Integration of Non-Traditional Membranes into MEAs

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UNCLASSIFIED

Outline

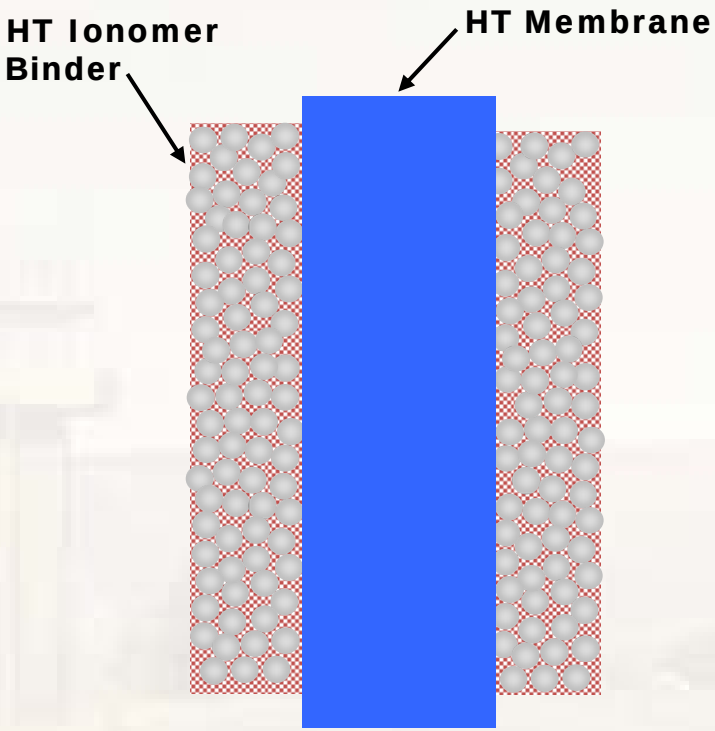
- **Background – MEA Fabrication**

- **Part 1. Membrane-Electrode Interface**
  - Interfacial resistance measurement
  - Impact of poor MEA adhesion
  - Method of improving MEA adhesion

- **Part 2. Non-PFSA Ionomers**
  - Ionomer to catalyst ratio
  - Dispersing agent
  - Oxygen permeability
  - Chain mobility

Ionomer Binder for Non-Traditional Membranes

MEA for PEMFCs



Membrane

- High proton conductivity at low RH
- Good thermal/electrochemical stability
- **Low reactant permeability**
- Low electronic conductivity

Ionomer Binder

- High proton conductivity at low RH
- Good thermal/electrochemical stability
- **High reactant permeability**
- Good catalyst-ionomer interaction

Ionomer binder having dissimilar structure with membranes may be desirable.

Struggling for Robust MEA Fabrications

- Gubler et al., *"Hotpressing of radiation grafted membranes was not successful in our laboratory…. Successful fabrication of hotpressed MEAS was possible when thinner membranes with lower degree of grafting were used"* ***Fuel Cells***, (2005) 5, 317.
- Bae et al., "*The MEA composed of SPS-g-PP composite membrane may suffer from the heterogeneous interfacial structure increasing the contact resistance between membrane and catalyst layer*" ***J. Memb. Sci***. (2003), 220, 75.
- Lufrano et al. *"…Poor electrode/electrolyte (sulfonated polysulfone) contact caused from the assembly of a nonperfluorinated membrane with a catalytic layer containing Nafion ionomer and low chains mobility of these glassy polymers"* ***J. Appl. Sci***. (2000) 77, 1250.
- Le Ninivin et al. *"Optimization of Electrode-membrane interfaces (sulfonated polyphenylene) is necessary*" ***J. Appl. Electrochem***. (2004) 34, 1159.
- Vernon et al. *"..With this in mind optimization of MEA fabrication processes as well as the development of more compatible ionomer materials in the electrodes may produce very significant improvements in performance for the hybrid membrane MEA"* ***J. Power Sources*** (2005) 139, 141-151.
- Besse et al. *".. We have observed that the fuel cell performances of our polyimide membranes are relatively dependent of prelimianry acid treatment. In order to improve the electrode/membrane interface, a thin sulfonated polyimide layer was deposited on the electrode surface before making the assembly"* ***New Mater. Electrochem. Sys.*** (2001), 346.

LANL MEA Processing for Non-Traditional Membranes

- **Direct Membrane Painting**

  Y.S.Kim, J. Electrochem. Soc. 151, A2150 (2004)

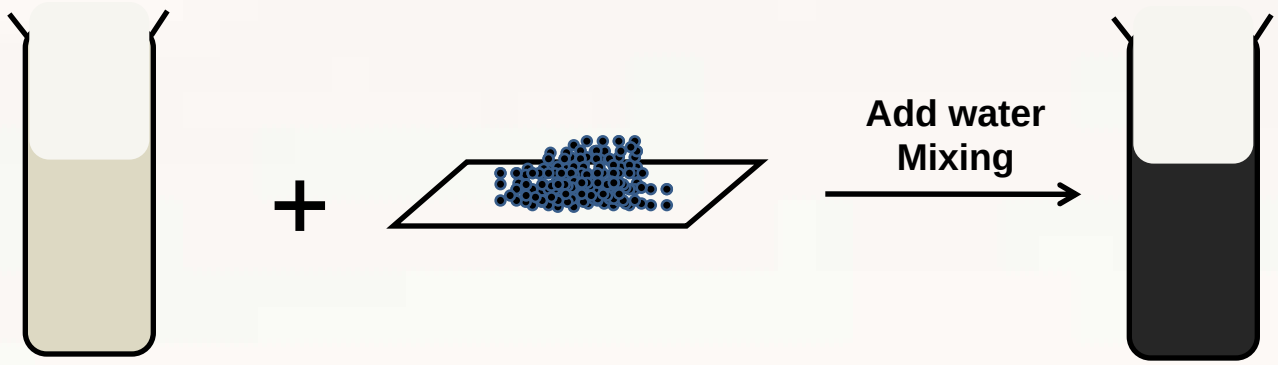
- Catalyst ink is directly painted on to membranes using vacuum plate
- Simple process
- Difficult to control catalyst loading
- Difficult to process highly water swollen membrane
- Easy to isolate membrane property
- Mostly used for DMFC applications

- **Decal transfer (Hot pressing)**

  Wilson, US Patent 5,211,984 (1993)

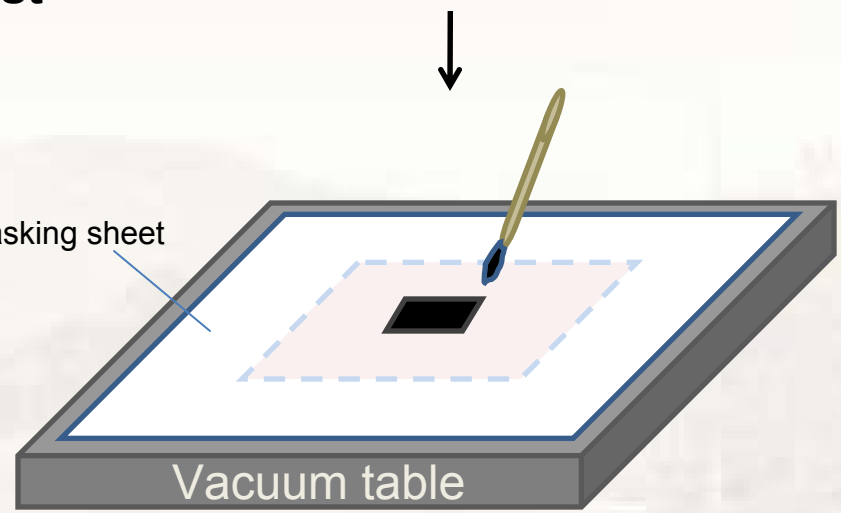
- Catalyst ink is painted on decal then transfer to membrane using hot pressing
- Complex procedure
- Precise control of catalyst loading
- Easy to process highly water swollen membrane
- Electrode adhesion to membrane is critical
- Difficult to isolate membrane property
- Mostly used for PEMFC applications

