

Advanced Fuel Cell Membranes Based on Heteropolyacids

John A. Turner and F. J. John Pern

Hydrogen and Electricity, Systems and Infrastructure Group
National Renewable Energy Laboratory
Golden, CO 80401-3393

Andrew M. Herring* and Steven F. Dec**

* Department of Chemical Engineering and

** Department of Chemistry and Geochemistry
Colorado School of Mines
Golden, CO 80401-1887

May 18, 2006

Project ID #
FC4

This presentation does not contain any proprietary or confidential information

Disclaimer and Government License

This work has been authored by Midwest Research Institute (MRI) under Contract No. DE-AC36-99GO10337 with the U.S. Department of Energy (the "DOE"). The United States Government (the "Government") retains and the publisher, by accepting the work for publication, acknowledges that the Government retains a non-exclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this work, or allow others to do so, for Government purposes.

Neither MRI, the DOE, the Government, nor any other agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe any privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not constitute or imply its endorsement, recommendation, or favoring by the Government or any agency thereof. The views and opinions of the authors and/or presenters expressed herein do not necessarily state or reflect those of MRI, the DOE, the Government, or any agency thereof.

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/m²

Barriers

- Barriers addressed
 - O. Stack materials and manufacturing costs
 - P. Durability

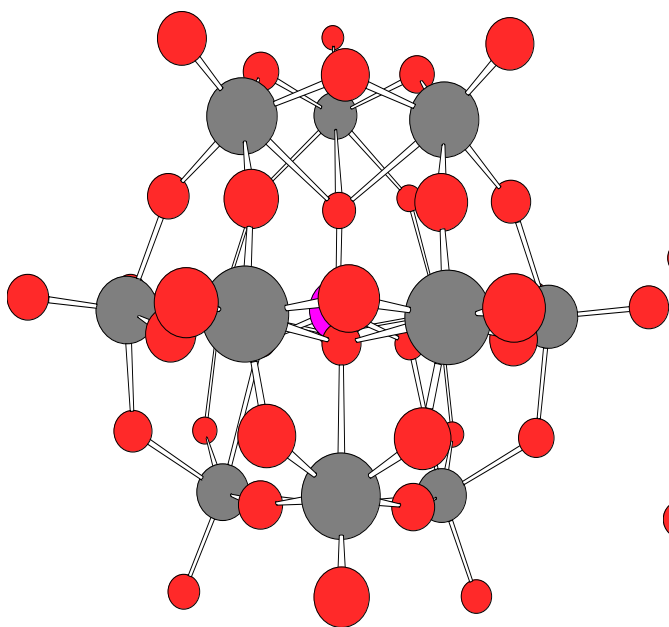
Partner/Subcontract

- Colorado School of Mines
 - Prof. Andrew M. Herring
 - Dr. Steven F. Dec

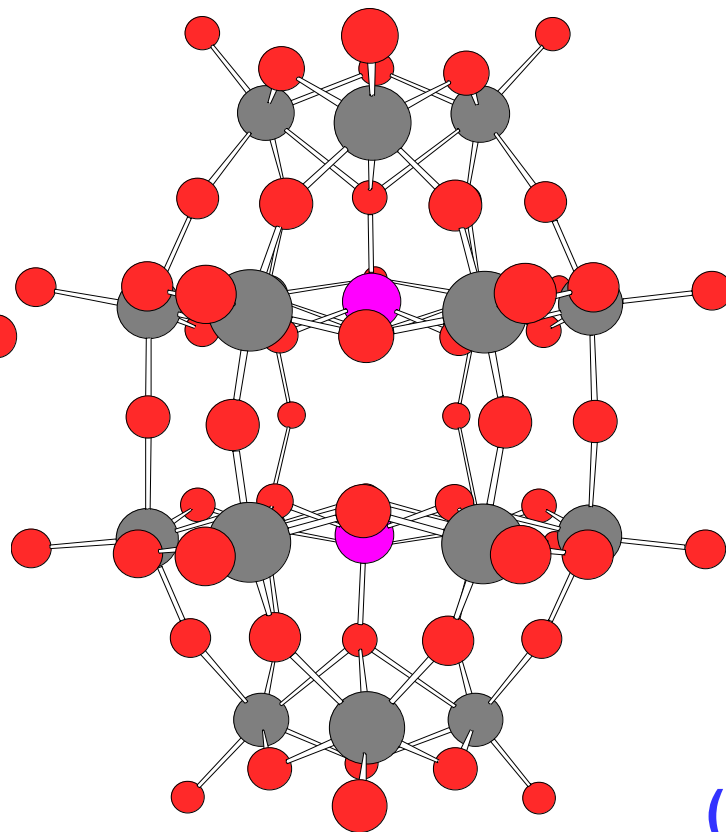
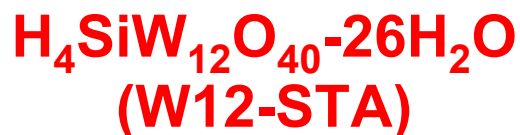
Objectives

