State of the Art and Challenges in Polymer Electrolyte Fuel Cell Membranes

NIST NCMC-14 Meeting

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Outline

- Fuel Cell Types and Related Separators
- PEM Fuel Cell Types
  - Hydrogen PEMFC
  - Direct Methanol PEMFC
  - Other: Alkaline, Alternative Fuels
- Membrane Requirements
- PFSA Membranes
- Hydrocarbon Membranes
- Challenges and Future Directions

Fuel Cell Types

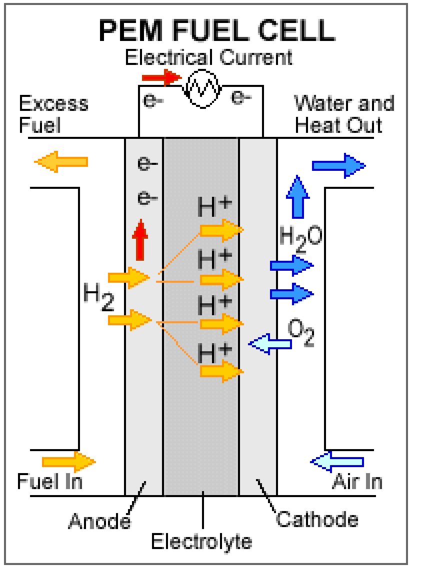
Fuel Cell Type	Common Electrolyte	Operating Temperature	System Output	Electrical Efficiency	Applications	Advantages	Disadvantages
Polymer Electrolyte Membrane (PEM)*	Solid organic polymer poly-perfluorosulfonic acid	50 - 100°C 122 - 212°F	<1kW – 250kW	53-58% (transportation) 25-35% (stationary)	▪ Backup power ▪ Portable power ▪ Small distributed generation ▪ Transportation	▪ Solid electrolyte reduces corrosion & electrolyte management problems ▪ Low temperature ▪ Quick start-up	▪ Requires expensive catalysts ▪ High sensitivity to fuel impurities ▪ Waste heat temperature not suitable for combined heat and power (CHP)
Alkaline (AFC)	Aqueous solution of potassium hydroxide soaked in a matrix	90 - 100°C 194 - 212°F	10kW – 100kW	60%	▪ Military ▪ Space	▪ Cathode reaction faster in alkaline electrolyte, leads to higher performance	▪ Expensive removal of CO_2 from fuel and air streams required (CO_2 degrades the electrolyte)
Phosphoric Acid (PAFC)	Liquid phosphoric acid soaked in a matrix	150 - 200°C 302 - 392°F	50kW – 1MW (250kW module typical)	>40%	▪ Distributed generation	▪ Higher overall efficiency with CHP ▪ Increased tolerance to impurities in hydrogen	▪ Requires expensive platinum catalysts ▪ Low current and power ▪ Large size/weight
Molten Carbonate (MCFC)	Liquid solution of lithium, sodium, and/or potassium carbonates, soaked in a matrix	600 - 700°C 1112 - 1292°F	<1kW – 1MW (250kW module typical)	45-47%	▪ Electric utility ▪ Large distributed generation	▪ High efficiency ▪ Fuel flexibility ▪ Can use a variety of catalysts ▪ Suitable for CHP	▪ High temperature speeds corrosion and breakdown of cell components ▪ Complex electrolyte management ▪ Slow start-up
Solid Oxide (SOFC)	Yttria stabilized zirconia	600 - 1000°C 1202 - 1832°F	<1kW – 3MW	35-43%	▪ Auxiliary power ▪ Electric utility ▪ Large distributed generation	▪ High efficiency ▪ Fuel flexibility ▪ Can use a variety of catalysts ▪ Solid electrolyte reduces electrolyte management problems ▪ Suitable for CHP ▪ Hybrid/GT cycle	▪ High temperature enhances corrosion and breakdown of cell components ▪ Slow start-up ▪ Brittleness of ceramic electrolyte with thermal cycling

**Direct Methanol Fuel Cells (DMFC) are a subset of PEM typically used for small portable power applications with a size range of about a subwatt to 100W and operating at 60 - 90°C.*

http://www1.eere.energy.gov/hydrogenandfuelcells/fuelcells/fc_types.html#comparison

PEM Fuel Cells

- Polymer Electrolyte Membrane Fuel Cells
  - H_2 or methanol fuel
    - Stored, or from reformed hydrocarbons
  - Relatively low temperature operation
    - 60-90 °C is typical
    - 80 °C for H_2 PEM
  - Solid polymer separator (membrane)
    - Proton conductive
    - Mechanically strong
    - Hydrolytically and oxidatively stable
    - Low in-plane swelling
    - Low fuel and oxidant cross-over
    - Electrically insulating
    - Inexpensive (~10m² membrane / vehicle)



PEM Requirements – "A Tough Challenge"

Property	Metric	Typical Value	Material
Proton conductive	4-point *ex-situ* (hydrated 60-80C) 4-point *ex-situ* (25% to 90% RH)	160-200mS/cm 5-100mS/cm	PFSA
Mechanically strong	Tensile strength (23°C, 50% RH) Modulus (23°C, 50% RH)	~25 MPa* ~285 MPa*	Nafion®
(Electro)Chemically stable	Time @ OCV (*in-situ*) [a]	100-200h † 300-400h	PFSA Hydrocarbon
Low in-plane swelling	(%) x-y dimensional swelling	< 5% 15-20%	Reinforced Non-reinforced
Low fuel and gas cross-over	Electrochemical (mA/cm^2)	1.5 mA/cm^2 0.5 mA/cm^2	Nafion® Arkema M41
Inexpensive	$ retail $ @ commercial volume	$465 / m^2** $20 / m^2***	Nafion®

*DuPont technical data sheet for Nafion® NR-211 membrane.
**Retail price for NR-211 from Ion Power, Inc on 10/29/2008 (www.ion-power.com)
***US DOE target for automotive applications.
† www.hydrogen.energy.gov/pdfs/progress07/v_m_5_foure.pdf

