Advanced Fuel Cell Membranes Based on Heteropolyacids

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Project ID # FC4

This presentation does not contain any proprietary or confidential information

Overview

Timeline

- Project start date: FY 2005
- Project end date: tbd
- Percent complete: tbd

Budget

- Total project funding
  – DOE share: $300K
- Funding received in FY05:
  – $150K (0.3 FTE)
- Funding for FY06:
  – $150K (0.3 FTE)

Targets

- Low humidity operation (25% RH).
- High conductivity ~0.1 S/cm
- Cost $40/m^2

Barriers

- Barriers addressed

A. Durability.

B. Cost.

D. Thermal, Air and Water Management.

Partner/Subcontract

- Colorado School of Mines

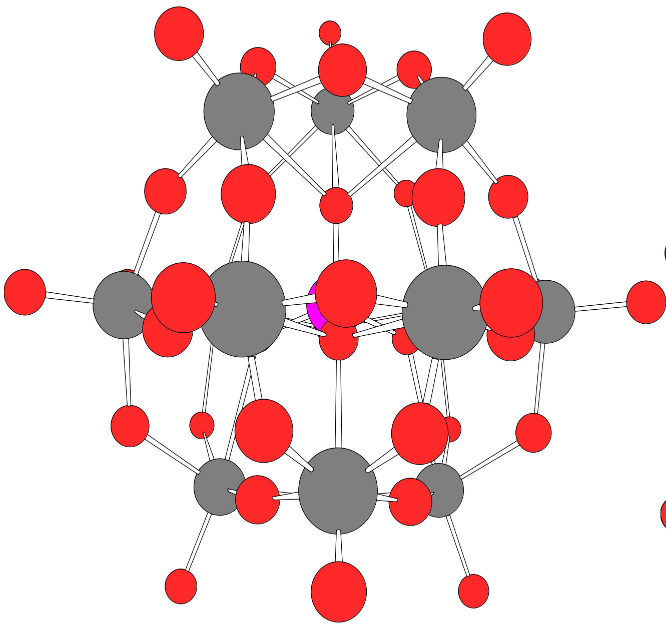
– Prof. Andrew M. Herring

– Dr. Steven F. Dec

Objectives

- **Develop the methodology for the fabrication of 3D cross-linked, hydrocarbon-based membranes using immobilized heteropolyacids (HPAs) as the proton conducting moiety.**
  - Conductivity ~0.1 S/cm at 120ºC and <1.5 kPa H_2O
- **Develop immobilization technology based on covalent attachment of HPAs to oxide nano-particles.**
- **Acquire an improved understanding of HPAs and their salts made by custom synthesis.**
  - HPAs make up a class of inorganic proton conductors that exhibit high proton conductivity at low humidity (below 25% RH) and at elevated temperatures (well above 100°C).
- **Conduct relevant characterizations of the membranes to better understand their structural, chemical, and thermal properties/stability and proton conductivity.**

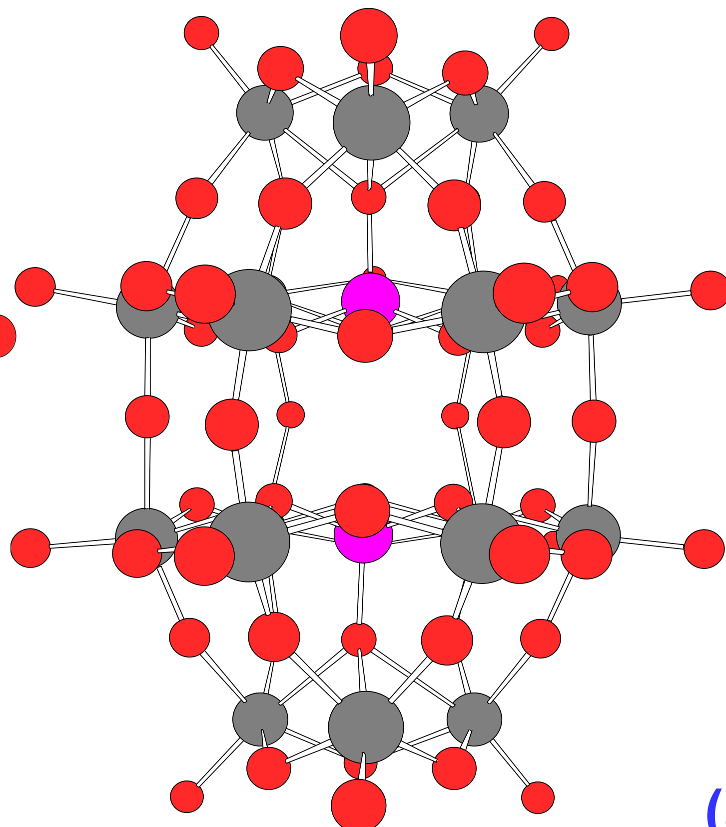
HPAs: High H^+ Conductivity, High Thermal Stability; Vast Structural Diversity; Known Redox Catalysts



Keggin

$[SiW_{12}O_{40}]^{4-}$

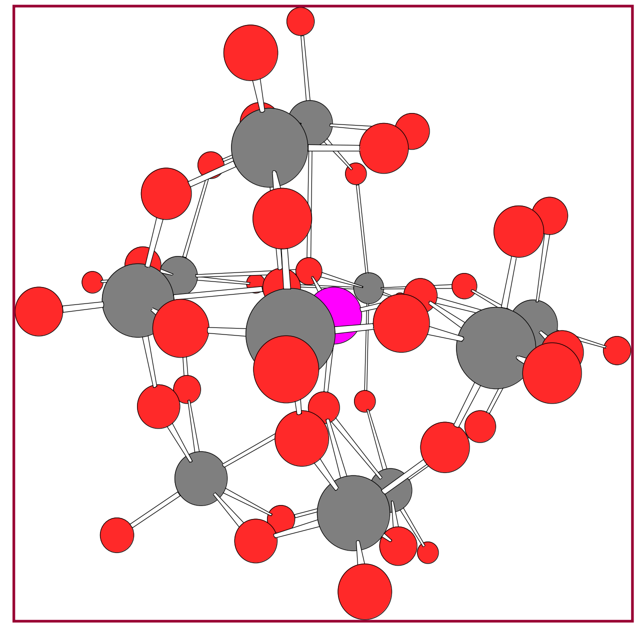
$H_4SiW_{12}O_{40}$-$26H_2O$
(W12-STA)



Dawson

$[P_2W_{18}O_{62}]^{6-}$

$H_6P_2W_{18}O_{62}$-xH_2O



Lacunary
(allows easy attachment points)

$[SiW_{11}O_{39}]^{8-}$

$H_8SiW_{11}O_{39}$-$26H_2O$
(W11-STA)

Strategies for Immobilizing HPAs

A. Binding Approaches:

1. Covalent bonding to oxide nano-particles insitu, which can bond covalently to, or embed physically in, a polymeric matrix
2. Direct embedding in a polymeric matrix
3. Covalent bonding directly to a polymeric matrix (CSM/3M collaboration, poster #FCP-6)