- **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 120°C 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.**

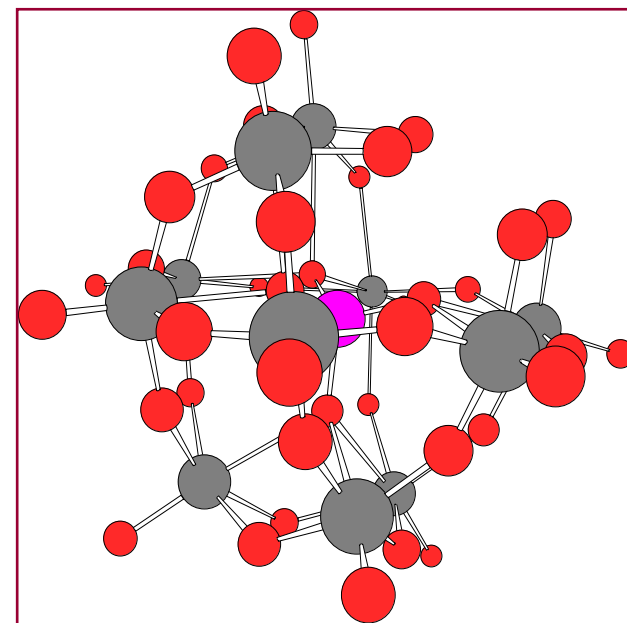
HPAs: High H⁺ Conductivity, High Thermal Stability; Vast Structural Diversity; Known Redox Catalysts



Keggin

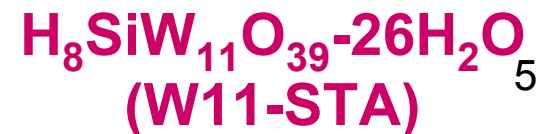


Dawson



Lacunary

(allows easy attachment points)



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:

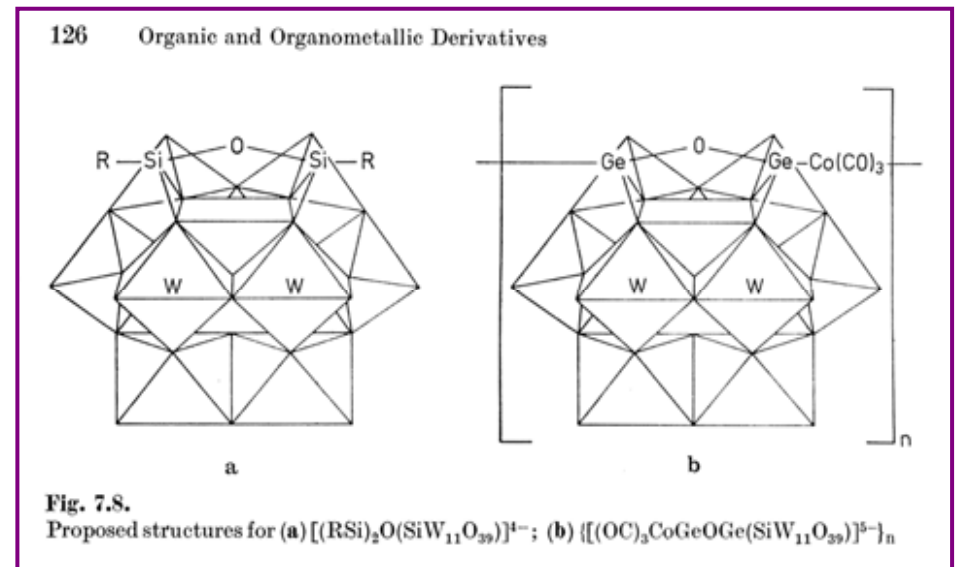
1. By bonding with functional silanes that can then be cross-linked or polymerized