Direct Membrane Painting

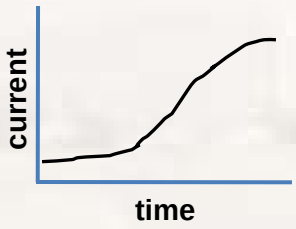


Electrolyte dispersion
Nafion 5%
Water/alcohol >90%

Pt black catalyst



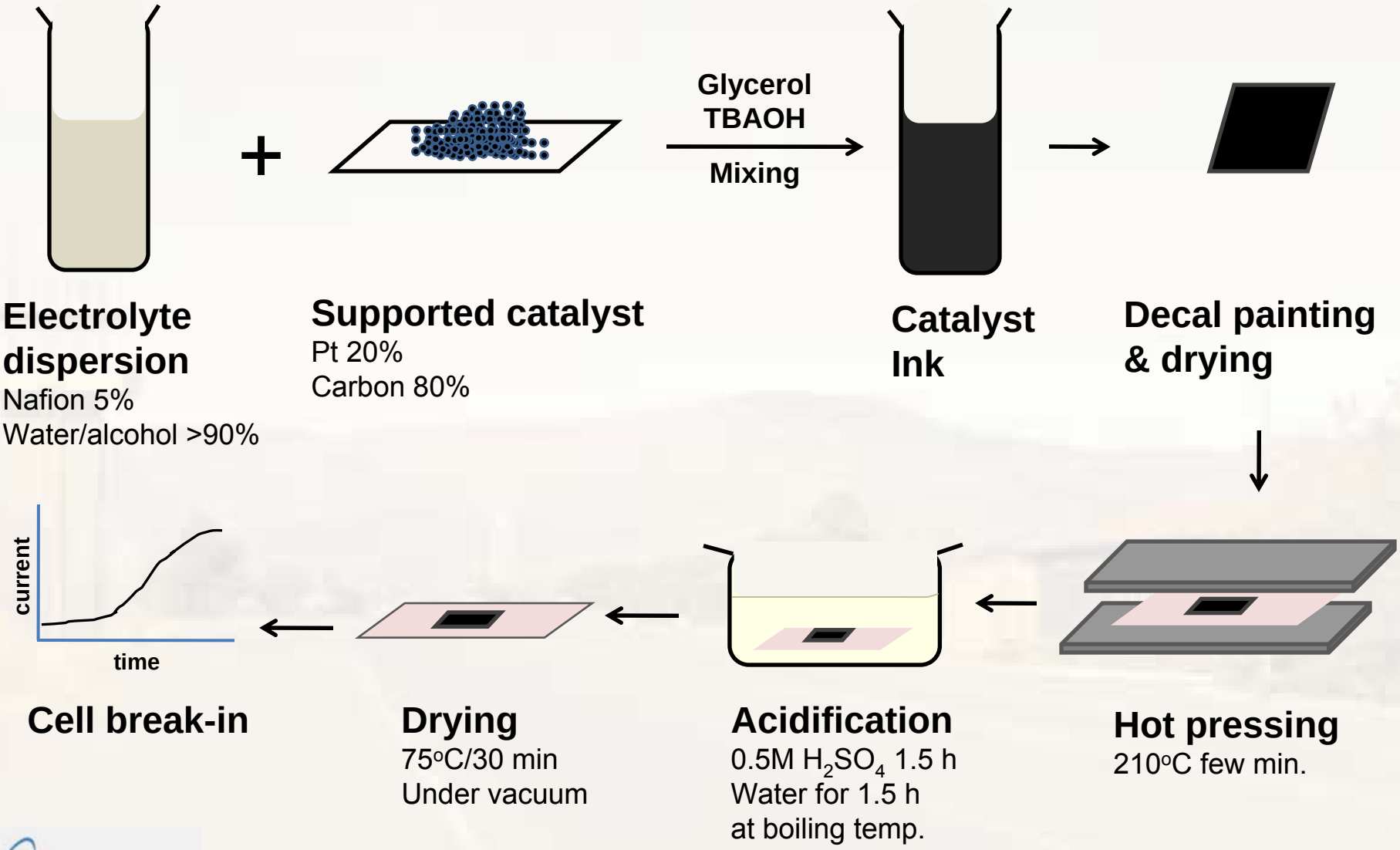
Ink Painting
75-80°C



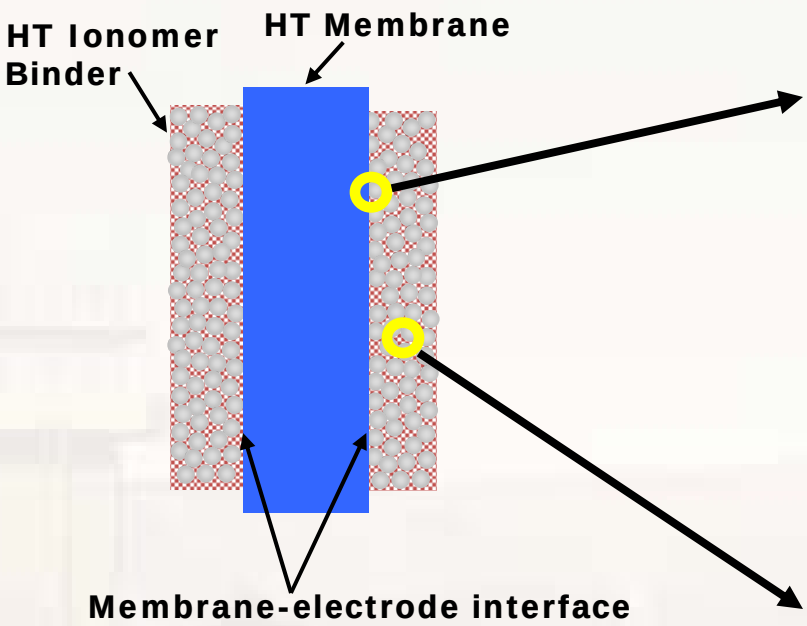
Cell break-in

Los Alamos
NATIONAL LABORATORY
EST. 1943

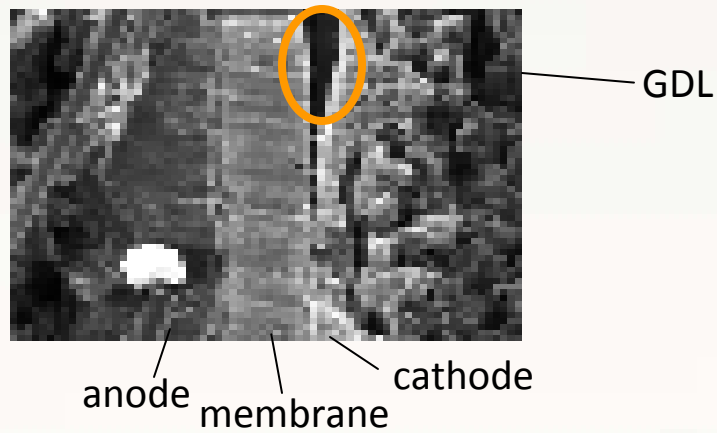
Decal Transfer (Hot pressing)



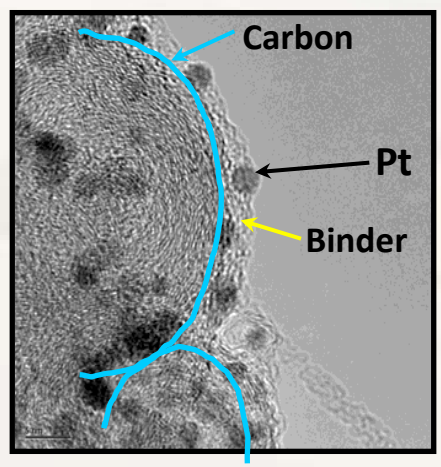
Two Major Issues with Dissimilar Ionomer Binders



