Novel Membranes and Ionomers

Michael A. Hickner
Professor, Department of Materials Science and Engineering
Department of Chemical Engineering and Department of Chemistry
Associate Director – Materials Research Institute
The Pennsylvania State University
hickner@matse.psu.edu

H2-AMP Workshop, March 30-31, 2022

Acknowledgements

- Bryan Pivovar – NREL
- Mike Yandrasits – 3M (retired)
- Andrew Park – Chemours
- Earl Wagener – Tetramer
- Scott Mauger – NREL
- Corky Mittelsteadt – Plug Power
- Kathy Ayers – Nel Hydrogen

Hickner Research Group @ Penn State

@hicknergroup hicknerresearchgroup

PEMs in Electrolyzers

- PFSA (perfluorosulfonic acid)
- Thick (100+ microns) – generally unsupported
- Demonstrated in commercial systems with 20,000+ hour lifetimes
- Little fundamental (molecular) study around electrolyzer operation and degradation
- Can be a cost driver in the stack and a major source of IR loss
- *Generally viewed as ripe for improvement in advanced membrane electrolysis systems*

Most Proton Exchange Membrane Knowledge is Derived from Fuel Cells

- PFSA and non-PFSA alternatives have been examined in detail in the fuel cell context
- Very few examples of purposed-designed electrolyzer membranes
- We know membranes likely need to be supported
- We know there will have to be additives
- Difficult to come up with universal accelerated tests for lifetime
- *There is a feeling that non-PFSA membranes may work, IF they can meet lifetime requirements*

Membranes Ohmic Losses are the #1 Loss at High Current Density Operation in PEMWEs

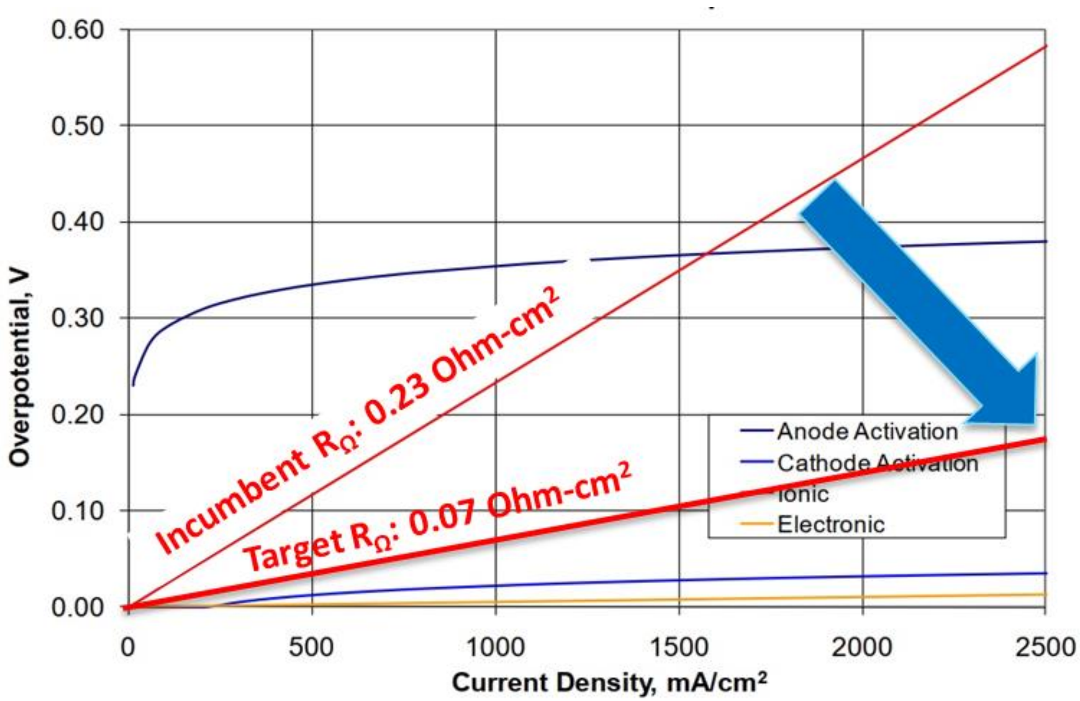
Table 3.4.6 Technical Targets: Membranes for Transportation Applications			
Characteristic	**Units**	**2015 Status**	**2020 Targets**
Maximum oxygen crossover[a]	mA / cm^2	2.4[b]	2
Maximum hydrogen crossover[a]	mA / cm^2	1.1[c]	2
Area specific proton resistance at:			
Maximum operating temperature and water partial pressures from 40–80 kPa	ohm cm^2	0.072 (120°C, 40 kPa)[c]	0.02
80°C and water partial pressures from 25–45 kPa	ohm cm^2	0.027 (25 kPa)[c]	0.02
30°C and water partial pressures up to 4 kPa	ohm cm^2	0.027 (4 kPa)[c]	0.03
-20°C	ohm cm^2	0.1[b]	0.2
Maximum operating temperature	°C	120[c]	120
Minimum electrical resistance	ohm cm^2	>5,600[c]	1,000
Cost[d]	\$ / m^2	17[e]	20
Durability[f]			
Mechanical	Cycles until >15 mA/cm^2 H_2 crossover[g]	23,000[c]	20,000
Chemical	Hours until >15 mA/cm^2 crossover or >20% loss in OCV	742[c]	>500
Combined chemical/mechanical	Cycles until >15 mA/cm^2 crossover or >20% loss in OCV	–	20,000

https://www.energy.gov/sites/default/files/2017/05/f34/fcto_myrdd_fuel_cells.pdf

Bryan Pivovar - NREL

New PEMWE Membranes

- PEMWE devices are the most proven technology to drive the adoption of H2@Scale.
- Reducing areal resistance of membranes in PEMWE environments (increasing voltage efficiency) is a critical contributor to their envisioned cost reduction toward \$1/kg H_2.