B. Modification of Lacunary HPAs:

1. By bonding with functional silanes that can then be cross-linked or polymerized

C. Fabrication Approaches:

1. Sol gel method
2. Immobilized via silylation onto supporting particles
3. Simple blending

D. Polymeric Matrix:

1. Organic
2. Inorganic
3. Organic-inorganic hybrid

126 Organic and Organometallic Derivatives

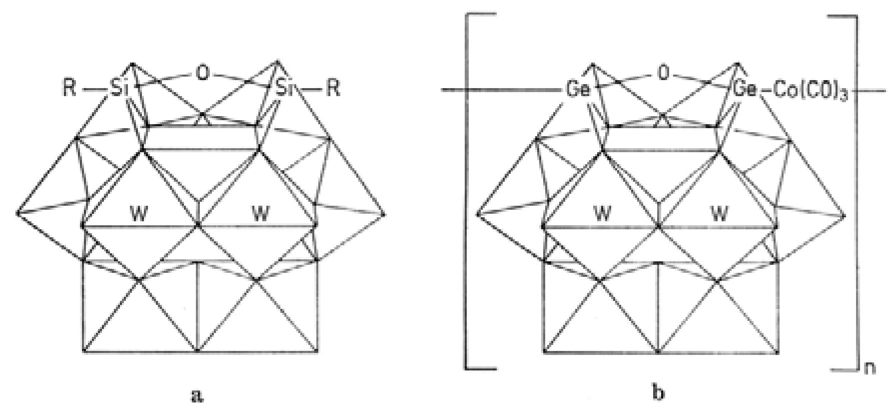
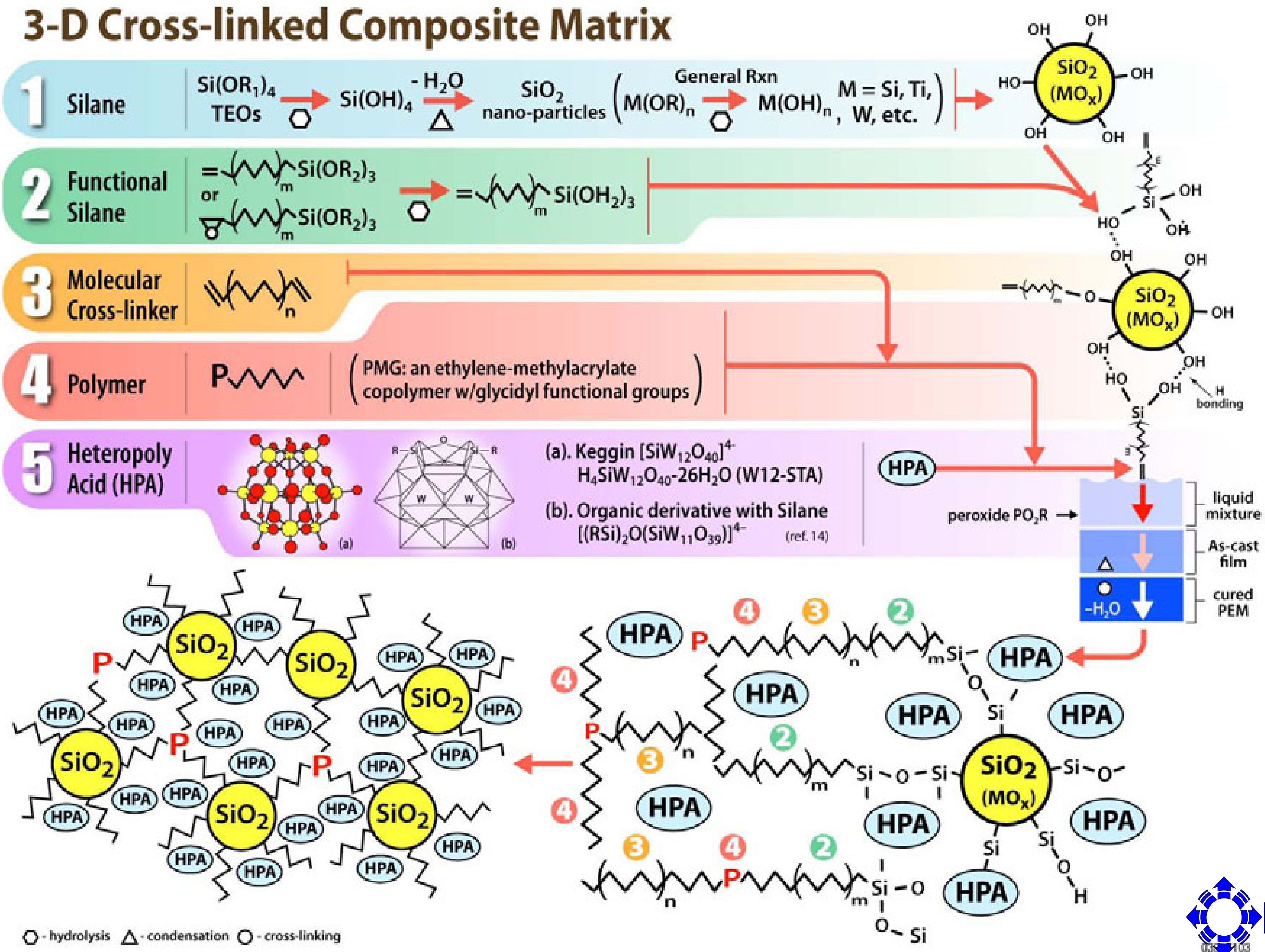


Fig. 7.8.
Proposed structures for (a) $[(RSi)_2O(SiW_{11}O_{39})]^{4-}$; (b) $\{[(OC)_3CoGeOGe(SiW_{11}O_{39})]^{5-}\}_n$

Ref. 14: “Heteropoly and Isopoly Oxometalates,” by M. T. Pope, Springer-Verlag, New York, 1983, Chap. 7, Fig. 7.8, p. 126.

Key Concept and Components in Composite Membrane Fabrication



Procedure for Fabricating 3D Cross-Linked HPA/SiO_2/Functional Silane Sol Gel Composite & PEM Membrane with PMG

TEOS + Functional Silane + pH = 1.35 H_2O + HPA

aged (gelled) solution → **Sol Gel Composite** → **Bonded STA%, IEC, & Other Analyses/Tests**

diluted with THF or EtOH → **Sol Solution**

Silanes: Methacrylate-type: Z-6030
Epoxy-type: A-186, A-187

HPAs: $H_4SiW_{12}O_{40}$ (W12-STA)
$H_8SiW_{11}O_{39}$ (W11-STA)
$K_8SiW_{10}O_{36}$ (KW10-STA)

Sol Solution + **Host Polymer Dissolved in THF or EtOH** → **Liquid Mixture** ← **Curing Agent, X-linker**