Interfacial Delamination



Poor Performance due to lack of Understanding of electrode structure

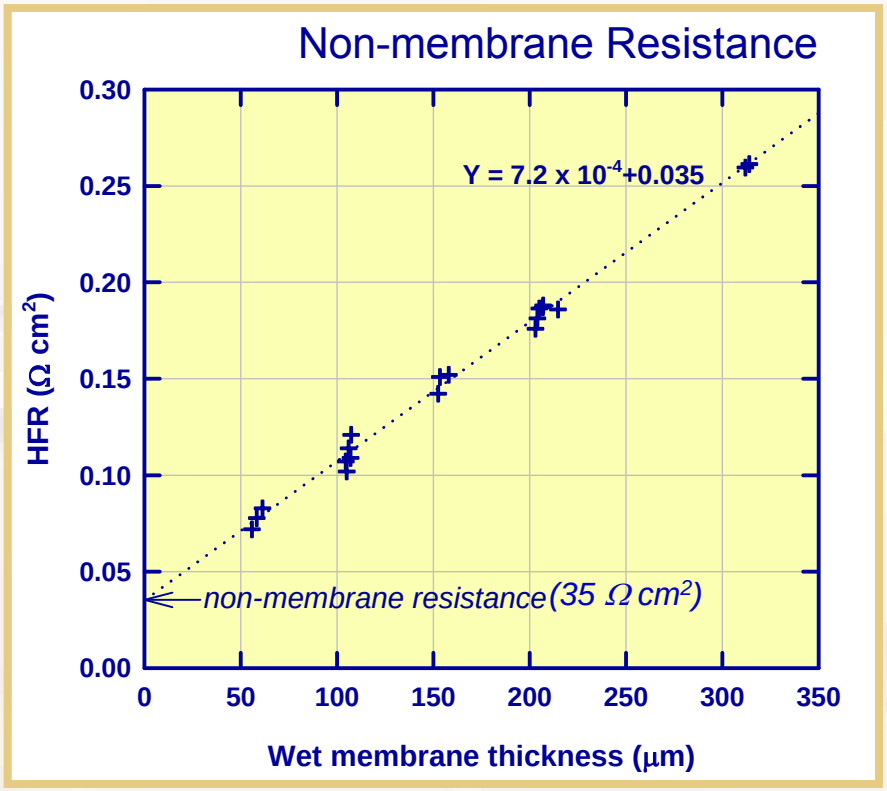


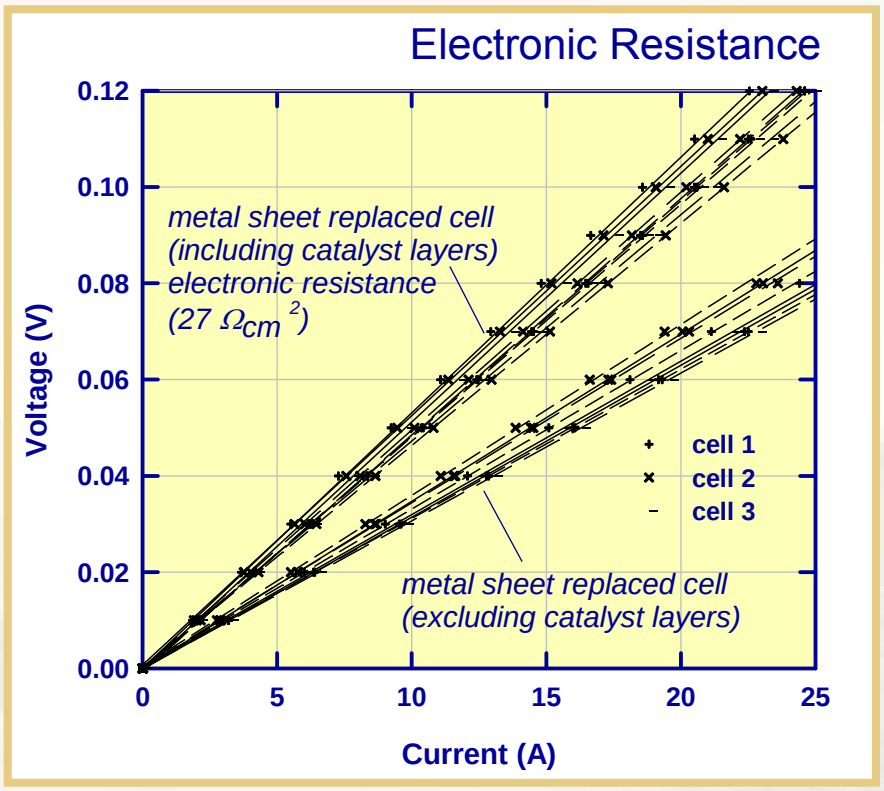
Catalyst/support dispersity
Catalyst-ionomer interaction
Ionomer morphology
Porosity
Reactant/water permeability
Catalyst solubility
Ionomer relaxation
etc

(K. More, DOE Hydrogen and Fuel Cells Annual Report (2005))

Measurement of Interfacial Resistance, $R_{interface}$

$R_{interface}$ = Non-membrane Resistance - Electronic Resistance

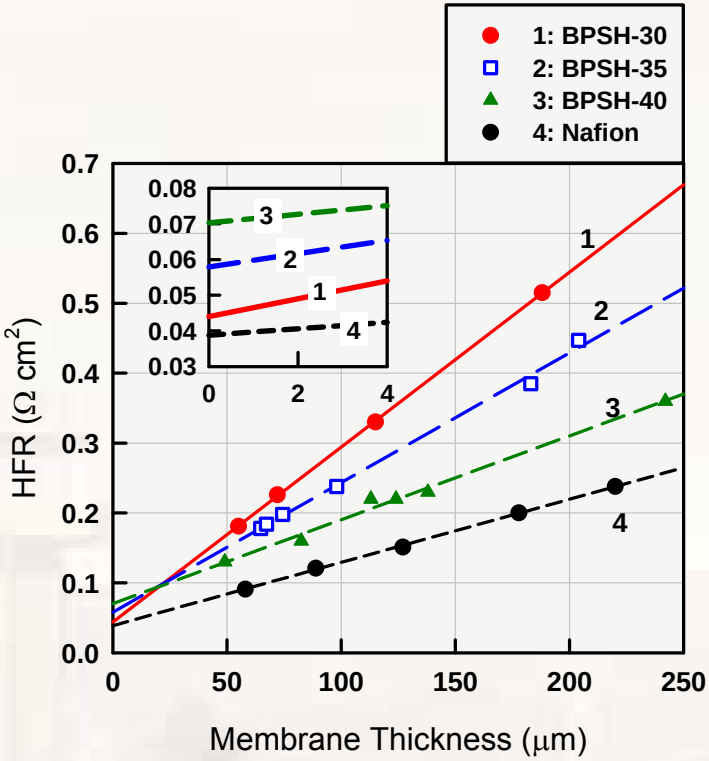




$R_{interface}$ for the example is 8 mΩ·cm²

Ref. Y.S. Kim and B.S. Pivovar, J. Electrochem. Soc. (2007) 154, B739.

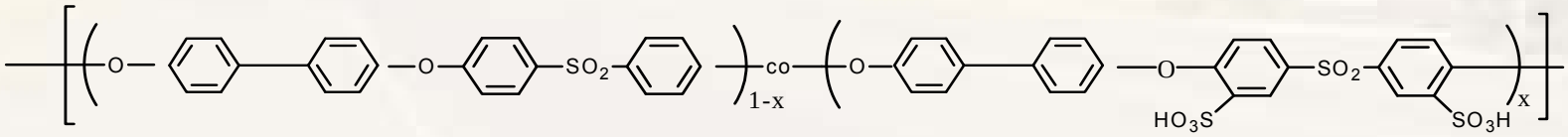
$R_{interface}$ between HC membrane and Nafion Electrode



Conductivity, σ, and Interfacial Resistance, $R_{interface}$

Membrane	σ *(mS/cm)*	$R_{interface}$ *(mΩ·cm²)*
BPSH-30	39	**17**
BPSH-35	54	**31**
BPSH-40	78	**43**
Nafion	111	**8**

Sulfonated Poly(Arylene ether) Sulfone (BPSH-x)*

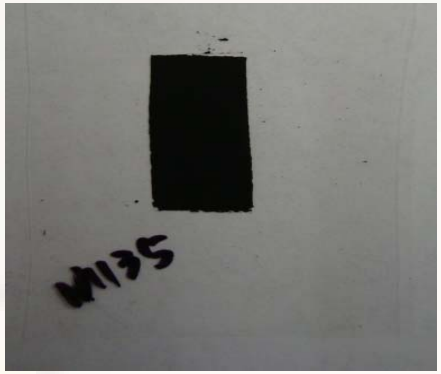


*Ref. M. Hickner et al. Chem. Rev. 104, 4587, 2004

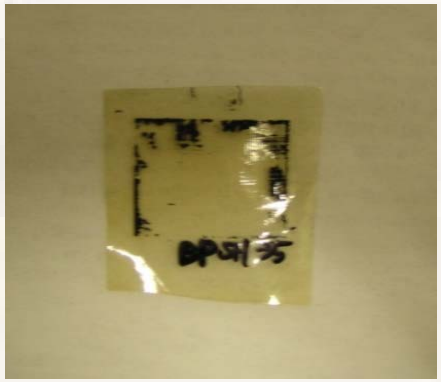
Impact of Membrane-Electrode Incompatibility on Decal Transfer

Electrode transfer @ 210°C hot pressing

Nafion memb./Nafion electrode



BPSH/Nafion electrode



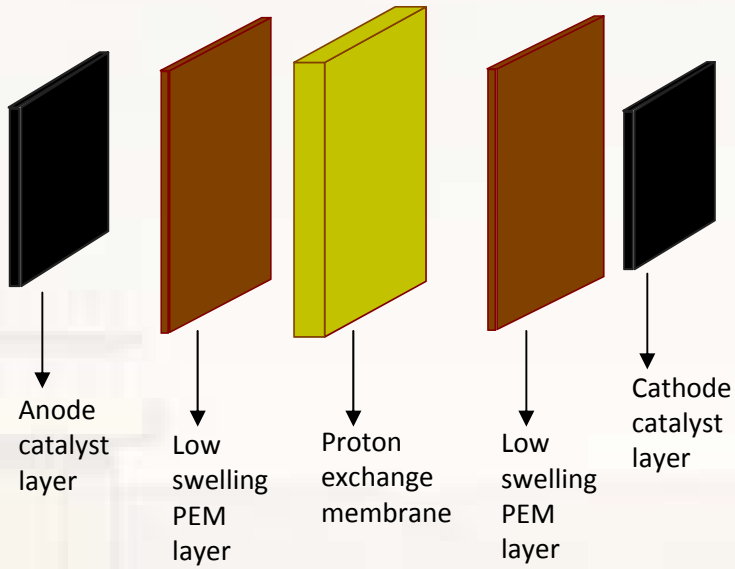
Membrane	*T_g* (°C)*	*Required hot pressing Temp. (°C)*
BPSH-30	260	**280**
BPSH-35	266	**285**
BPSH-40	271	**>295**
Nafion	120	**140-210**

