Automotive Perspective on Membrane Evaluation

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Overview

- Purpose: To provide automotive OEM perspective on the proper metrics for validating performance and durability of a fuel cell membrane suitable for vehicular fuel cell stack application.

- Metrics and condition ranges
- Degradation mechanisms and durability tests
  - Chemical
  - Mechanical
  - Other (Thermal, Hydrolytic)
- Recommendations on testing facilitation
- Brief note on cost

Metrics

Targets to be achieved both before and after an in-situ durability test.

Condition	Area-specific proton resistance ($m\Omega*cm^2$)[1]	Hydrogen crossover (mA/cm^2)[2]	Electrical resistance ($\Omega*cm^2$)[3]
120ºC P_w = 40-80 kPa (20-40% RH)	20	2	> 1000
80ºC P_w = 25-45 kPa (53-95% RH)	20	2	> 1000
30ºC P_w = 4 kPa (94% RH)	30	2	> 1000
-20ºC PEM water content TBD[4]	20	measure	measure

1. Through-plane preferred
2. Tested in MEA at 1 atm H_2/N_2, 0.5 V.
3. Tested in MEA with N_2/N_2, 0.5 V.
4. Water content may be implicitly set by standard cooldown procedure. Test method development required.

High Temperature Target

- While 120ºC remains the long-term high temperature target, there is significant benefit to OEMs to meeting targets at 95ºC.
- Programs focusing on polymers containing sulfonic / phosphonic acid proton-conducting groups should refocus on meeting targets at 95ºC (34-68 kPa, 40-80% RH)
  - 120ºC unlikely to be met if water is still the primary means for conduction
- Programs focused on alternative conduction mechanisms should still focus on 120ºC.

Other Testing Notes

- If applicable, fluorine release should still be measured in a chemical durability test
  - If release of other species from a membrane is expected or observed, this should be measured as well
- Specifying only area specific resistances (and not material conductivity) allows researchers to use judgment in designing membrane thickness
  - Low thickness is good for low proton resistance, but bad for minimizing H2 crossover and electrical resistance
- Other useful ex-situ tests are still recommended:
  - Dimensional stability, water uptake vs. RH, DMA/DSC, TGA, tensile/tear strength (or other mechanical tests), chemical analysis

Degradation Mechanisms: Chemical

- Motivation: PEMFC membrane polymer chains are well-known to degrade under circumstances likely to form radicals (e.g. $^{\bullet}OH$, $^{\bullet}OOH$, $^{\bullet}O_2^-$)
- Many reaction pathways can generate radicals
  - $Pt\text{-}H + O_2 \rightarrow {}^{\bullet}OOH$
  - $O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$ ($E^o = 0.695$ V)
  - $H_2O_2 \rightarrow 2\ {}^{\bullet}OH$
  - ${}^{\bullet}OH + H_2O_2 \rightarrow {}^{\bullet}OOH + H_2O$
  - ${}^{\bullet}OOH + H_2O \rightarrow {}^{\bullet}O_2^- + H_3O^+$
  - $H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + HO^- + {}^{\bullet}OH$

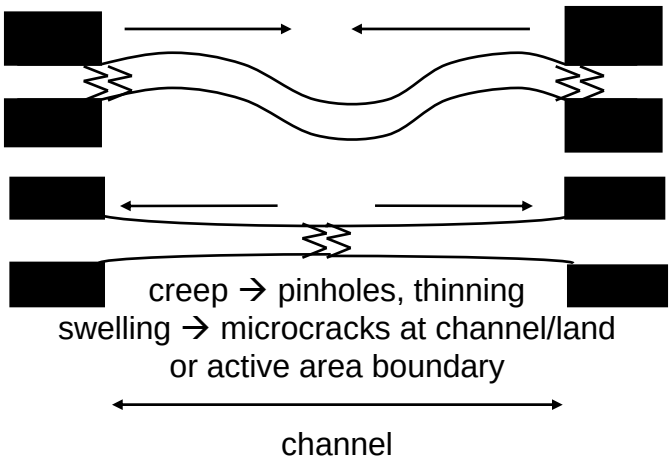
Probability of reaction pathways may be enhanced by Pt dissolution and deposition into the bulk membrane.

In-Situ Durability Test: Chemical

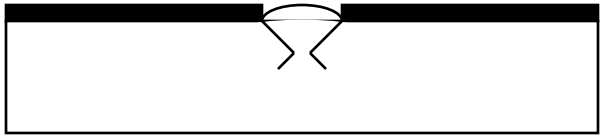
- Stressors for chemical degradation include:
  - Low RH. Condensed water may "wash out" bad actors such as metal cations, H_2O_2. (Borup *et al.*, *Chem. Rev.* **107** (2007) 3904-51)
  - High temperature. Increases activity of degradation reactions.
  - OCV. Allows availability of reactants (e.g. H_2, O_2) to begin degradation mechanisms.
- Published DOE test accounts for these stressors:
  - OCV, 90ºC, 30/30% RH A/C
  - DOE test duration: 200 hours
  - Auto OEMs have recommended to lengthen test to 500 hours

Degradation Mechanisms: Mechanical

Tensile stresses from expansion, contraction with RH cycling



Ratcheting near catalyst defects



GDL fiber protrusion

Can be minimized with proper materials and cell design

- In-situ failures known to occur despite minimal changes in ex-situ measured parameters (e.g. tensile strength, tear strength)
- Proper durability test seeks to isolate membrane performance from effects of chemical degradation, electrode materials and cell design

In-Situ Durability Test: Mechanical

- Humidity cycle:
  - 2 minutes dry
  - 2 minutes at 90ºC dew point
- Air on both sides of cell to avoid confounding with chemical degradation
- Other conditions are similar to normal cell operation (80ºC, near-ambient pressure, 2 LPM on each side)
- 20,000 cycles = 1333 hours

Thermal and Hydrolytic Stability

- Mechanisms:
  - High temperatures can enable the loss of functional groups (e.g. $–SO_3H$ from sulfonated PEMs)
  - Water environments can cause hydrolysis of imide rings in polyimides or leaching of conductive groups such as heteropolyacids
- At this time, no formal in-situ durability protocols exist for addressing thermal and hydrolytic stability
- Ex-situ screening methods are expected (e.g. TGA), but do not constitute confirmation of durability during fuel cell operation

Recommendations for Testing

- There should be one facility equipped to perform standard testing
  - All investigators would send membrane material to this facility
- This facility would use the same hardware, GDEs, sealing/gaskets, range of compression
  - Ideally, this would be done such that edge failures are not accelerated
  - OEMs can review outside designs

Cost

- At this time, the OEMs do not feel a rigorous cost analysis is required from DOE-funded projects, but there should be a reasonable expectation that the $20/m^2 target will be met at 500,000 stacks/year production volume
- The OEMs favor lowering the $20/m^2 target in the near future

Summary

- OEMs favor in-situ tests to verify PEM durability.
- At present, chemical and mechanical tests have been established to address known mechanisms
- Simple metrics can be used that are linked to a membrane's ideal function
  - Low area-specific proton resistance
  - Low hydrogen crossover
  - Low electrical conductivity
- To maintain consistency, tests should be done at a set facility with consistent hardware, electrode components, cell design and cell compression