemical Degradation of Ionomer

Hypothesis: Membrane degrades via reaction of (•OH) with ionomer

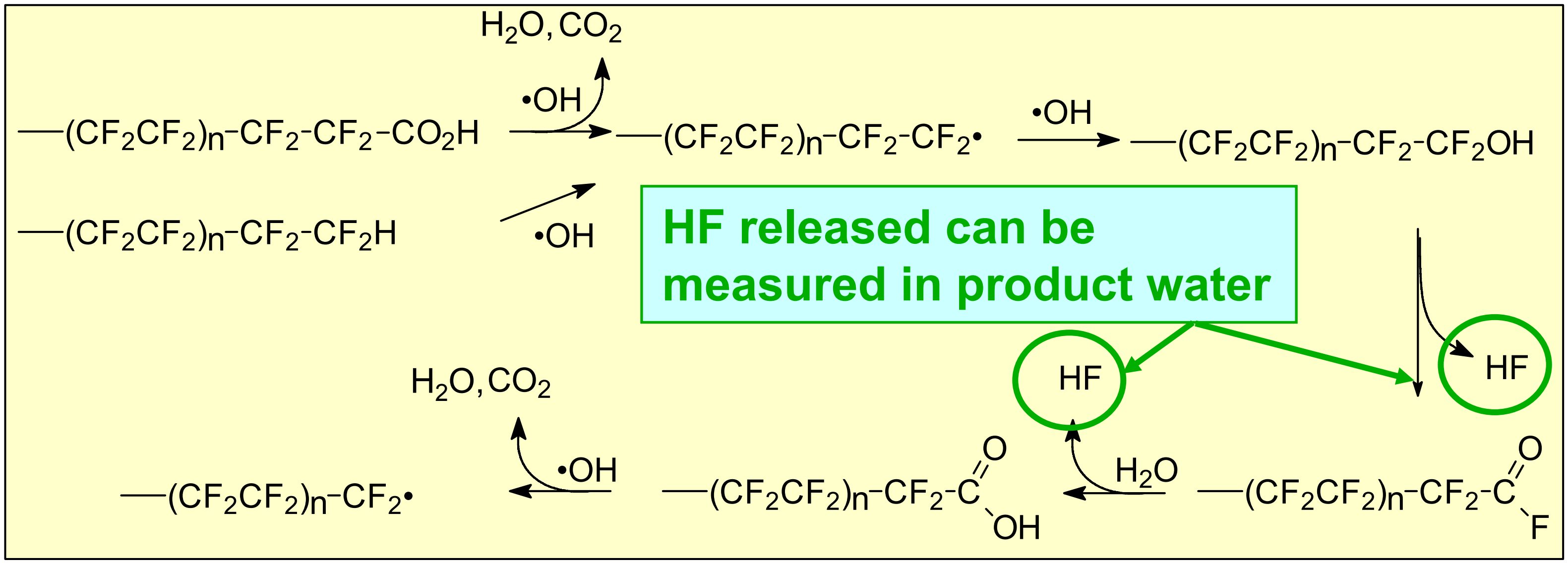
- Peroxide is formed as byproduct of oxygen reduction

$$O_2 + 2H^+ + 2e^- \longrightarrow H_2O_2$$

- Peroxyl radical can be formed through decomposition of hydrogen peroxide (H_2O_2)

$$H_2O_2 \xrightarrow{Fe^{++}} 2\,OH^{\bullet}$$

- Chain "unzipping" occurs via non-fluorinated end groups (example)