- **High Tg HC membranes require higher hot pressing temperature.**
- **Hot pressing temp. increases with degree of sulfonation.**
- **Low surface adhesion property of HC membranes makes difficult to 100% electrode transfer.**

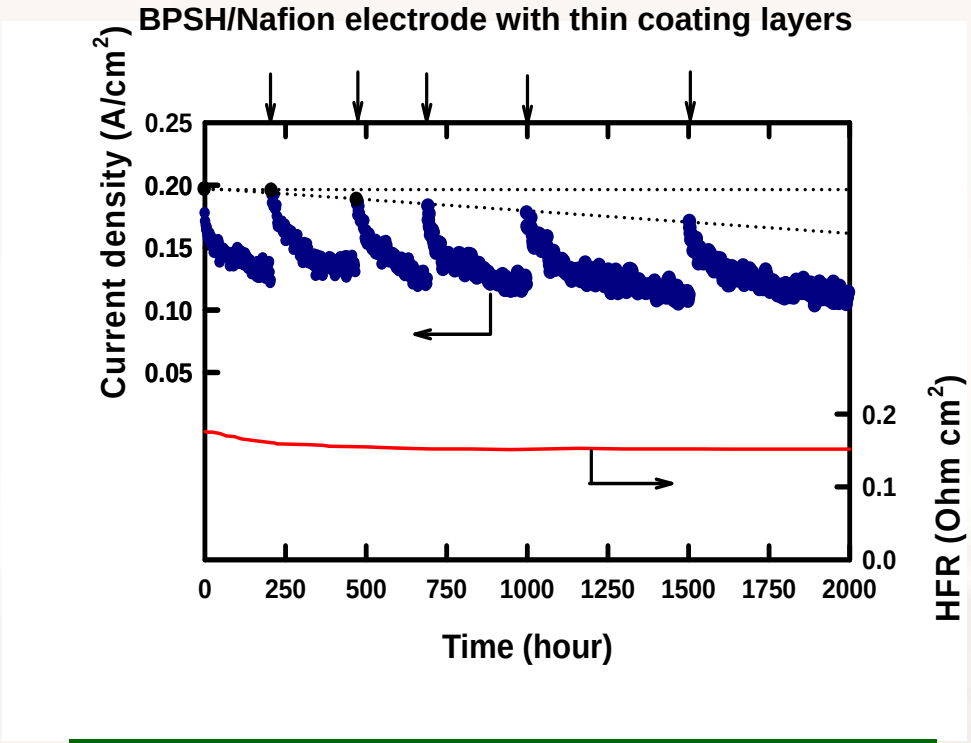
Ref. F.Wang et al. J. Memb. Sci. (2002), 197, 231.

Method of Improving Interfacial Adhesion: 1. Thin Coating Layer

Thin coating layer system*

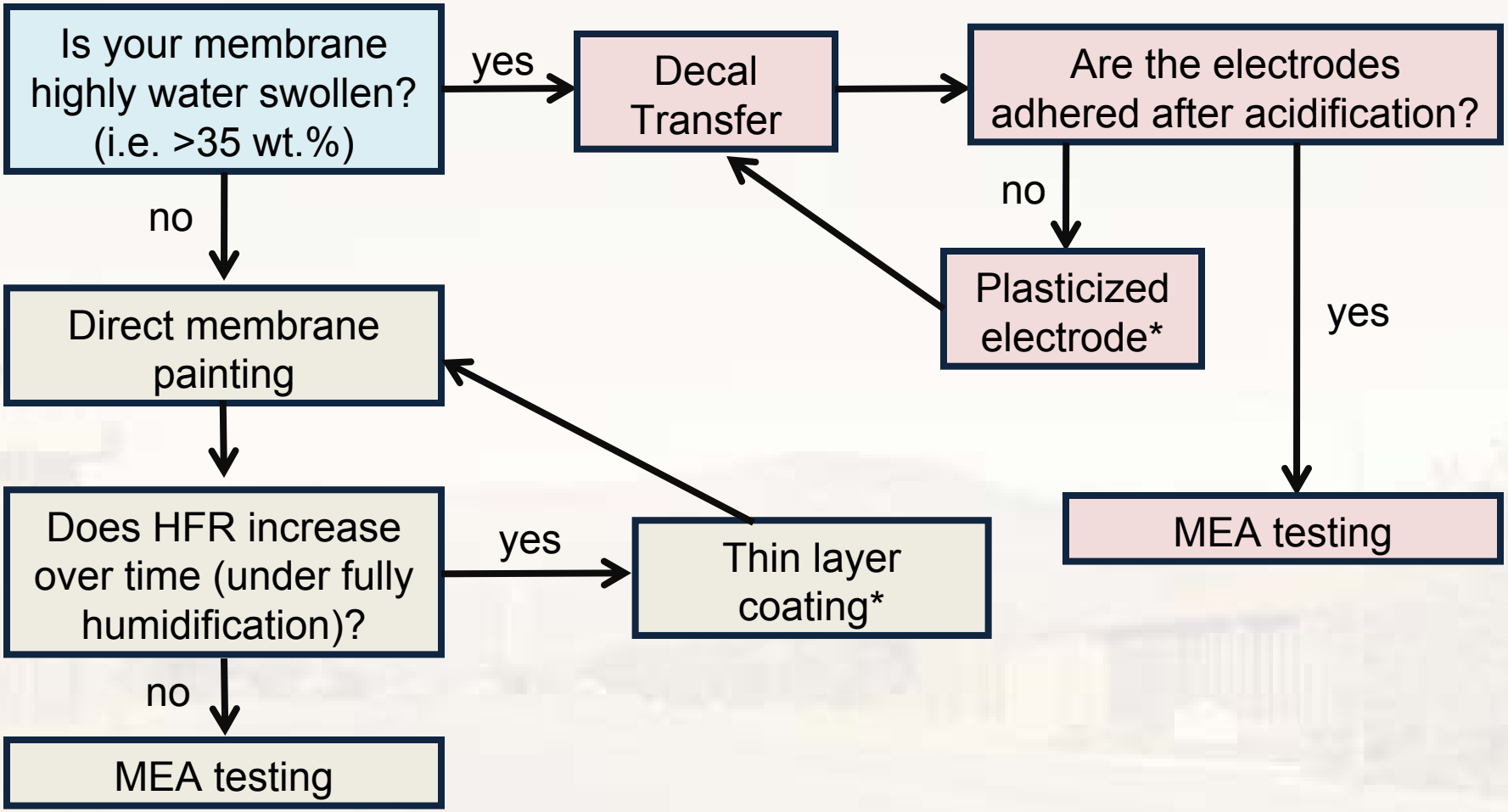


Y.S. Kim and B.S. Pivovar, US Patent Applications, LANL (2006)



- **Stable DMFC performance (and HFR) was obtained with thin coating layer system.**

LANL MEA Fabrication Steps using Non-traditional Membranes



** LANL Intellectual properties*

- **Part 1. Membrane-Electrode Interface**
  - Interfacial resistance measurement
  - Impact of poor MEA adhesion
  - Method of improving MEA adhesion

