High Temperature Proton Exchange Membrane Nanocomposites for Fuel Cells

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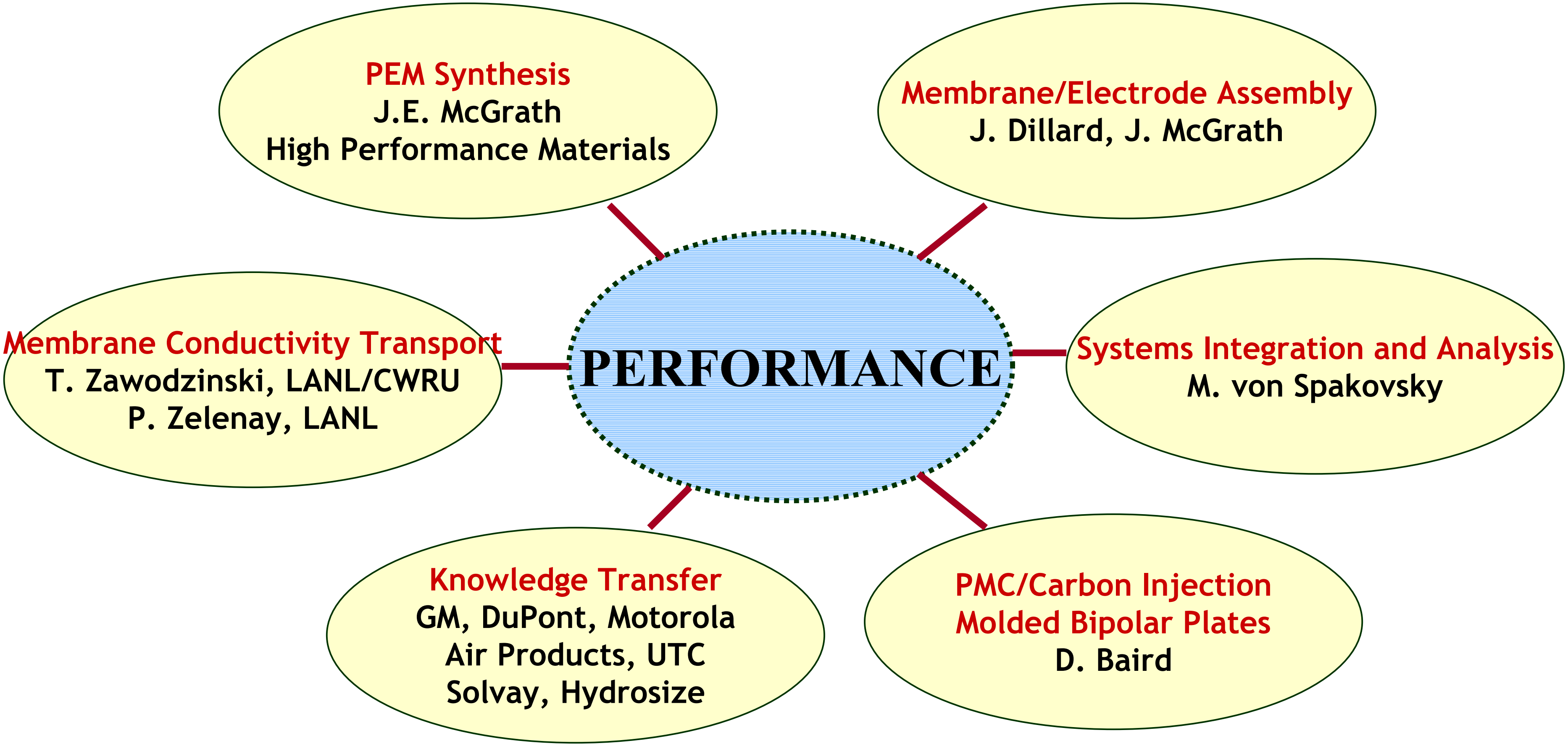
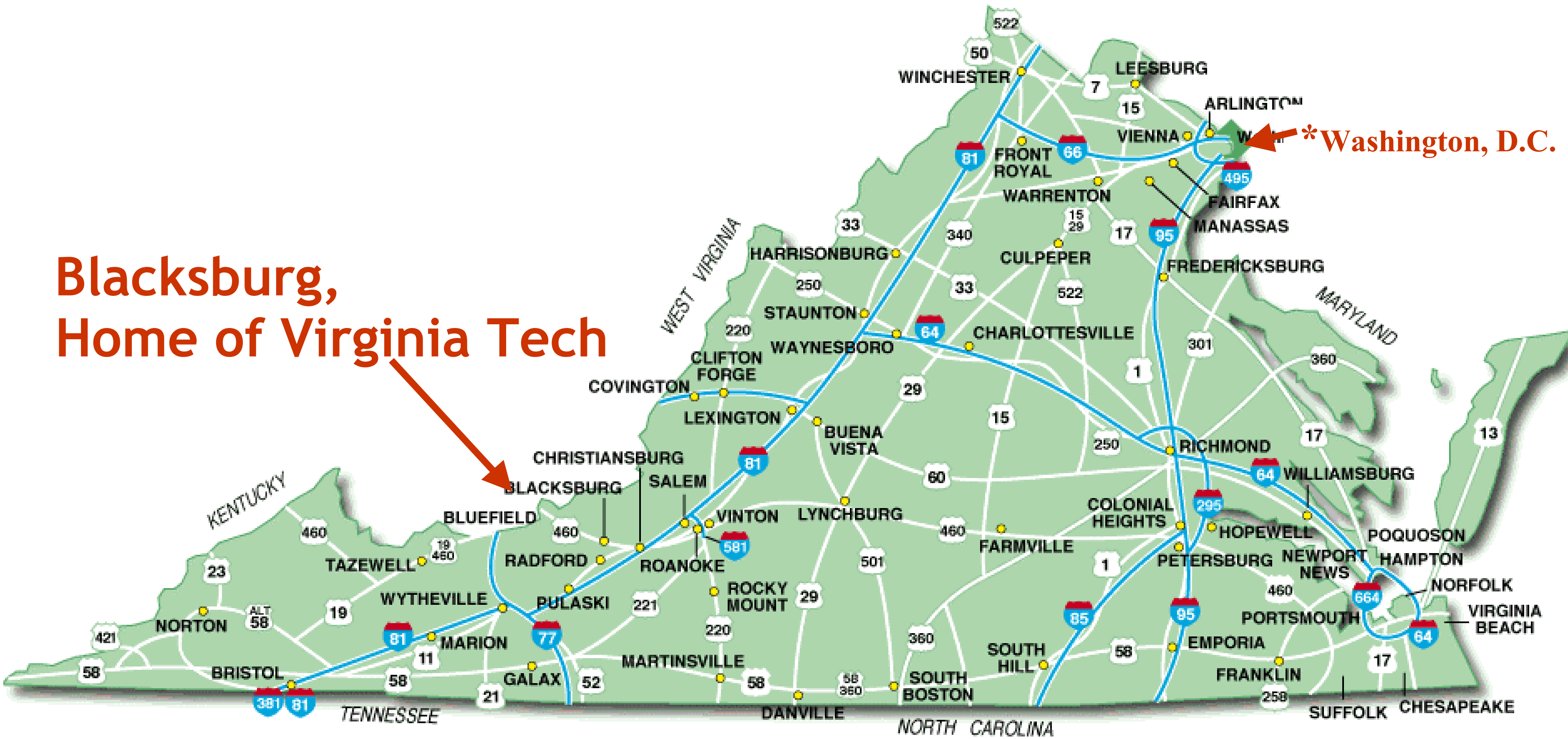
Funding Agency	Project Title	PI(s)	Timing
U.S. Dept. of Energy, Golden, CO	"Advanced Materials for PEM-Based Fuel Cell Material Systems"	J. McGrath, D. Baird, J. Dillard, P. Zelenay, T. Zawodzinski, M. von Spakovsky	Oct. 2001 to Sept. 2003



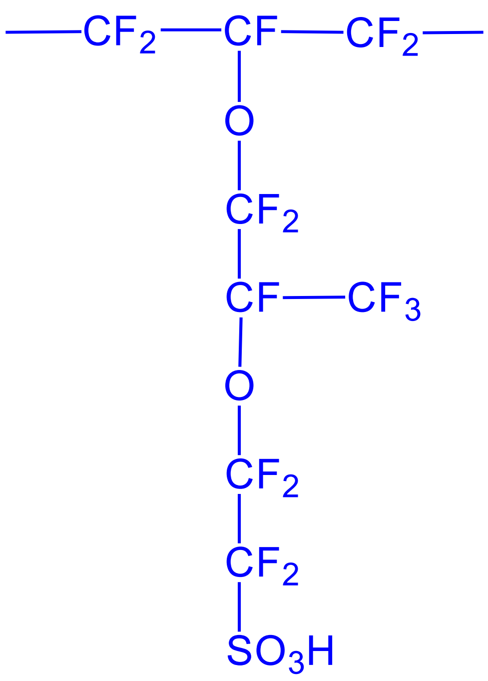
Commonwealth of Virginia

Blacksburg,
Home of Virginia Tech



Views of Virginia Tech

Currently Used Proton Exchange Membrane (PEM) - Nafion™



Chemical structure of poly(perfluorosulfonic acid) - Nafion

Advantage

- **Excellent Proton Conductivity**
- **Good Mechanical & Chemical Properties**
- **Long term stability**

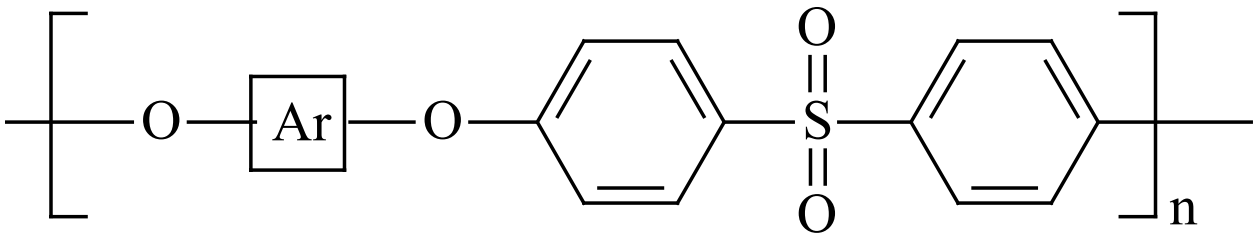
Disadvantage

- **Expensive**
- **High methanol permeability**
- **Loss of membrane performance at elevated temperature (>80^{o}C)**

Objectives

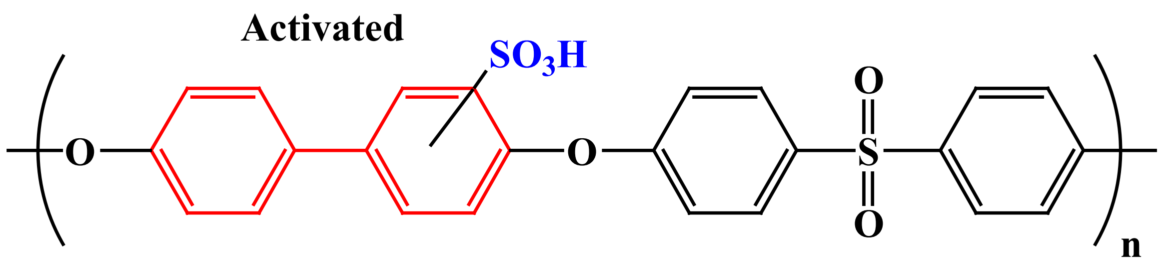
- Fundamental investigations to identify viable alternative PEM systems
  - H_2/AIR, 80ºC or higher (preferably 120-150ºC)
  - Direct methanol (DMFC) PEM Systems with reduced permeability

Why Poly(arylene Ether Sulfone)s?