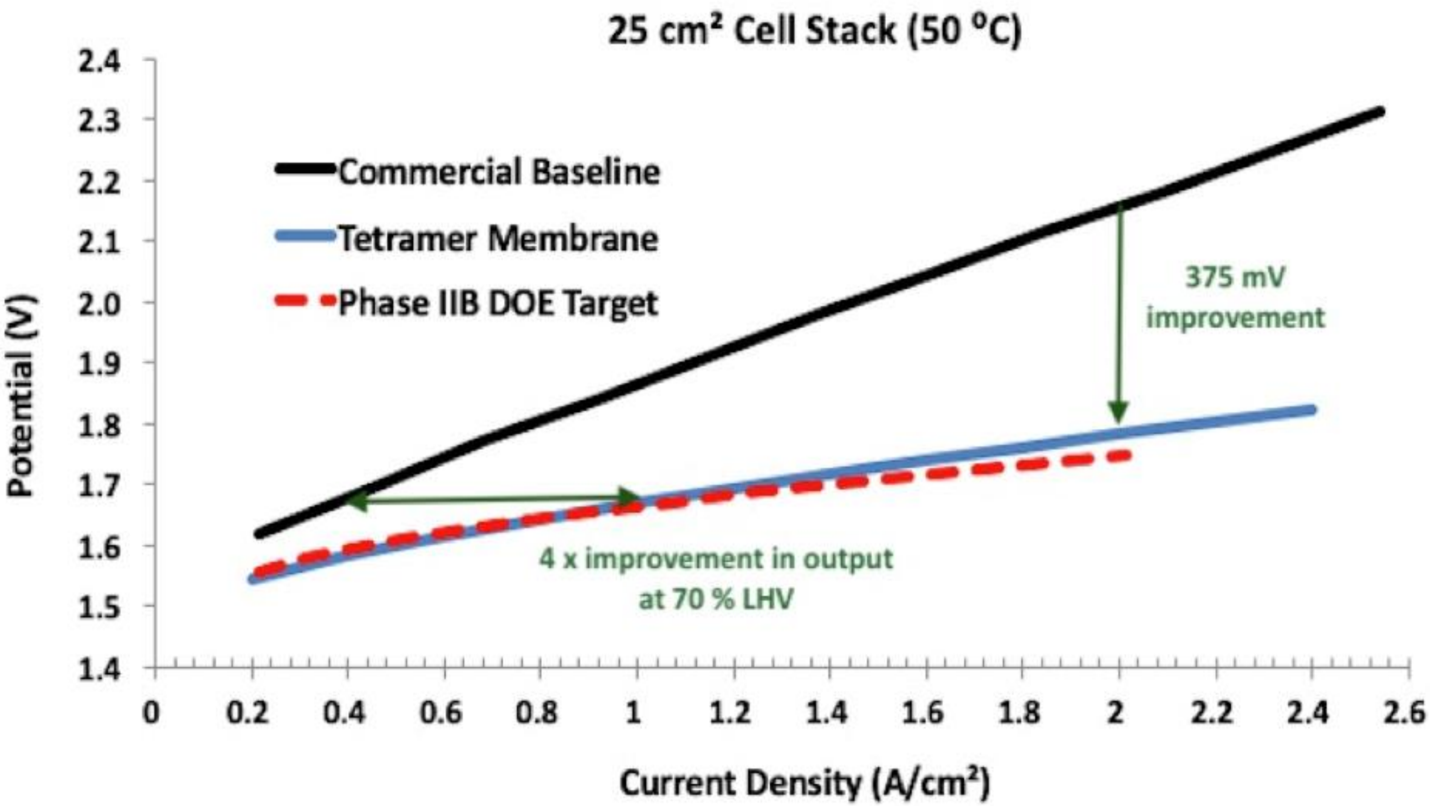


- *Additives will be required to enable thin membranes in a high differential pressure stack*
- Understanding durability implications of gas recombination catalysts (GRCs) and radical scavengers will enable “moving on” from incumbent thick membranes in PEMWE.

Andrew Park - Chemours

Designing PEMWE Membranes

Can achieve low cell potentials with new membranes.



Earl Wagener – Tetramer
Kathy Ayers – Nel Hydrogen

Thin PEMWE Membranes

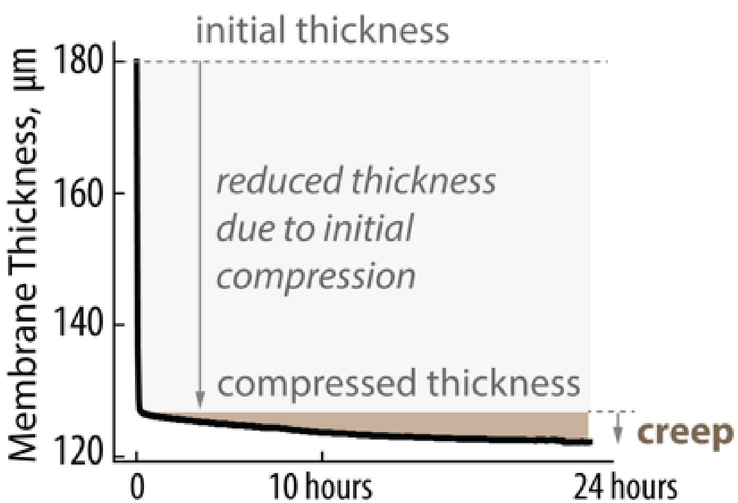
- Have too high gas crossover under differential pressure
- Need to be mechanically supported
- Demonstrated in some cases with reasonable lifetimes (less than 10,000 hours)
- Need to consider gas crossover and other losses due to thin membranes – more consideration of the trade-offs
- Thin membranes can reduce cost
- *High priority for next-generation PFSA-based PEMWE membranes*

PFSA Membrane Creep

Both hydration and pressure impact the creep response
Nafion creeps more in liquid water

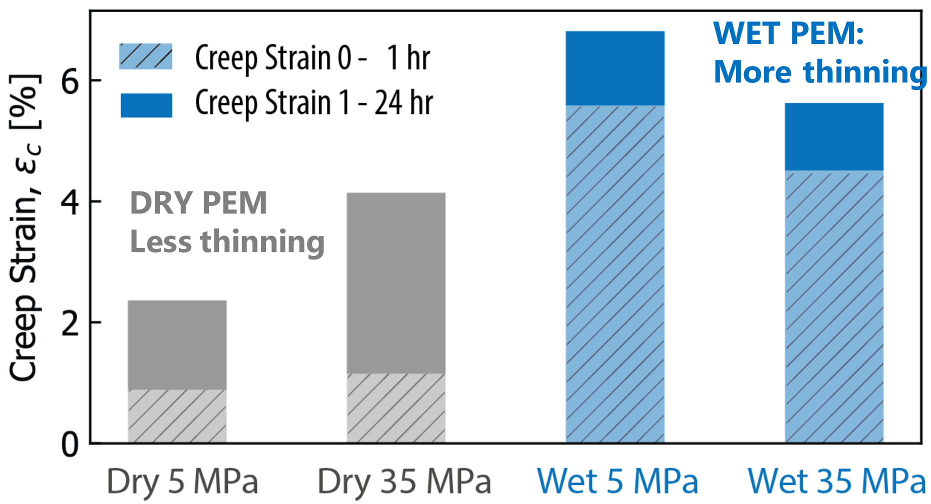
An in-situ compression creep procedure for is demonstrated and applied to Nafion