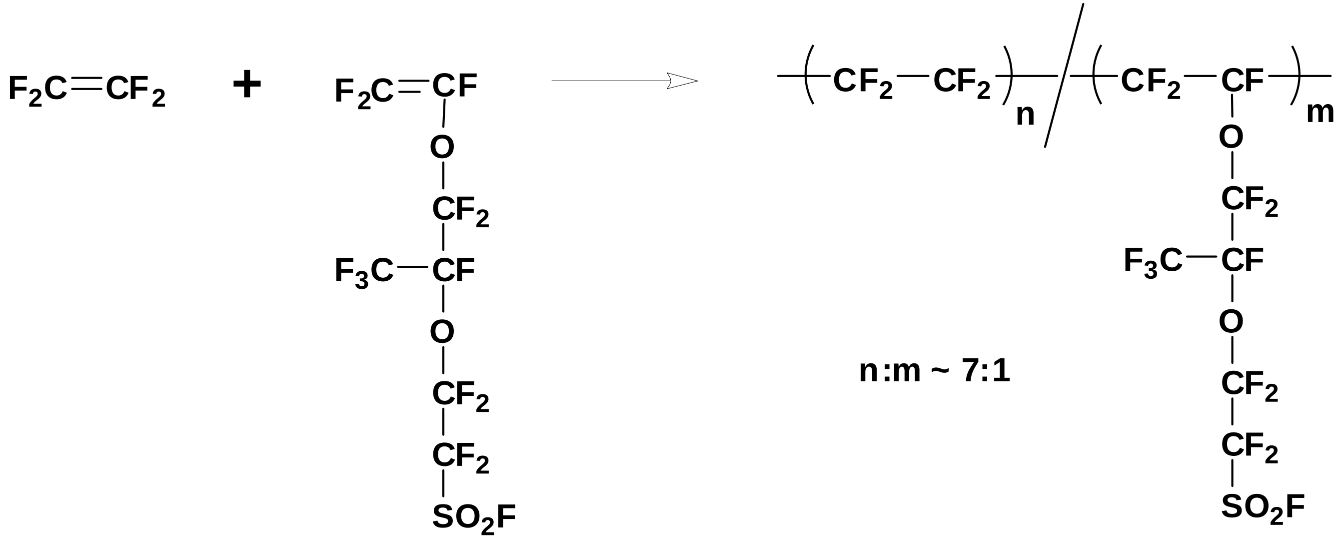
[a] Zhang, J., et.al., J. Power Sources, 2006, (163), 532-537.

Membrane Types

- Membrane Chemistry
  - PFSA
    - Perfluorinated copolymers
  - Hydrocarbon
    - Aromatic backbone copolymers
    - Aliphatic backbone copolymers
    - Polymer blends
    - Controlled-architecture (block and graft copolymers)
- Application
  - H_2 PEM – Stationary
  - H_2 PEM – Automotive
  - H_2 PEM – Portable (backup power)
  - DMFC

PFSA Membranes

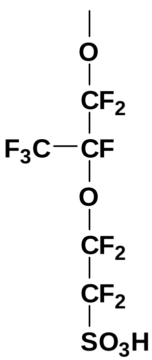
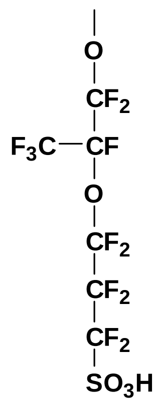
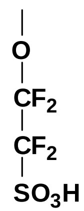
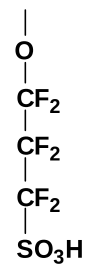
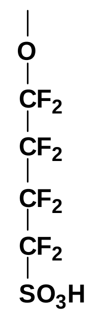
- Perfluorinated Sulfonic Acid
  - Nafion®
  - A single copolymer
  - Developed (1963) for chlor-alkali applications
    - Tetrafluoroethylene + perfluorinated vinyl ether



- EW ~ 1000-1100 g/mol H^+
- IEC ~ 1.0 – 0.91 molH^+/g

PFSA Membranes

- Non-Nafion® PFSA Materials
  - Similar production process as Nafion®
  - Varied side-chain type

	Nafion® (DuPont)	Aciplex® (Asahi Chemical)	Hyflon® Ion (Solvay-Solexis)	Flemion® (Asahi Glass)	3M
Side Group					
Typical EW	1000-1100	1000-1100	750-900	800-900	800-900

EW = grams of material / mol SO_3H

Grot, W., in "Perfluorinated Ionomers", 2007, ISBN 978-0-8155-1541-8.

R.L. Ames et al. / Journal of Membrane Science 249 (2005) 65–73

PFSA Membranes – In-Situ Performance

- Nafion® (DuPont)

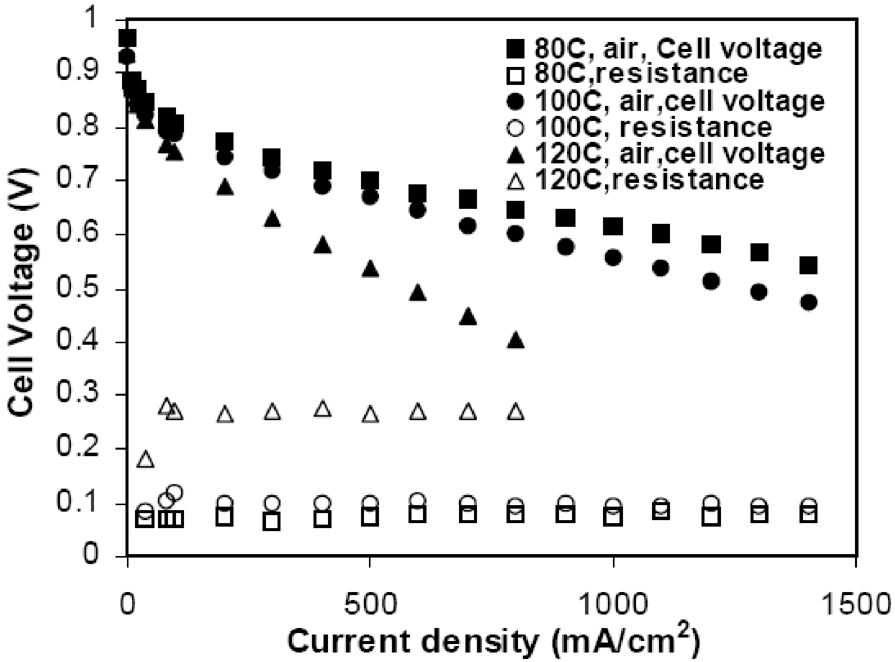


Fig.1 Cell performance at three different conditions at atmospheric pressure on air
Cell temperature was 80°C (75%R.H. cathode), 100°C (70%R.H. cathode) and 120°C (35%R.H.cathode)

PFSA Membranes – State of the Art - Durability

- OCV Hold Accelerated Durability Testing*
  - DOE Protocol*: 90 ^oC, O_2, OCV, 30% RH
  - Failure Criterion: 20% loss in OCV
  - Chemical degradation leads to membrane thinning
  - Typical PFSA membranes fail in 100-200h

- RH Cycling*
  - DOE Protocol*: 25-50cm^2 cell, 80^{o}C, cycle air 2min./2min. @ 0/100% RH
  - Failure Criterion: air crossover > 10sccm or 20,000 cycles
  - RH cycling leads to mechanical membrane failure
  - Only 1 PFSA membrane meets 20,000 cycle target (PFSA 111-IP)

Tang, H., et.al., “A Degradation Study of Nafion Proton Exchange Membrane of PEM Fuel Cells”, *J. Power Sources,* **2007**, (170), 85–92.

Schiraldi, D.A., “Perfluorinated Polymer Electrolyte Membrane Durability”, *J.Macromol. Sci., Part C: Polym. Rev.*, **2006**, (46), 315–327.

*US DOE testing protocols, Funding Opportunity Announcement DE-PS36-08GO98009 (5/27/2008).