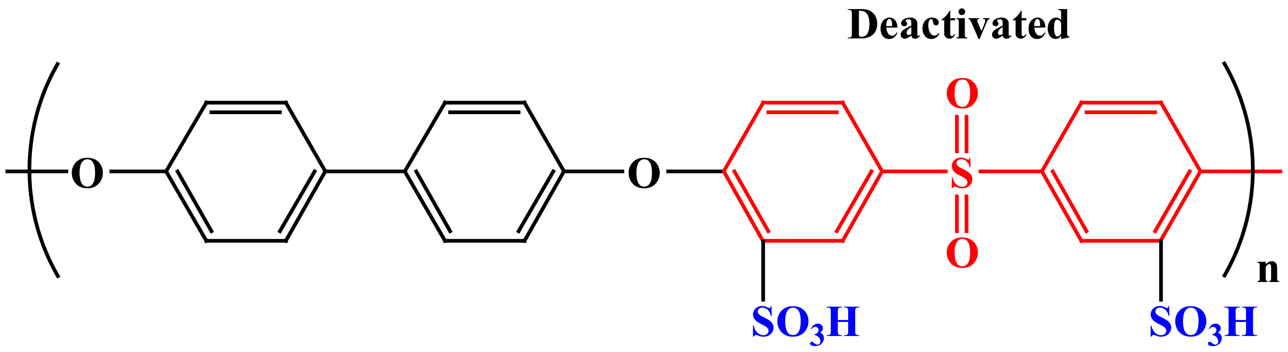


- High thermal stability
- Good stability against acid, bases and oxidants
- Good mechanical properties
- Film-forming, high-performance thermoplastics
- Melt processible
- Several monomers are commercially available

Comparison of Polymeric -SO_3H Group Stability from Post and Monomer Sulfonation Methods

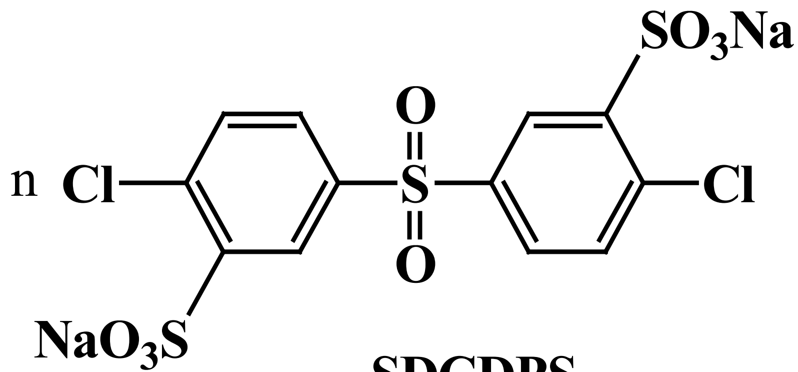


- Post sulfonation occurs on the most reactive, but least stable, position
- High electron density leads to relatively easy desulfonation



- Monomer sulfonation on the deactivated position
- Enhanced stability due to low electron density

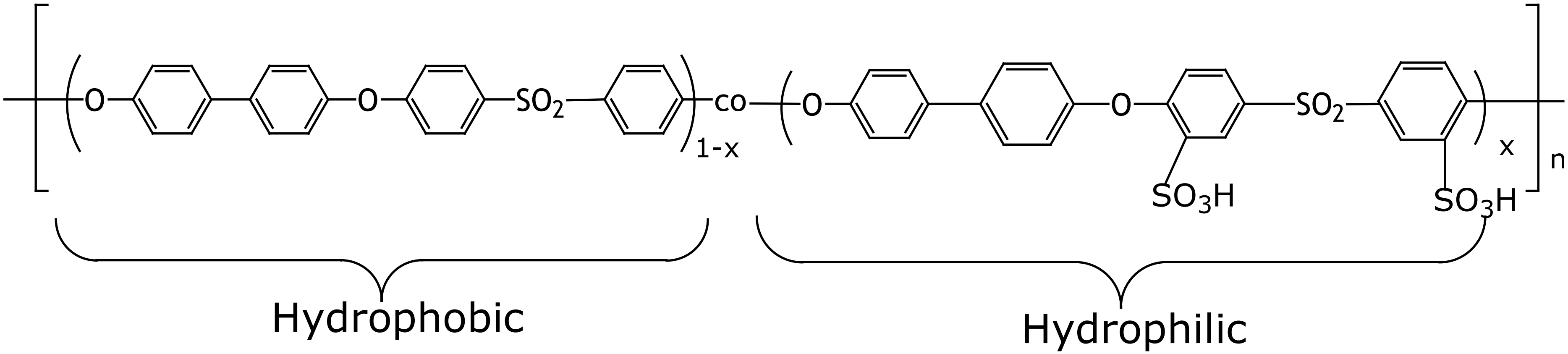
Advantages of Direct Polymerization



SDCDPS

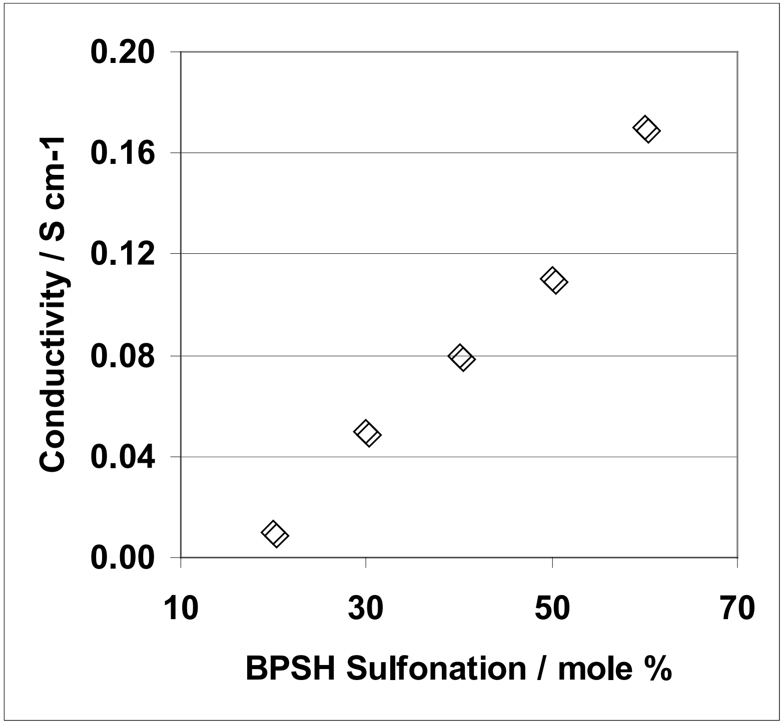
- High yields from 40MM lb/year precursors
- Precise control of ionic concentration during synthesis
- Well-defined ion conductor location; morphology control
- High H^+ conductivity
- Enhanced stability due to deactivated position of $-SO_3H$
- Compatible with additives for >100ºC studies
- Very high molecular weight copolymers possible

Wholly Aromatic Random (Statistical) Poly(arylene ether sulfone) / Poly(arylene ether disulfonated sulfone) Copolymers Via Direct Copolymerization (BPSH-x)



- <u>B</u>i<u>p</u>henyl <u>S</u>ulfone: <u>H</u> Form (BPSH)
- x = molar fraction of disulfonic acid unit, e.g., 30, 40, etc.

Effect of Sulfonation on Conductivity



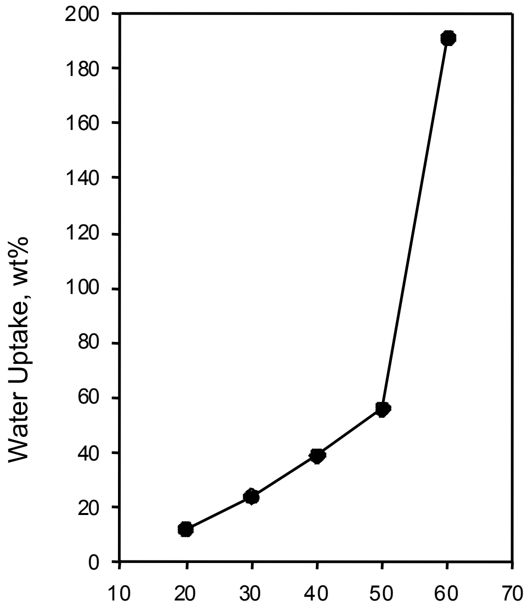
30°C in liquid water

Conductivity is both a strong function of *sulfonation* and *water content*

Influence of Sulfonation Degree on Water Uptake of Polymer Membranes

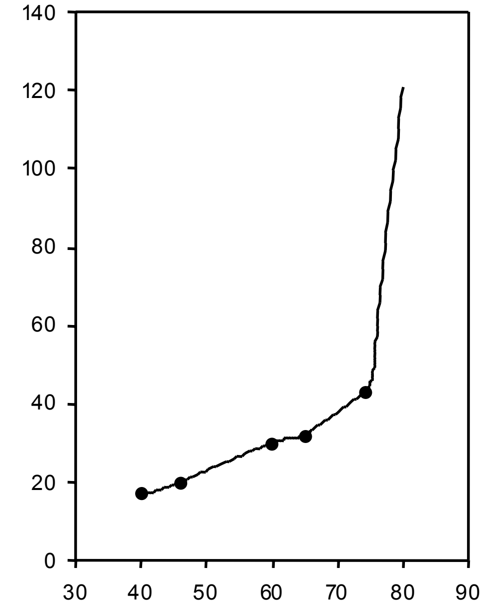
H_20 Sorbed

BPSH (a)



% Disulfonation

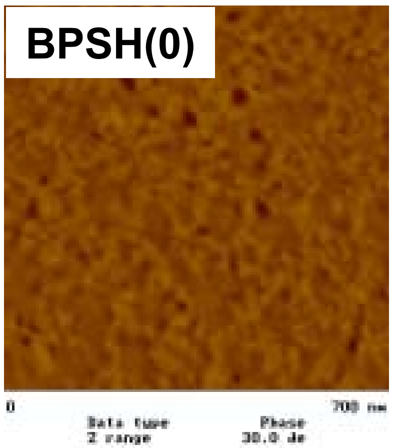
PEEK (b)

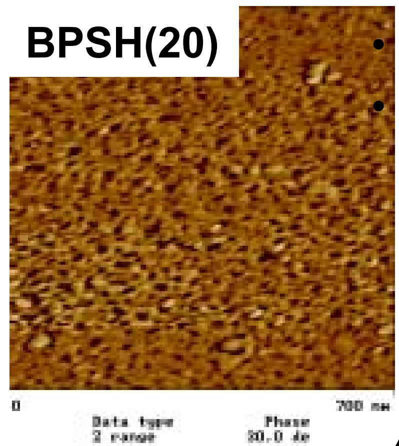


(a) F. Wang, M. Hickner, Y.S. Kim, T. Zawodzinski and J.E. McGrath, "Synthesis and Characterization of Sulfonated Poly(arylene ether sulfone) Random (Statistical) Copolymers Via Direct Polymerization: Candidates for New Proton Exchange Membranes," ***Journal of Membrane Science,*** **197 (2002), 231-242.**

(b) Kaliaguire, S. et al. J. Memb. Sci., 173, (2002).