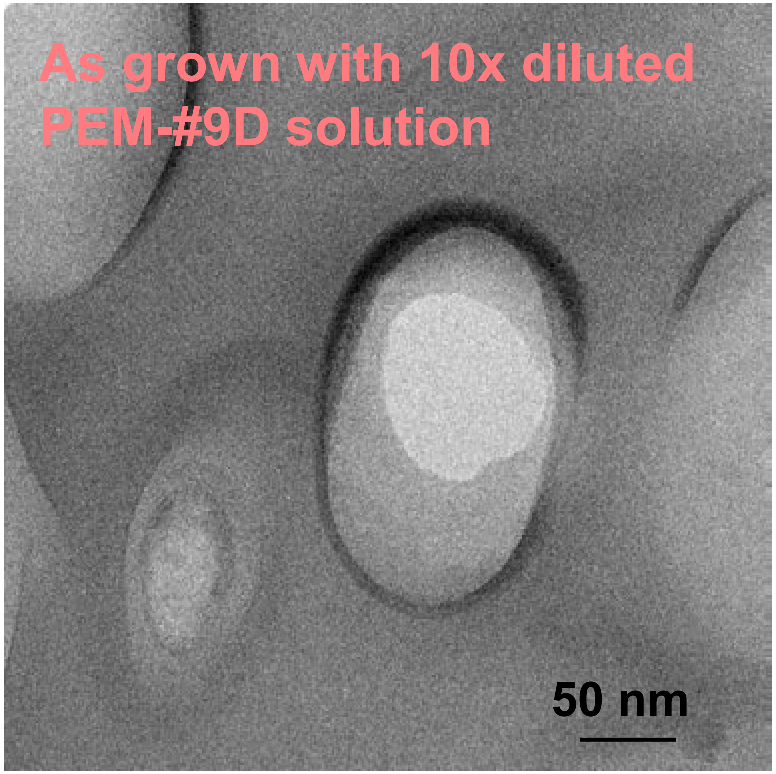
Liquid Mixture → solution cast → **As-cast Film**

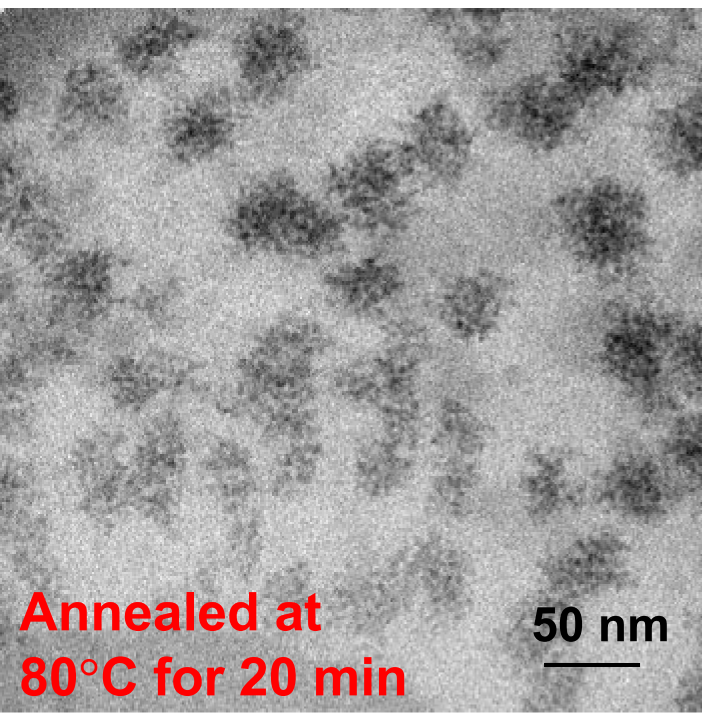
Polymer: PMG or BSPPO

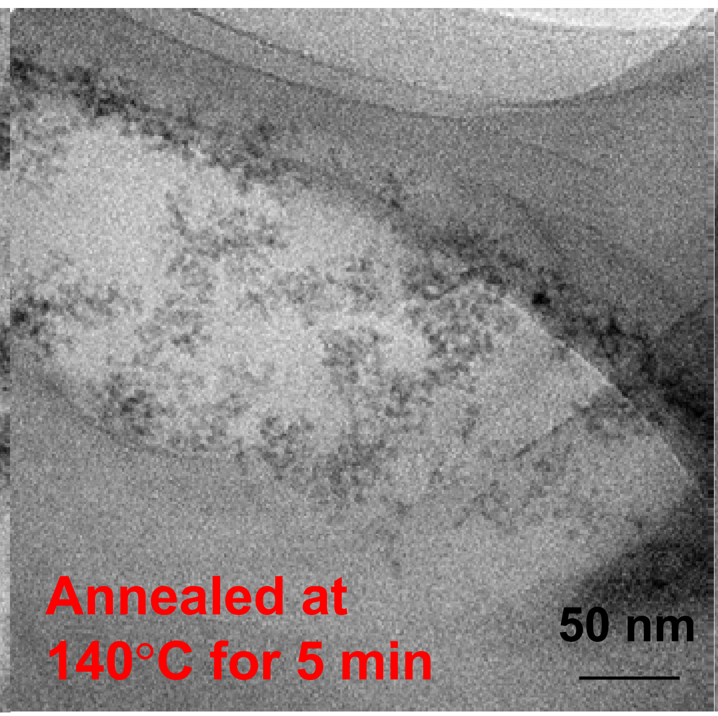
As-cast Film → thermal or UV X-linking → **Cured PEM** → **Bonded STA%, IEC, & Other Analyses/Tests**

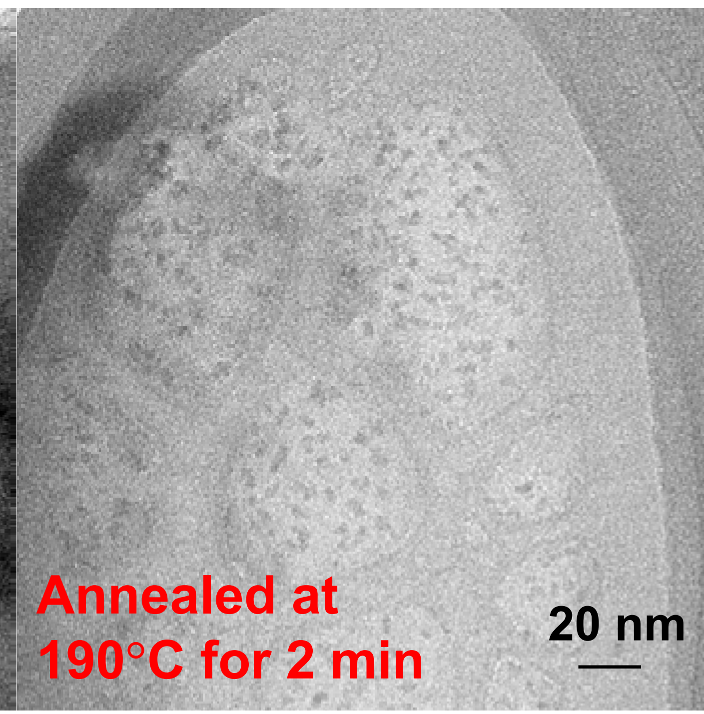
(3D Network of SiO_2/silane/HPA/PMG)

Formation of SiO_2 Nano-Particles in Composite Matrix upon Thermal Treatments (TEM Analysis)