PFSA Membranes – State of the Art – Overall

- Asahi Glass – New ‘NPC’ PFSA Membrane

Experimental Conditions

Cell Temp : 120°C

RH : 18% (H_2 & Air)

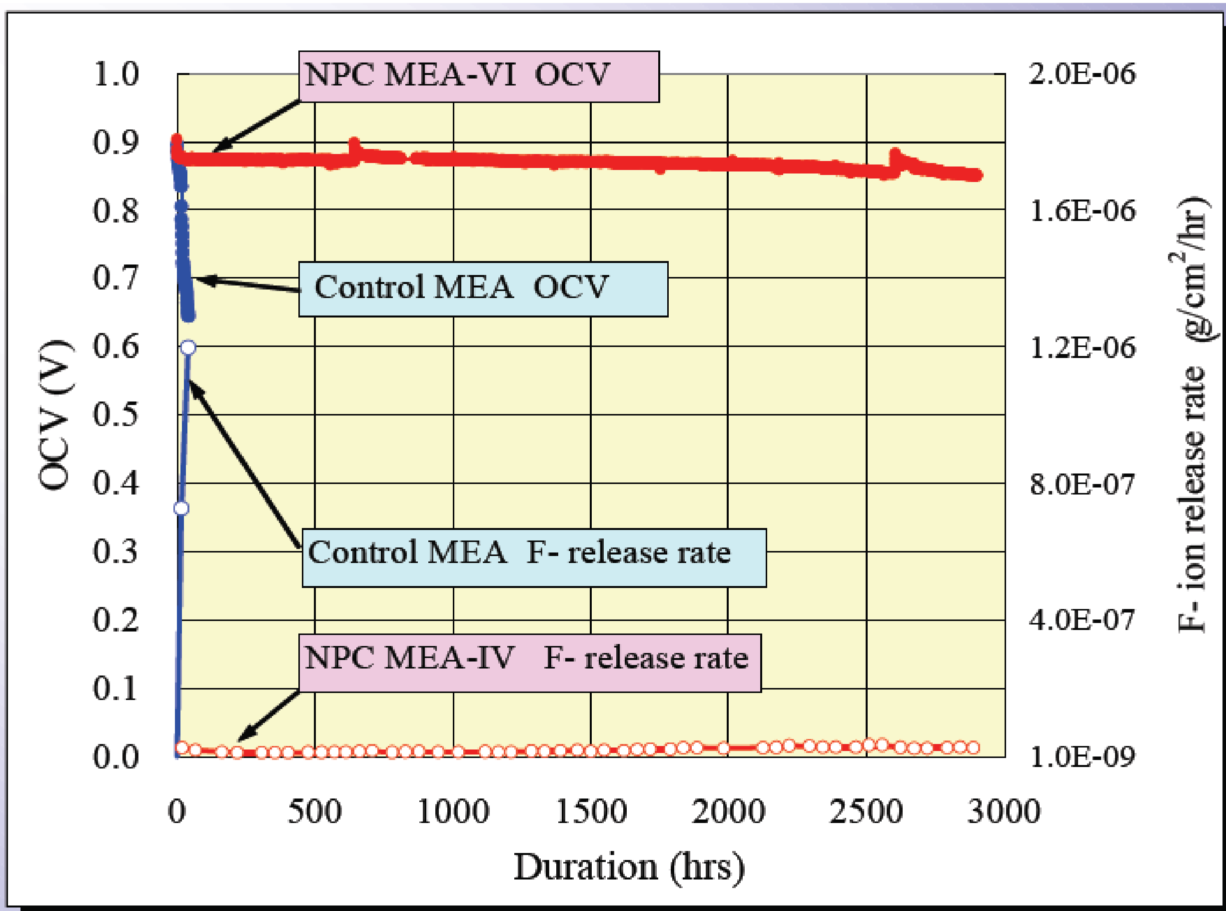
Press : Ambient

Control MEA

Flemion SH25 : 25 μm

Cathode Pt : 0.2mg/cm²

Anode Pt : 0.2mg/cm²



Endoh, E., “Progress of Highly Durable MEA for PEMFC Under High Temperature and Low Humidity Conditions”, 2007 *Fuel Cell Seminar Presentation.*

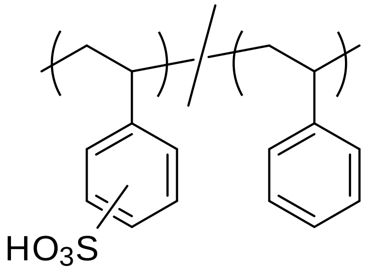
PFSA Membranes – "Wish List"

- Low EW Ionomer → Conductivity
- Mechanically Reinforced → Low Swelling
- Stabilized end groups → Chem. Stability
- Redox-active additive → Chem. Stability (*in-situ*)
- High conductivity at low RH → Auto. applications
- Low gas cross-over → High fuel utilization
- Inexpensive (<$20/$m^2$) → Commercially viable

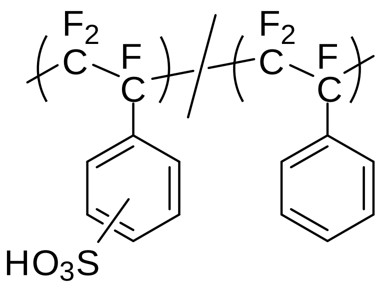
- <u>Low RH conductivity and low cost are difficult for PFSAs</u>

Hydrocarbon Membranes

- Aliphatic Backbones
  - sPS (GE, 1960s)
    - Direct sulfonation of polystyrene
    - Very inexpensive, simple to produce
    - Oxidatively unstable
    - Limited IEC range

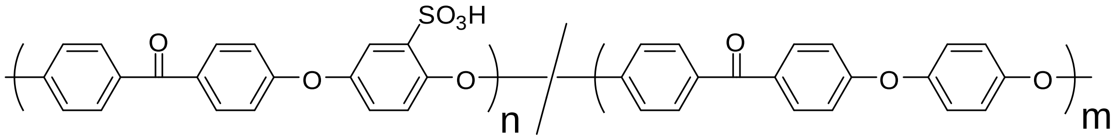


  - BAM3G (Ballard)
    - Copolymerization of α,α,β-trifluorostyrenes
    - Better oxidative stability
    - Limited IEC range
    - Specialized monomer

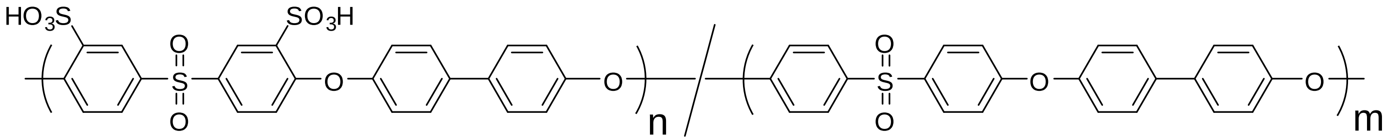


Hydrocarbon Membranes

- Aromatic Backbones
  - sPEEK



    - Direct sulfonation of engineering thermoplastic
  - BPSH



    - Copolymerization of pre-sulfonated monomers
  - Sulfonated polyarylsulfide (sulfone)