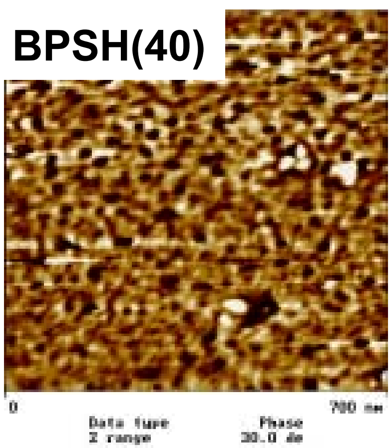
AFM Phase Images of BPSH Membrane

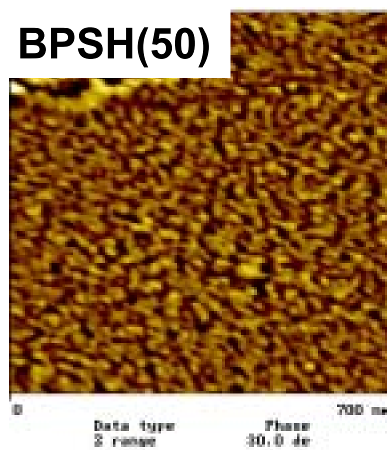


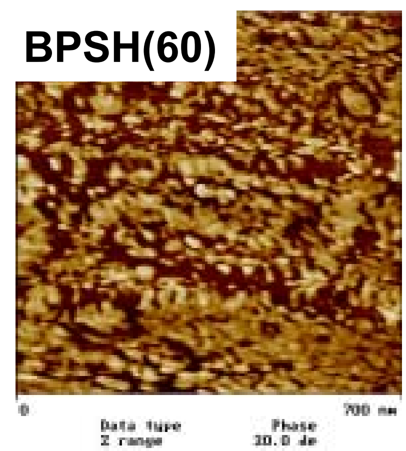


- Scale: 700 nm
- Phase angle: 30 degree

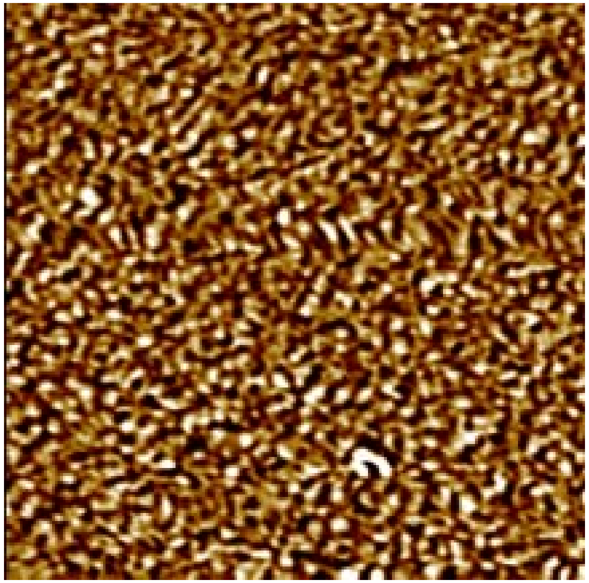
Percolation Threshold





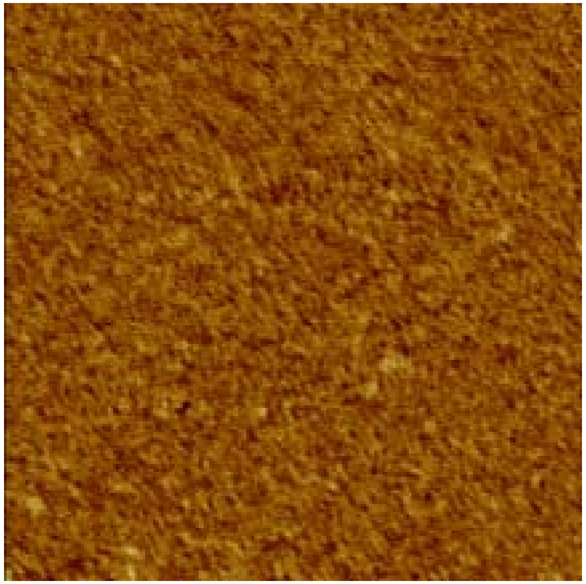


BPSH and Nafion™



1 μm

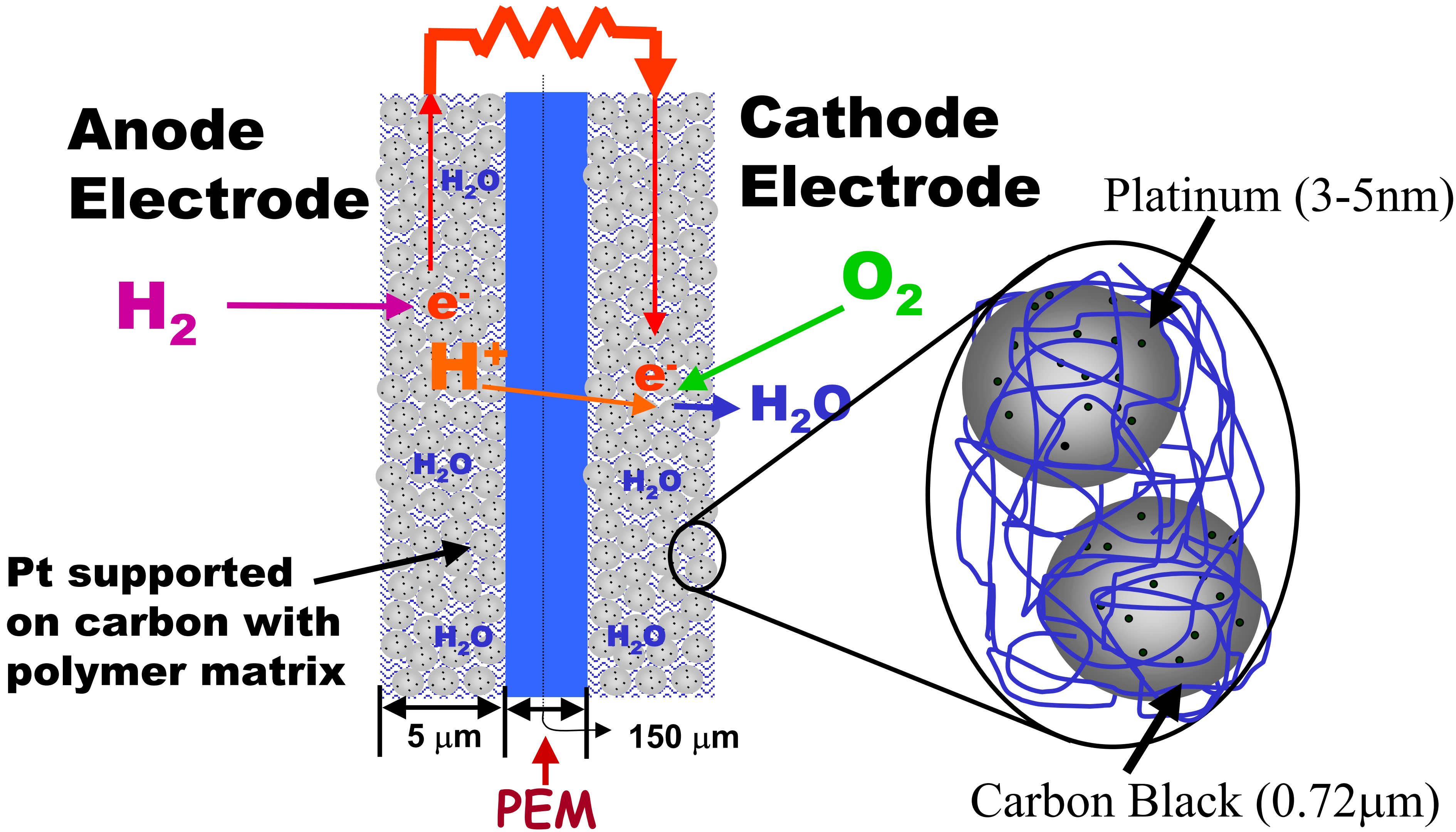
Phase Image of BPSH-40



700 nm

Phase Image of Nafion 117

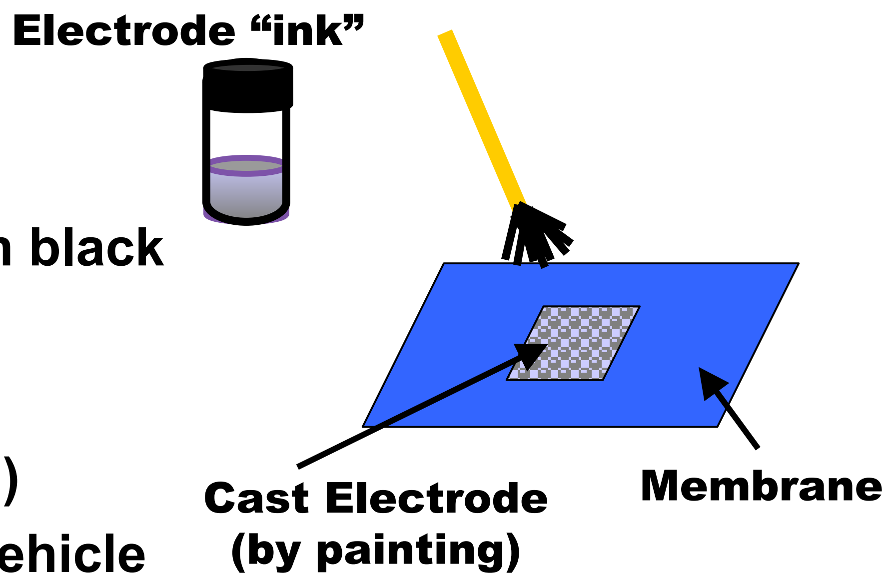
Membrane Electrode Assembly



Direct Painting Fabrication of Membrane Electrode Assembly

Ink

1) Catalyst
   - Platinum or Pt/Ruthenium black (nanocrystalline metal)
2) Polymer Dispersion
   - BPSH polymer (acid form)
   - 50/50 water/IPA solvent vehicle

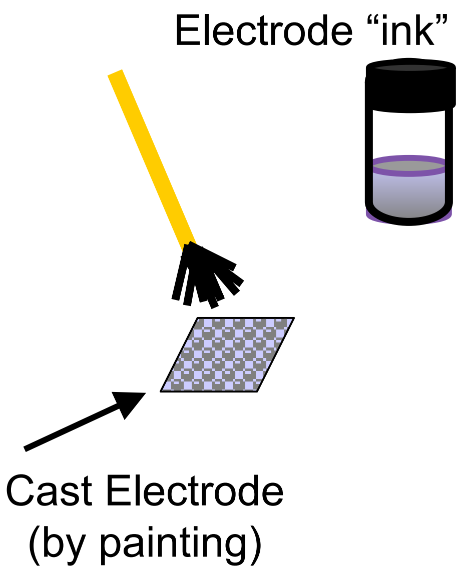


M. Wilson thin film electrode
US #5211984

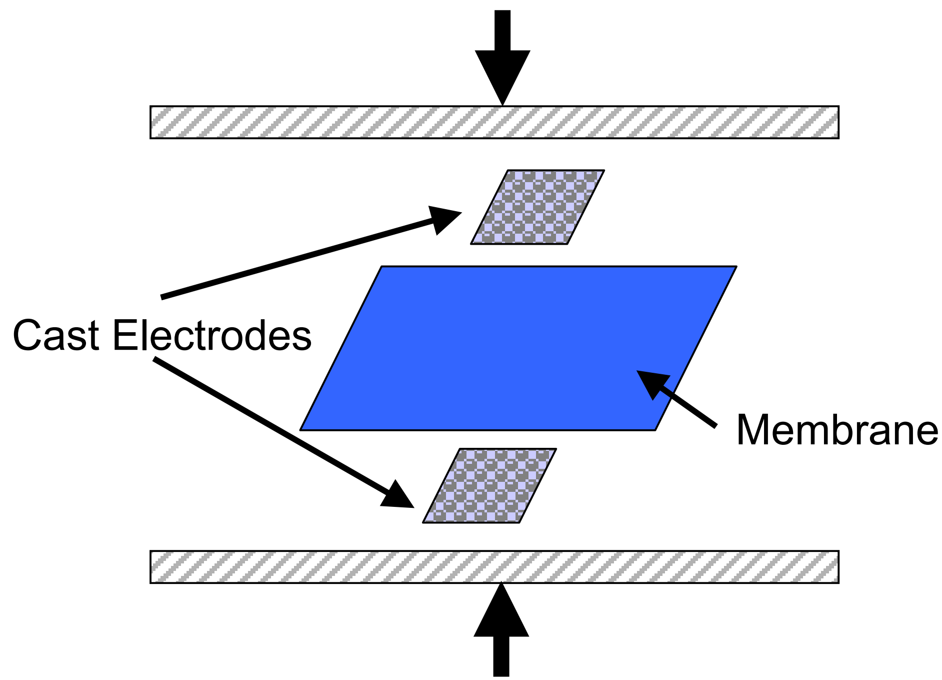
- Catalyst ink painted directly onto dried acid form membrane at 60°C
- Polymer : Catalyst weight ratio is ~ 1:7 (50:50 volume ratio)
- Catalyst loading (mg Pt/cm^2) is determined by amount of ink applied to active area
- Used primarily for DMFC MEA fabrication with high catalyst loadings

Hot-Press Fabrication of Membrane Electrode Assembly

Step 1: Painting of catalyst ink onto a release substrate (Teflon or Kapton)

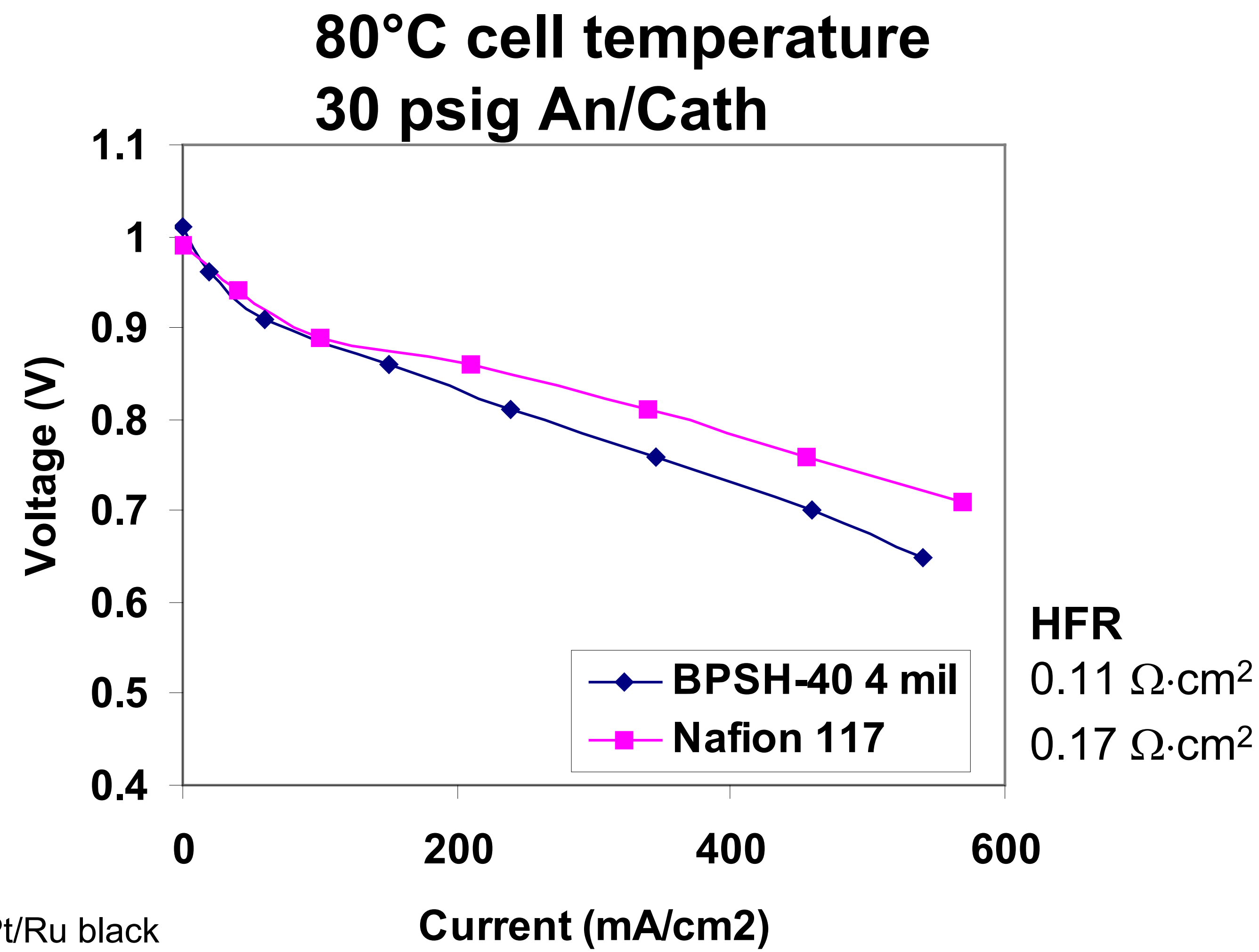


Step 2: Hot-pressing of electrodes onto membrane at 200°C and 200 psi for 5 min.