Creep is evidenced over the course of days



Creep leads to thinning under compression

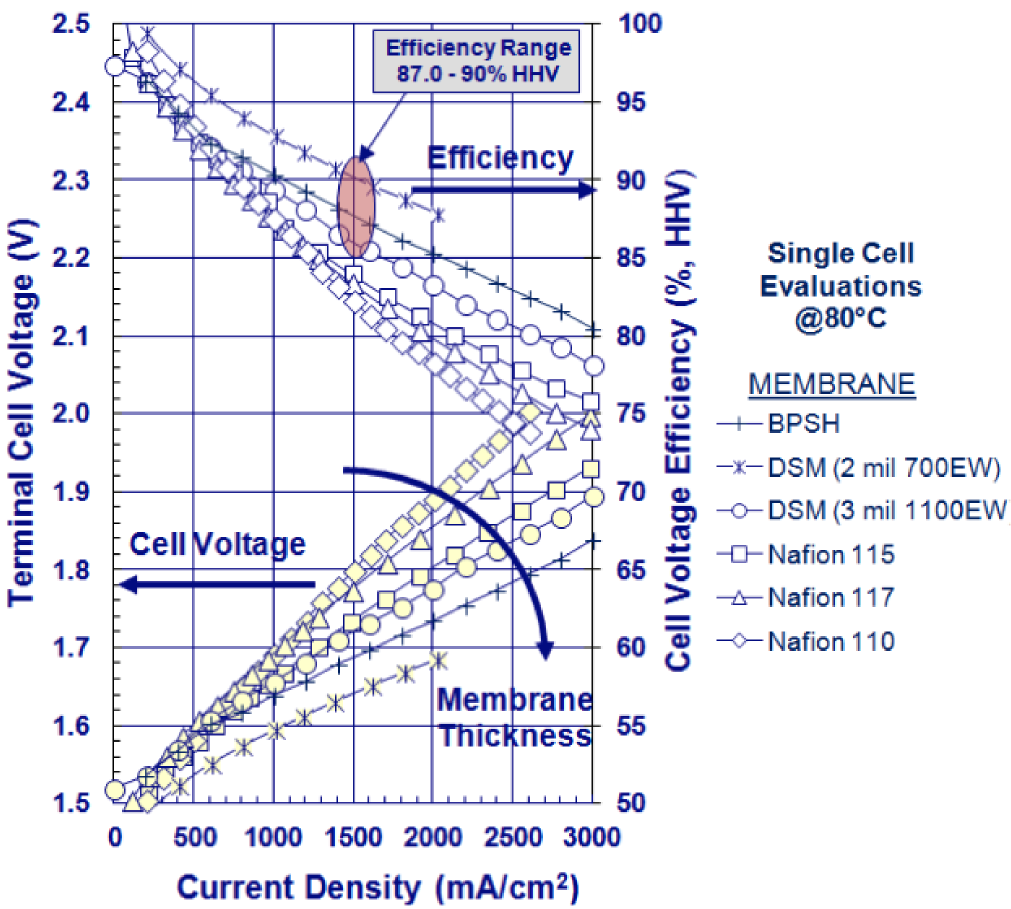
- 5 MPa (725 psi) & 35 MPa (5000 psi) for 24 hrs
- Hydrated Nafion creeps more (in water)
- It slows down after the first hour
- Increasing compression reduces the subsequent creep strain, by restricting the polymer mobility

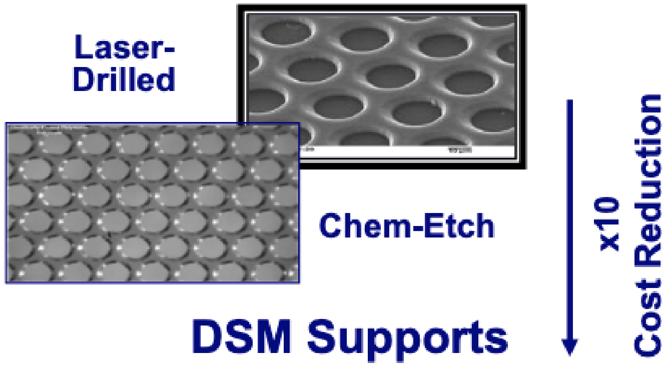


C. Arthurs and A. Kusoglu (2021). ACS Applied Energy Materials, 4, 4, 3249–3254.

Thin Supported Membranes

Membrane Progress:
Membrane/Catalyst Evaluations

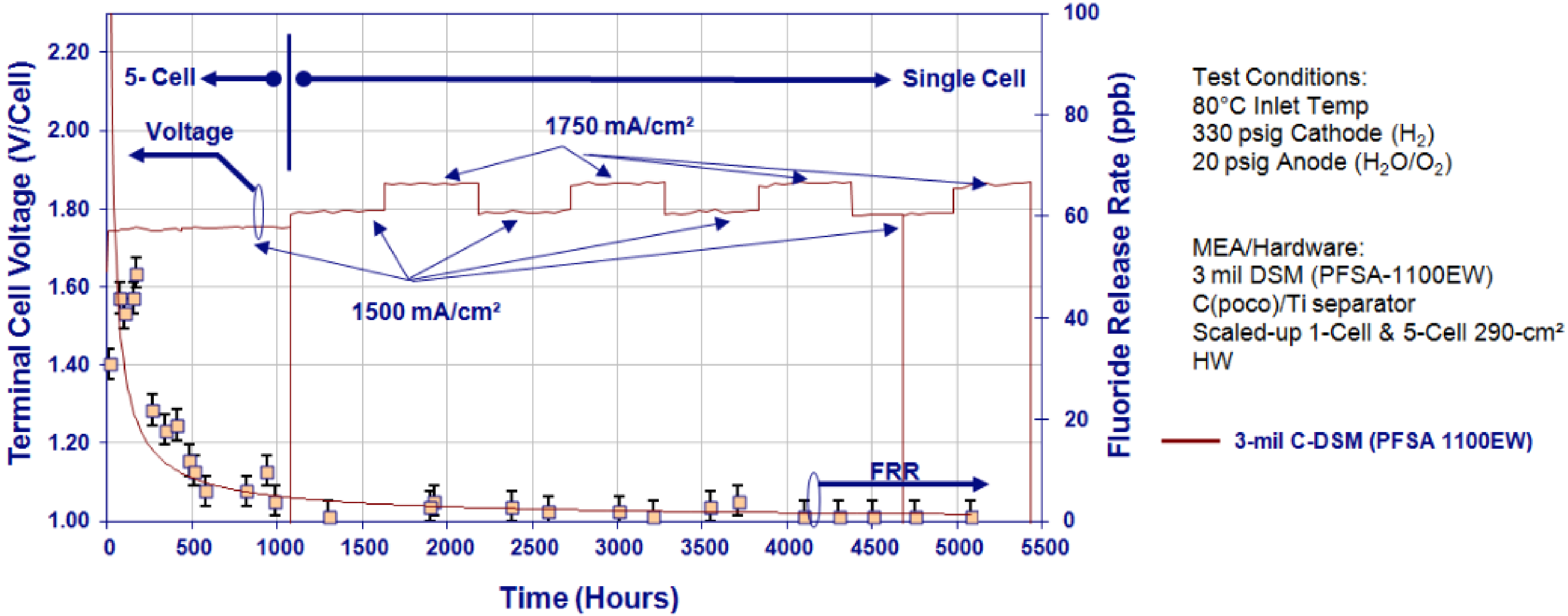




- Developed high efficiency DSM membranes
  - Chem-etched substrates used to lower cost, aid ease of fabrication
- Developed electrode structures with reduced catalyst loadings: 0.7 mg Pt/cm² (Pt/Ir-Anode), 0.4 mg Pt/cm² (Pt/carbon-Cathode)
  - Previously 8 mg Pt/cm²
- Successful testing of 3M NSTF Pt (cathode) and PtIr (anode) catalyst: 3M catalysts are one-order magnitude lower (~0.10 to 0.15 mg Pt/cm² Anode/Cathode)
- Alternative BPSH hydrocarbon membranes exhibited high degradation rates but are effective in reducing cross-over