    - Copolymerization / sulfonation of intermediates

Hydrocarbon Membranes

- Random Copolymers
  - Advantages
    - Potentially very low cost
    - Increased chemical durability
  - Disadvantages
    - Direct sulfonation ~ limited *in-situ* stability
      - Pre-sulfonation / copolymerization necessary
    - Limited sulfonate content
      - Swelling / conductivity tradeoff
    - Rapid drop in proton conductivity at reduced RH
- Block Copolymers
  - Control size of hydrophilic domains
    - Increase local concentration of acidic functionality

Hydrocarbon Membranes

- BPSH Random Copolymers

Y.S. Kim et al. / Journal of Membrane Science 243 (2004) 317–326 321

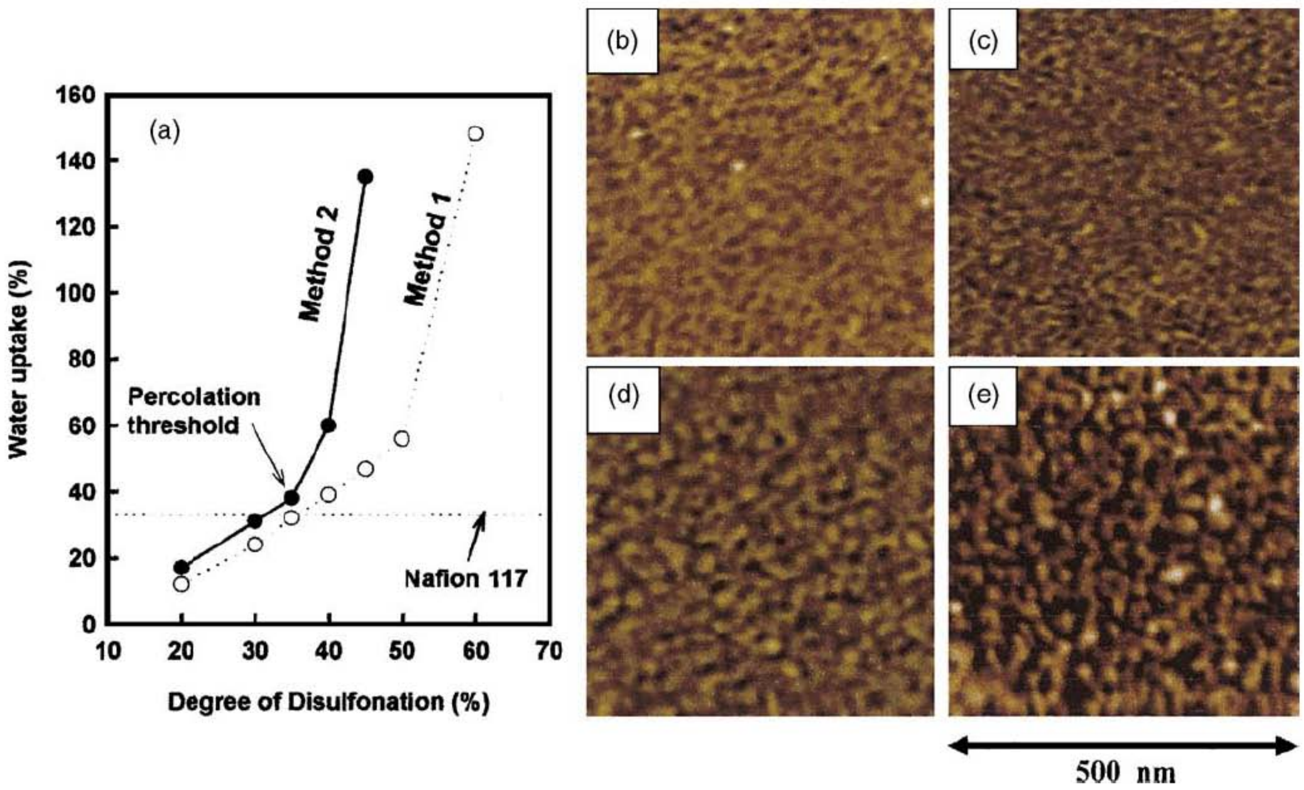


Fig. 4. (a) Percent water uptake and (b)–(e) morphology as a function of degree of disulfonation at 25 °C of BPSH treated by *Method 2* acidification; (b) BPSH-30, (c) BPSH-35, (d) BPSH-40 and (e) BPSH-45. The micrograph (d) was reproduced from [15].

Hydrocarbon Membranes

- Controlled Morphology
  - Polymer architecture determines phase-separated morphology