C. Fabrication Approaches:

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

D. Polymeric Matrix:

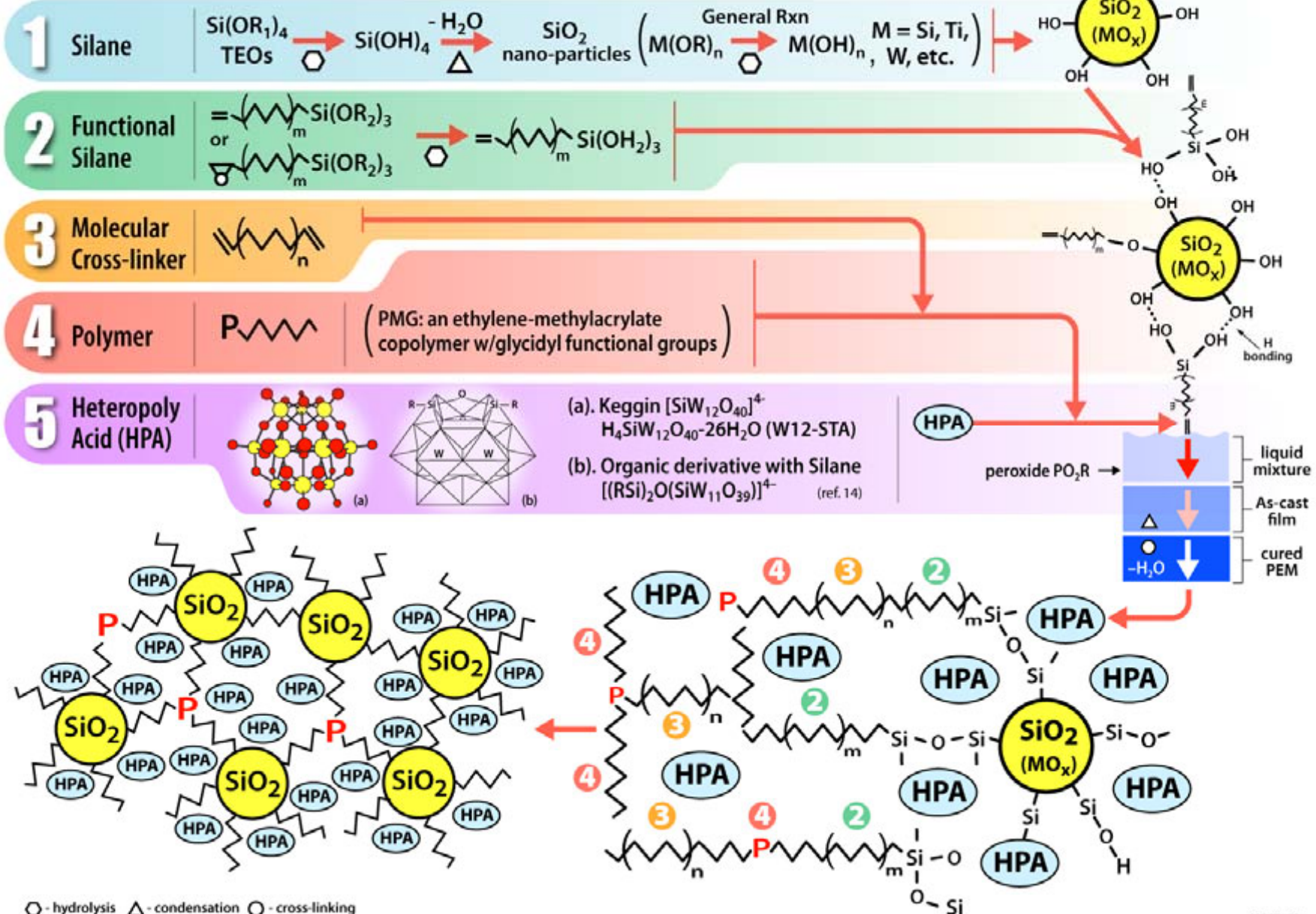
1. Organic
2. Inorganic
3. Organic-inorganic hybrid