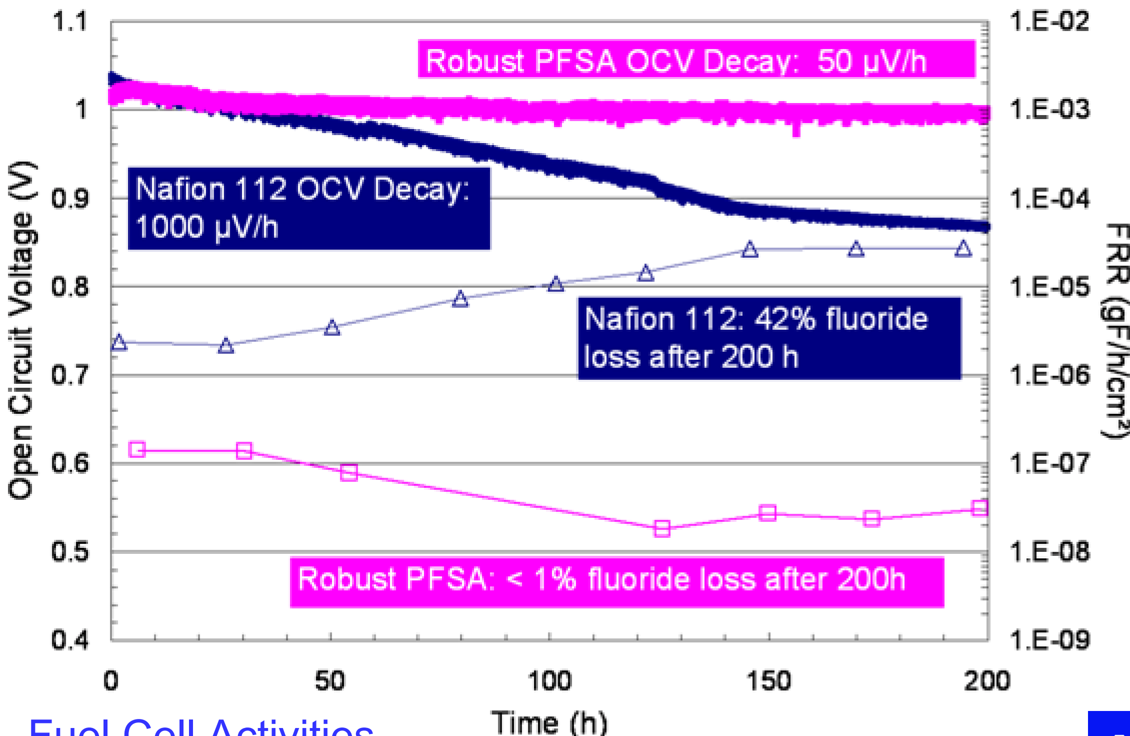
Journal of Power Sources, Volume 131, Issues 1-2, 14 May 2004, Pages 41-48, Curtin et al

Accelerated Membrane Chemical Durability

Objective: Test for chemical failure with minimal mechanical stress

Method: Operate at conditions that accelerate Chemical Degradation - no RH fluctuations

Materials:	MEA (Pt/C electrodes) & Carbon Fiber Paper GDM
Cell Build:	50 cm^2 cell w/ serpentine flow field
Conditions:	OCV, 95°C, 50% RH, 50 kPag, 5/5 stoich at 0.2 A/cm^2 equivalent flow
Diagnostics:	OCV, H_2 crossover current, physical leak, FRR



Target:

- PFSA: < 10^{-8} g/hr-cm^2 Fluoride release rate (FRR)
- Non-PFSA: crossover diagnostic used as opposed to effluent chemical analysis