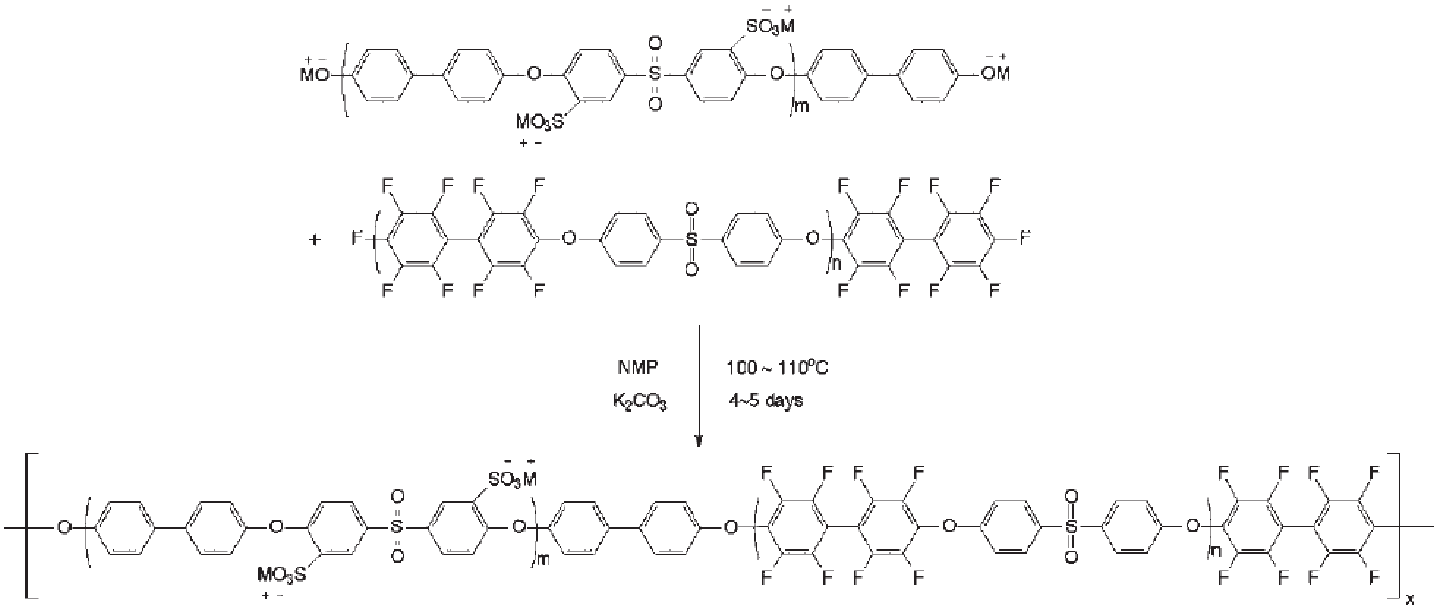
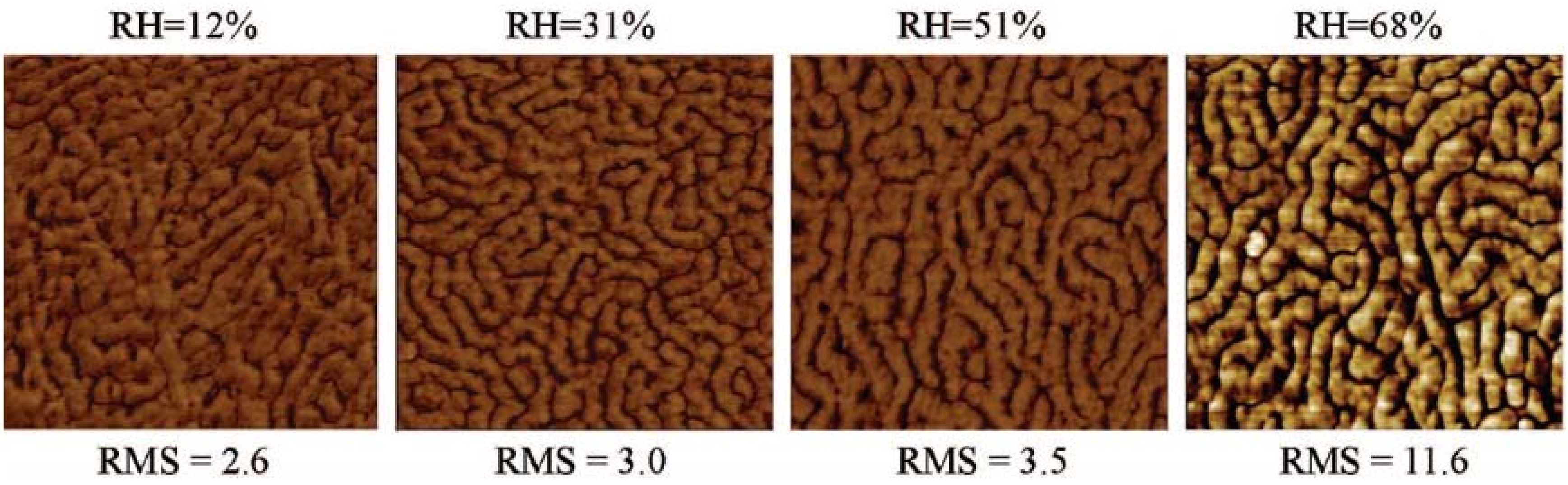


Figure 7.
Synthesis of BisSF-BPSH multiblock copolymers.

McGrath, J.E., et.al., *Macromol. Symp.,* **2006**, (245-246), 439-449.

Hydrocarbon Membranes

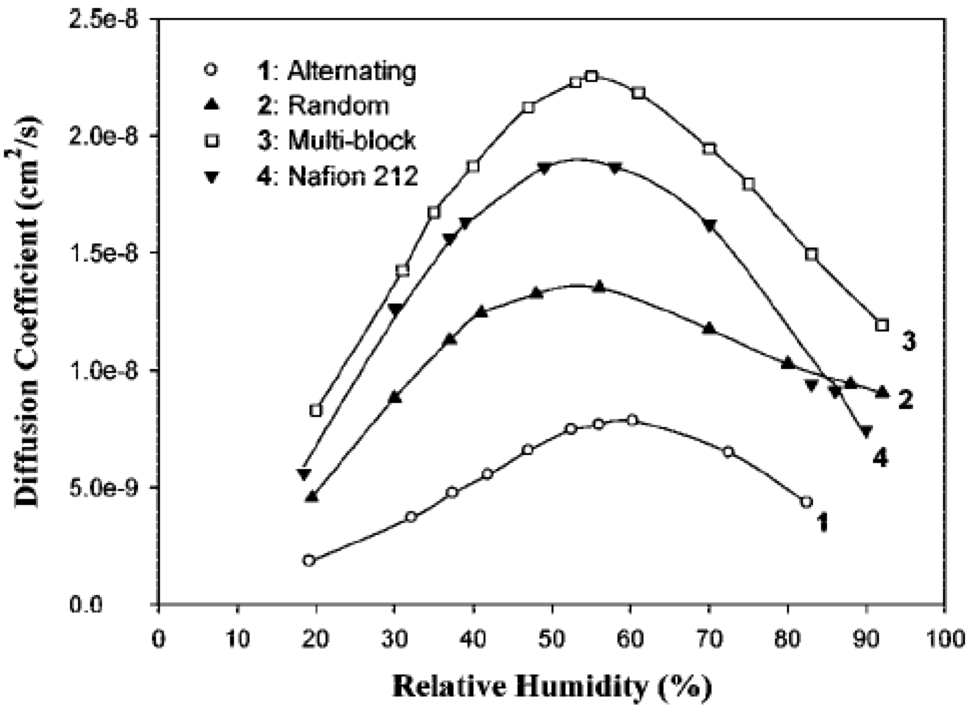
- Controlled Morphology
  - Polymer architecture determines phase-separated morphology
  - BPSH block copolymers



Einsla, M.L., et.al., Chem. Mater, 2008, 20, 5636-5642.