- **Used primarily for H_2/Air MEA fabrication with low catalyst loadings**

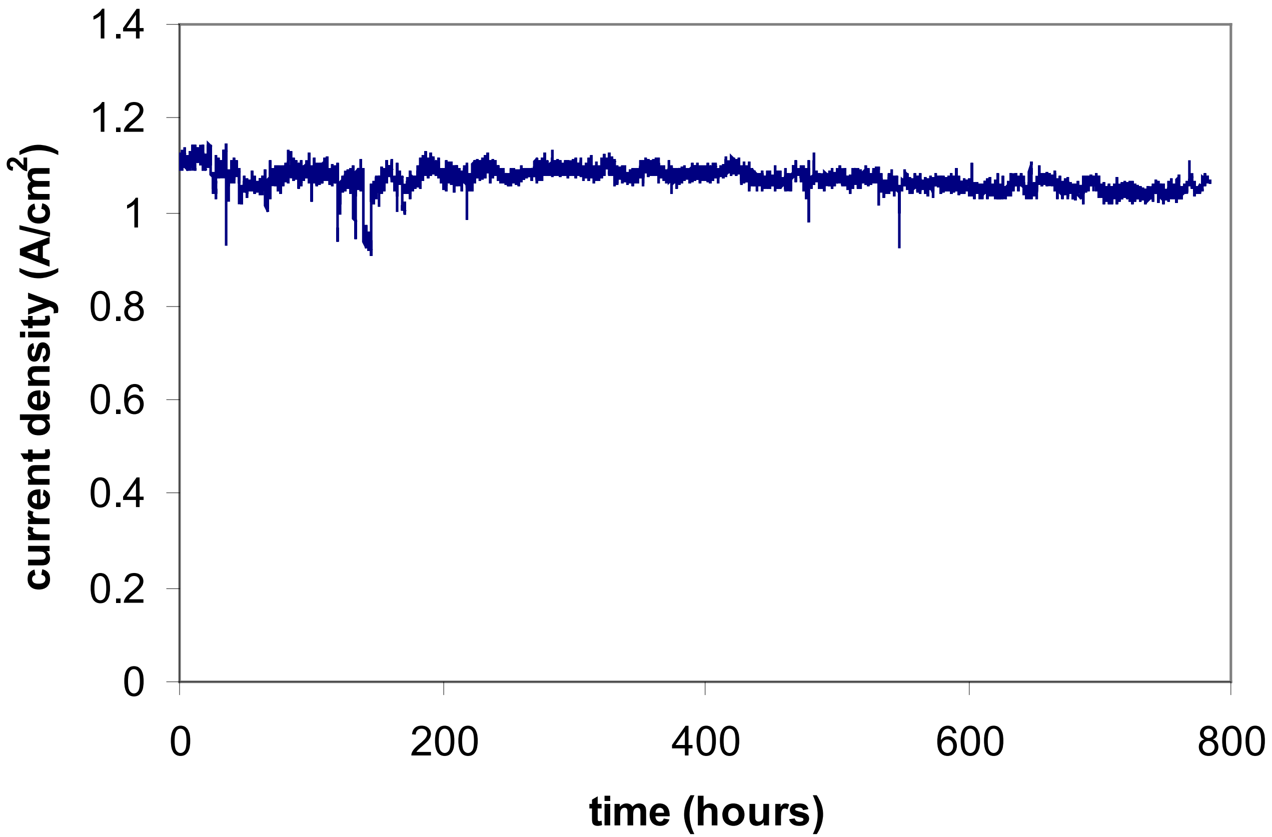
H_2/Air Fuel Cell Performance



Anode: 10 mg/cm² Pt/Ru black
Cathode: 6 mg/cm² Pt black

note: BPSH-40 membrane has BPS anode and Nafion cathode

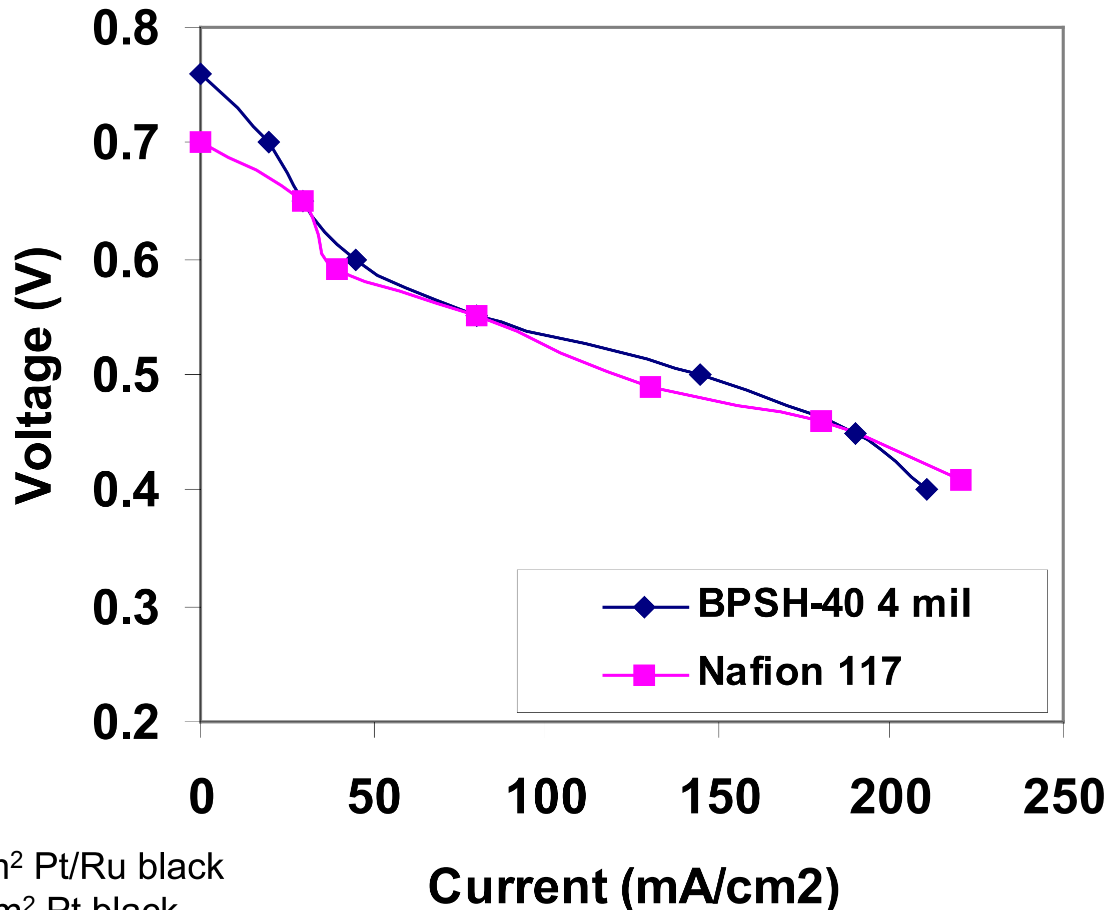
BPSH-30 H2/Air Fuel Cell Life Test: *Membrane is stable ≥ 800 hours*



Conditions:
0.5 V cell voltage
80°C cell temp.
full humidification
Anode:
hydrogen 30 psig
0.2 mg Pt/cm^2
carbon supported catalyst
Cathode:
air 30 psig
0.4 mg Pt/cm^2
carbon supported catalyst

note: no change in cell resistance over the entire test indicates no change in membrane – minor performance drop most likely a result of electrode degradation

Direct Methanol Fuel Cell Performance

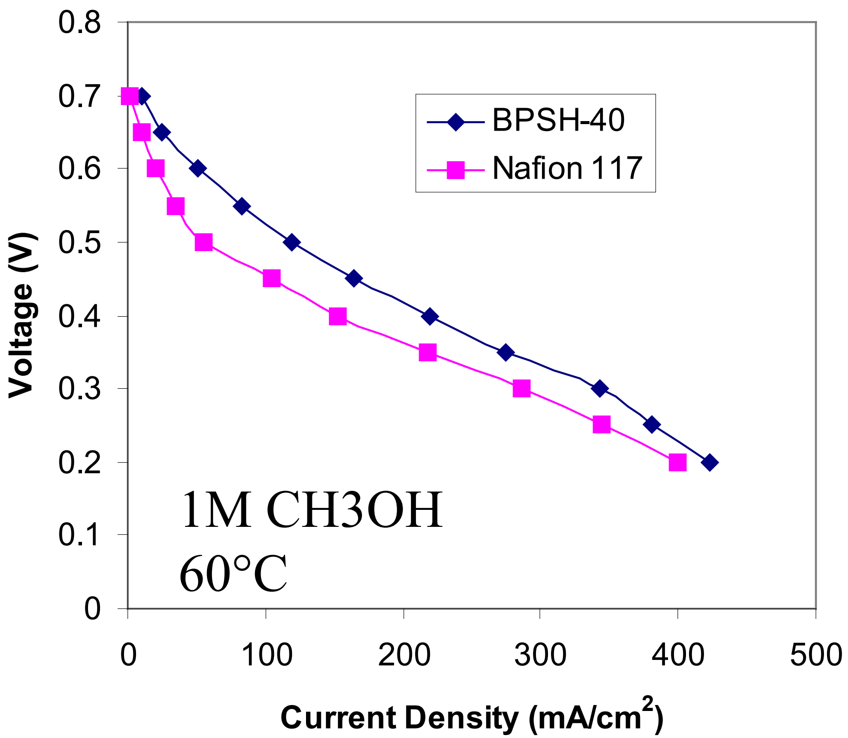


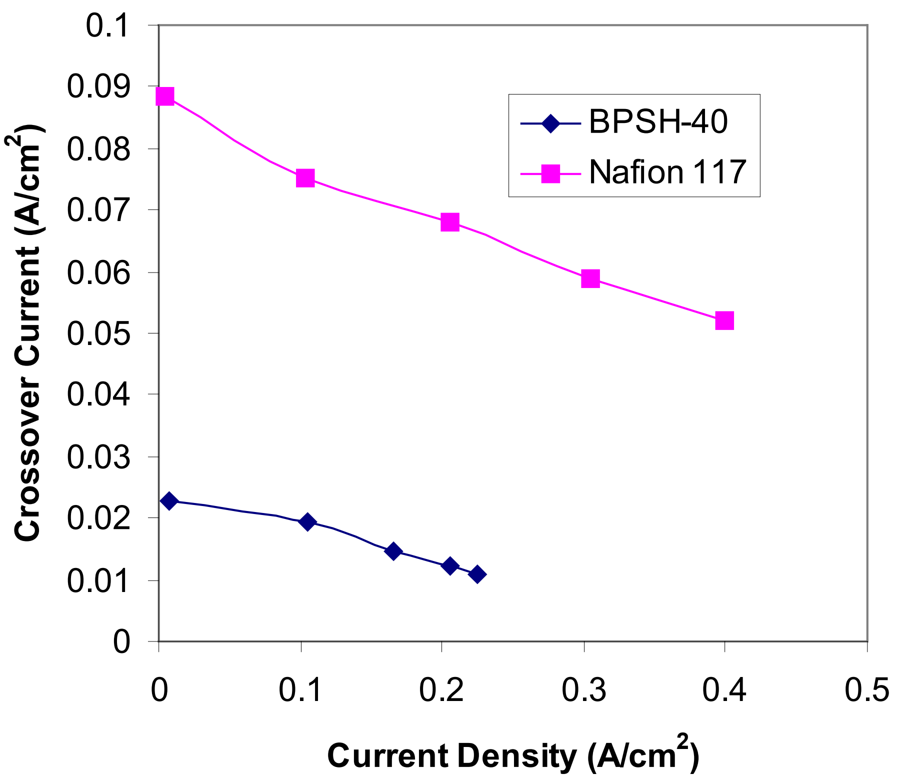
Conditions:
0.5 M CH_3OH
unhumidified air
0 psig
80°C cell temp.

HFR
0.11 $\Omega\cdot cm^2$
0.17 $\Omega\cdot cm^2$

Anode: 10 mg/cm^2 Pt/Ru black
Cathode: 6 mg/cm^2 Pt black

DMFC - Fuel Crossover
Why We Are Interested



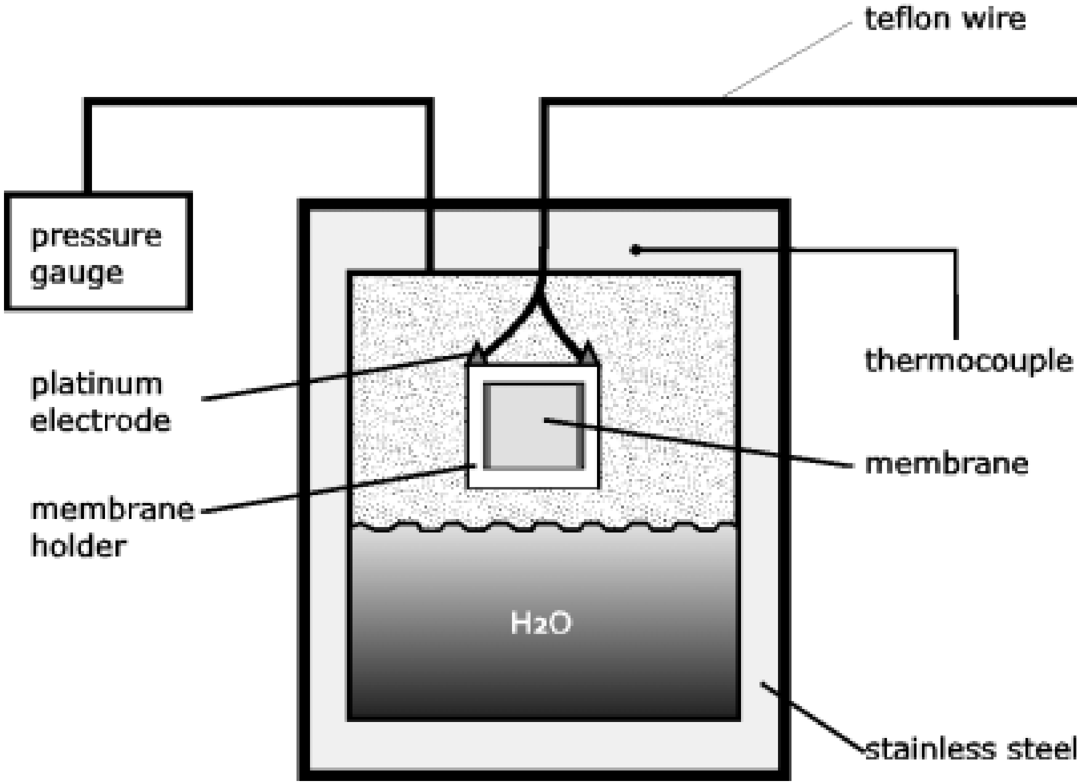


BPSH polymers give similar performance to N117 with much lower methanol crossover

Objectives

- Explore the conductivity behavior of Nafion and BPSH membranes at elevated temperature (>100^{o}C) in fully humidified conditions
- Investigate the influence of acidification treatment on electrochemical properties
- Establish the optimum sulfonation level of BPSH for elevated temperature operation of fuel cell
- Investigate the effect of HPA (phosphotungstic acid and zirconium hydrophosphate) incorporated systems on proton conductivity and water management for the use in elevated temperature fuel cell applications

Schematic Setup of Sealed-off Cell



- **Limit conditions**
  Temperature: 140^{o}C
  Relative Humidity:100%

- **Equilibrium conditions**:
  Placed sample in humidity oven at least 4 hrs at less than 100 ^{o}C and 2 hrs at above 100 ^{o}C at 100% relative humidity.