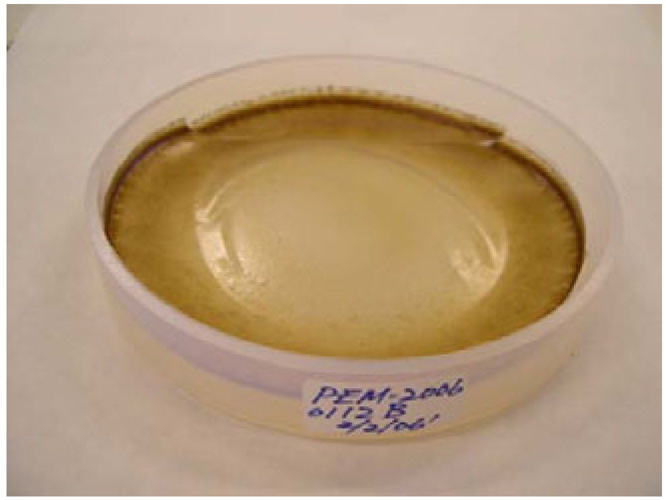


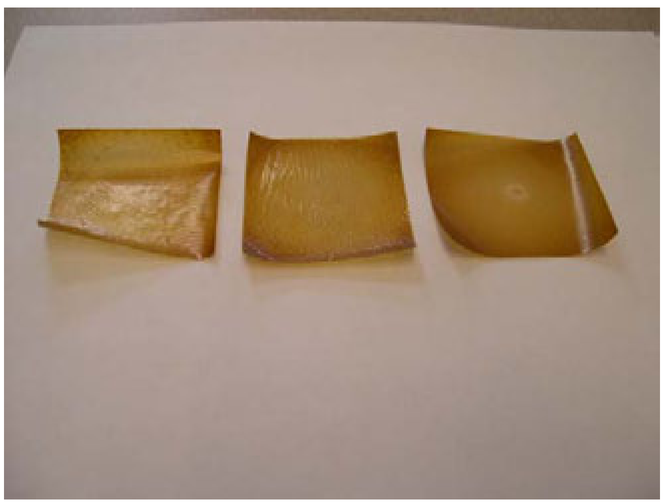


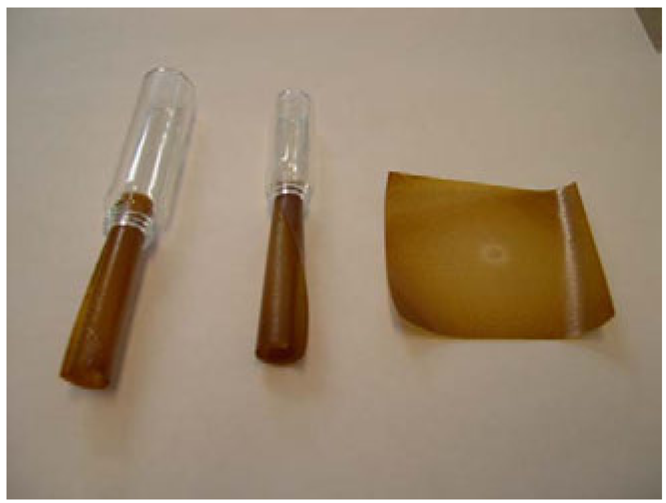


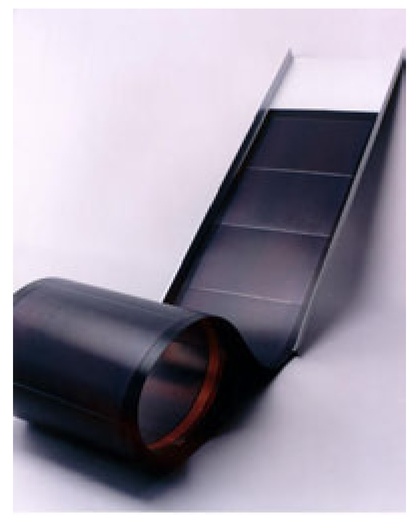


Flexibility of PEM Membranes Fabricated with High HPA Loading







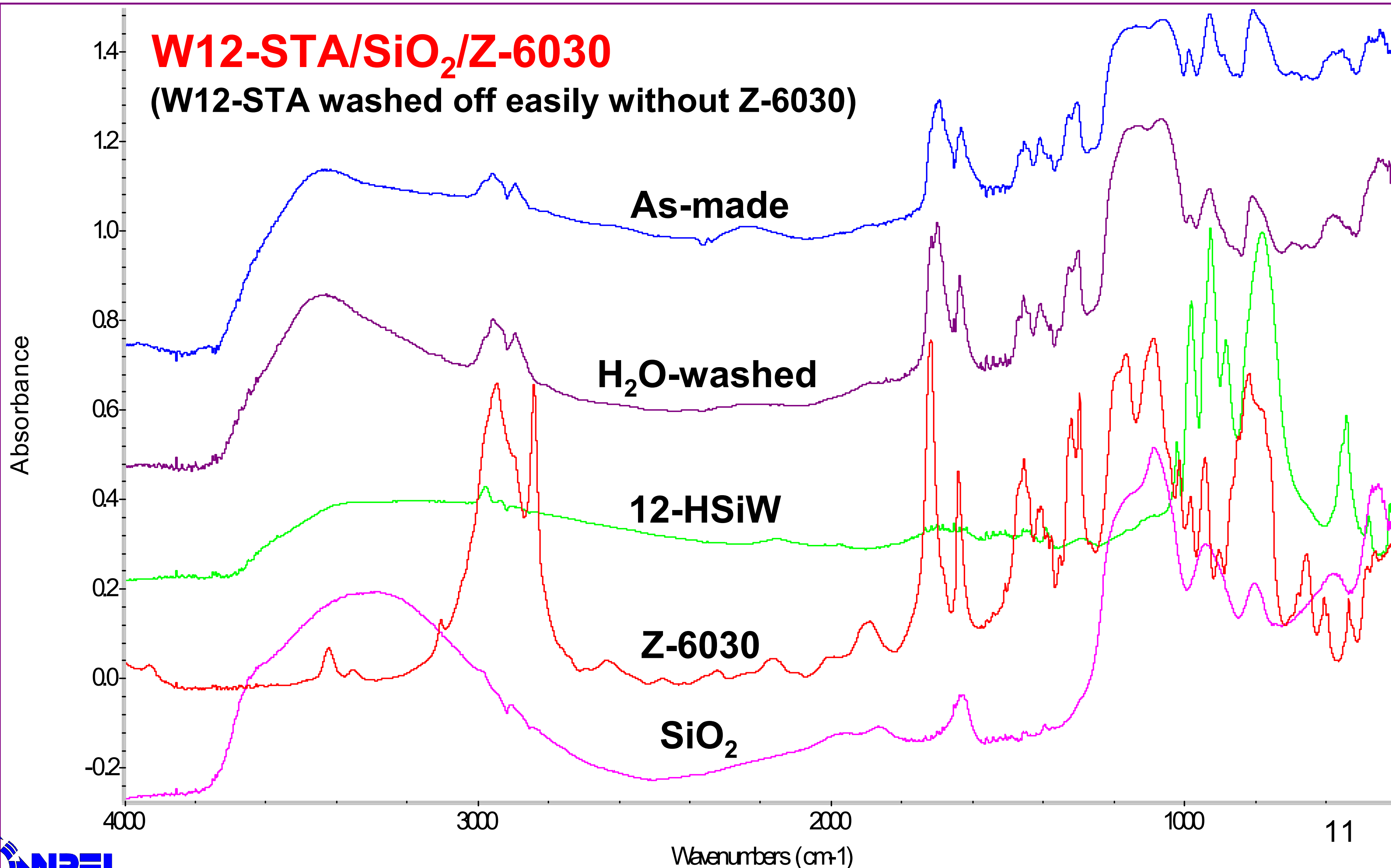


PEM-#9B,C,D Films: W12-STA/(PMG + Cross-Linker) = 174 Wt%