Hydrocarbon Membranes

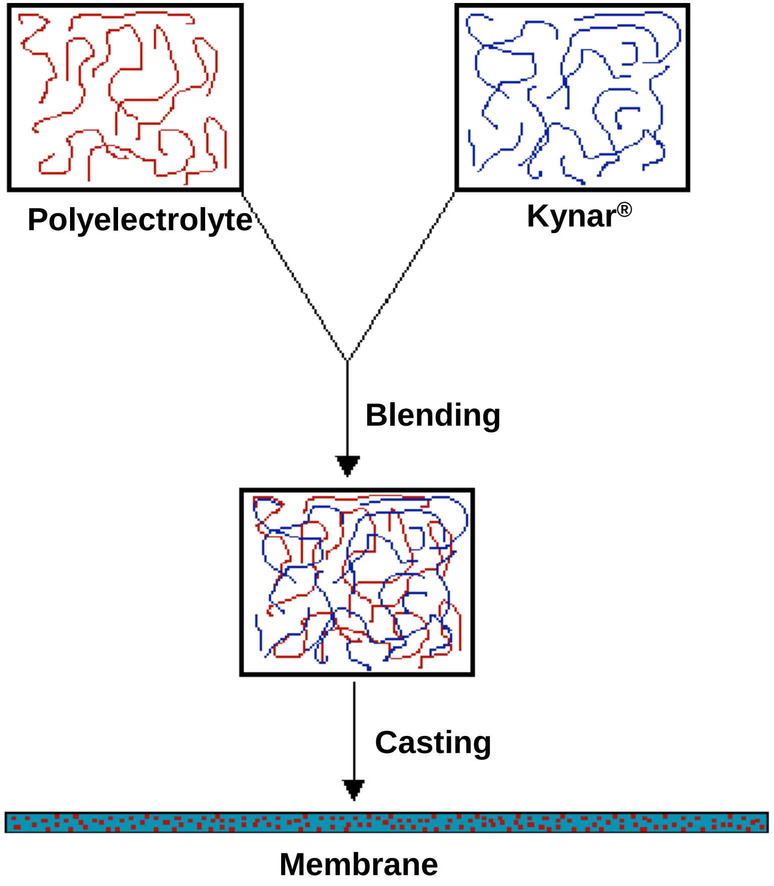
- Water diffusion coefficient comparison for BPSH materials
- Critical for proton transport



Einsla, M.L., et.al., Chem. Mater, 2008, 20, 5636-5642.

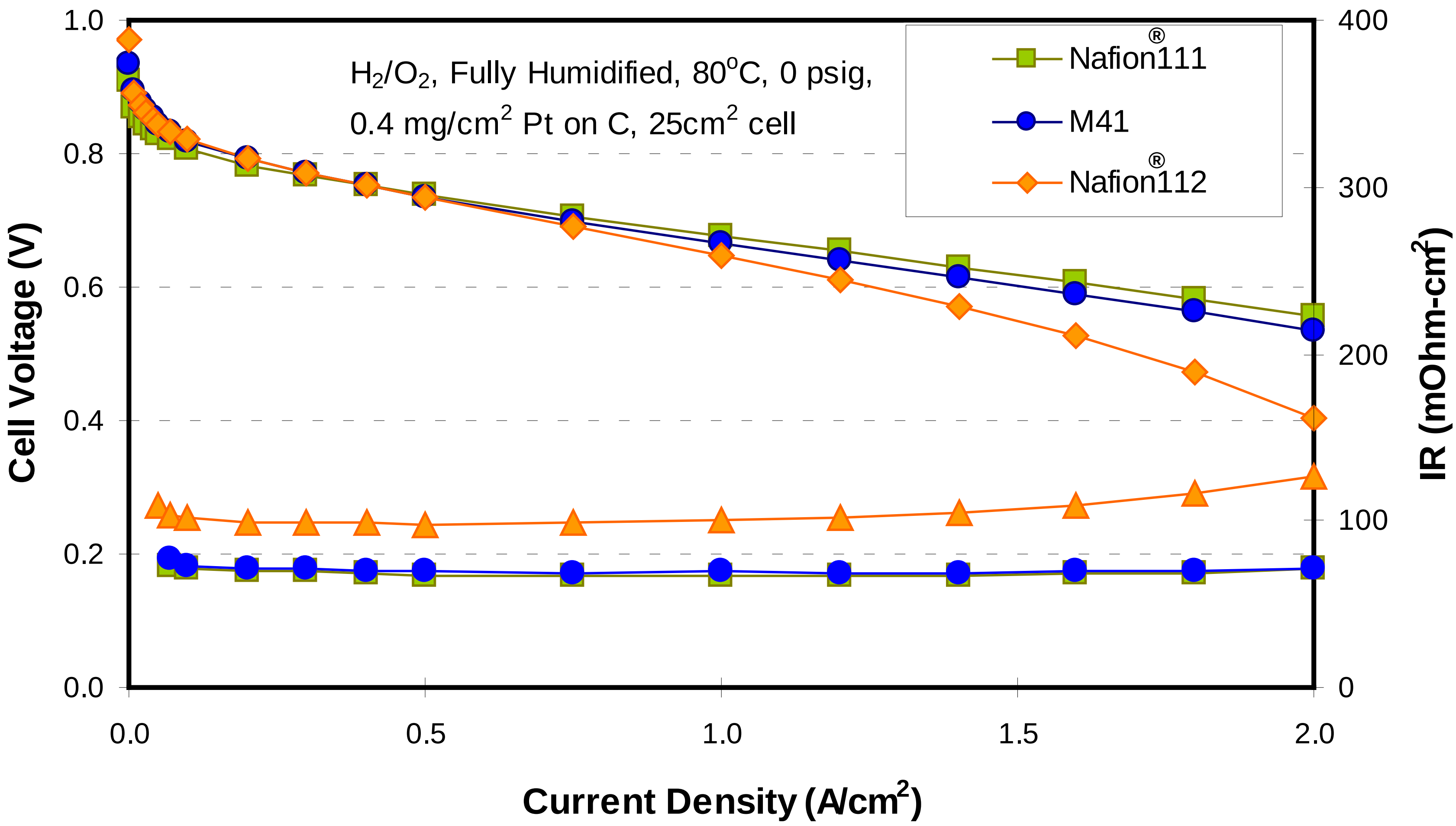
Hydrocarbon Membranes – Arkema's Approach

- Polymer blend system
- Decouple proton conductivity from mechanical requirements
  - Kynar® PVDF
    - Commercial product
    - Mechanical support
    - Chemical resistance
    - Electrochemical stability
  - Polyelectrolyte
    - H^+ conduction
- Process Flexibility
- A lower-cost approach
  - Kynar® PVDF - commercial product
  - Polyelectrolyte – minor component