Monjid Hamdan – Giner
2013 DOE Merit Review

Membrane Progress: Durability Testing (5,000 hours)



Performance

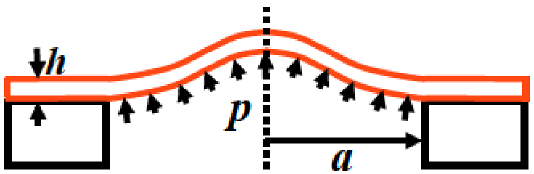
- Completed 1,000 & 5,000 Hour Life-Test Milestones
  - Scaled-up 5-cell (290-cm²)
  - 1.73-1.75V (~88% HHV)
- DSM MEA from 5-cell short stack re-assembled into a single-cell stack, total operating time = 5430 hours
- Scaled-up cells include low-cost components used in final stack assembly

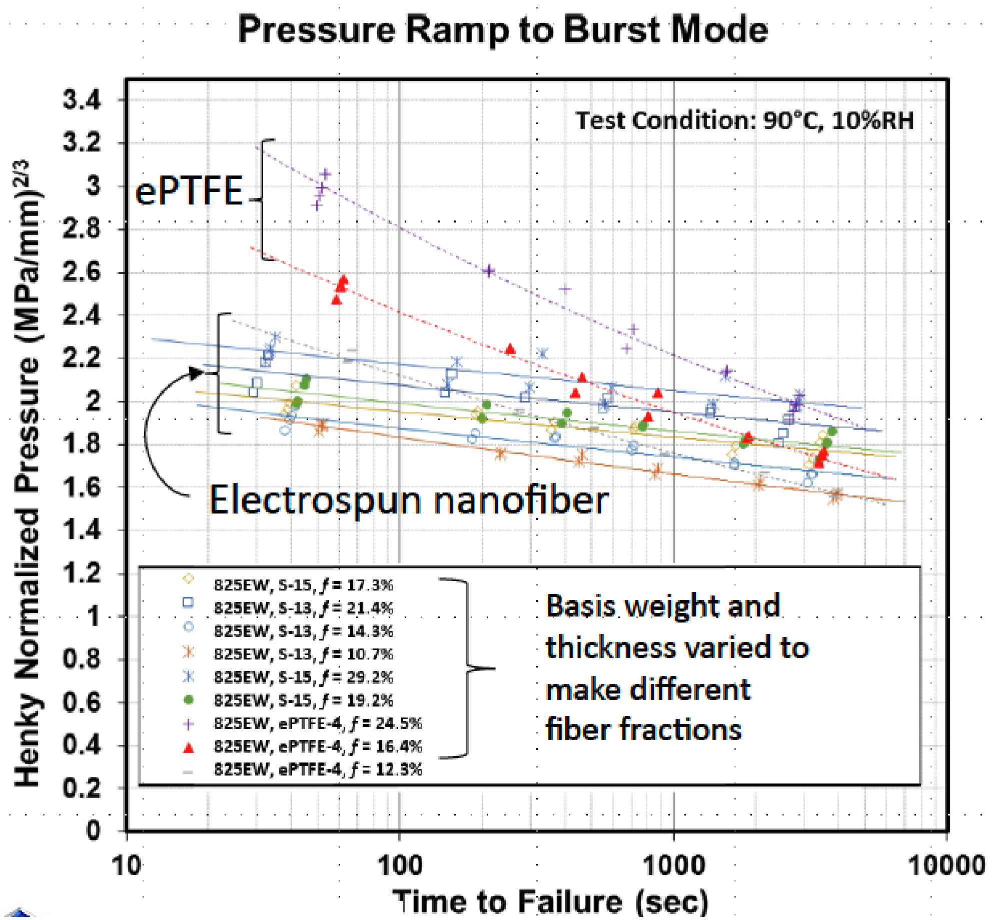
Membrane Degradation (Estimated Lifetime)

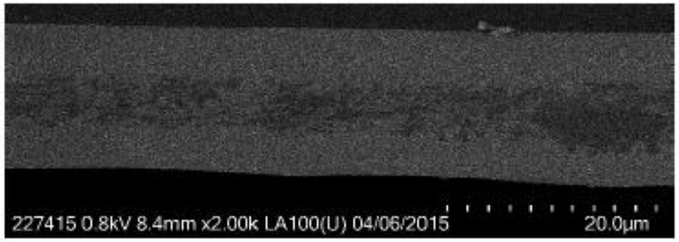
- F ion Release Rate: 3.7 µg/hr (<10 ppb)
- DSM -1100EW (Stabilized Ionomer): ~55,000 hours

Monjid Hamdan – Giner
2013 DOE Merit Review

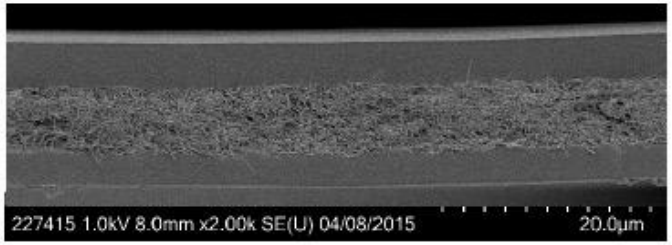
Membrane Support Testing







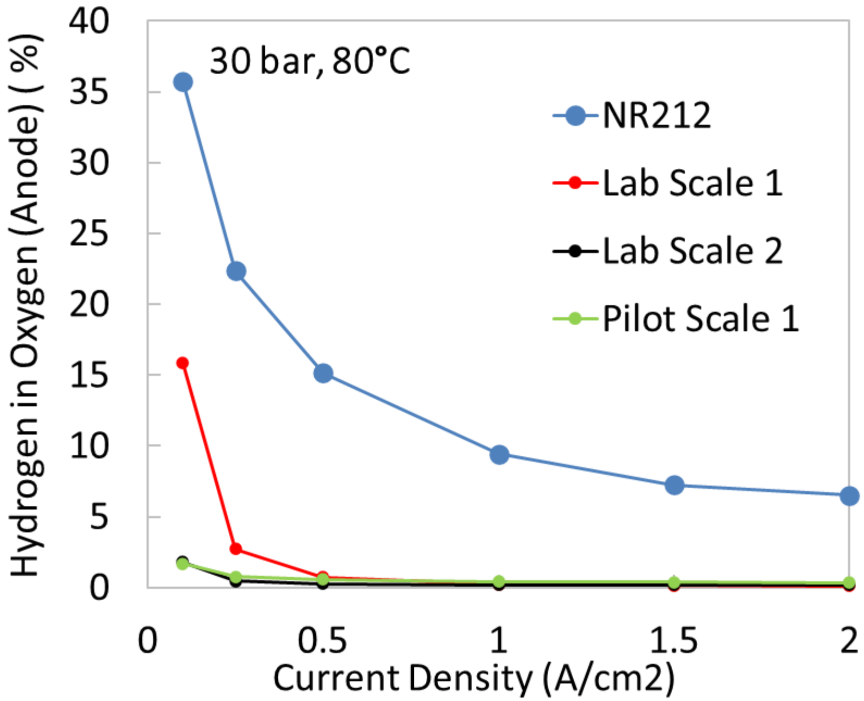
Electrospun nanofiber supported membrane (~16.1% fiber vol fraction)



ePTFE supported membrane (~16.4% fiber vol fraction)