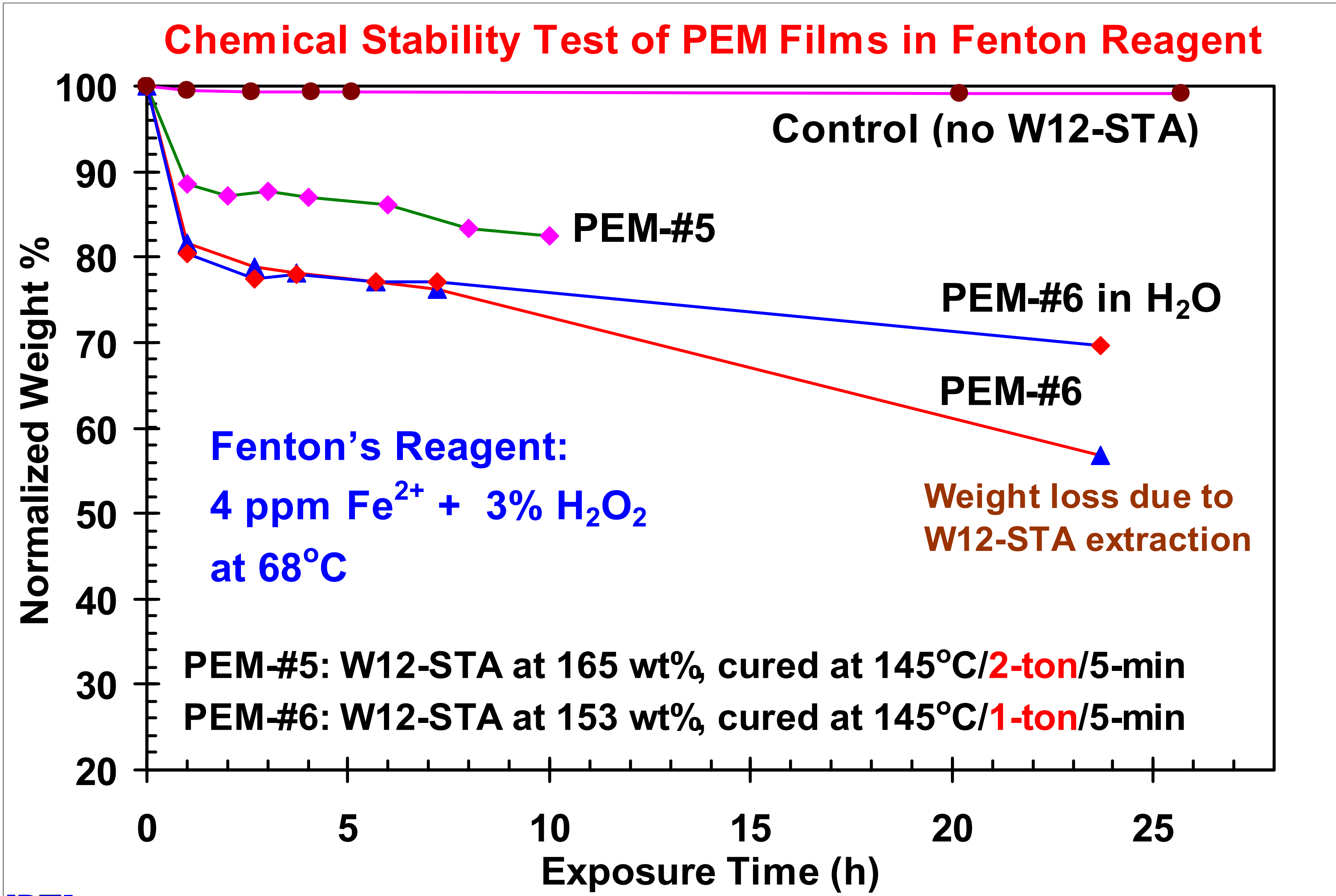
Immobilizing the HPA

Binding HPA with Z-6030 Silane in Sol Gel Composite

→ W12-STA Retained



Chemical Stability of Membrane and Composite PEM



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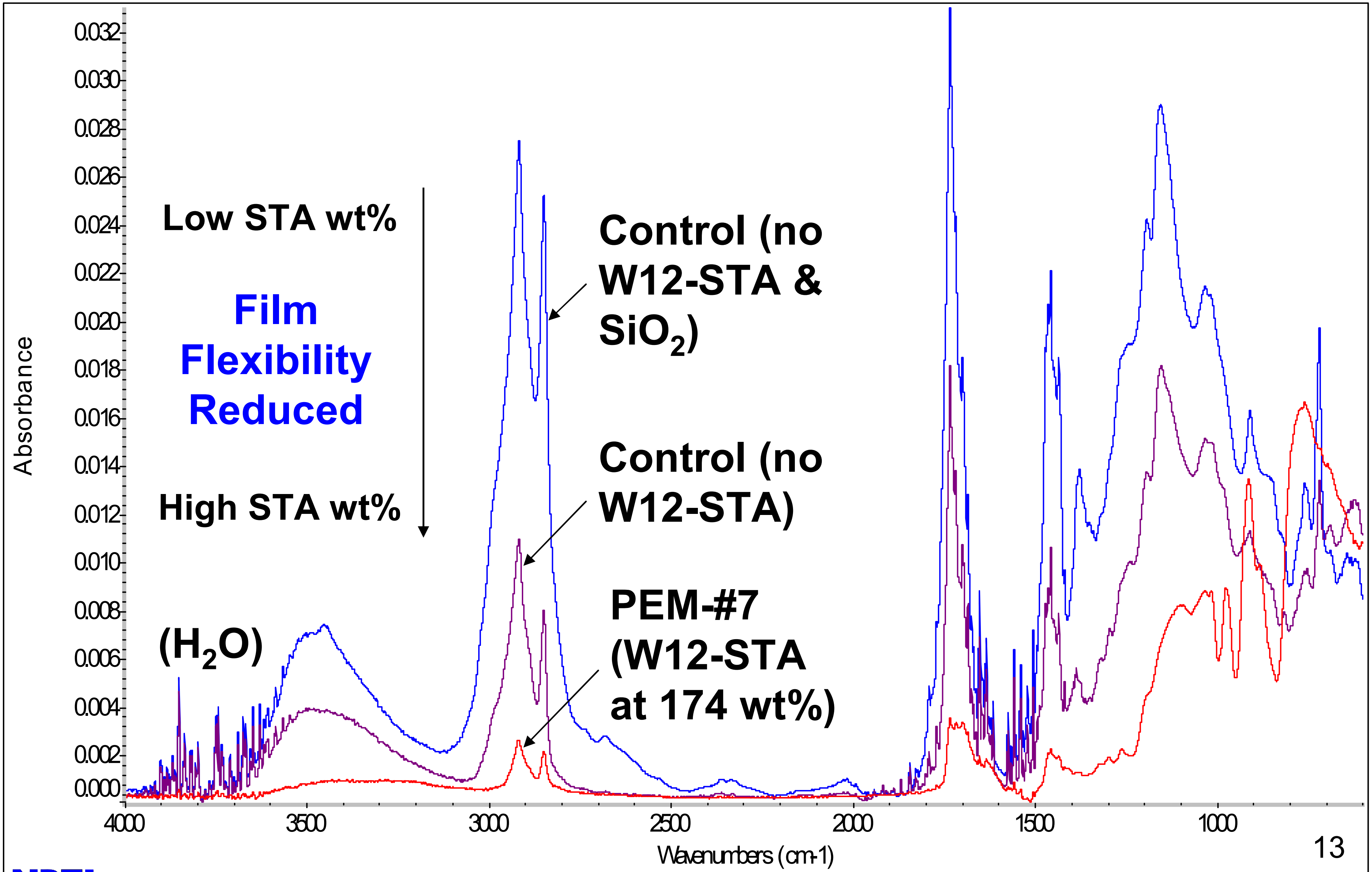
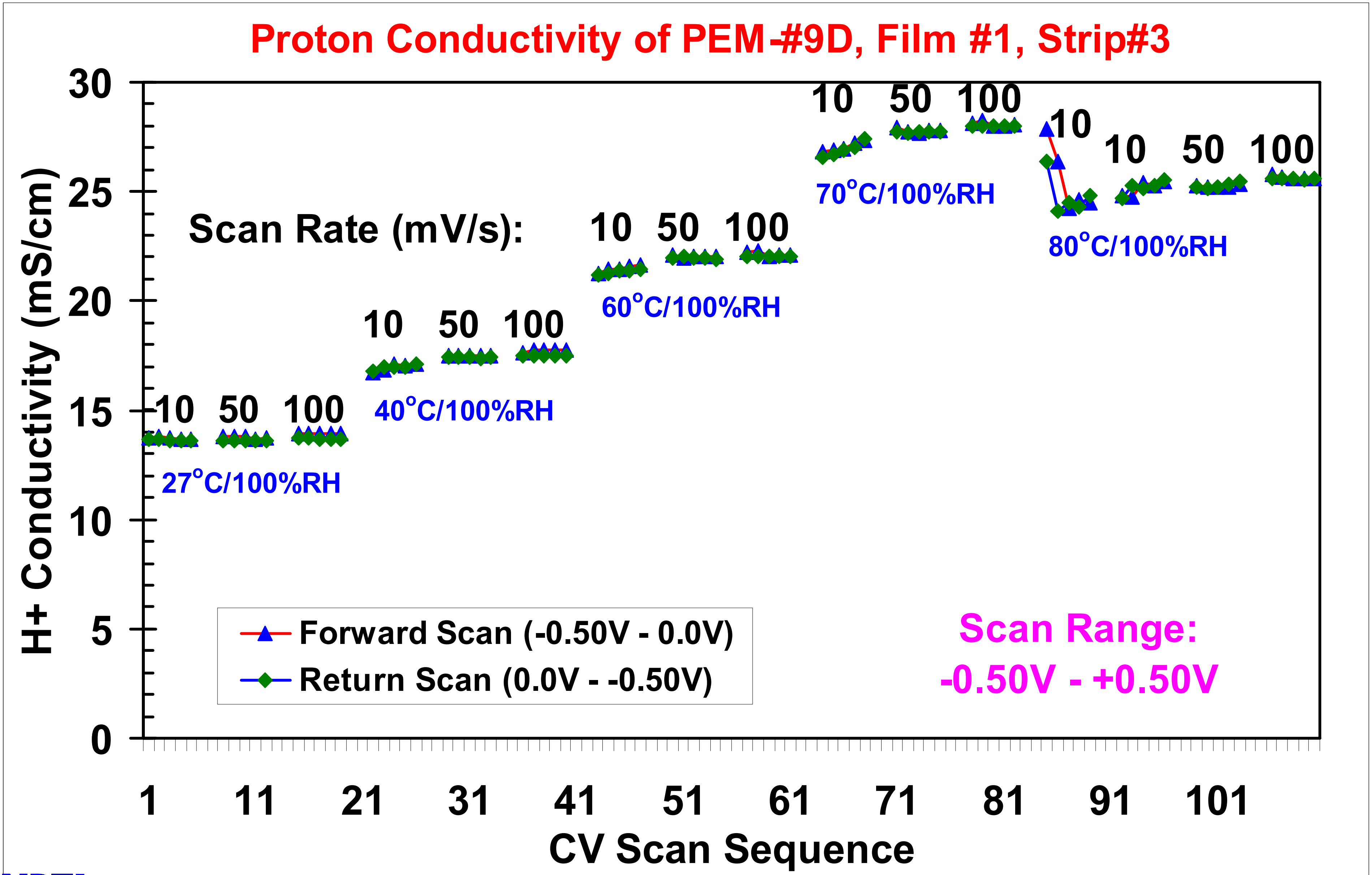