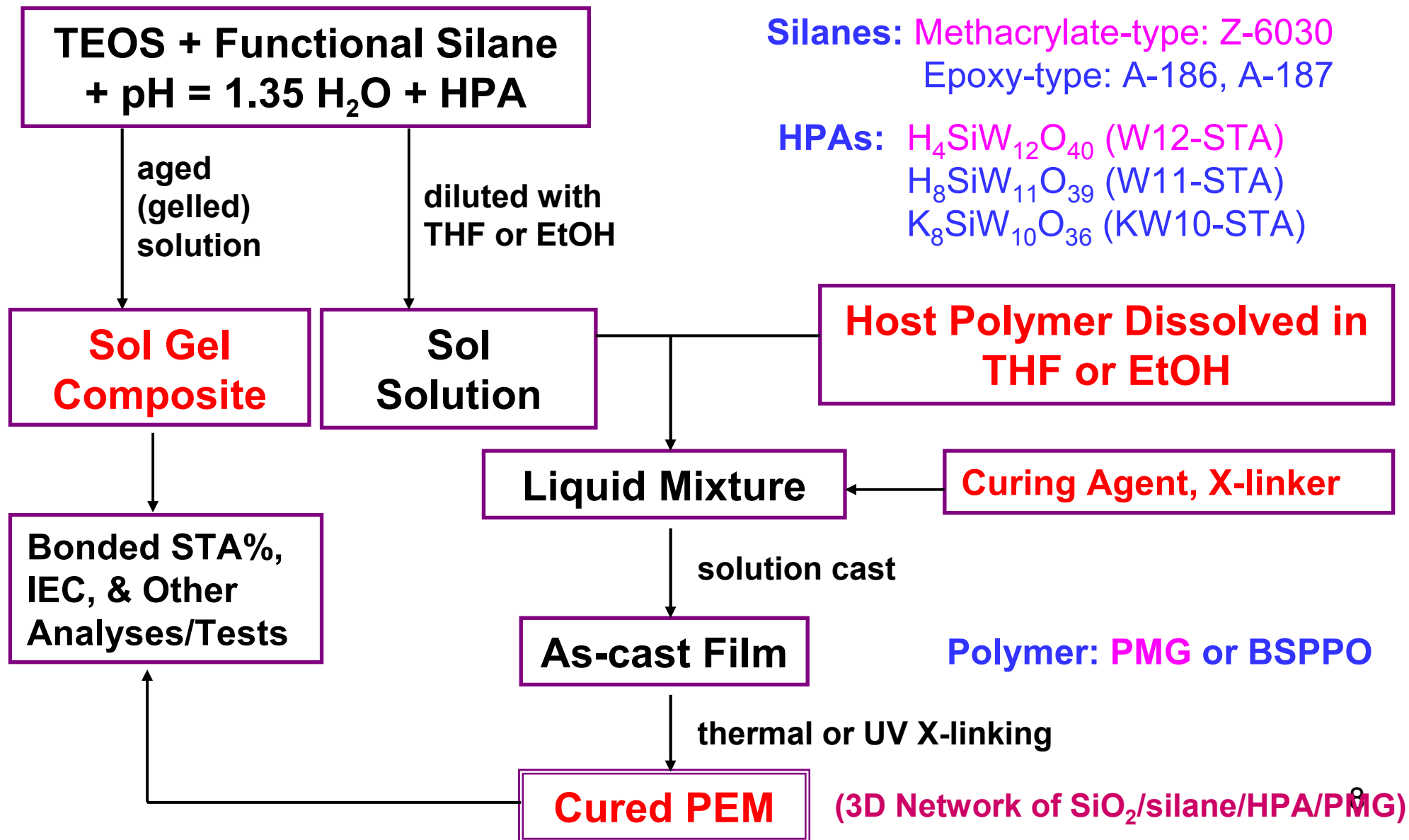
Ref. 14: "Heteropoly and Isopoly Oxometalates,"
by M. T. Pope, Springer-Verlag, New York, 1983,
Chap. 7, Fig. 7.8, p. 126.