  ***Total test hours*:~24 hrs.**

Sample Preparation and Measurement

Acidification

- Method 1: 1.5M H_2SO_4, 30°C, 24 hrs,
- deionized H_2O 30°C, 24hrs.

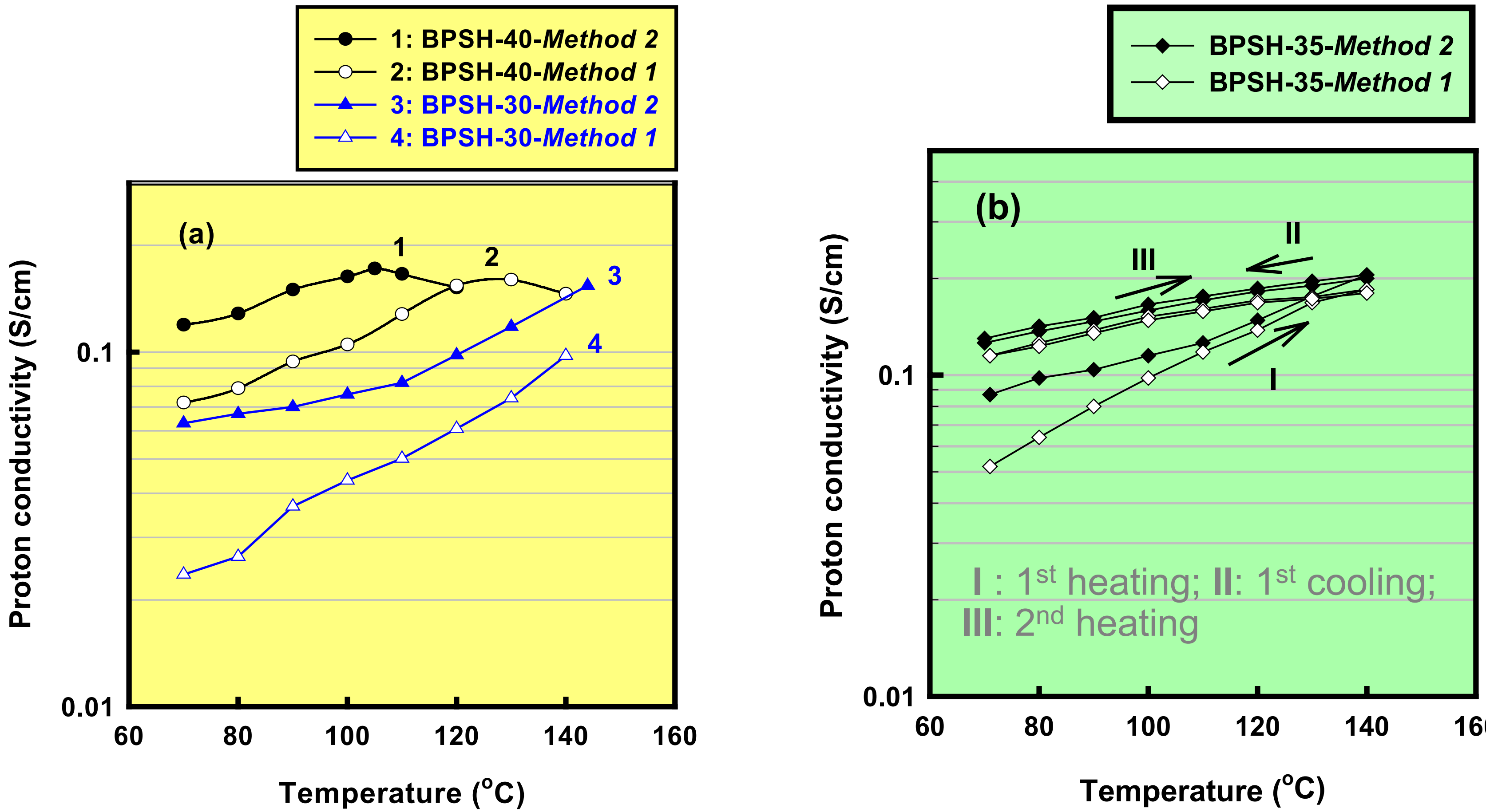
- Method 2: 0.5M H_2SO_4, boil, 2 hrs.
- boiled deionized H_2O, 2hrs.

- All films were stored in deionized H_2O at least 2 days before any test

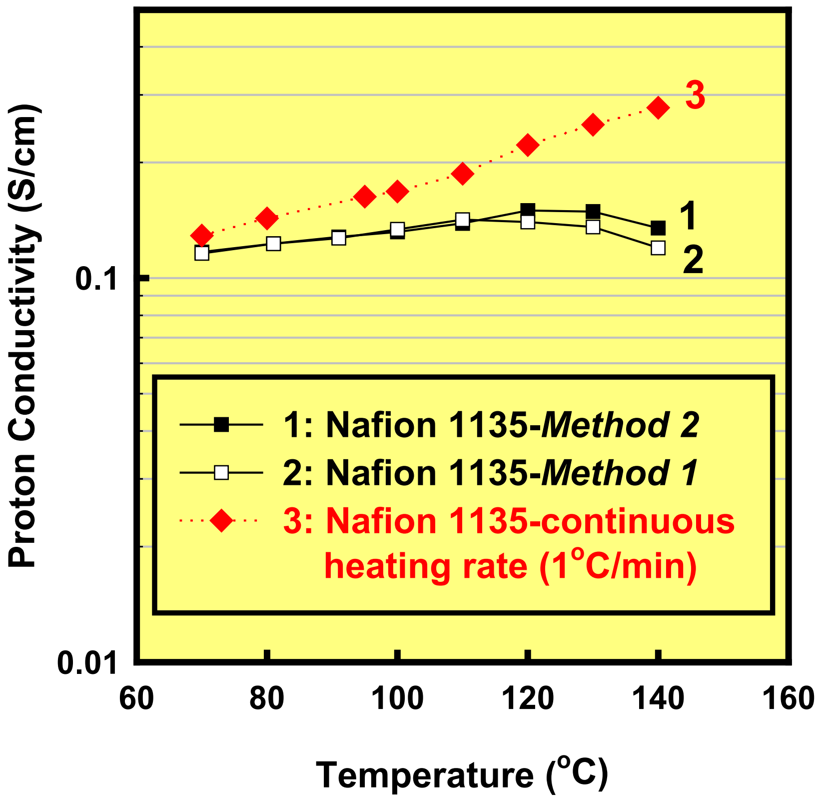
Measurement

- Humidity chamber (ESPEC-SH240)
- Stainless steel sealed-off cell

Proton Conductivity of BPSH as a Function of Temperature (70-140ºC)



Proton Conductivity of Nafion™ as a Function of Temperature (70-140°C)

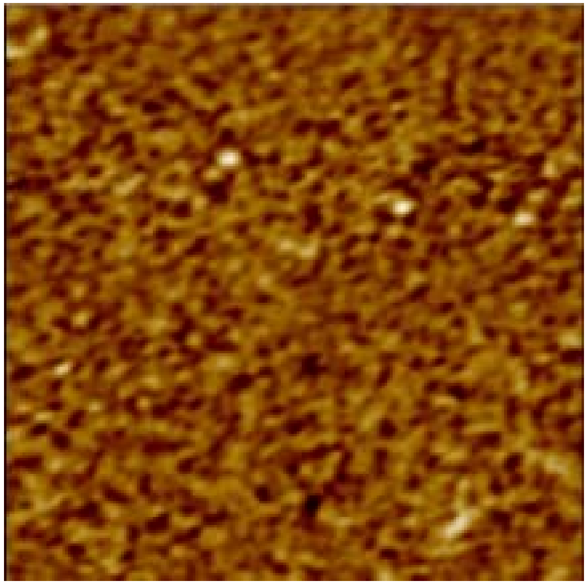


Nafion	E_a (kJ/mol)
1 and 2	5.4-5.8
3	13.1
Ref. 1	7.0
Ref. 2	7.8
Ref. 3	9.4
Ref. 4	9.7
Ref. 5	13.4

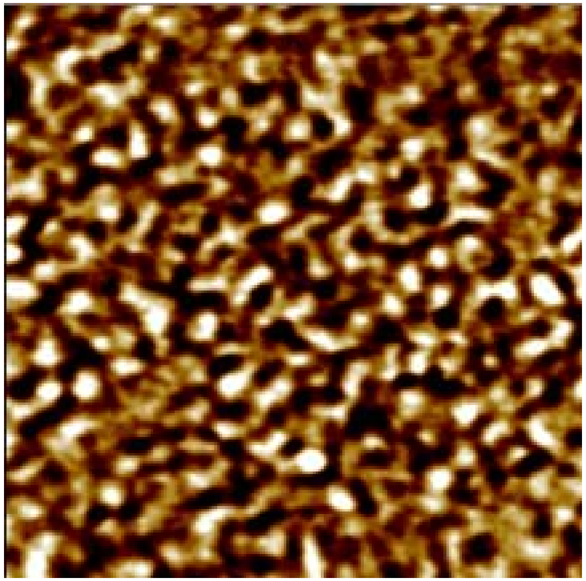
Ref. 1 Alberti, J. Memb. Sci. 73 (2001)
Ref. 2 Kopitzke, J. Electrochem. Soc. 1677 (2000)
Ref. 3 Yeo, J. Electrochem. Soc. 533 (1983)
Ref. 4 Lufrano, Solid State Ionics 47 (2001)
Ref. 5 Halim, Electrochim. Acta. 1303 (1994)

BPSH-40 TM-AFM Phase Images

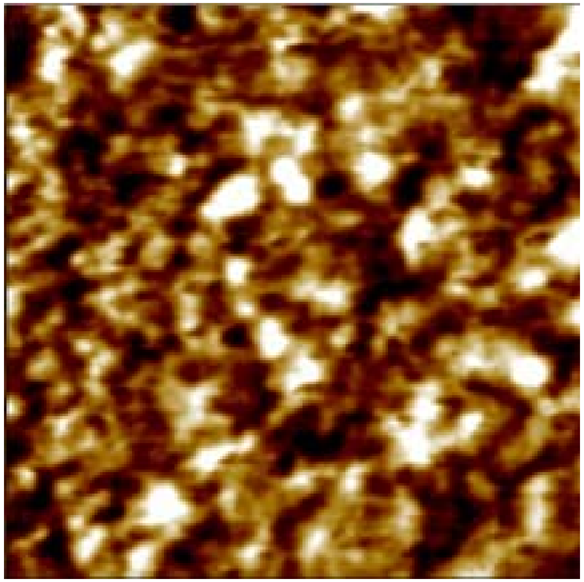
Sample treatment: drying at 100^{o}C for 12 hours then samples were allowed equilibrate by exposure to 50% relative humidity at 30^{o}C for 2 hours, then imaged immediately in relative humidity of about 40%. Scan size: 500nm; Z-range: 10^{o}



after *Method 1*



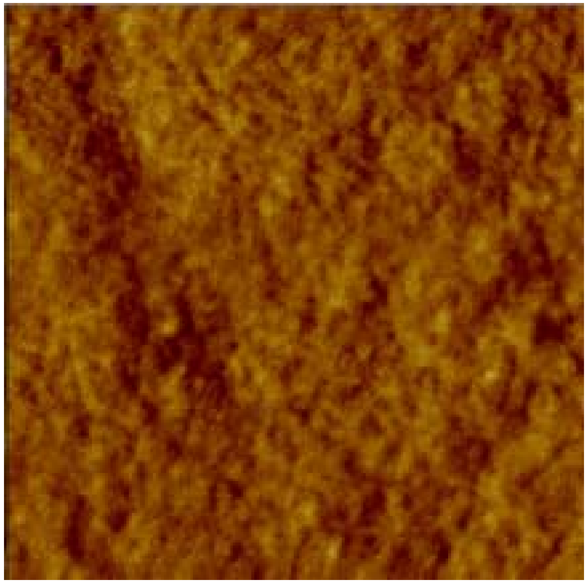
after *Method 2*



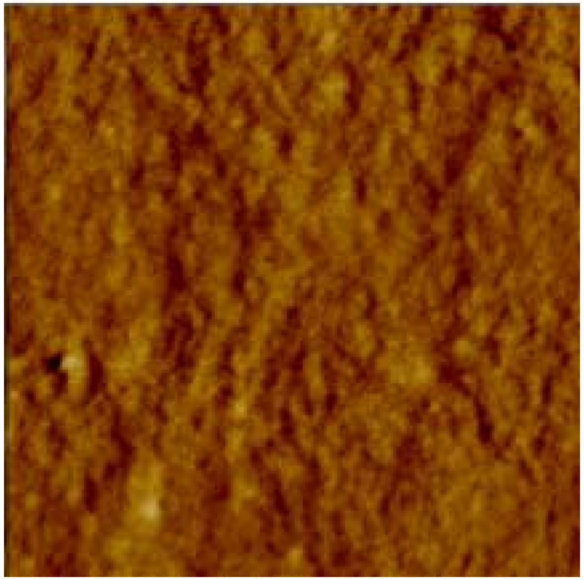
after high temperature exposure (140^{o}C max.)