Mike Yandrasits – 3M
2015 DOE Merit Review

Gas Recombination Catalyst Additives



Active area: 50 cm², Cell temperature: 80 °C, Anode: 0.4 mg/cm² IrO_2, Cathode: 0.1 mg/cm² Pt/HSC, partial pressures: ~0.8 bar (O_2), 30 bar (H_2),

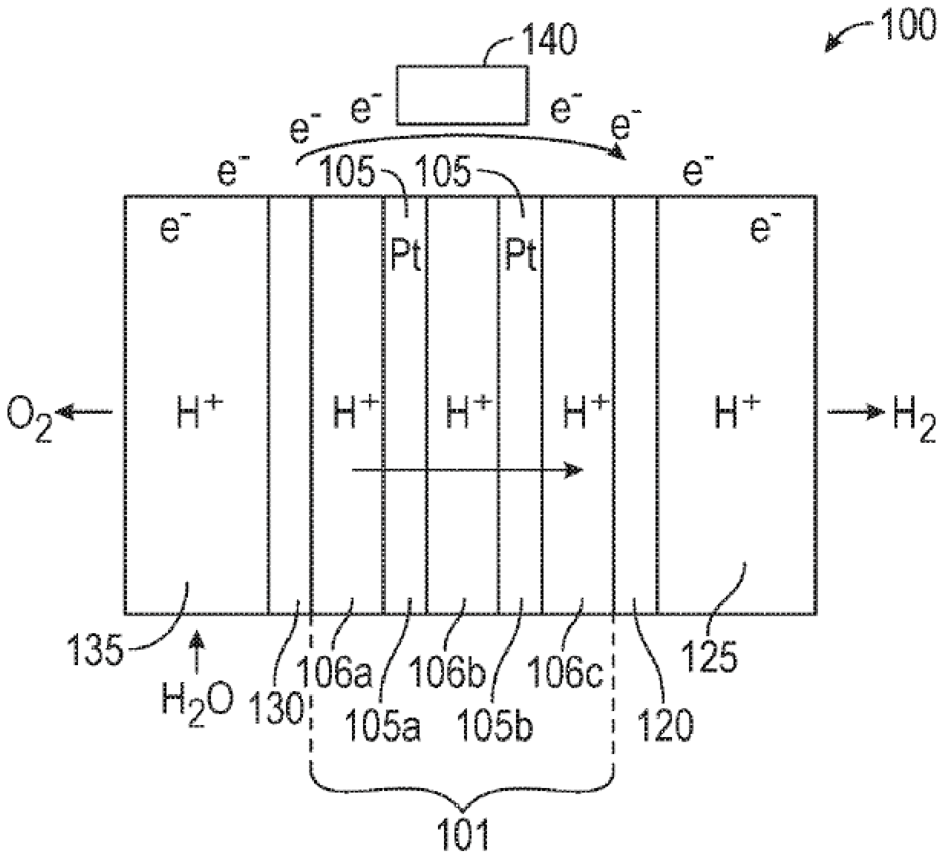
- PEM MEAs utilizing 50 µm membranes require hydrogen crossover mitigation
- Gas recombination catalysts (GRCs) in membrane are effective tools to mitigate hydrogen crossover
- At 80C and 30 bar p_{H2} (most extreme conditions yet tested), mitigated prototype membranes exhibit:
  - <20% LFL from 0.25 A/cm² to 2 A/cm²
  - <50% LFL from 0.1 A/cm² to 0.25 A/cm²
- Time effect on membrane performance under evaluation

Membrane	GRC Loading (mg/cm²)	H_2 in O_2 Content in Anode at 0.25 A/cm² (%)
NR212	0	22.4
Lab Scale 1	<<0.1	2.7
Lab Scale 2	<<0.1	0.5
Pilot Scale 1	<<0.1	0.75

50 µm reinforced membrane with GRC demonstrates up to 50x reduction in effective H_2 crossover at 80C, 30 bar p_{H2}

Andrew Park - Chemours

Multilayer PEMWE Membranes



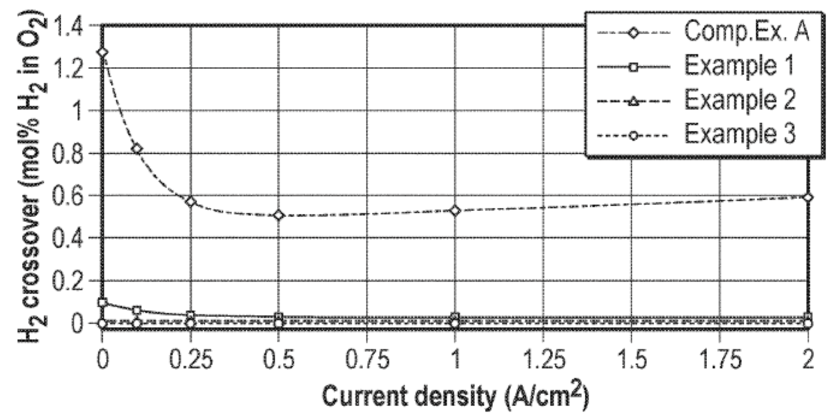
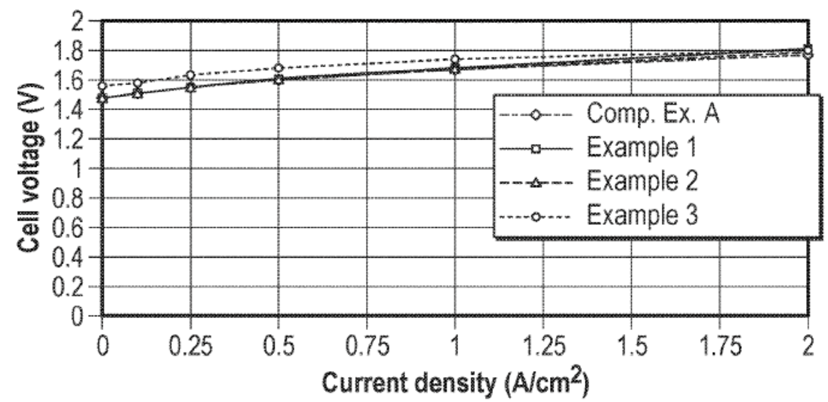