Key Concept and Components in Composite Membrane Fabrication

3-D Cross-linked Composite Matrix

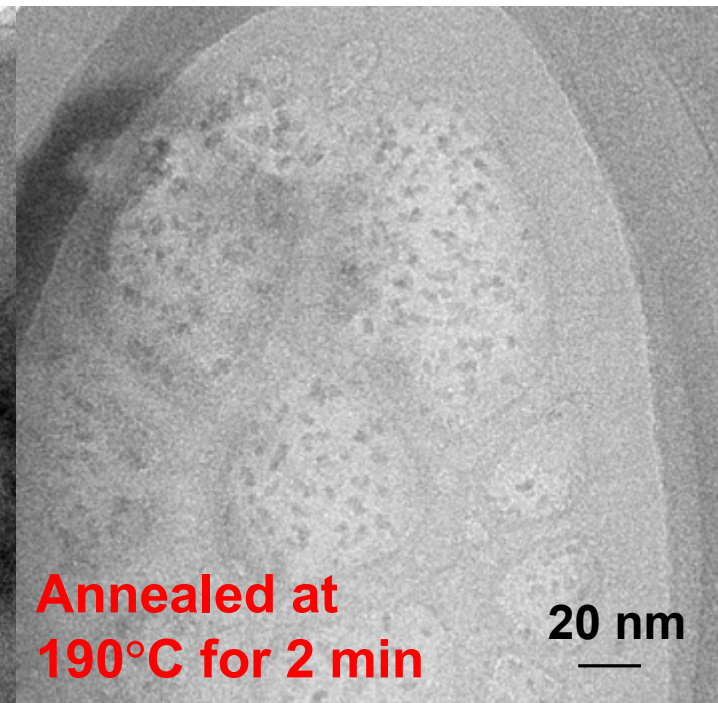
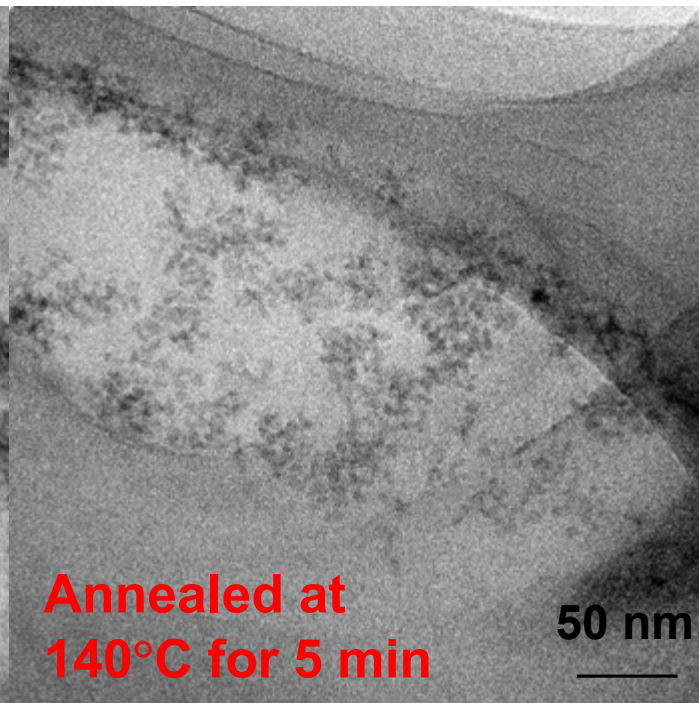
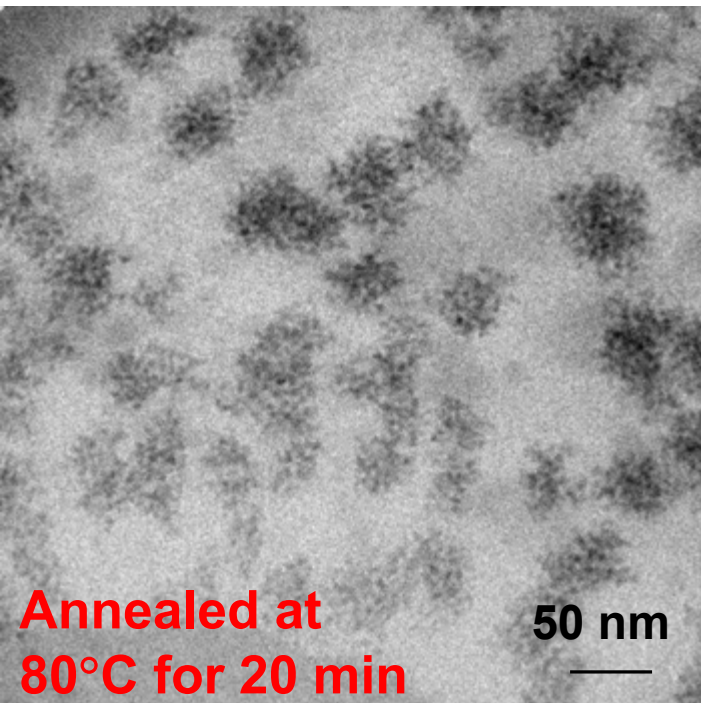
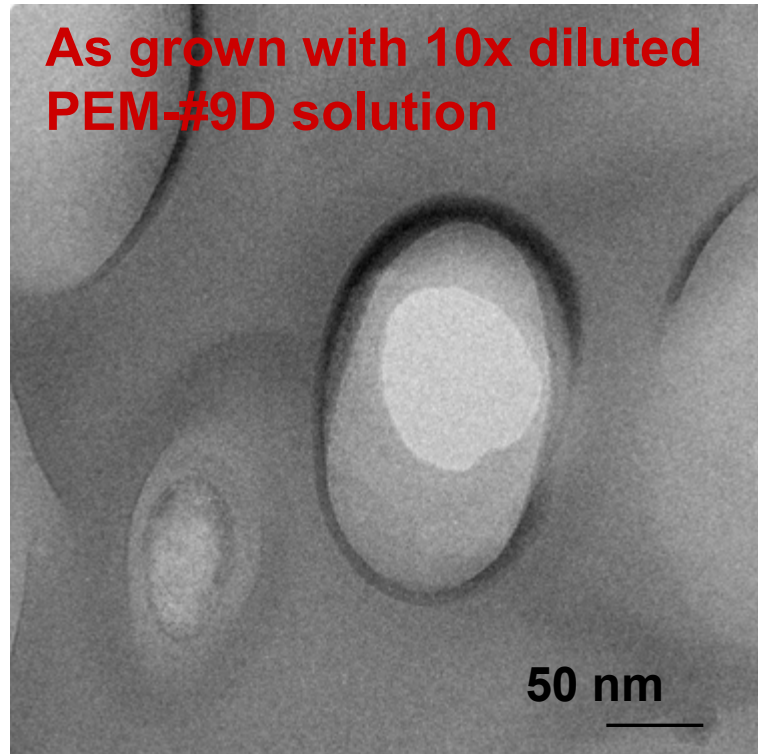