Nafion 1135
TM-AFM Phase Images

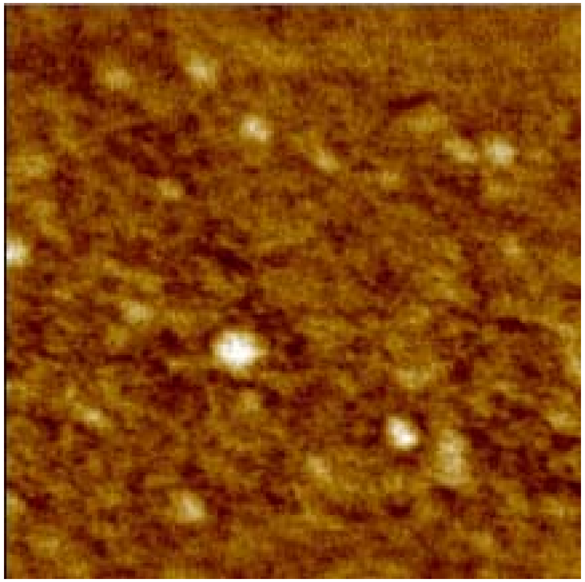
Sample treatment: drying at 100^{o}C for 12 hours then samples were allowed equilibrate by exposure to 50% relative humidity at 30^{o}C for 2 hours, then imaged immediately in relative humidity of about 40%. Scan size: 500nm; Z-range: 10^{o}



after *Method 1*



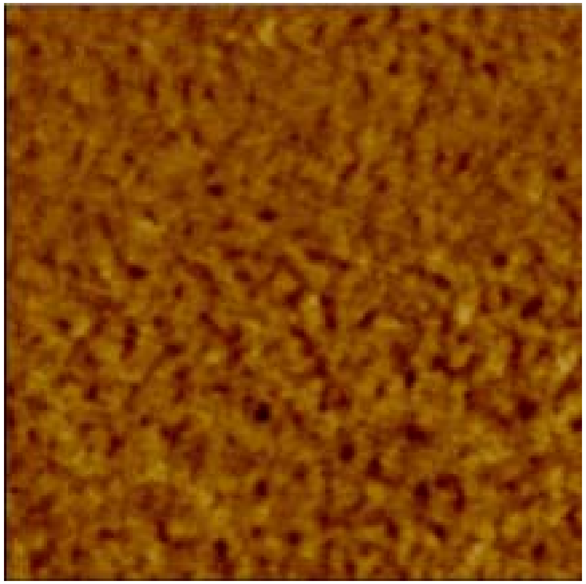
after *Method 2*



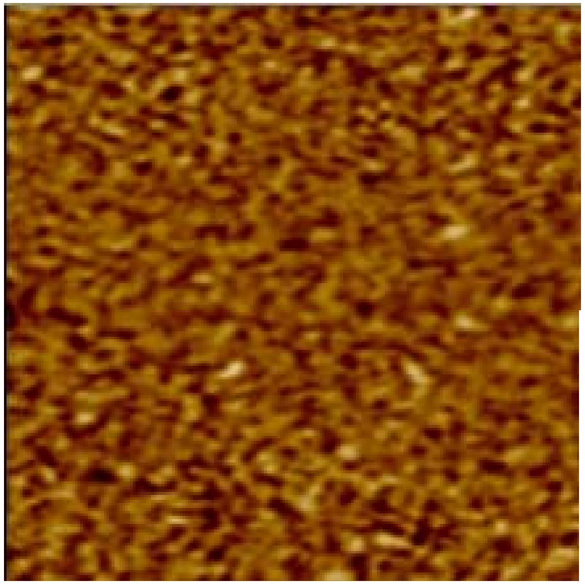
after high temperature exposure (140^{o}C max.)

BPSH-35 TM-AFM Phase Images

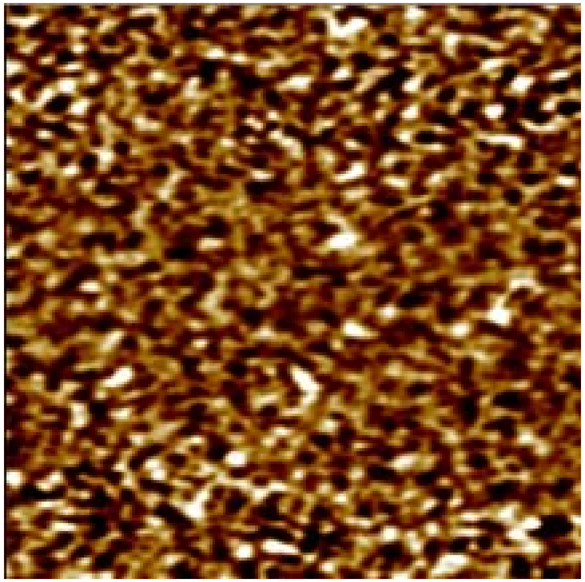
Sample treatment: drying at 100°C for 12 hours then samples were allowed equilibrate by exposure to 50% relative humidity at 30°C for 2 hours, then imaged immediately in relative humidity of about 40%. Scan size: 500nm; Z-range: 10°



after *Method 1*



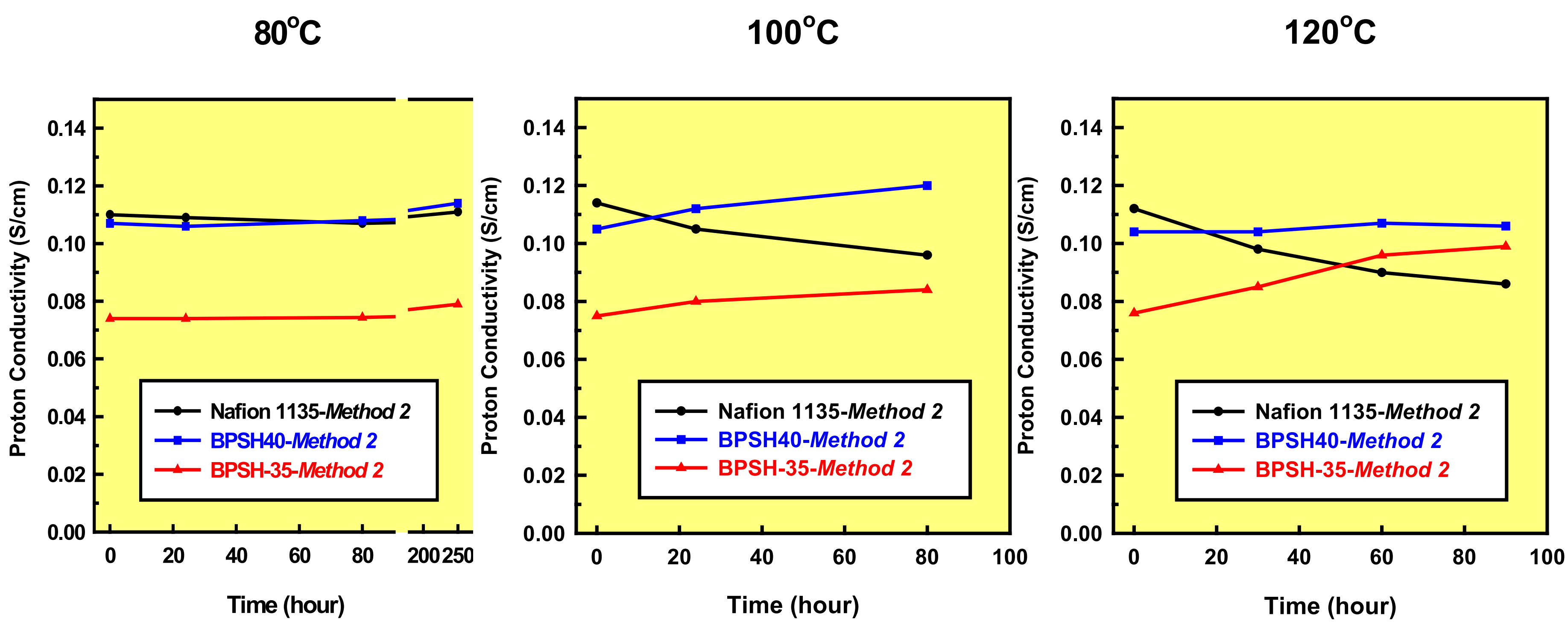
after *Method 2*



after high temperature exposure (140°C max.)

Influence of Aging Temperature on Electrochemical Stability

Aging procedure: Samples treated by *Method 2* were placed in fully humidified condition at a given aging temperature. After a certain time being, samples were taken and treated by *Method 1* in order to remove any contaminants during aging procedure. Then measured the proton conductivity in liquid H_2O at 30°C.



Water Absorption Change in Terms of Treatment Conditions

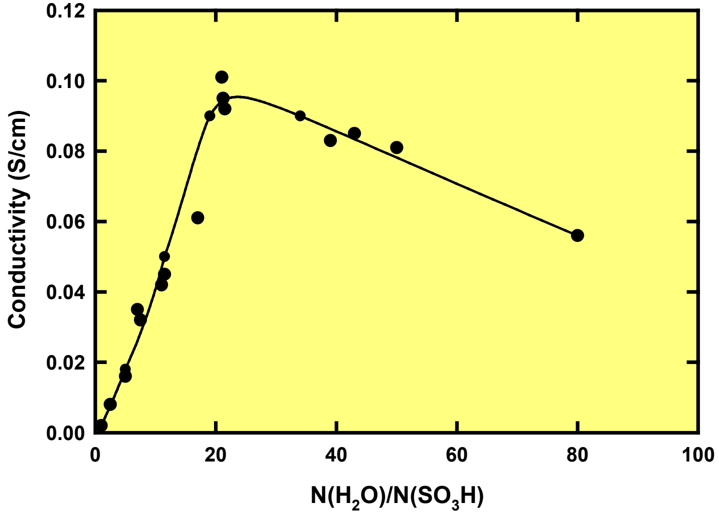
Water Absorption (%)

treatment	*Method 1*	*Method 2*	Test A[a]	Test B[b]
BPSH-30	24	31	43	NA
BPSH-35	32	38	51	73
BPSH-40	39	58	74	170[c]
BPSH-60	148	>1000[c]	NA	NA
Nafion 1135	19	19	29	36[c]

[a] Test A: high temperature conductivity (70-140^{o}C, 24 hr)

[b] Test B: Aging (120^{o}C, 60hr)

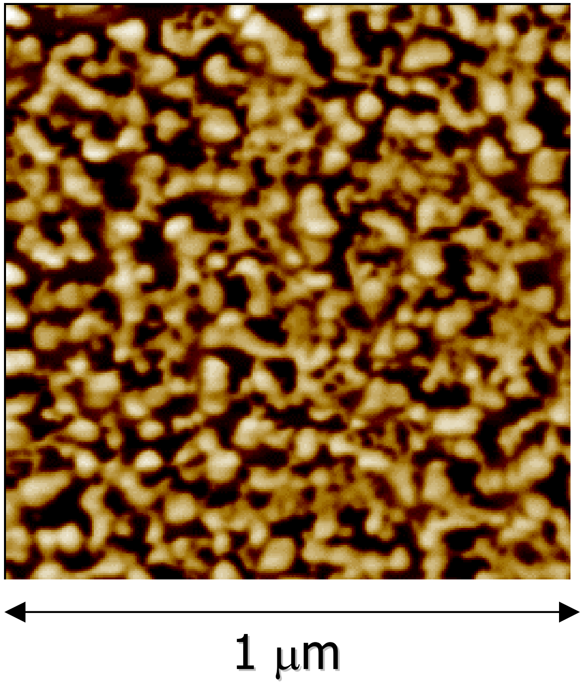
[c] Mechanically unstable at wet condition



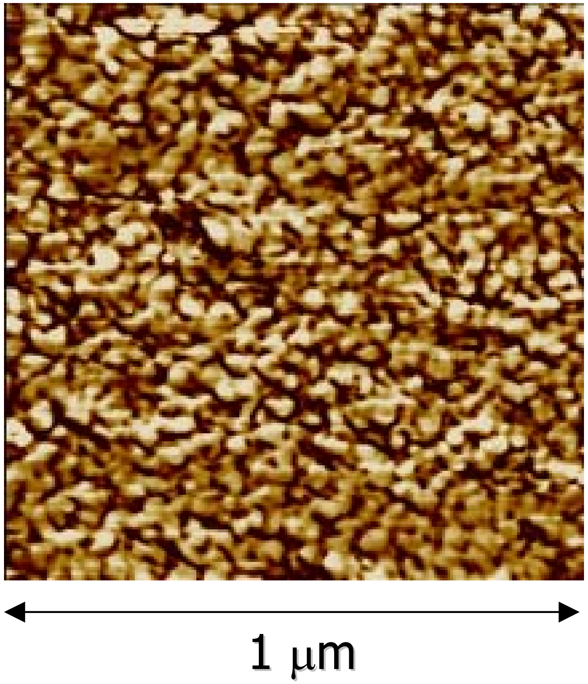
Proton conductivity versus water content for Nafion™ 117 Membranes at 30^{o}C, indicating data for membranes pre-swollen in glycerol.