PEM Mechanical Strength and Flexibility Reduced by Increasing HPA Loading

FTIR-ATR Spectra of Cured Control Blanks and PEM-#7



H⁺ Conductivity as a Function of Cell Temperature at 100% RH



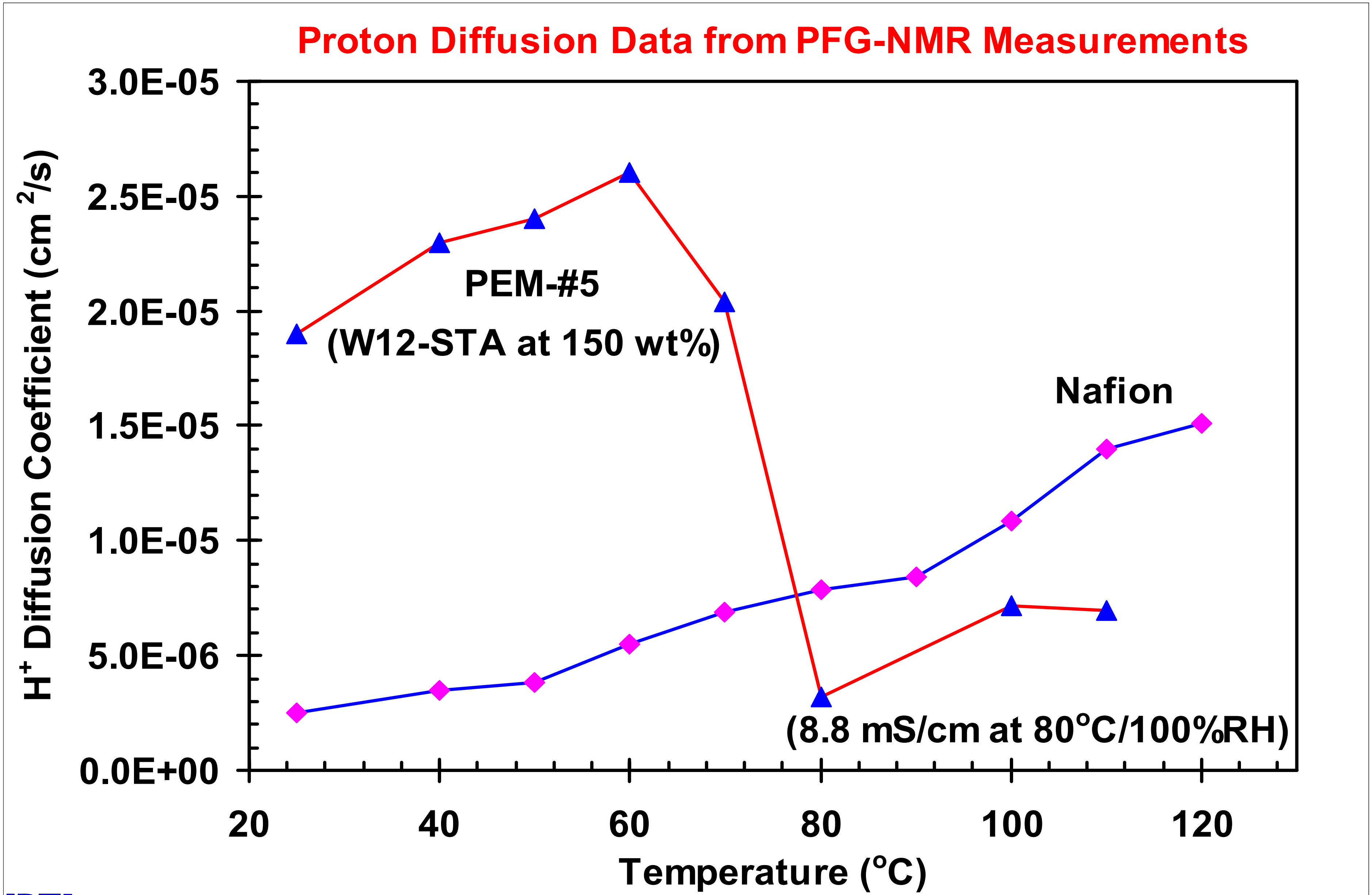
Improving H^+ Conductivity with Higher HPA Loading and Better Membrane Fabrication