Combining Mechanical & Chemical Stresses

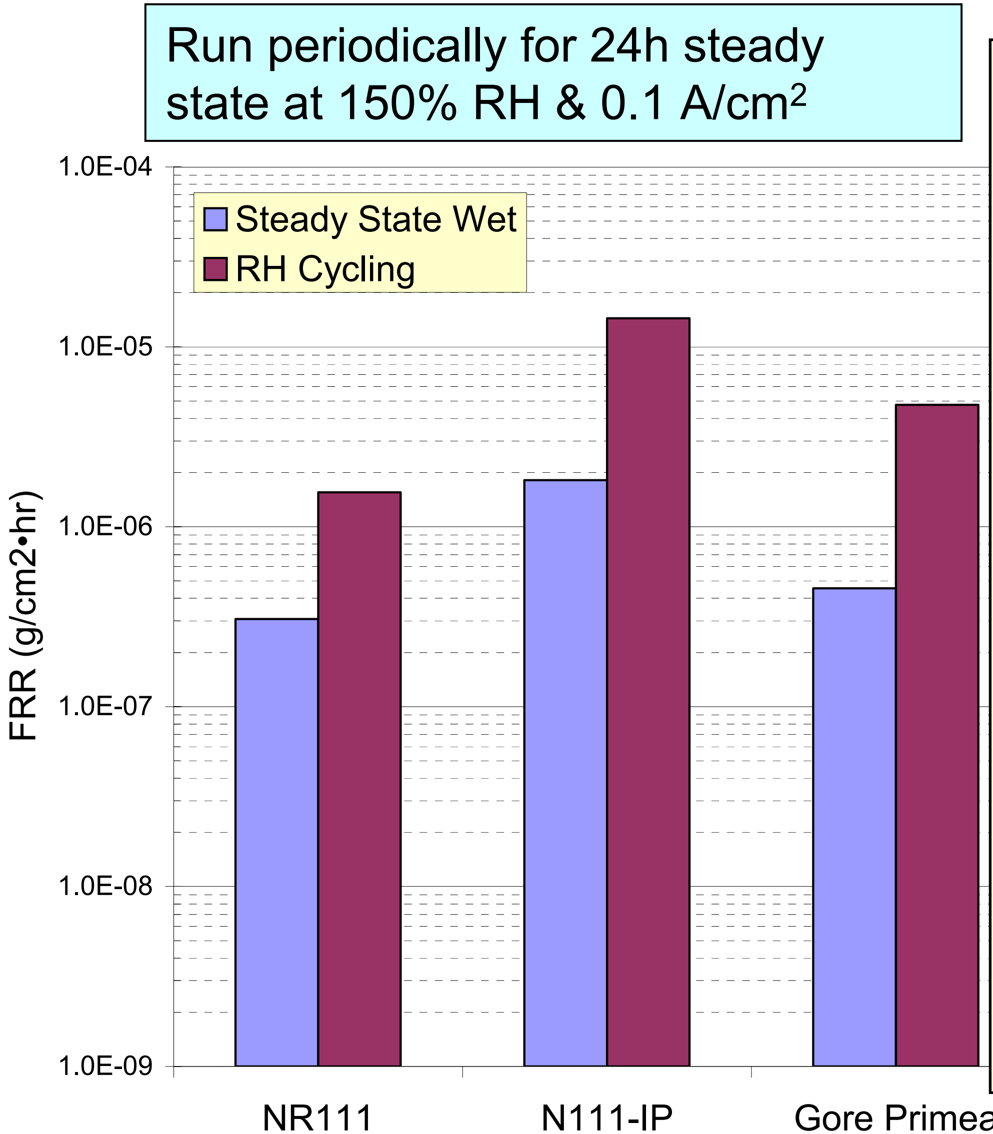
Objective: Does Electrochemical Reaction Accelerate Mechanical Failure?

- Repeat Humidity Cycling Protocol in a H_2/Air Fuel Cell
- Run constant current test at 0.1 A/cm_2

MEA	Cycles to Failure w/o load	Cycles to Failure @ 0.1 A/cm^2
DuPont™ Nafion® (NR-111)	**4000-4500**	**800-1000**
Ion Power™ Nafion® (N111-IP)	**20000+**	**1800**
Gore™ Primea	**6000-7000**	**1300**

- Commercial PFSA: failure accelerated >5 times under electrochemical load
- GM Benchmark: Lifetime under load = 0.7 X Lifetime in with no electrochemical load

Chemical Degradation During Humidity Cycling



- <u>Commercial PFSA</u>
  - ~10X higher FRR during cycling
  - >5X acceleration of membrane failure at 0.1 A/cm^2
  - Mechanical stresses accelerate chemical degradation
- <u>Robust PFSA Benchmark</u>
  - FRR 100-1000X lower than other PFSAs
  - FRR does not increase with RH cycling
  - Mechanical stresses do not accelerate chemical degradation

Summary

- Membrane Performance
  - High membrane conductivity at low RH (< 50%) required to enable an "auto-competitive" Fuel cell System
  - 120°C remains long term target, but 95°C enables initial commercialization
  - Low EW PFSAs have potential to meet performance requirements
  - HC benzene sulfonic acid membranes not expected to meet targets
- Membrane Durability
  - Humidity cycling durability must be considered when developing membrane materials
  - Humidity cycling durability strongly dependent on processing method
  - Mechanical reinforcement not sufficient to prevent RH cycling failures
  - Humidity cycling failure is accelerated by chemical degradation
  - Mitigations strategies must be incorporated to prevent radical attack on the membrane
- High Performance Membranes exist, Mechanically Robust membranes exist, and Chemically Stable Membranes exist

→ Now we need to combine these properties into a single material

Acknowledgements

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