FIG. 4



3M US Patent Appl.
US 2020/0102659 A1

PEM Lifetime Additives

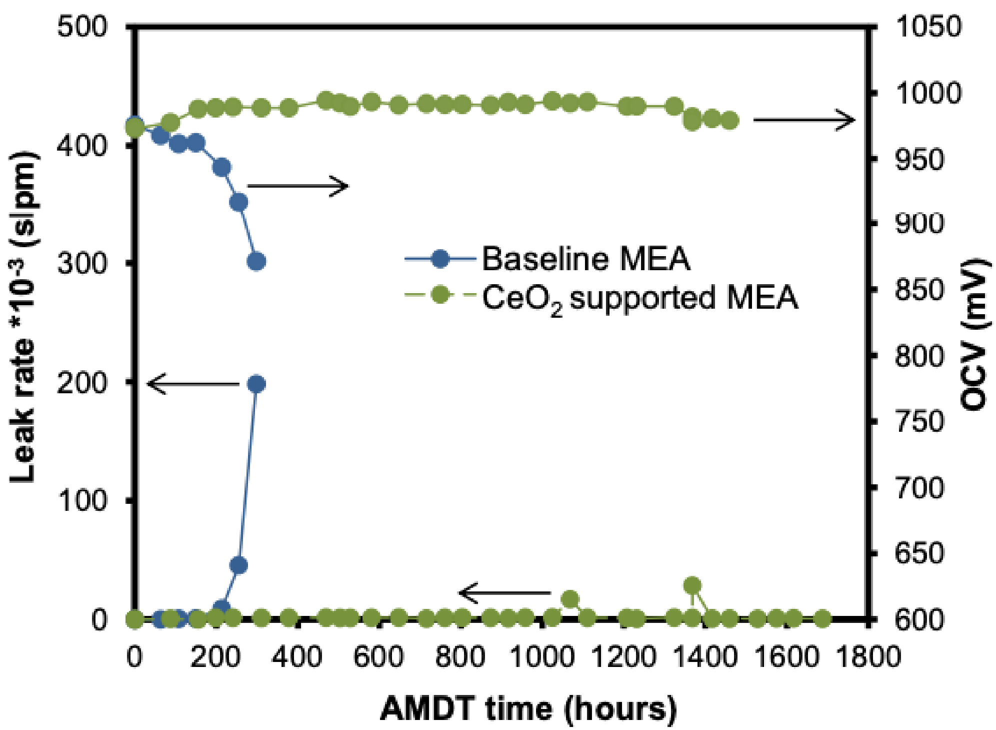


Figure 1. Hydrogen leak rate and open circuit voltage (OCV) development of baseline and CeO_2 supported MEAs during the accelerated membrane durability test (AMDT).

$$Ce^{3+} + HO^{\cdot} + H^+ \rightarrow Ce^{4+} + H_2O$$

$$Ce^{4+} + H_2O_2 \rightarrow Ce^{3+} + HOO^{\cdot} + H^+$$

$$Ce^{4+} + HOO^{\cdot} \rightarrow Ce^{3+} + O_2 + H^+$$

CeO_2 addresses both HO• and HOO• radicals as well as H_2O_2.

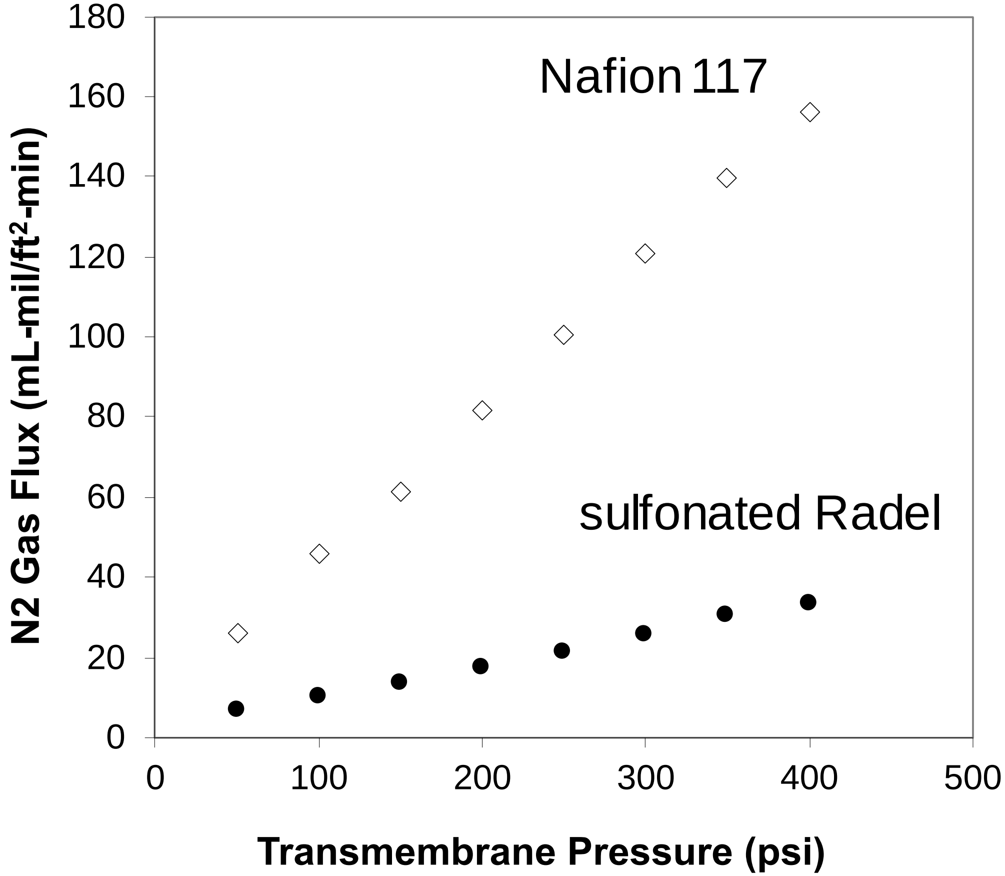
What are the key degradation-causing side products in PEMWEs? Need to investigate mechanisms and then design mitigation strategies.

J. Electrochem Soc., 165 (10) F780-F785 (2018)

Non-PFSA Alternatives

- Growing concerns around PFAS and manufacture/degradation of fluorinated polymers
- Have some proven attributes:
  - Low gas crossover
  - High modulus
  - Adjustable properties
- Very limited performance and lifetime data
- Little support and additive engineering work for new polymer structures

Non-PFSA Gas Crossover



Can decrease gas crossover 5-10x compared to PFSAs without much trouble.