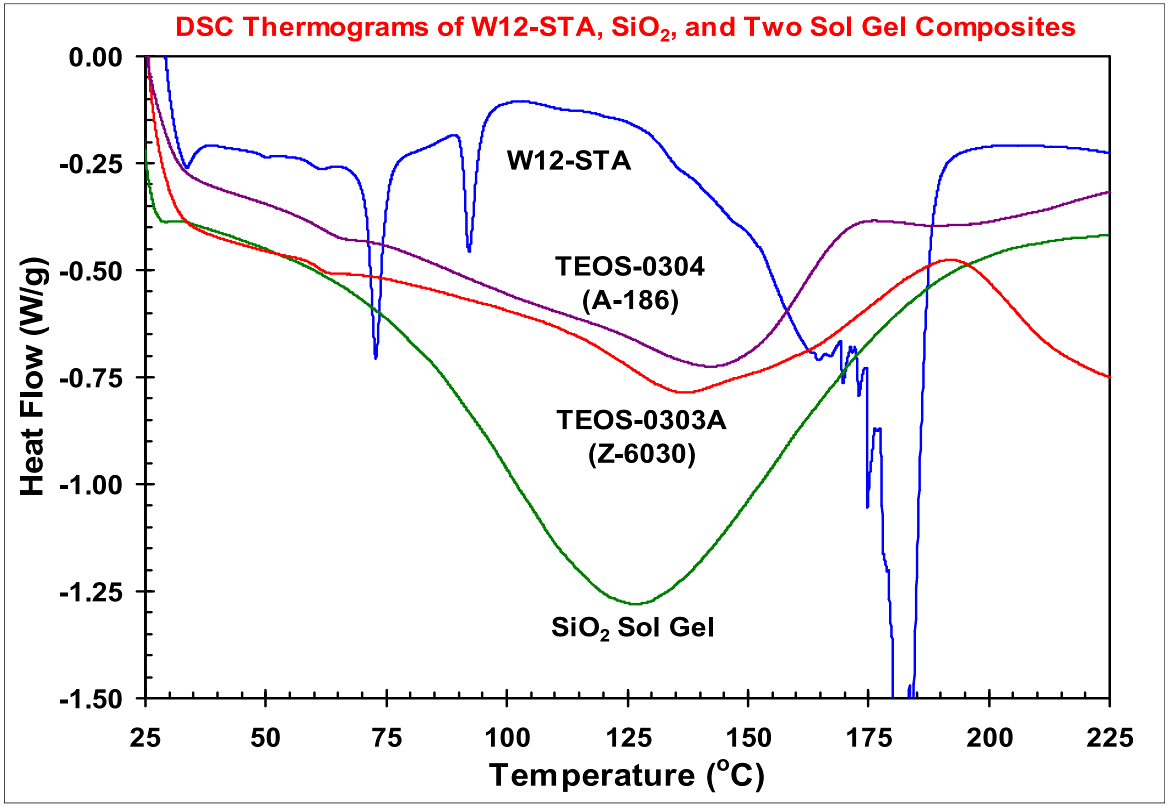
Table 1. PEM Compositions vs Proton Condutivity Derived from I-V Curves of CV Scans

PEM ID	HPA	Components: Host Polymer	Components: X-Linker	Weight Ratio: HPA/(PMG + X-Linker)	Best Proton Conductivity (mS/cm): 80°C/100%RH	Best Proton Conductivity (mS/cm): 100°C/46%RH	Best Proton Conductivity (mS/cm): 120°C/23%RH[1]
1	HSiW12Ox	BSPPO	No	0.56	0.15		
2	HSiW12Ox	PMG	Yes	0.81	6.9		
3	HSiW11Ox	PMG	Yes	1.09	6.4, 10.46	2.41	0.85
4	KSiW10Ox	PMG	Yes	1.05	7.56, 13.3	1.61	0.25
5	HSiW12Ox	PMG	Yes	1.50	8.8		
6	HSiW12Ox	PMG	Yes	1.54	15.57		
7	HSiW12Ox	PMG	Yes	1.74	14.55	2.1	
8	HSiW12Ox	PMG	Yes	1.74	19.17	3.81	
9B	HSiW12Ox	PMG	Yes	1.74	22.28		
9C	HSiW12Ox	PMG	Yes	1.74	21.15		
9D	HSiW12Ox	PMG	Yes	1.74	25.45	[28.25 at 70°C/100%RH]	
Nafion 112	SO3H				149.9	98.99	49.25

[1] Values of the proton conductivity at 120°C/23%RH are with large uncertainty because of rapidly lost linearity on I-V curves

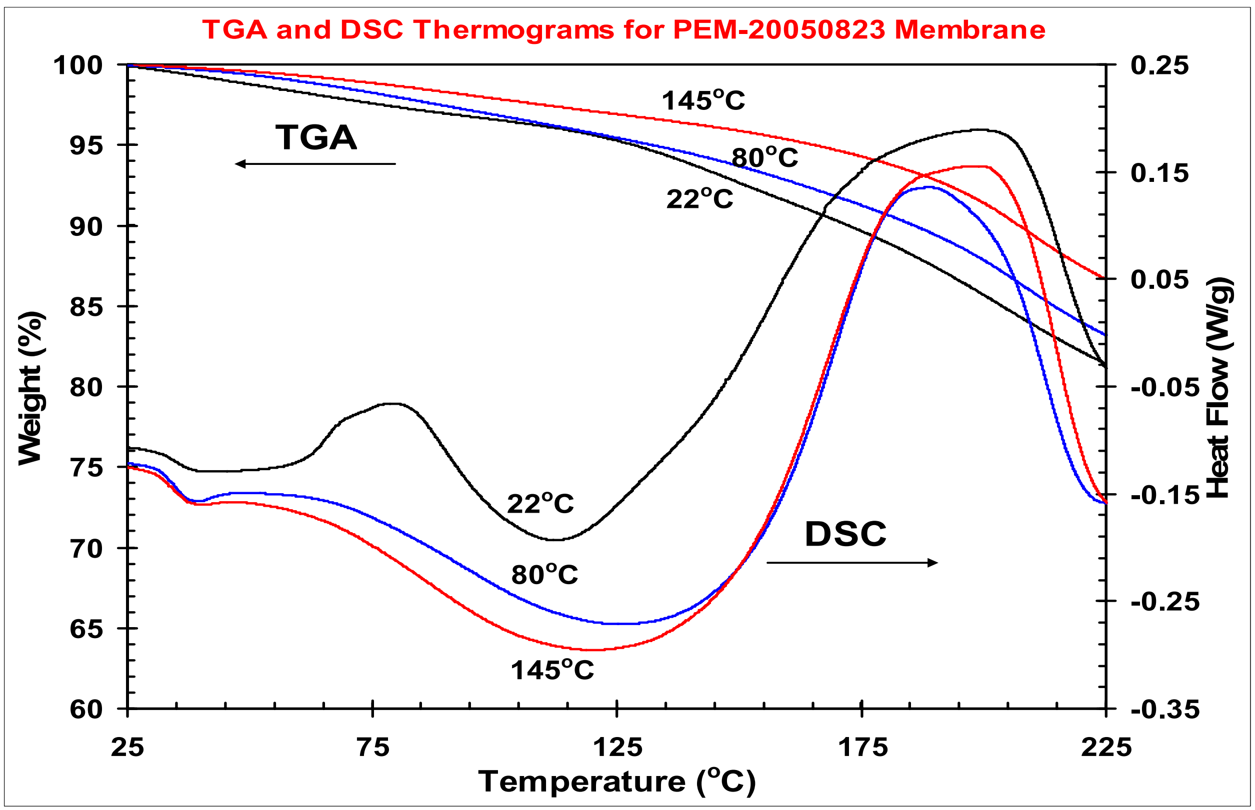
High H^+ Diffusion Coefficients for Composite Membrane