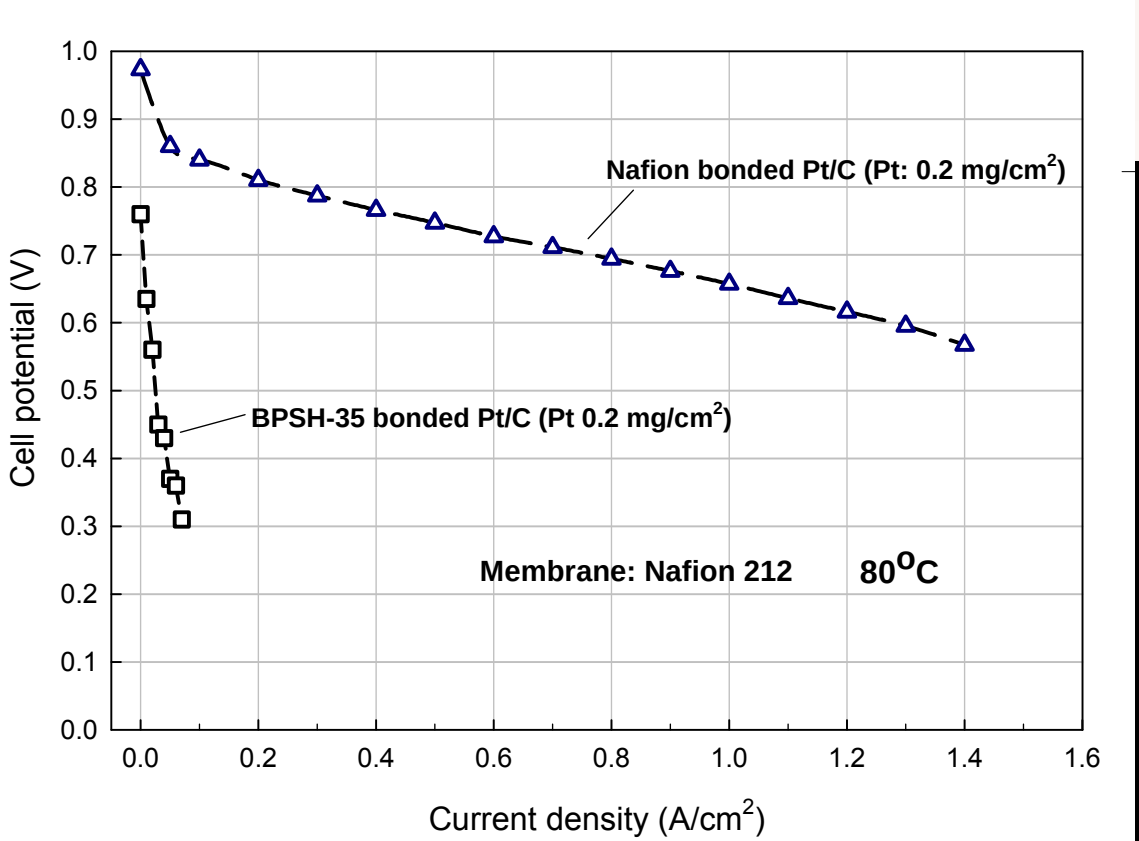
- **Part 2. Non-PFSA Ionomers**
  - Ionomer to Catalyst Ratio
  - Dispersing Agent
  - Oxygen Permeability
  - Chain Mobility

Electrode formulation & testing conditions for electrode studies

Catalyst: **Carbon supported platinum (20 wt.%)**
Catalyst loading: **0.2 mg/cm^2**
Anode ionomer: **Commercial Nafion dispersion**
Membrane: **Nafion 212**
MEA fabrication: **LANL proprietary**

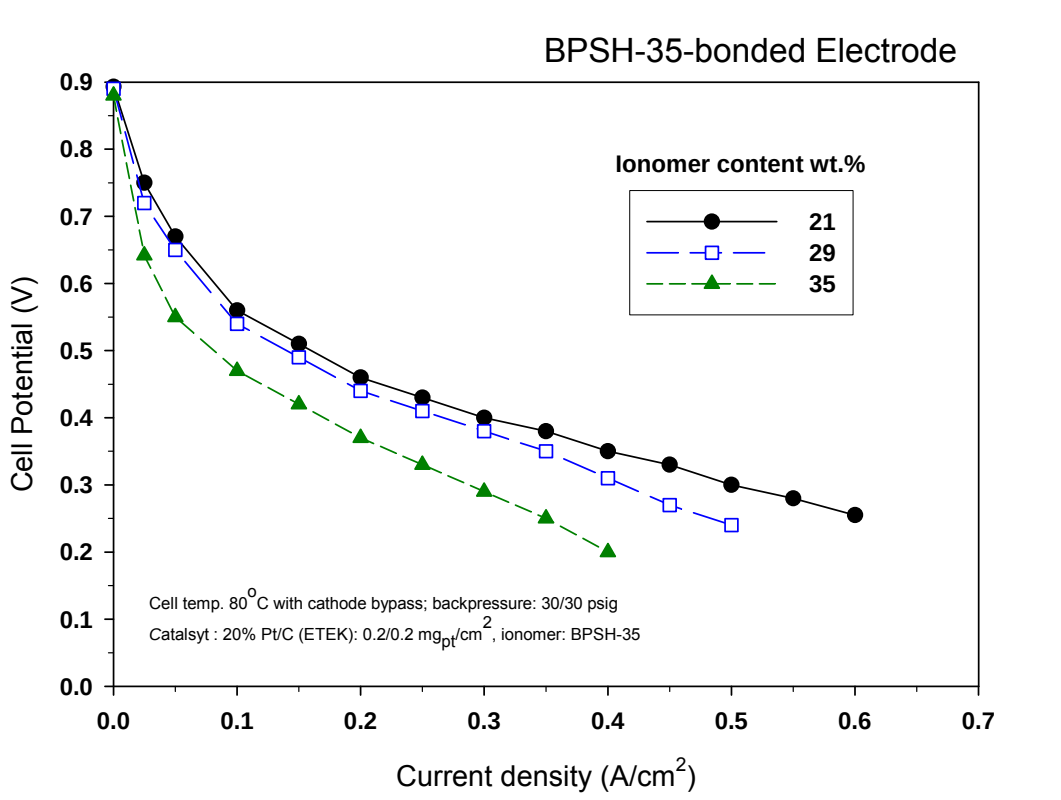
Cell temperature: **80°C**
Anode humidity bottle temperature: **105°C**
Back pressure: **20 or 30 psi**
Break in time: **>14 h**

Non-PFSA Electrode – Fact & Motivation



BPSH-35

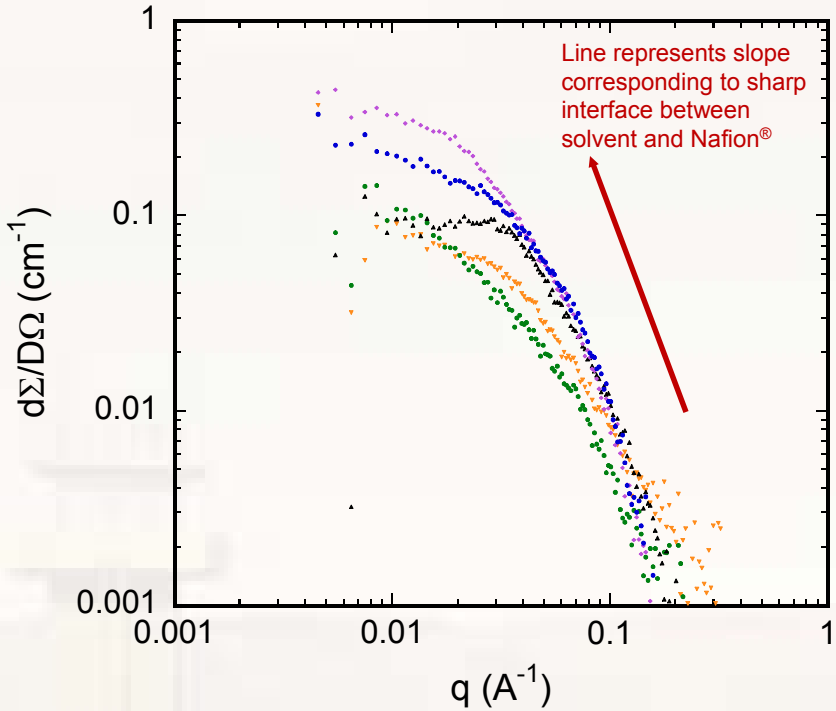
Effect of Ionomer Content on Fuel Cell Performance



ionomer	Density (g/cm^3)	Wt.%	Vol.%
Nafion	2	29	30
BPSH-35	1.3	21	27
		29	40
		35	53

- **Due to the lower density of BPSH-35, electrode with less amount of BPSH-35 performed better.**
- **Optimum BPSH-35 content is ~21wt.% (~27 vol.%).**

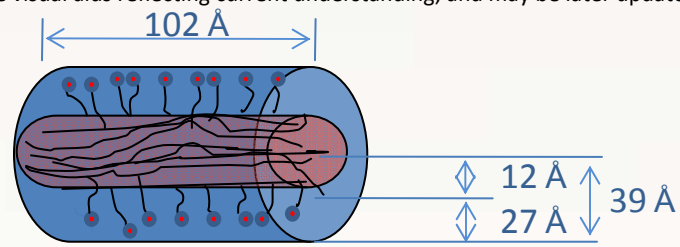
SANS Study of Nafion® Dispersion



Solvent	Slope
NMP	-1.7
Ethylene glycol	-2.0
Water/IPA (2:3)	-2.0
Butanediol	-3.3
Glycerol	-3.5

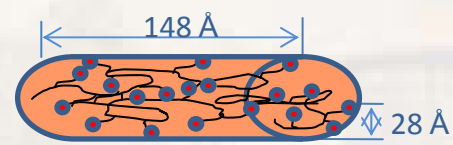
NMP dispersion: **Core-Shell Cylinder**

*Structures are visual aids reflecting current understanding, and may be later updated



- Sharp interface between core and shell
- SLD* of core = ~calculated Nafion® backbone
- SLD of shell = ~solvent
- No solvent penetration into the core
- Solvent penetrates side chains (low slope)