Procedure for Fabricating 3D Cross-Linked HPA/SiO₂/Functional Silane Sol Gel Composite & PEM Membrane with PMG

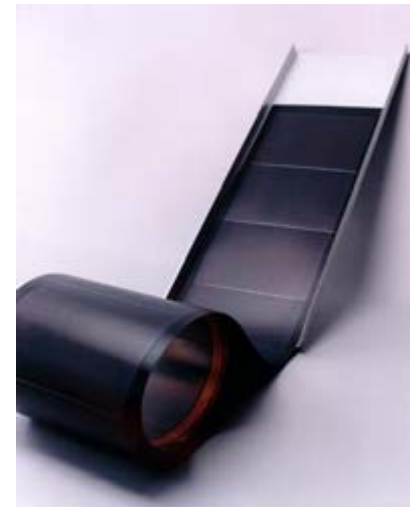
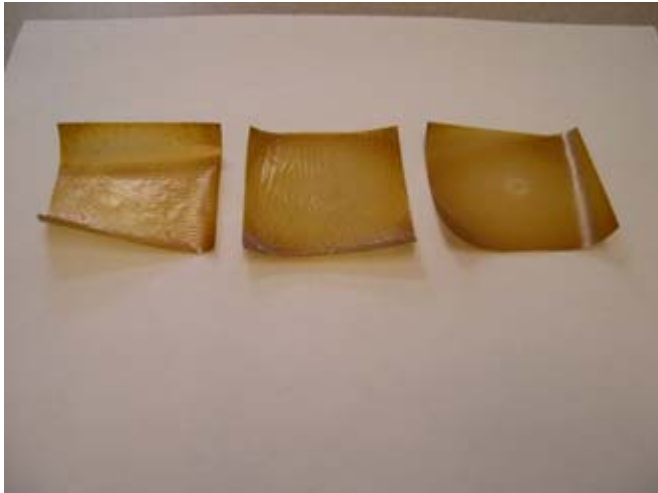
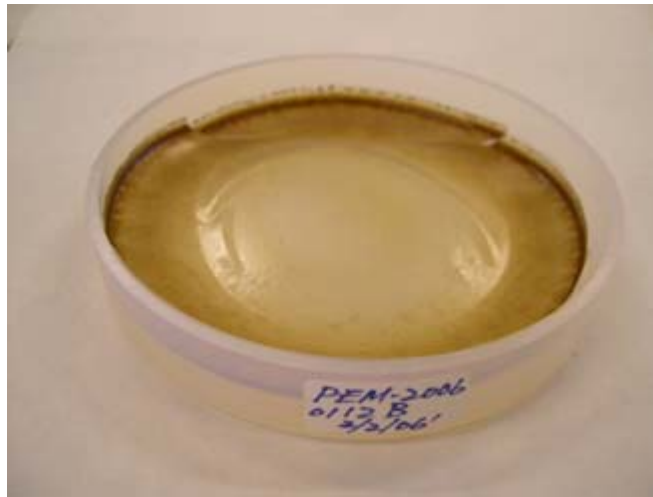