Moisture Retaining Capability of W12-STA and Sol Gel Composites (DSC Analysis)

W12-STA/SiO_2/Z-6030
W12-STA/SiO_2/A-186



TGA and DSC of as-cast, 80°C-pressed, and 145°C-cured PEM

PEM-#6: W12-STA loading level at 153 wt%/ (PMG+ X-linker)

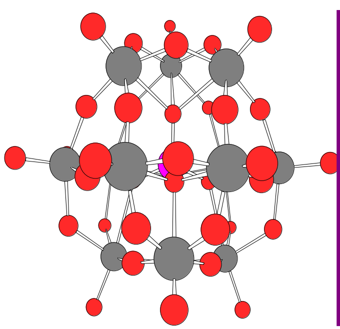
Summary of Accomplishments

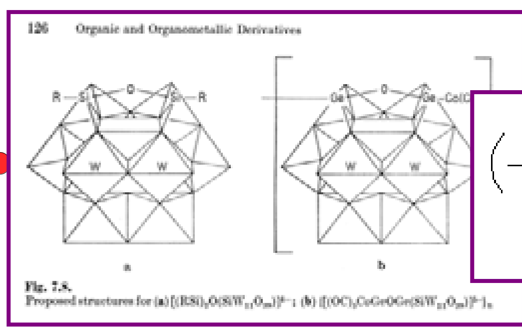
PEM Fabrication and Performance

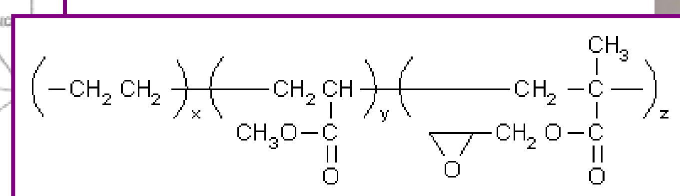
- **We have shown the ability to retain HPAs into a polymer-composite matrix of our design.**

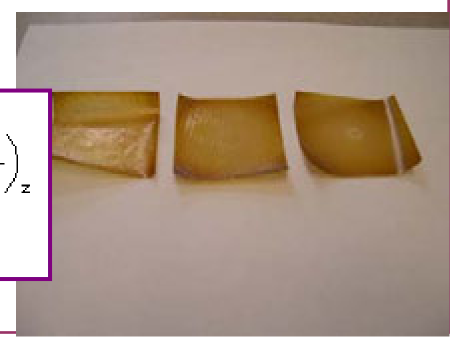
- **Properties of HPA-based composite PEMs:**
  - high chemical stability (Fenton's reagent test)
  - good thermal stability (with highly reactive W12-STA)
  - good mechanical flexibility
  - effective binding of silicotungstic acids (Wn-STA) with select functional silanes (n = 10, 11, 12)
  - high Wn-STA loading [HPA/(PMG + X-Linker) > 150 wt%]
  - moderate proton conductivity (25 mS/cm at $80^{o}C$/100%RH)

- **Clear progress towards meeting the DOE targets**









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Achieving Fundamental Goals

Future Work

- **To continue to improve/modify/optimize the current PEM composite formulation, fabrication, and processing conditions**
  - to enhance PEM's thermal stability in the 90-120^{o}C range
  - to improve mechanical strength and flexibility
  - to reduce membrane thickness and improve film uniformity

- **To continue to develop immobilization strategies for various HPAs, custom-synthesized at CSM, that show high proton diffusion coefficients and thermal stability.**

- **To understand the binding mechanism of HPA with functional silanes and SiO_2 nano-particles in the polymer matrix.**

- **To understand the proton conduction mechanism in the 3D cross-linked composite membranes in order to further improve proton conductivity at low humidity and elevated temperatures.**

2005 Reviewers' Comments

"One of the few new, alternative ideas for membranes in the whole DOE program"

- Issues:
  - …needs to present conductivity values for membranes with "fixed" HPAs…
    - Done
  - HPA approach is sound as a demonstration but water solubility must be addressed…
    - Excellent progress has been made in this regard
  - Nafion doped in HPAs has been shown to be feasible…the PI is in need of new insight.
    - Not part of our project, those figures were for introduction to HPAs only
    - Our project is focused on developing a composite hydrocarbon membrane using HPAs as the proton conducting moiety that will meet the DOE targets for operation at low RH and higher temperatures
- Future:
  - Need durability studies in actual operating fuel cell conditions and …thermal and RH cycling…gas crossover measurements
    - PEMs of 3D cross-linked PMG matrix were not available yet at the time
    - These subjects will be investigated for HPA-based PEMs this summer

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Presentations and Publications

- F. J. Pern, J. A. Turner, Fanqin Meng, and A. M. Herring; "Sol-Gel SiO_2-Polymer Hybrid Heteropoly Acid-Based Proton Exchange Membranes," MRS 2005 Fall Meeting, Energy and The Environment Symposium, Session A: The Hydrogen Cycle—Generation, Storage, and Fuel Cells. In press.
- F. J. Pern, J. A. Turner, and A. M. Herring; "Hybrid Proton Exchange Membranes Based on Heteropoly-Acid and Sulfonic-Acid Proton Conductors," ECS 2006, Abstract (accepted for oral presentation)
- J. L. Horan , J. Turner , A. M. Herring, and S. Dec; "Structure and Dynamics of Non-Commercial Heteropoly Acids for Fuel Cell Applications," ECS 2006, Abstract
- N. V. Aieta, M. Kuo, F. Meng, J. Turner, and A. M. Herring; "The Use of Heteropolyacids as Additives for Low Humidity Operation of Nafion Membranes for PEM Fuel Cell Applications," ECS 2006, Abstract
- A. M. Herring, R. J. Stanis, J. Ferrell III, M. Kuo, J. Turner, and M. Samaroo; "The Use of Heteropoly Acids as Electrocatalysts for the Oxygen Reduction Reaction in PEM Fuel Cells," ECS 2006, Abstract
- R. J. Stanis, A. M. Herring, M. Kuo, and J. Turner; "Increased CO Tolerance of Pt Electrodes by Addition of Adsorbed Heteropoly Acids and Salts in PEM Fuel Cell Anode Catalysts," ECS 2006, Abstract