Glycerol dispersion: **Cylinder Model**

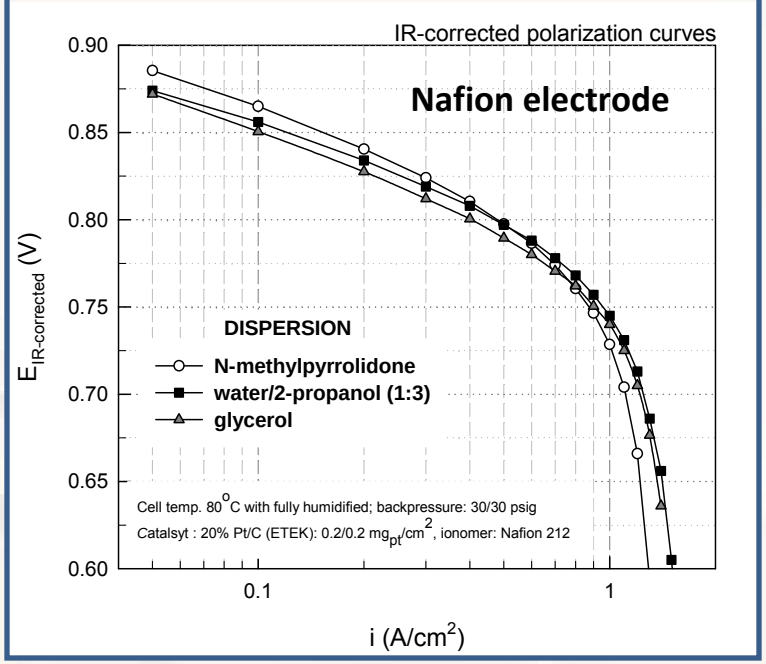


- Less phase separation between Nafion® backbone and side chains
- Glycerol appears to penetrate Nafion® less than NMP (high slope), but some penetration may occur

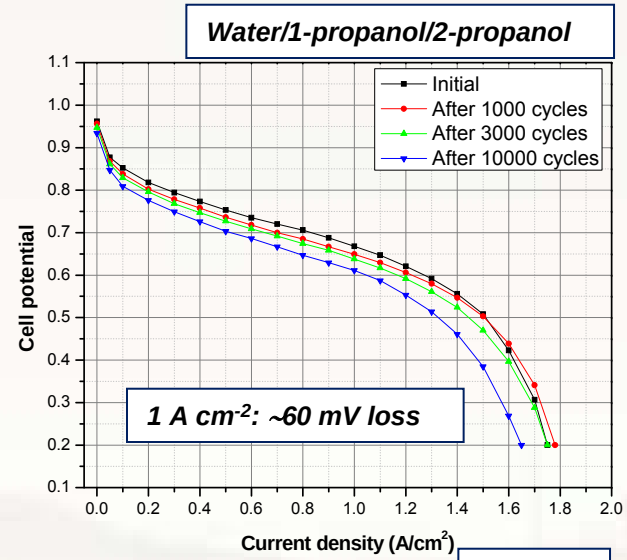
*** More information: FC_16 Christina Johnston, LANL, Wed. 9:00 AM.**

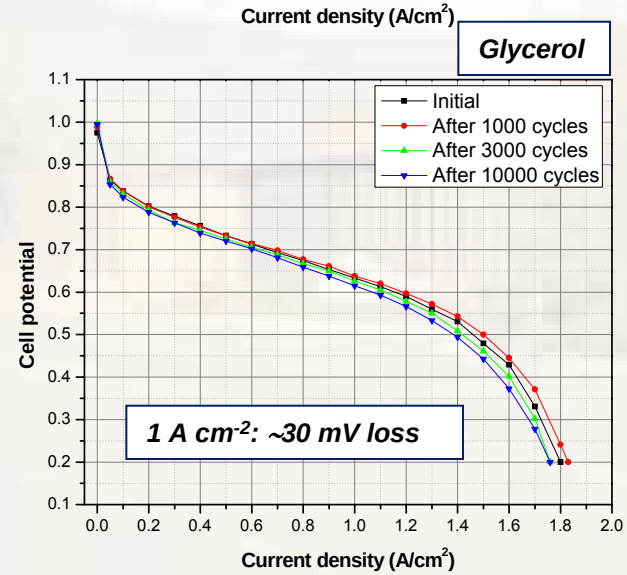
Effect of Dispersing Agent on Electrode Performance

Initial Performance



Durability (potential cycling)





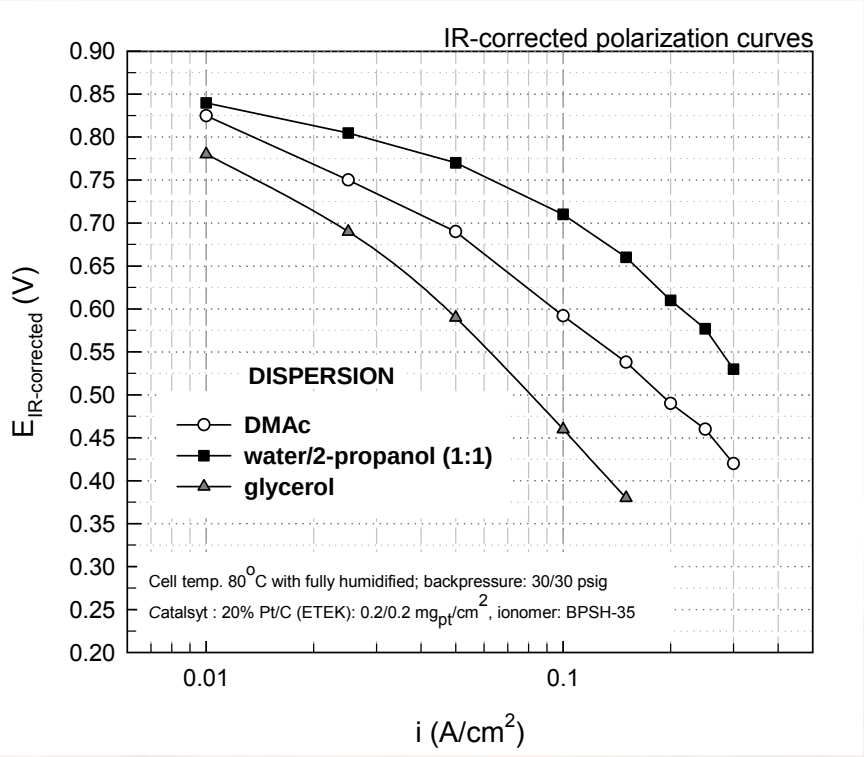
- **Electrodes from NMP (and water-isopropanol) dispersion exhibits good ORR kinetics while electrode from glycerol dispersion have relatively good mass transfer.**
- **Electrode from water/2-propanol showed poor potential cycling durability while electrode from glycerol showed good durability.**