ARPA-E GRIDS
w/Nel Hydrogen

Non-PFSA Mechanical Properties

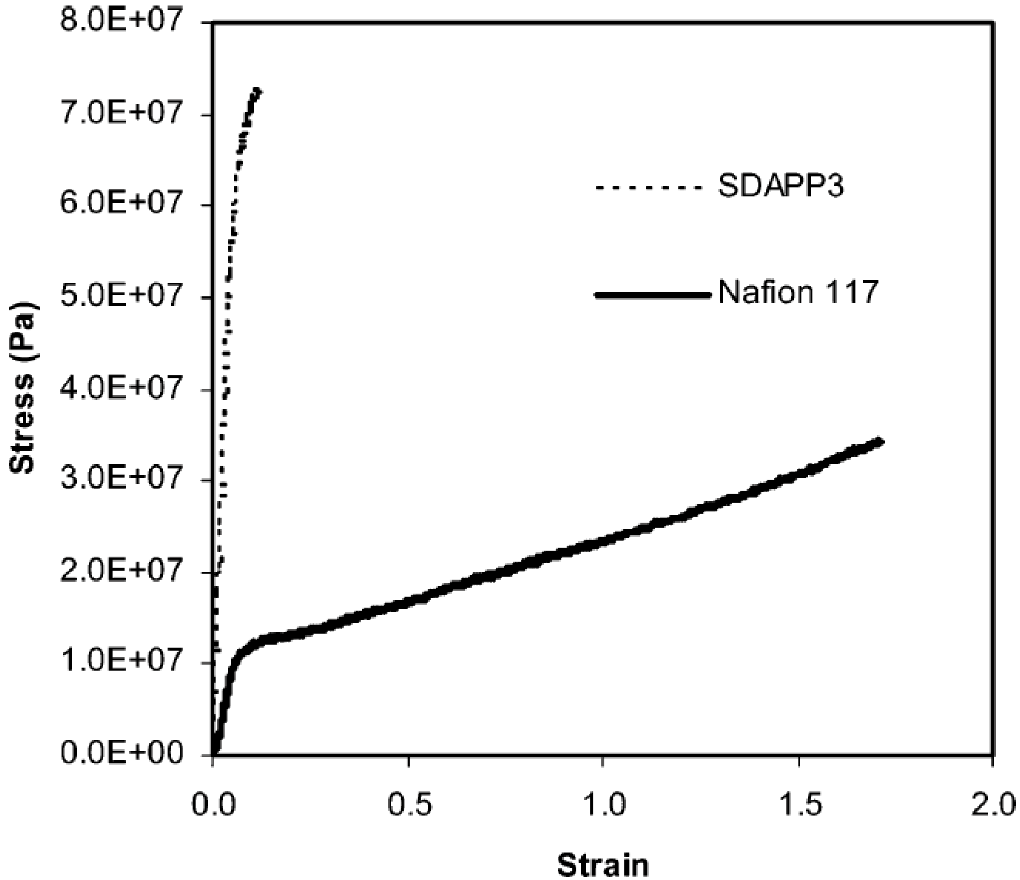


Figure 7. Tensile stress−strain properties of SDAPP3 and Nafion 117 dry films.

Higher modulus of aromatic membranes will lead to less creep.

However, membranes can be brittle and can fatigue crack during cycling.

Need strong (high modulus) and tough (high elongation) membranes.

Fujimoto, et al. Macromolecules 2005.

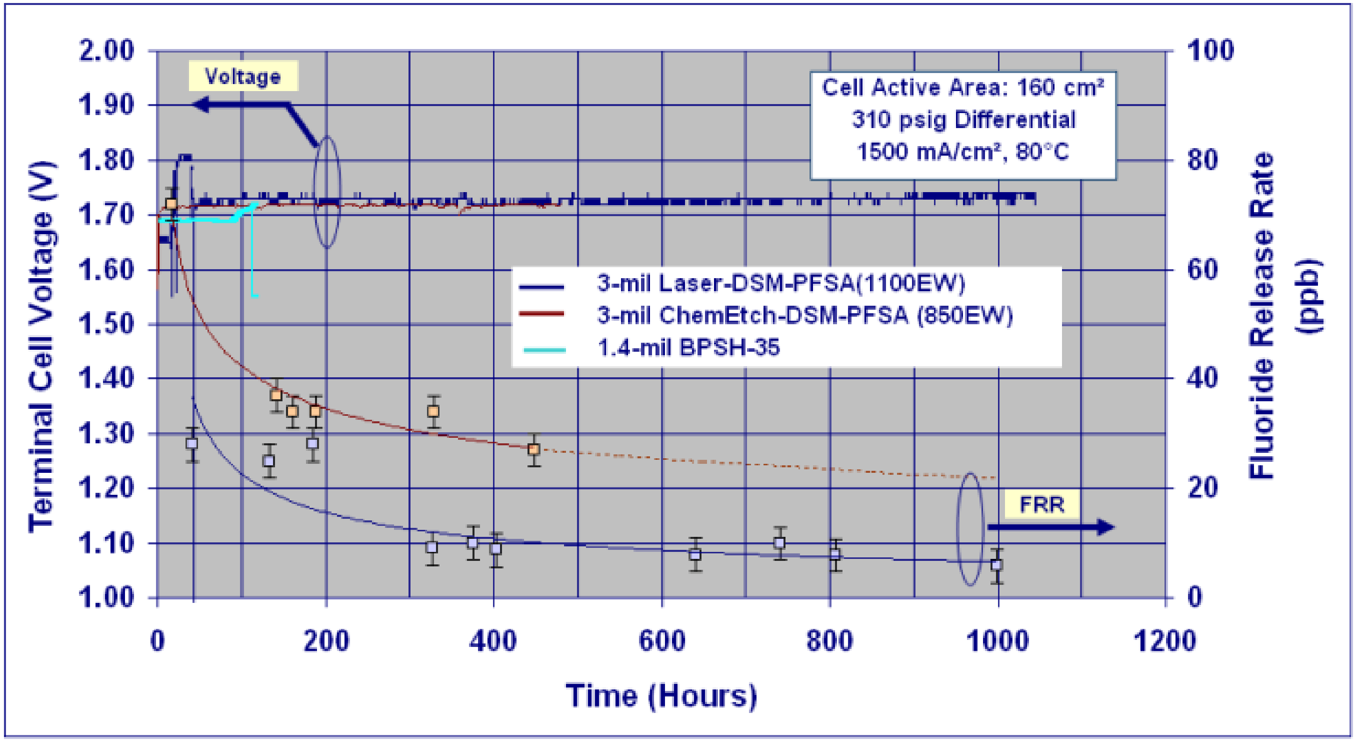
Non-PFSA Tunable Water Transport

There is a trade-off of conductivity, mechanical properties, gas crossover, and water transport that must be considered in non-PFSA PEMWE membranes.

	IEC ($mmol\ g^{-1}$)	**Water uptake (%)**	**Thickness (microns)**	**Water Permeability ($g\ cm\ cm^{-2}\ psi^{-1}\ s^{-1}$) 10^{-10}**
S-Radel 1.0	**1.05**	**7.45**	**62**	**0.13**
S-Radel 1.6	**1.59**	**21.8**	**76**	**0.61**
S-Radel 2.0	**1.95**	**26.5**	**95**	**2.1**
S-Radel 2.5	**2.54**	**69.6**	**121**	**15**
NRE212	**0.91**	**33**	**60**	**6.3**