Ref. T. Zawodzinski, *Advances in Electrochemical Science and Engineering,* Wiley-VCH, p264

HPA Composite Membranes

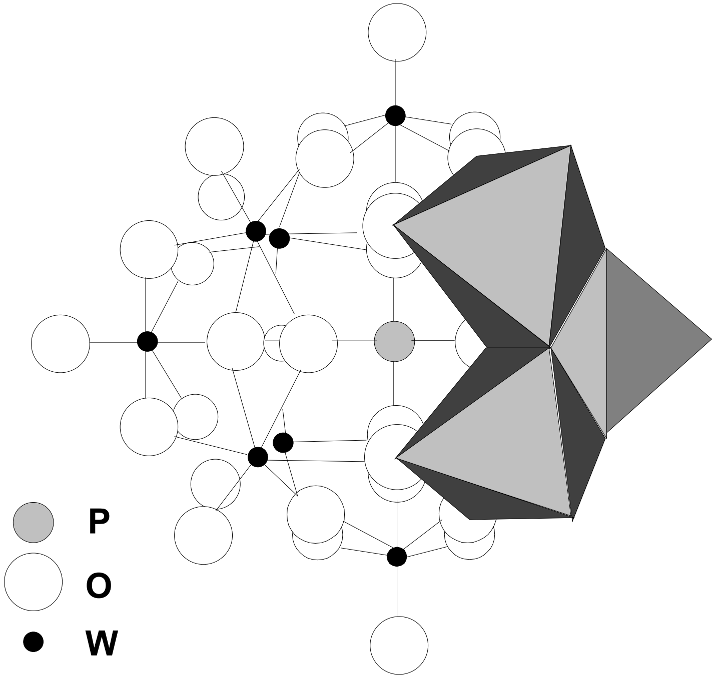


Phase Image of Phosphotunstic acid incorporated system



Phase Image of Zirconium hydrogen phosphate/ BPSH-40 composite

Heteropolyacid ($H_3PW_{12}O_{40}$)

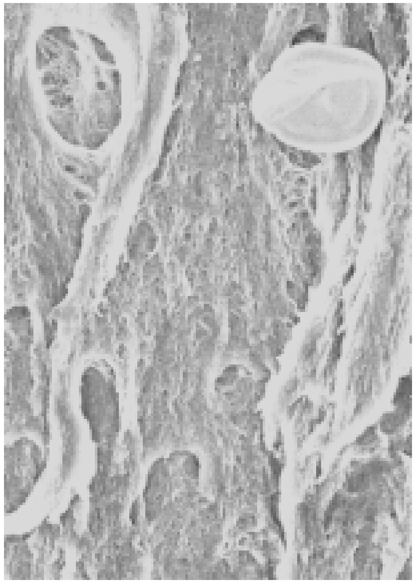


Structure of Keggin anion ($PW_{12}O_{40}^{3-}$)

- ✓ Conductive material (0.17 S/cm)
- ✓ Crystalline form ($H_3PW_{12}O_{40}$ $29H_2O$)
- ✓ Soluble in water or polar solvent
- ✓ Stable at temperatures higher than 100 ^oC

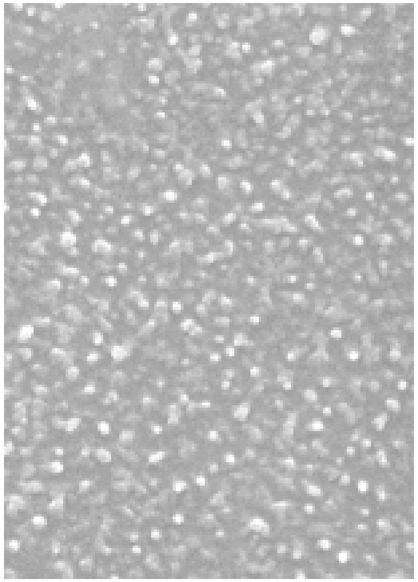
B.B. Bardin, S.V. et. al. *J. Phys. Chem. B*, 102, (1998) 10817.

Cross-Sectional Morphology of Nanocomposite Membranes by Scanning Electron Microscope



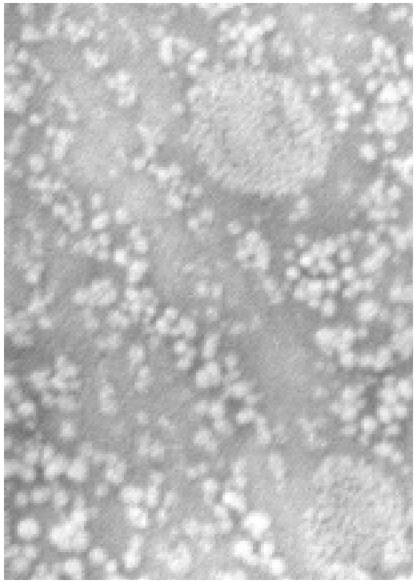
1 μm

HPA/PBPSH-0



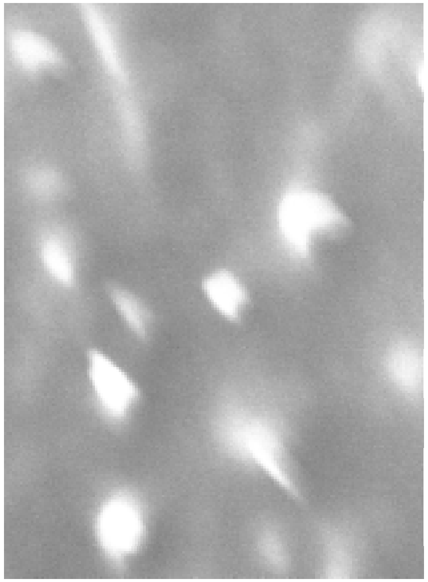
200 nm

HPA/PBPSH-20



200 nm

HPA/PBPSH-40



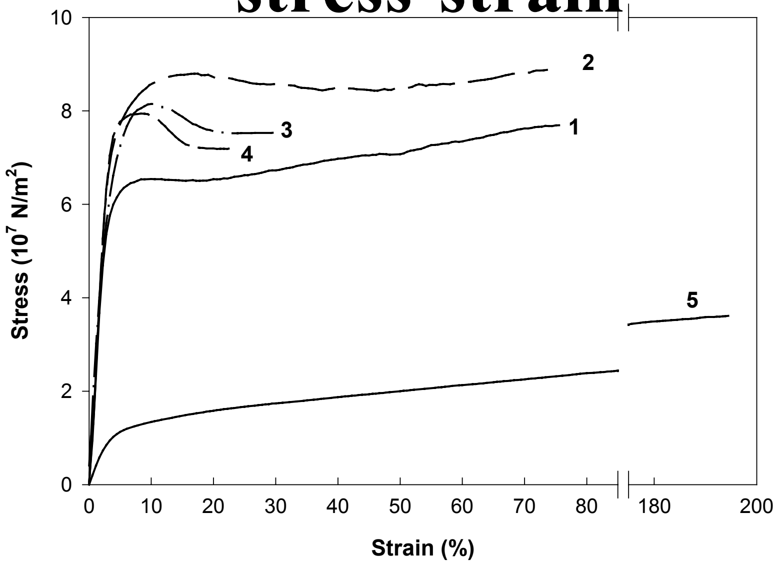
200 nm

HPA/PBPSH-60

*** HPA concentration= 30 wt.%**

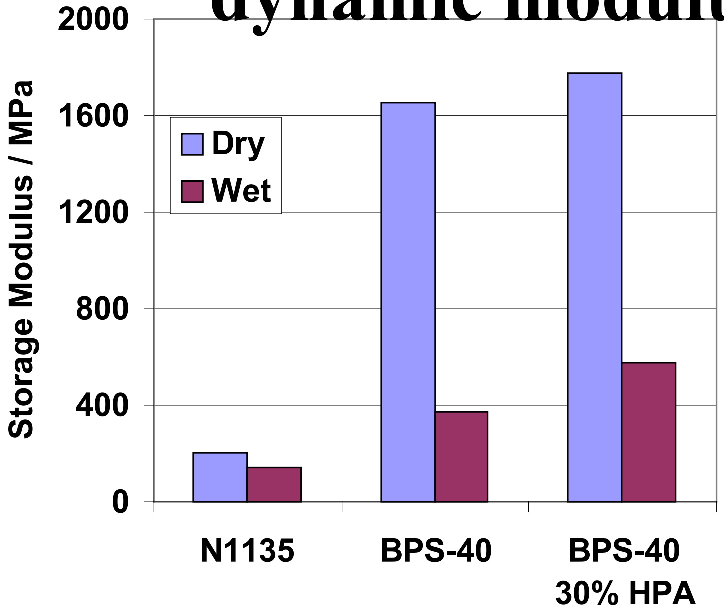
Stress-Strain Properties and Modulus by In-Situ DMA

stress-strain



1: PBPSH-40
2: HPA 30 %
3: HPA 45 %
4: HPA 60 %
5: Nafion 117

dynamic modulus



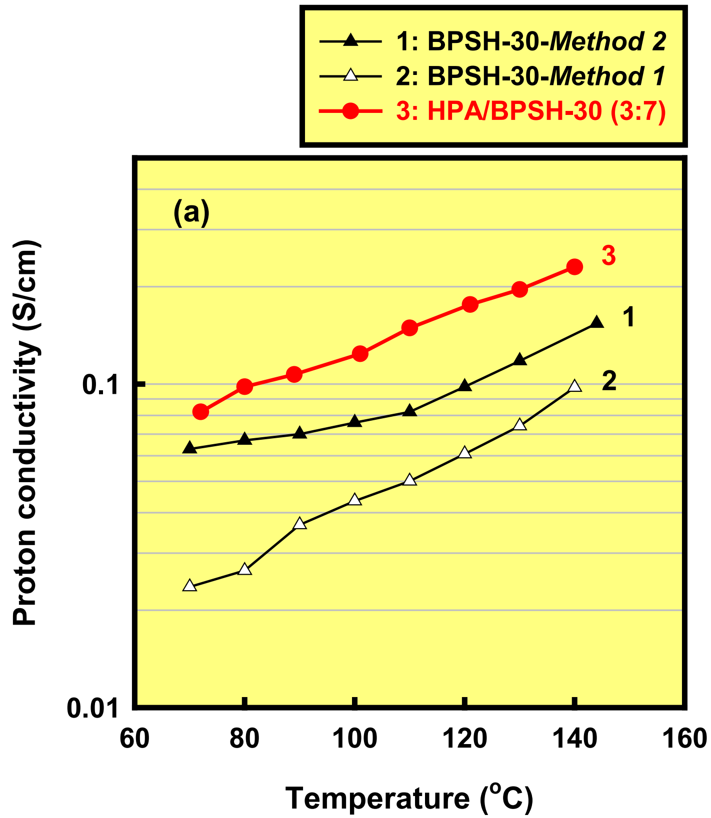
dry: 25C ambient humidity
wet: 30C liquid water

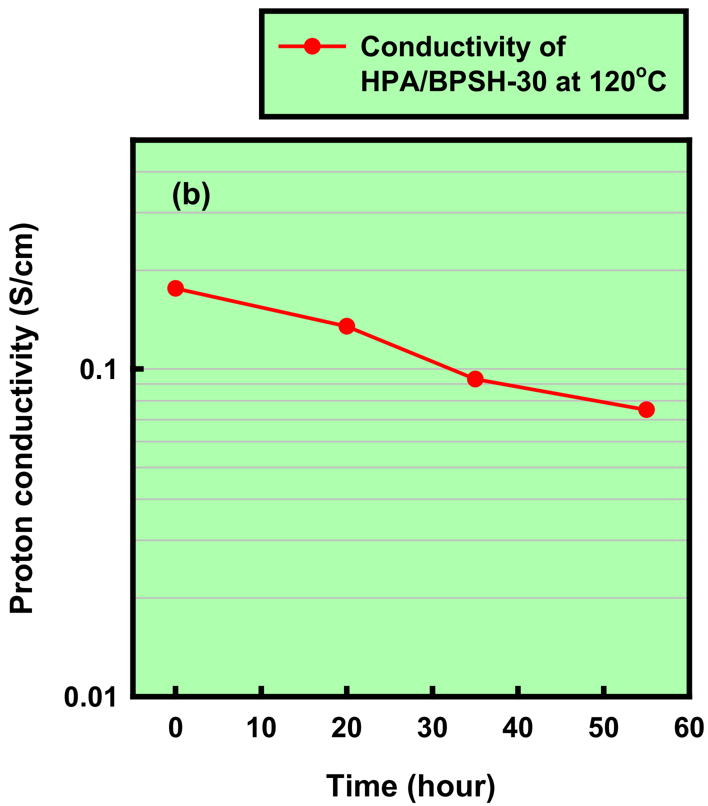
In Situ Synthesis of Composite Membranes Containing Zirconium Hydrophosphate Heteropolyacid (HPA)

$$ZrOCl_2 + 2H_3PO4 \xrightarrow[\text{80°C, 6hr}]{\text{Aqueous Medium}} Zr(HPO_4)_2 \bullet H_2O + 2HCl$$