*** More information: FC_16 Christina Johnston, LANL, Wed. 9:00 AM.**

HC Ionomer Dispersion in Various Dispersing Agent*

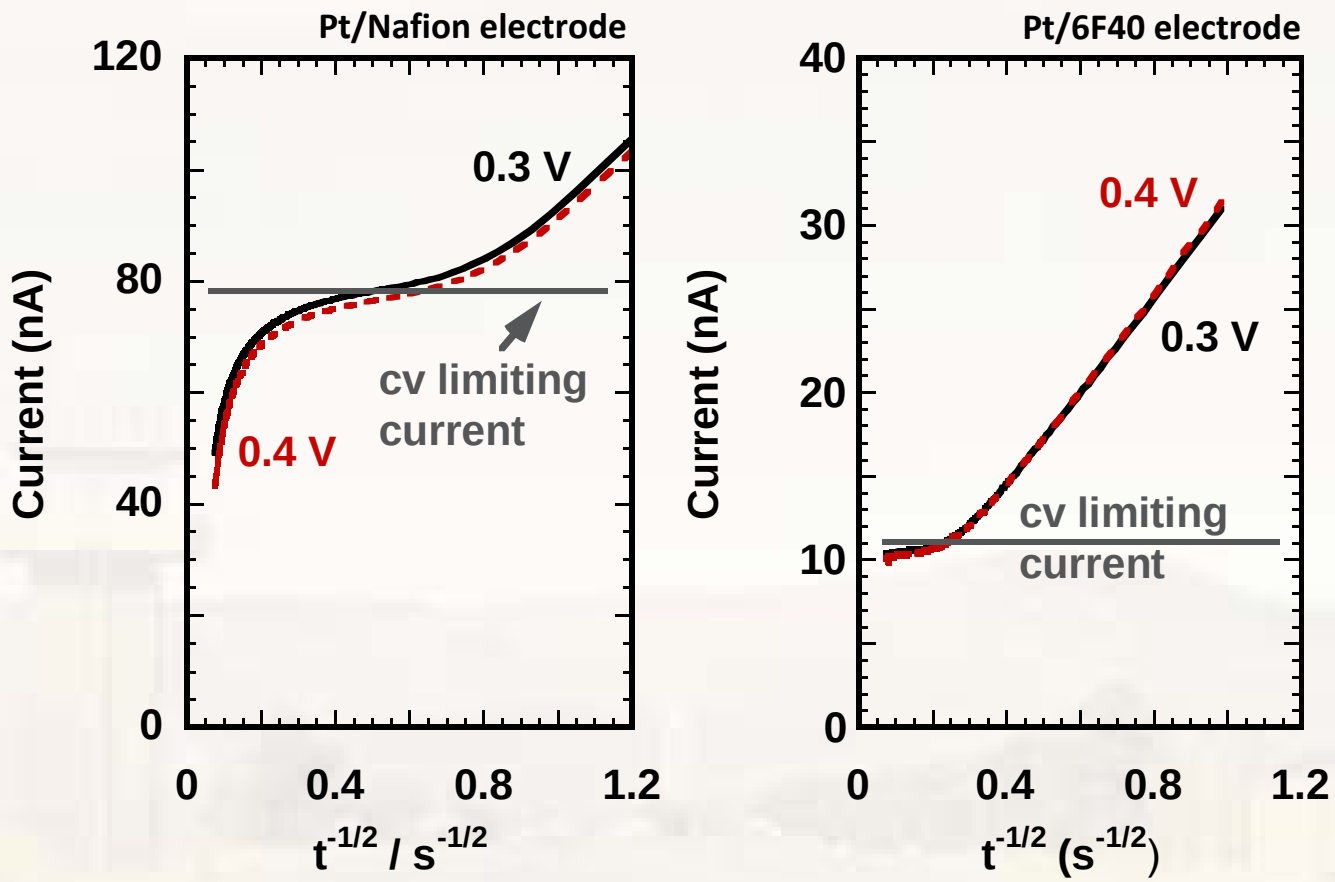
EW	Dispersing medium	Dispersion	Mechanical property	Wettability
670	1,4 butanediol	-	NA	NA
1519		-		
670	Ethylene glycol	+	Tough	Good
1519		-		
670	Propylene glycol	+	Tough	Good
1519		-		
670	Glycerol	+	Tough	Good
1519		+		
483		+		
670	Water/iso-propanol (1:1)	+	Brittle	Poor
670	NMP	+	Tough	Good
1519		+		
670	DMSO	+		
1519		+		
670	DMAc	+		
1519		+		

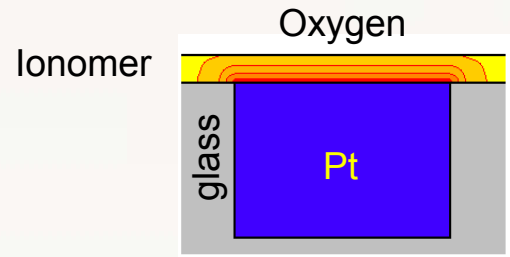
Y.S. Kim, T. Rockward, and K.S. Lee, US Patent Pending, LANL (2009)



- **Dispersing agent effect is much greater for BPSH-35 electrode than Nafion but similar trend.**
- **We have difficulties using water-based dispersion due to poor mechanical properties and poor wettability.**

Chronoamperometry of Oxygen on Pt/Nafion® and Pt/6F40

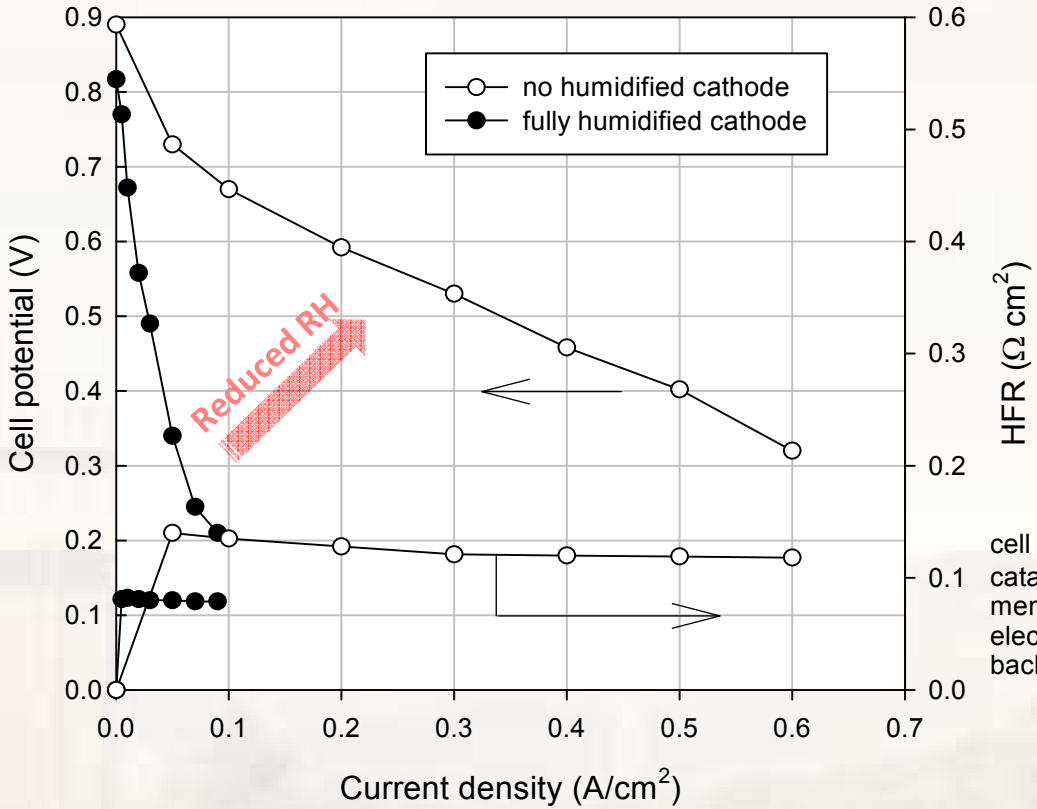




60 °C, 60% RH, 100 µm (diameter) Pt UME (microdisk)
Film thickness: Nafion – 13.5 µm, 6F40 - 26.5 µm ;

- **Significantly lower oxygen reduction currents for the Pt/6F40 than those for pt/Nafion indicates significantly lower oxygen permeability of 6F40 to oxygen.**
- **Non linearilty and current decrease of Pt/Nafion beyond the cv limiting current indicates significant polymer chain reorganization of Nafion during chromoamperometry process.**

Effect of Cathode Humidification on Fuel Cell Performance

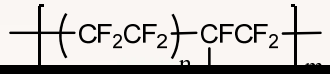


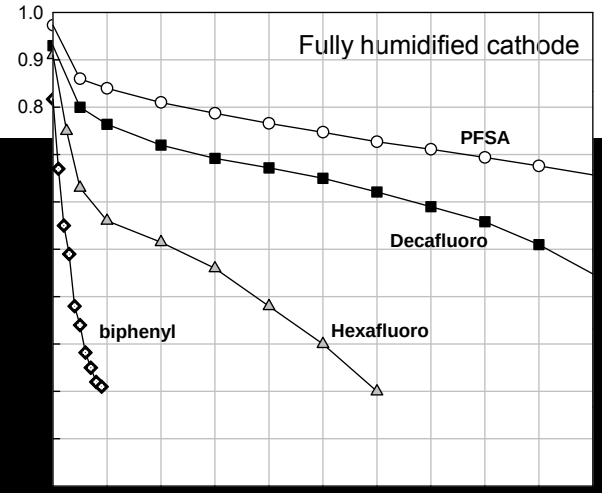
cell temp. 80°C
catalsyt : 0.2 mg/cm^2 Pt/C
membrane Nafion 212
electrode binder:BPSH-35 (27 vol.%)
back pressure 30 psig

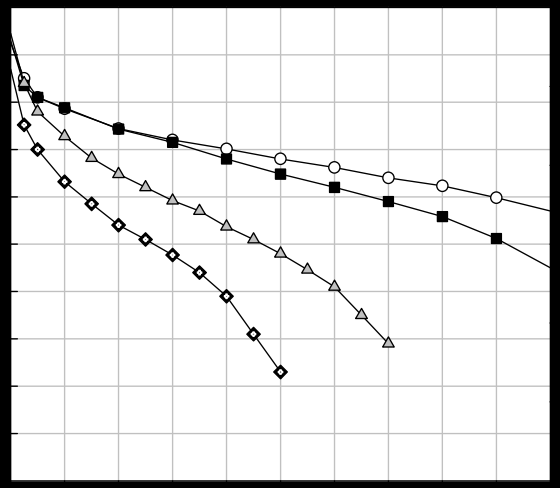
- **Hydrocarbon bonded electrode shows better performance at low RH conditions, due to better mass-transfer**
- **Good chance to replace PFSA-bonded electrode with thermally stable HC- bonded electrode for high temp. and less RH fuel cells**