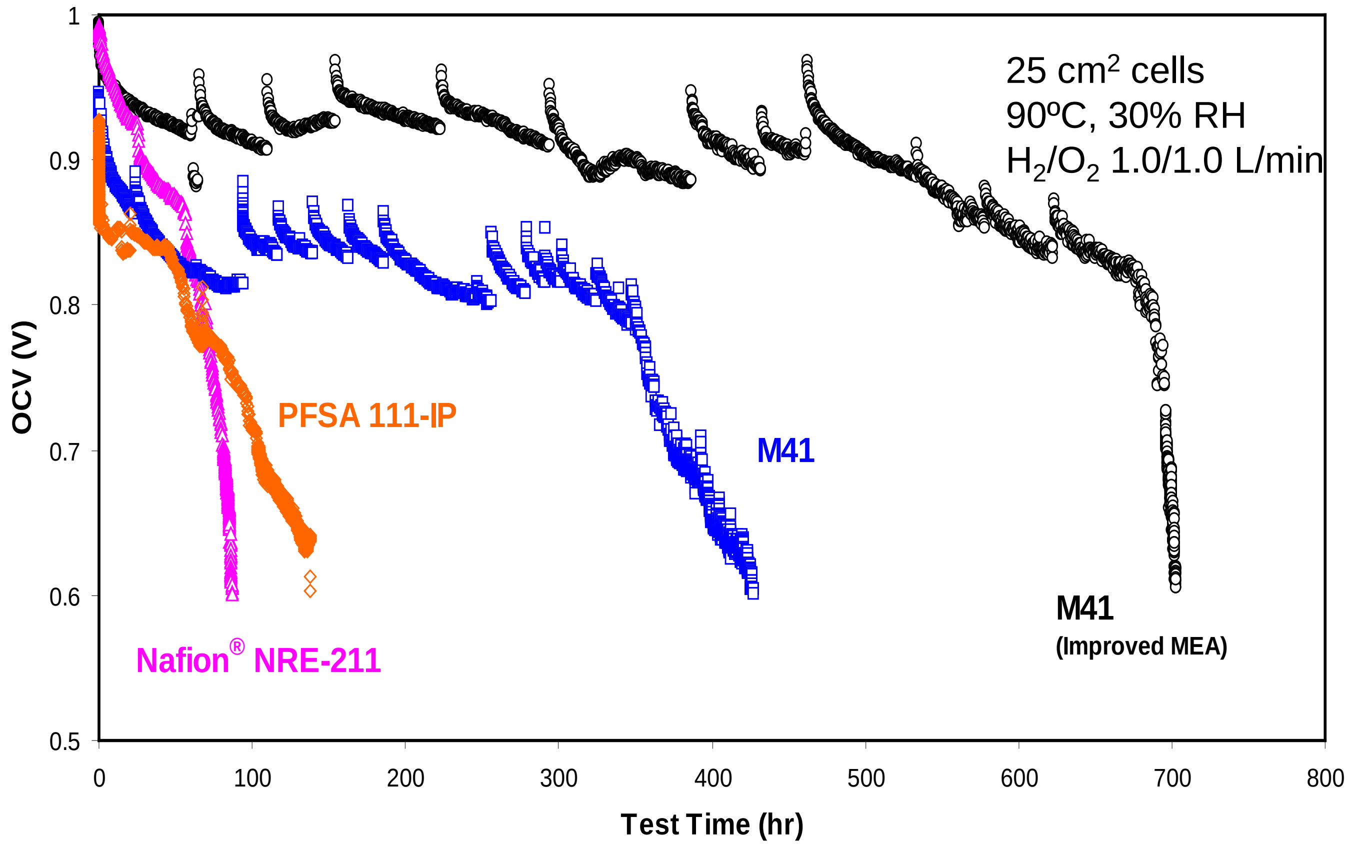
http://www.hydrogen.energy.gov/pdfs/review08/fc_12_goldbach.pdf

Arkema M41: BOL Performance



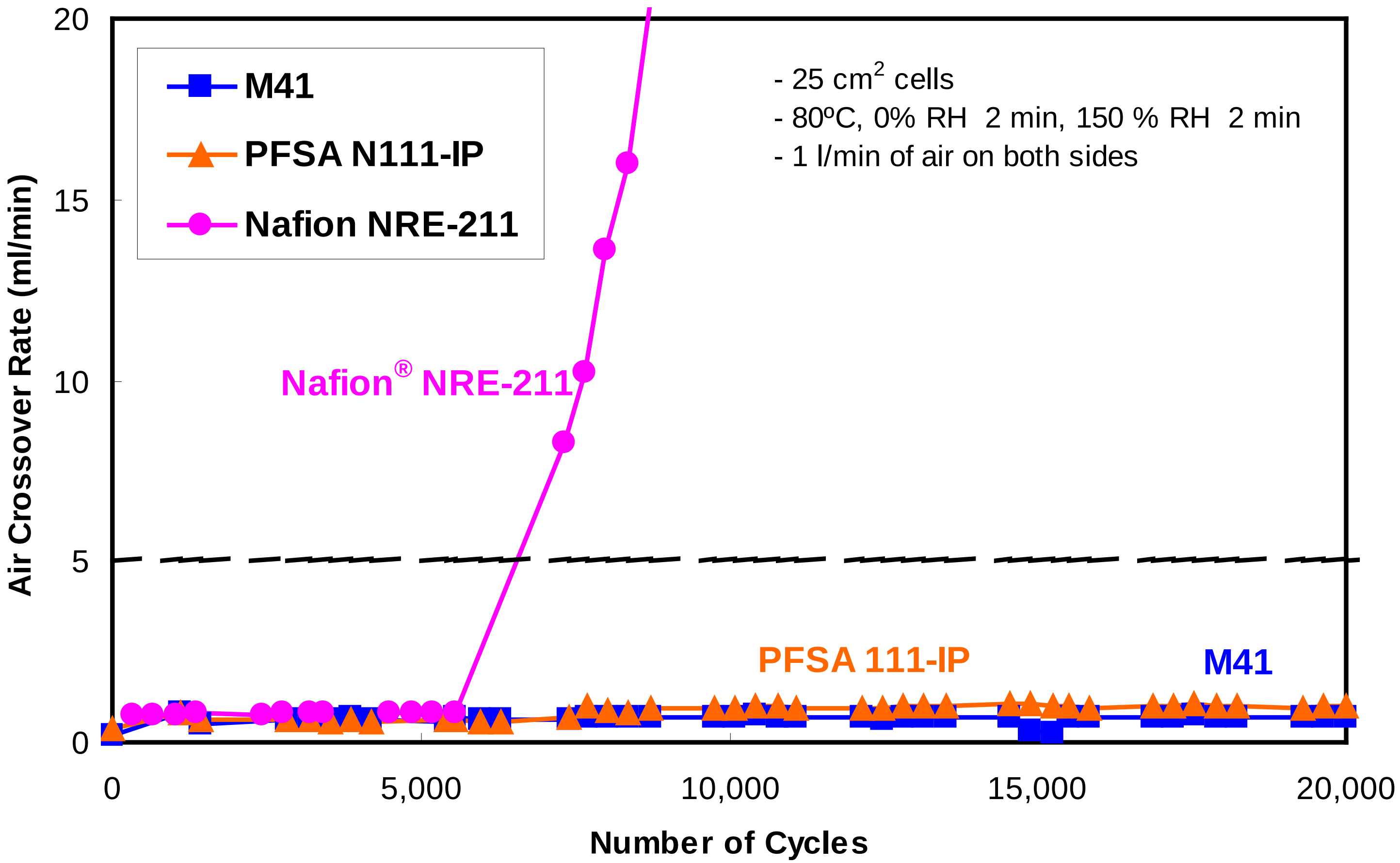
- Comparable in-cell performance to Nafion® 111 demonstrated

Arkema M41 – OCV Durability



- Short resistance decreases for PFSA and M41 membranes
- No fluoride and low sulfate emission from M41
- H_2 cross-over remains very low at failure for M41
- Fluoride emission and H_2 cross-over from PFSAs