- Process conducted on water swollen acid form membranes (e.g., BPSH-40) first swollen for 1 hour in boiling water
- Composite membranes washed with deionized water for 4 hours to remove excess H_3PO_4 and HCl
- Wt% HPA confirmed by TGA

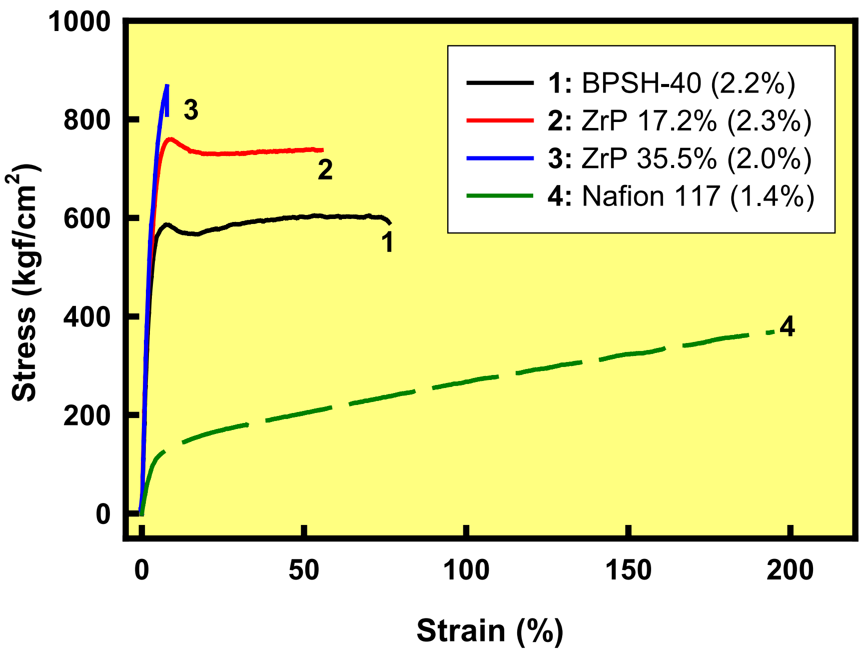
Proton Conductivity of Phospho Tungstic Acid/BPSH-30 at Elevated Temperature



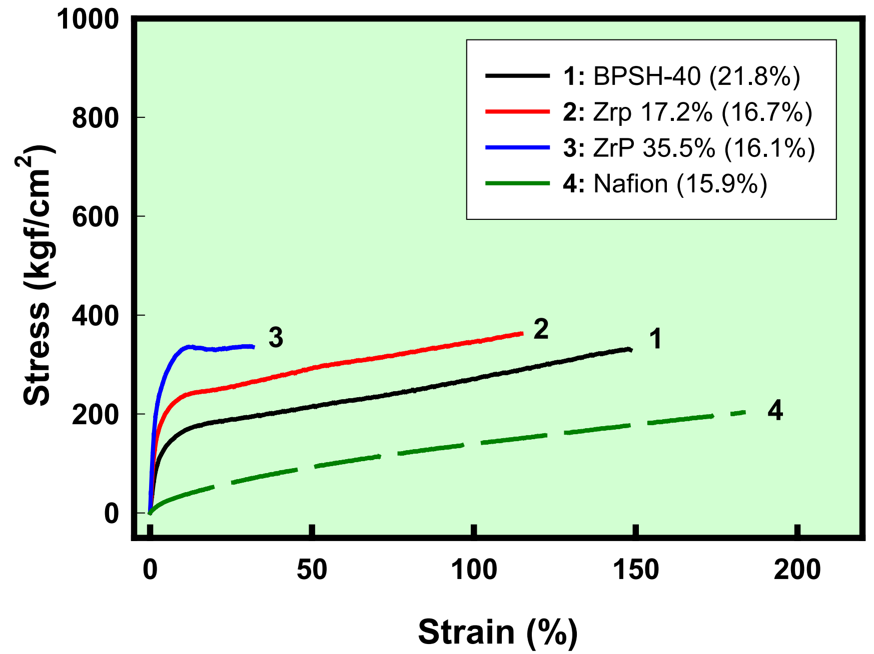


- Proton conductivity as a function of temperature
- Proton conductivity as a function of aging at 120°C

Stress-Strain Curves of ZrP/BPSH-40 Composite Membranes



Dry Conditions

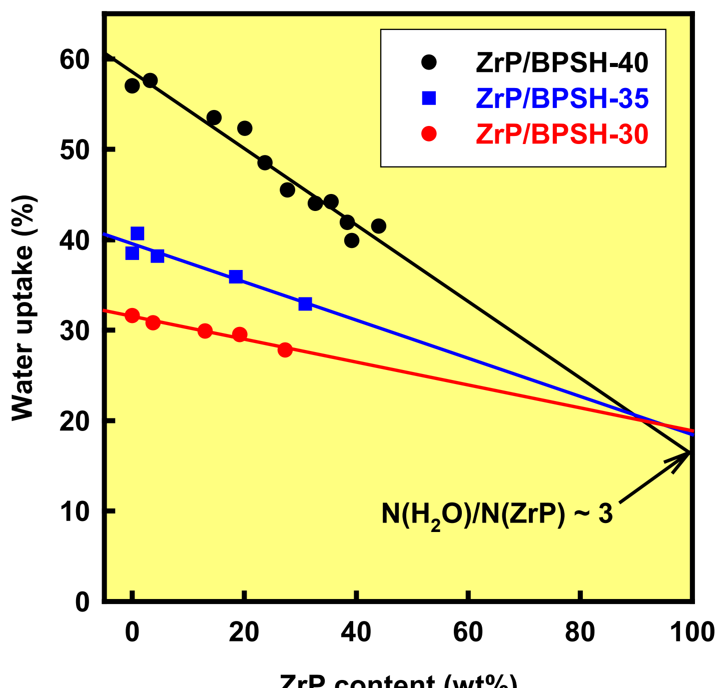


Wet Conditions

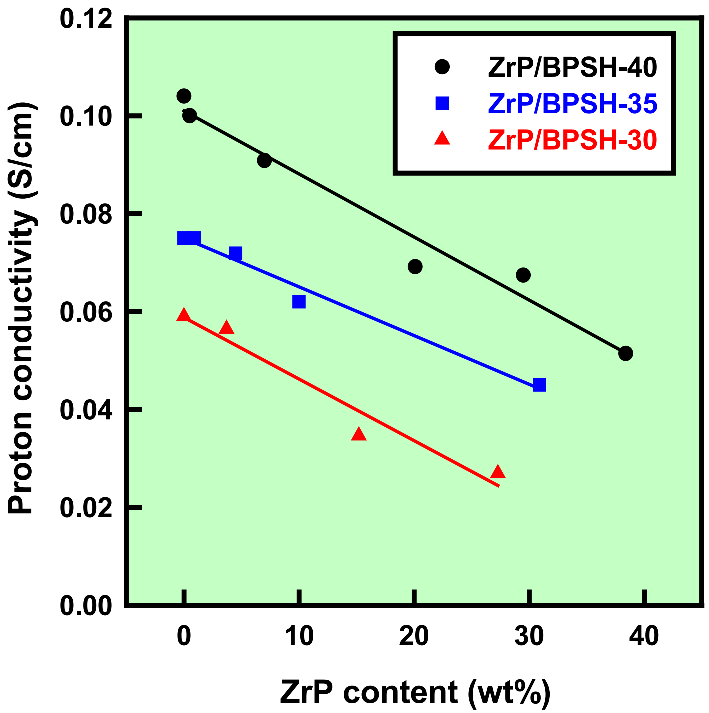
Parenthesis: water content in weight percent

Test conditions: 25^{o}C, 40% RH, Crosshead speed: 5mm/min, Number of specimen: 5

Influence of ZrP on Water Uptake and Proton Conductivity

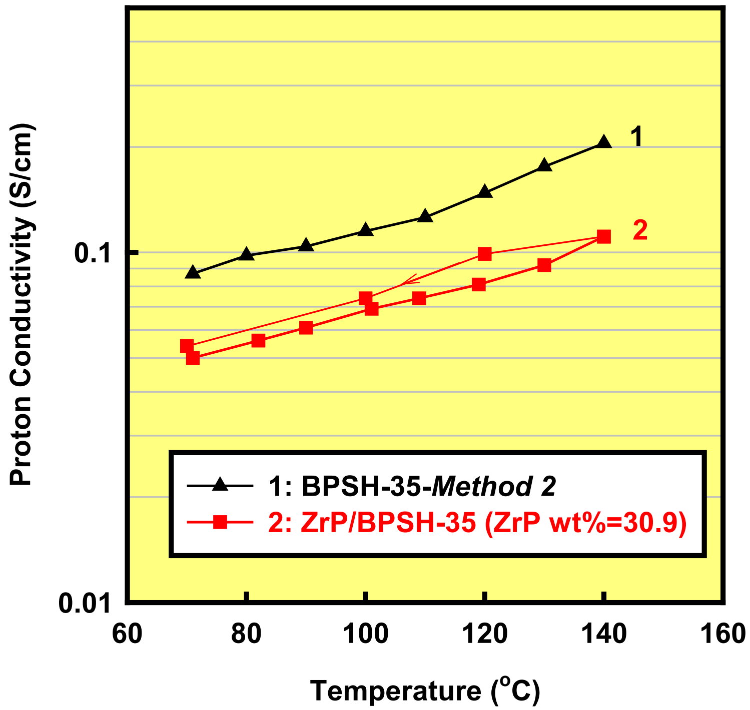


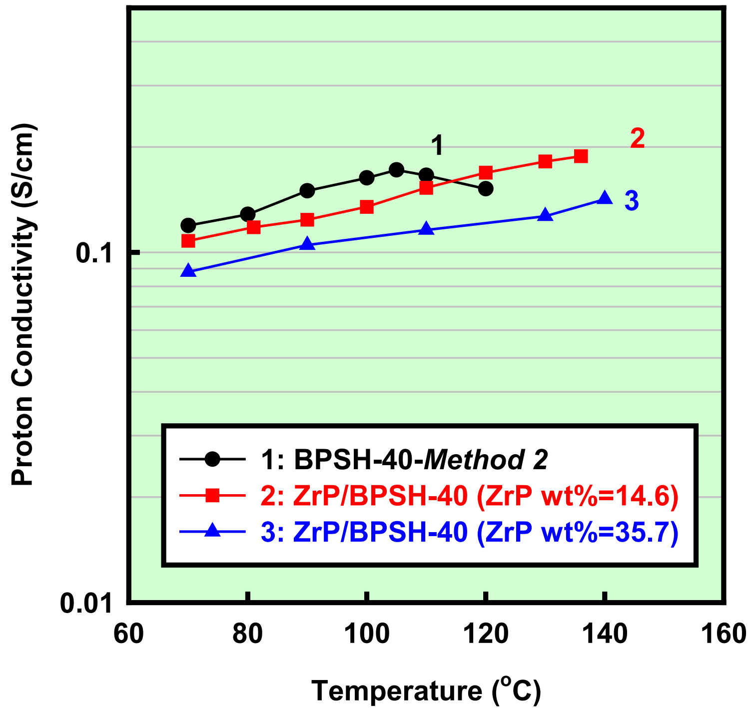
Water uptake at 30°C



Proton conductivity at 30°C in liquid water

Effect of Zirconium Hydrogen Phosphate Incorporation on Proton Conductivity at Elevated Temperature





- Proton conductivity of BPSH-35 and ZrP/BPSH-35 as a function of temperature
- Proton conductivity of BPSH-40 and ZrP/BPSH-40 as a function of temperature

Trade-off for HPA Incorporation for Elevated Temperature Fuel Cell Operation

	Phosphotungstic acid HPA	Zirconium hydrogen phosphate HPA
Conductivity	$\Uparrow$	$\Downarrow$
Morphological Stability	$\Uparrow$	$\Uparrow$
Dimensional Stability	$\Uparrow$	$\Uparrow$
Mechanical Properties	$\Uparrow$ **(strength)** $\Downarrow$ **(elongation)**	$\Downarrow$
Thermal Resistance	$\Uparrow$	$\Uparrow$
HPA Retention Stability	**Poor for high degree of disulfonation**	**Good**

Ref. Y.S. Kim et.al., J.Memb.Sci., submitted (2002)

Y.S.Kim et.al., 8th International symposium for polymer electrolyte (2002)

Summary

- Proton conductivity for BPSH was considerably dependent on the acidification temperature while that of Nafion 1135 remained constant.
- BPSH-40 and Nafion-1135 showed maximum conductivity at the temperature around 120^{o}C. TM-AFM results indicated that the conductivity decrease at high temperature was due to the excessive water absorption and and subsequent morphological instability.
- Aging test in fully humidified condition above 120^{o}C showed that the conductivity of Nafion 1135 decreased significantly after 60 hours, while BPSH-35 showed a slight increase in proton conductivity presumably due to the positive morphological change.

Summary

- Phosphoric tungstic HPA incorporated sulfonated BPSPPO composites had a strong hydrogen bonding interaction between tungstic oxide and sulfonic acid resulting in not only enhanced dimensional stability but also improved proton conductivity at the temperature range of 70-140^{o}C.

- Zirconium hydro phosphate HPA/BPSH composites showed enhanced dimensional stability with acceptable proton conductivity above 100^{o}C, compared to pure BPSH copolymer.

McGrath Research Group – June 2001

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**SURP: Summer Undergraduate Research Program*