Effect of Hydrophobicity of Polymers

PFSA

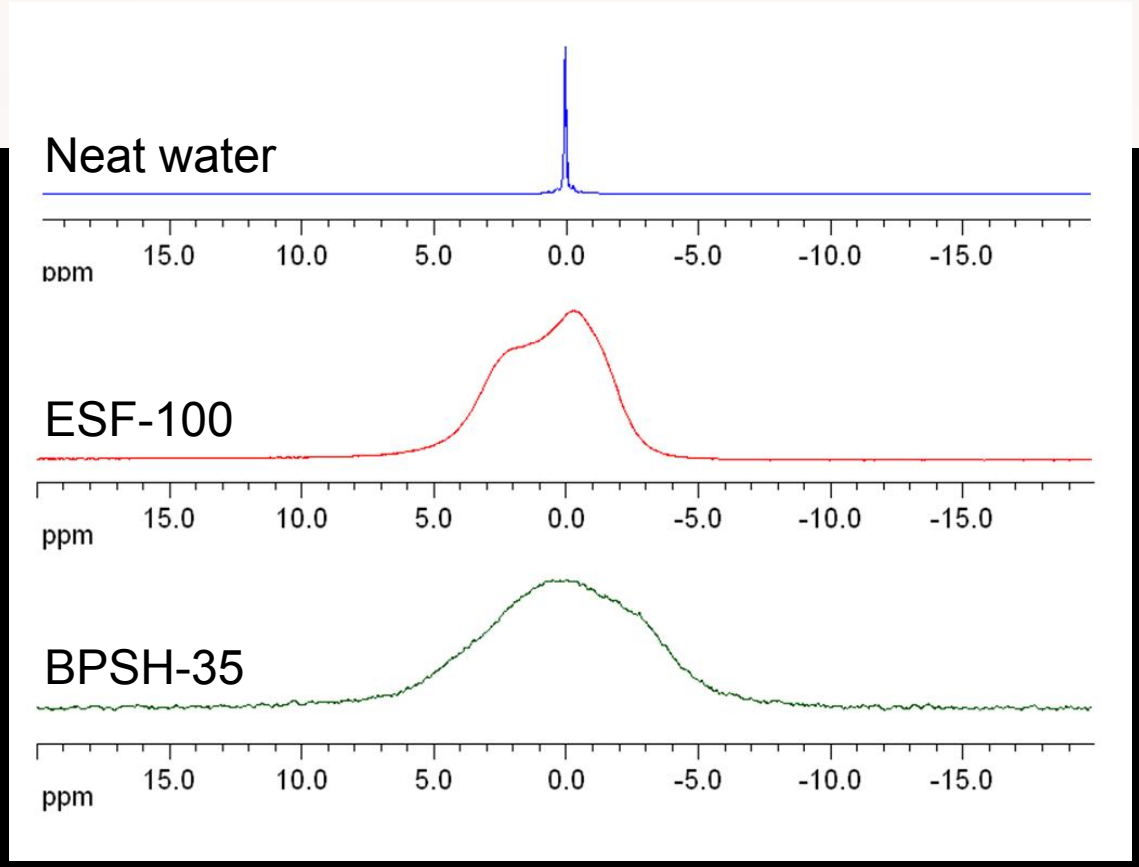




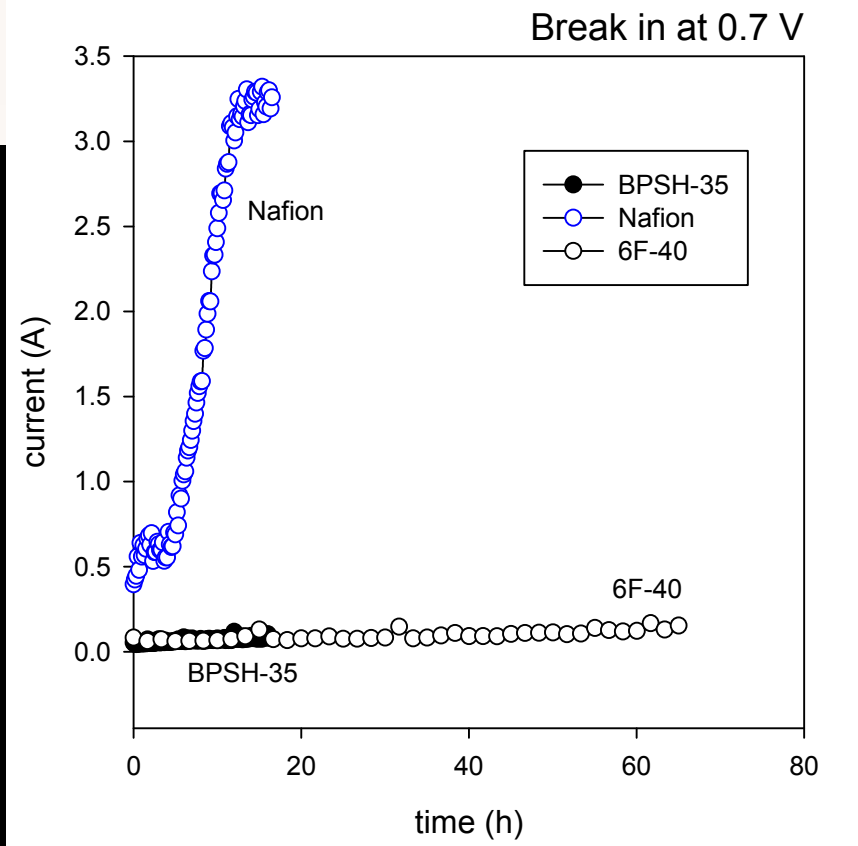


Courtesy: Profs

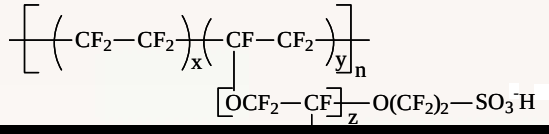
State of Water in ESF-100 and BPSH-35 using ^{2}H NMR

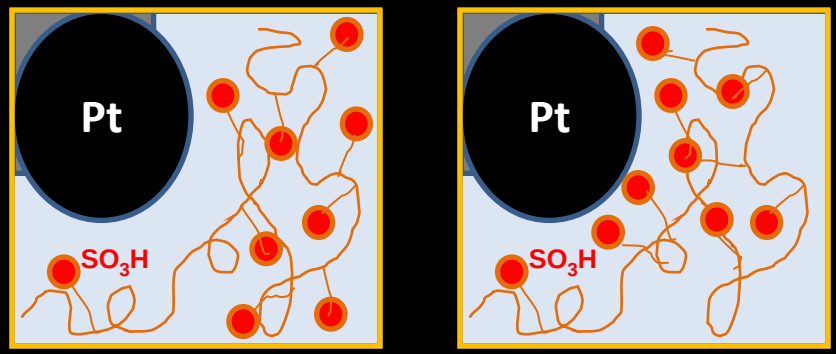


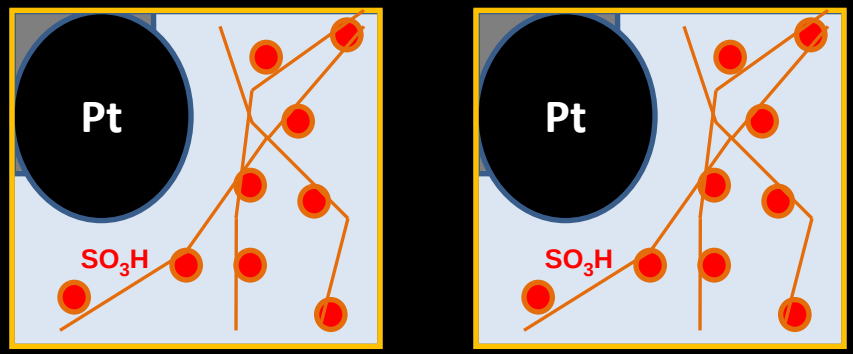
Effect of Chain Mobility on Break-in Process



Nafion







Summary

- Poor adhesion between membrane and electrode may result in premature MEA failure (poor electrode transfer) during MEA processing or gradual interfacial delamination during long-term fuel cell operation.
- Interfacial adhesion can be enhanced by thin coating layers or plasticization of electrode.
- To date, properties and interaction of non-PFSA ionomer binders with fuel cell catalyst are poorly understood.
- SANS results indicated that dispersed and solid ionomer had different structure (size, micelle formation and phase separation) and mechanical properties depending on dispersing agent.
- Solid NMR study indicated that state of water may be important factor for electrode flooding which have observed as a predominant factor. Electrode performance increased with fluorination of polymers.
- Side chain mobility may give critical influence on electrode performance. More investigation is needed in this area.

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Kwan Soo Lee (GIST, LANL)

Tommy Rockward (LANL)
Andrea Labourieu (LANL)
Bruce Orler (LANL)
Cindy Welch (LANL)
Marilyn Hawley (LANL)
Rex Hjelm (LANCE, LANL)
Christina Johnston (LANL)
Jerzy Chilstunoff (LANL)

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