Arkema M41: RH Cycling



- Nafion® NRE-211 failed at approximately 6,000 cycles
- M41 and PFSA 111-IP MEAs met target of 20,000 cycles
- M43 (improved M41 MEA) has exceeded 50,000 cycles

State of the Art – Availability

- PFSA Membranes
  - Nafion® (DuPont) - Widely available
    - Distributed in film and dispersion form
    - www.ion-power.com
  - Hyflon® Ion
    - Available from manufacturer - Solvay-Solexis
  - Flemion®
  - Aciplex®
  - 3M Ionomer

  → Not as widely distributed

- Hydrocarbon Membranes
  - PolyFuel Inc. – DMFC membranes to OEMs only
  - Arkema – to customers/collaborators under NDA only
  - BPSH – University project(s) – not commercial scale

State of the Art – All Membranes

- PFSA Membranes
  - Asahi Glass – NPC PFSA
  - Nafion® XL – reinforced Nafion® PFSA

- Hydrocarbon Membranes
  - BPSH block copolymer membranes (VA Tech, J. McGrath)
  - Arkema – M41 PVDF blend membranes
  - FumaTECH – FumaPEM P,E,K series membranes
  - PolyFuel Inc. – DMFC membranes

PEM Requirements – "The Automotive Challenge"

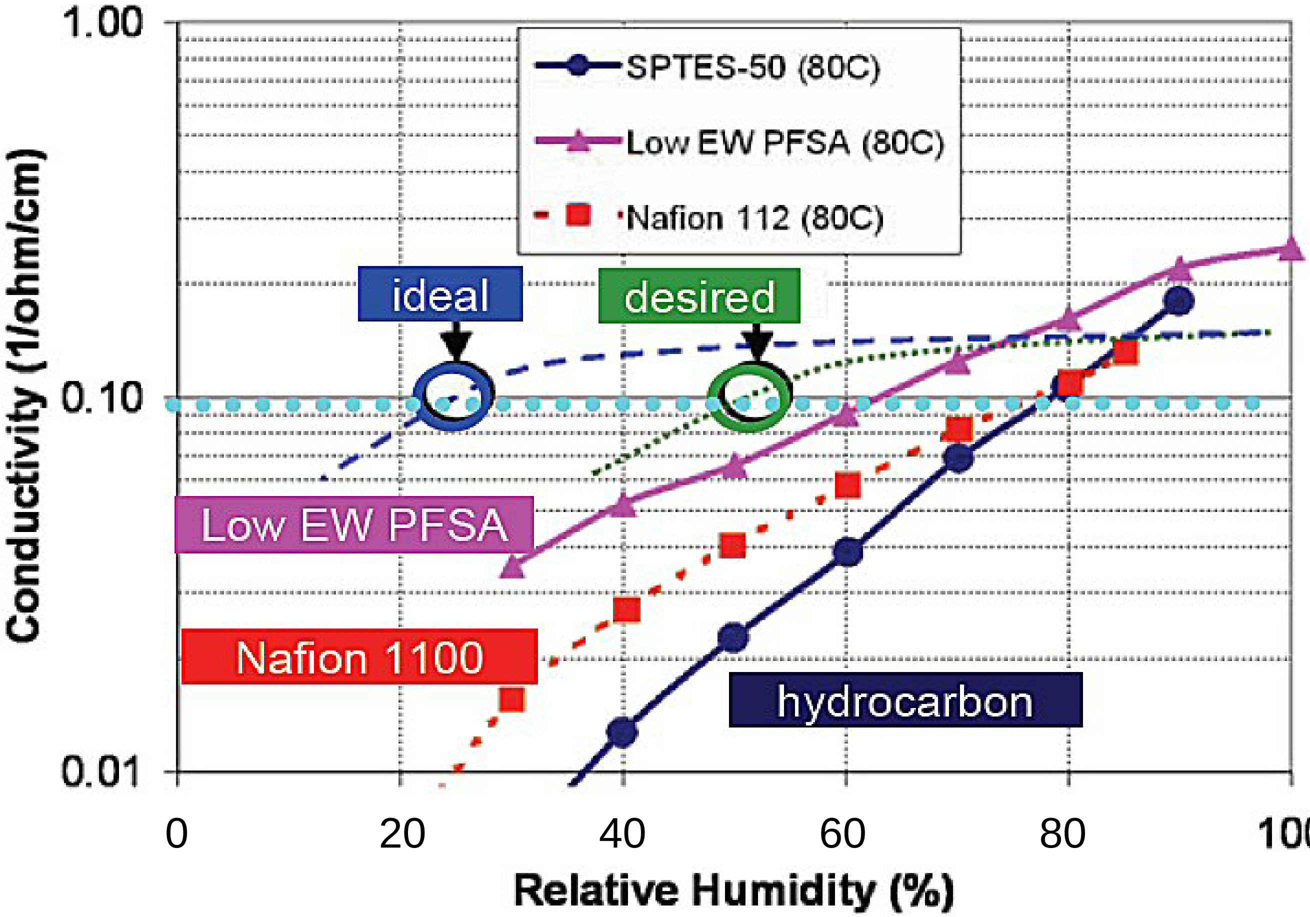
Characteristics	Units	Calendar year		
		2000 status[a]	2005	2010
Membrane conductivity, operating temperature	Ω-cm^{-1}	0.1	0.1	0.1
Room temperature	Ω-cm^{-1}			
-20^{o} C	Ω-cm^{-1}			
Oxygen cross-over[b]	mA/cm^2	5	5	2
Hydrogen cross-over[b]	mA/cm^2	5	5	2
Cost	$/kW		50	5
Operating Temperature	^{o}C	80	120	120
Durability	Hours	1000[d]	>4000[e]	>5000[f]
Survivability[c]	^{o}C	–20	–30	–40
Thermal cyclability in presence of condensed water		yes	yes	yes

Notes:
a) Status is present day 80^{o}C unless otherwise noted; targets are for new membranes/CCMs
b) Tested in CCM
c) Indicates temperature from which bootstrapping stack must be achieved
d) Continuous operation
e) Includes thermal cycling
f) Includes thermal and realistic driving cycles

US DOE HFCIT – High Temperature Membrane Working Group published targets.
http://www1.eere.energy.gov/hydrogenandfuelcells/htmwg.html#targets

PEM Requirements – "The Automotive Challenge"

- Proton Conductivity



US DOE HFCIT – High Temperature Membrane Working Group presentation – T. Greszler, "Membrane Performance and Durability Overview for Automotive Fuel Cell Applications", September 14, 2006.

GM General Motors

http://www1.eere.energy.gov/hydrogenandfuelcells/2006_htmwg_archives.html

Summary

- PEM fuel cell membranes must meet many challenges
- Nafion® is widely-distributed
- Alternatives in varying degrees of commercialization
- Many chemistries possible with hydrocarbon materials
- Application defines membrane properties
  - Automotive – stringent performance and durability requirements
  - Stationary / Backup – durability is critical
  - Portable – high fuel utilization is critical (DMFC)
- Rapid property screening and optimization needed
- LOW COST will be the key!