ARPA-E GRIDS
w/Nel Hydrogen

Non-PFSA Membrane Lifetime



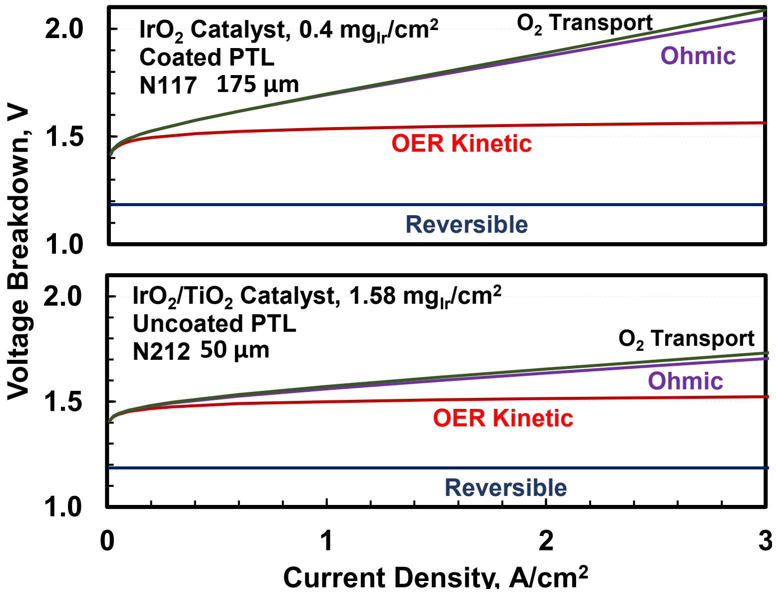
- **Membrane Performance**
  (3-mil Laser Drilled DSM PFSA(1100EW)
  - Voltage:1.71-1.73V
  - Efficiency: 75.1% LHV (88.8% HHV)
  - Completed 1000 Hour Life Milestone
- **Membrane Degradation (Estimated Lifetime)**
  - F ion Release Rate: 3.7 µg/hr (<10 ppb)
  - DSM -1100EW Stabilized Ionomer: ~55,000 hours
  - DSM – 850EW Non-Stabilized Ionomer: <20,000 hours
  - BPSH-35: Life test fail due to H_2 X-over (pinhole detected)

Scarce information on non-PFSA durability, what does exist isn't promising.

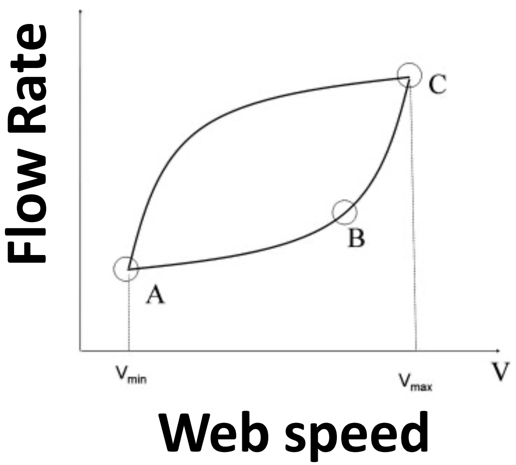
Monjid Hamdan – Giner
2010 DOE Merit Review

Membrane Processing Challenges

- Development of new chemistries challenging without right equipment and requires kg-scale quantities
- Specialized equipment needed for fabrication of composite or multilayer membranes
- Meeting overpotential technical targets will likely require transition from extrusion (t > 100 µm) to solution casting (t < 50 µm)
- Polymer solubility and density ($\rho_{Naf} = 2\ \frac{g}{cm^3}$) must be materials development considerations to enable manufacturing processes within operable limits (e.g. coating window, drying/oven lengths, solvent toxicity)



Coating Window

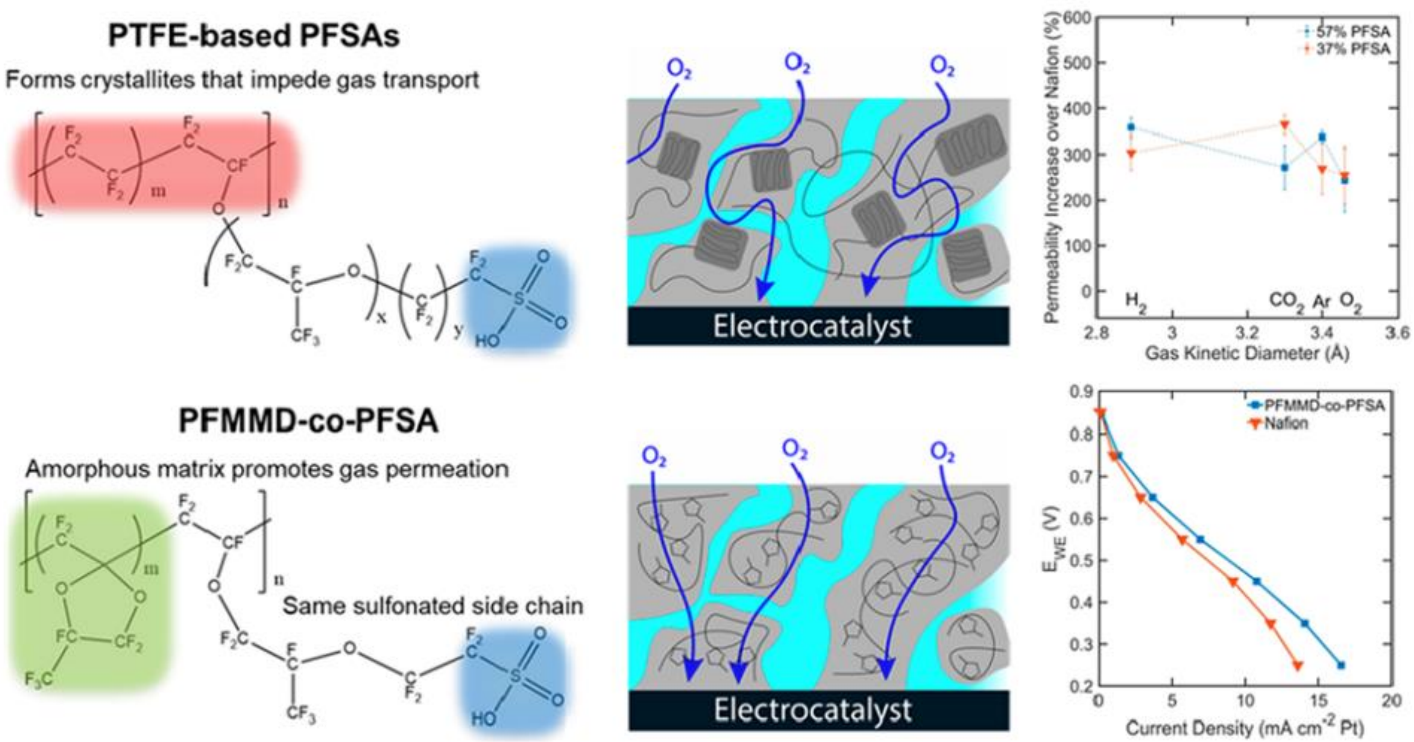


Drying Challenges

Scott Mauger - NREL

Ionomers for PEMWE Catalyst Layers

Likely need different properties from catalyst layer ionomers compared to membranes



Katzenberg, et al. JACS 2020.

Sustainability and Recycling

- Solvent processing is already a tremendous cost driver in the chemical industry
- Many electrochemical cell recycling projects discard the membrane/organics and focus on the inorganics
- How soon will PEMWE components be designed with recycling ease as a metric?
- Fluorinated polymer manufacturing may be targeted – not just their use.

Conclusions

- New PFSA PEMWE membranes are likely on their way.
- Need to consider longer-term solutions, including costs and recycling/sustainability.
- Interesting non-PFSA membrane work to study trade-offs, but lifetime is a key question.
- It will be important to know what we can borrow from PEMFCs and what new knowledge needs to be gained for effective PEMWE membrane and ionomer design.