Formation of SiO₂ Nano-Particles in Composite Matrix upon Thermal Treatments (TEM Analysis)

As grown with 10x diluted PEM-#9D solution



Flexibility of PEM Membranes Fabricated with High HPA Loading

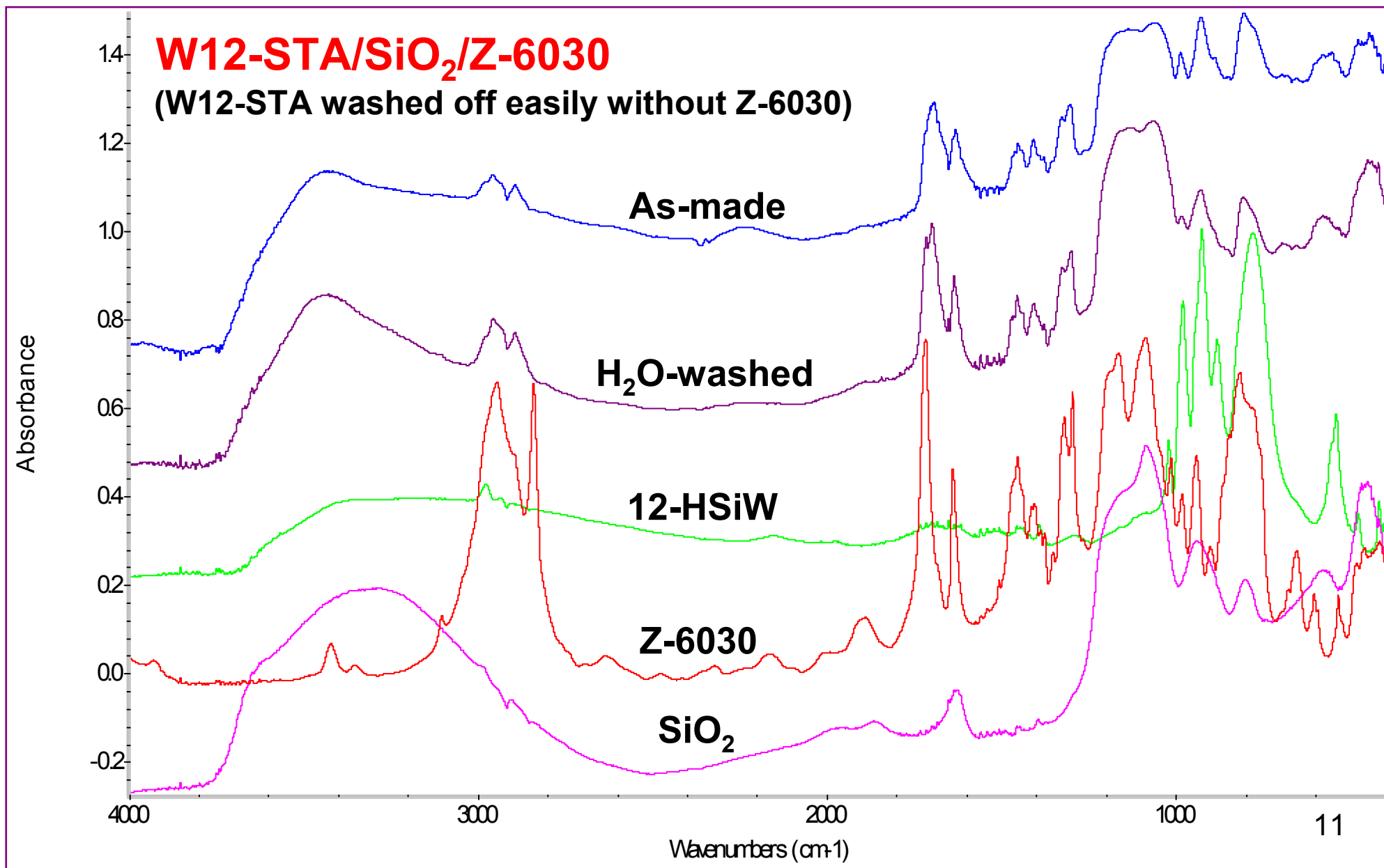


PEM-#9B,C,D Films: W12-STA/(PMG + Cross-Linker) = 174 Wt%

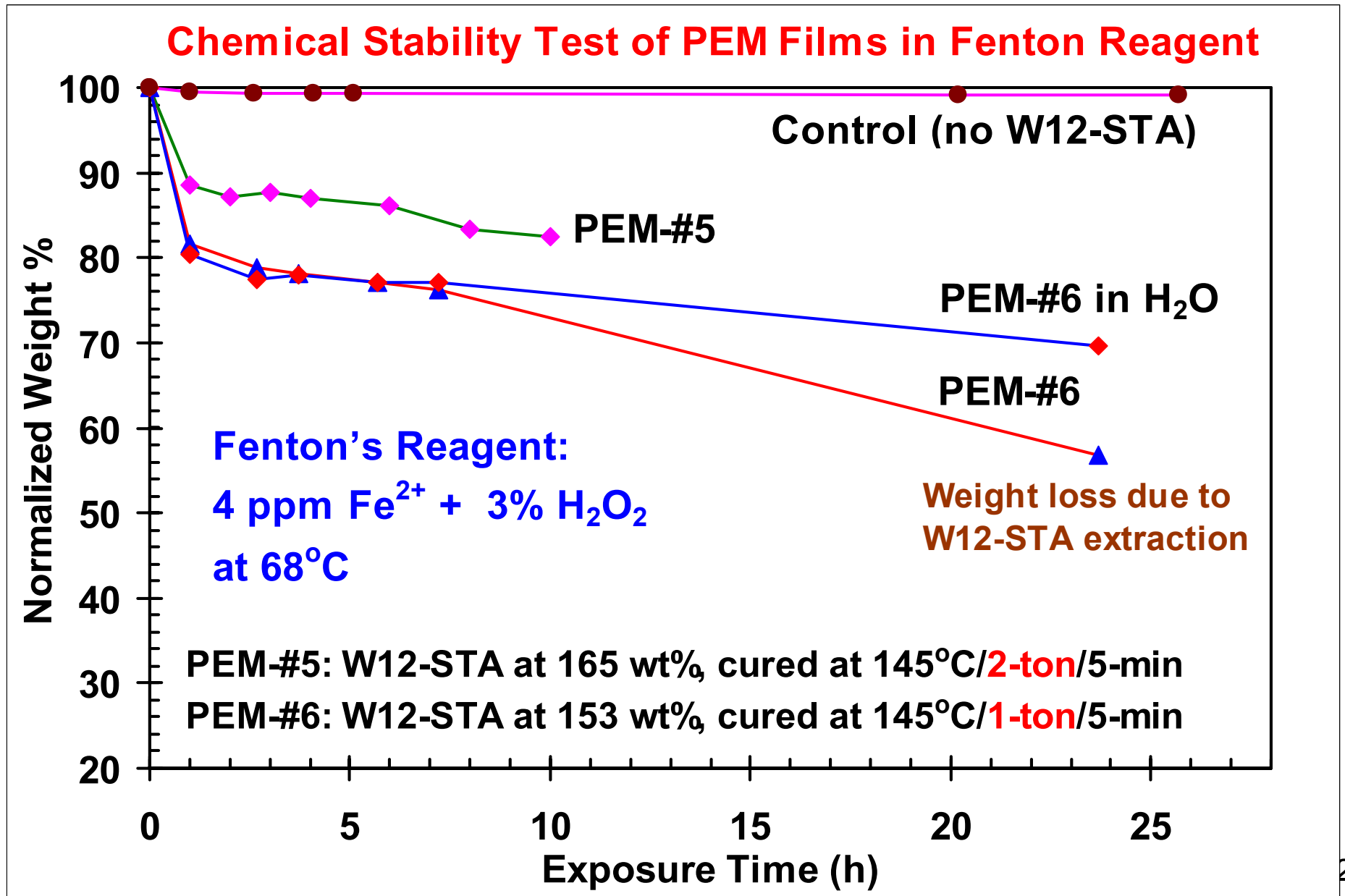
Immobilizing the HPA

Binding HPA with Z-6030 Silane in Sol Gel Composite

→ W12-STA Retained

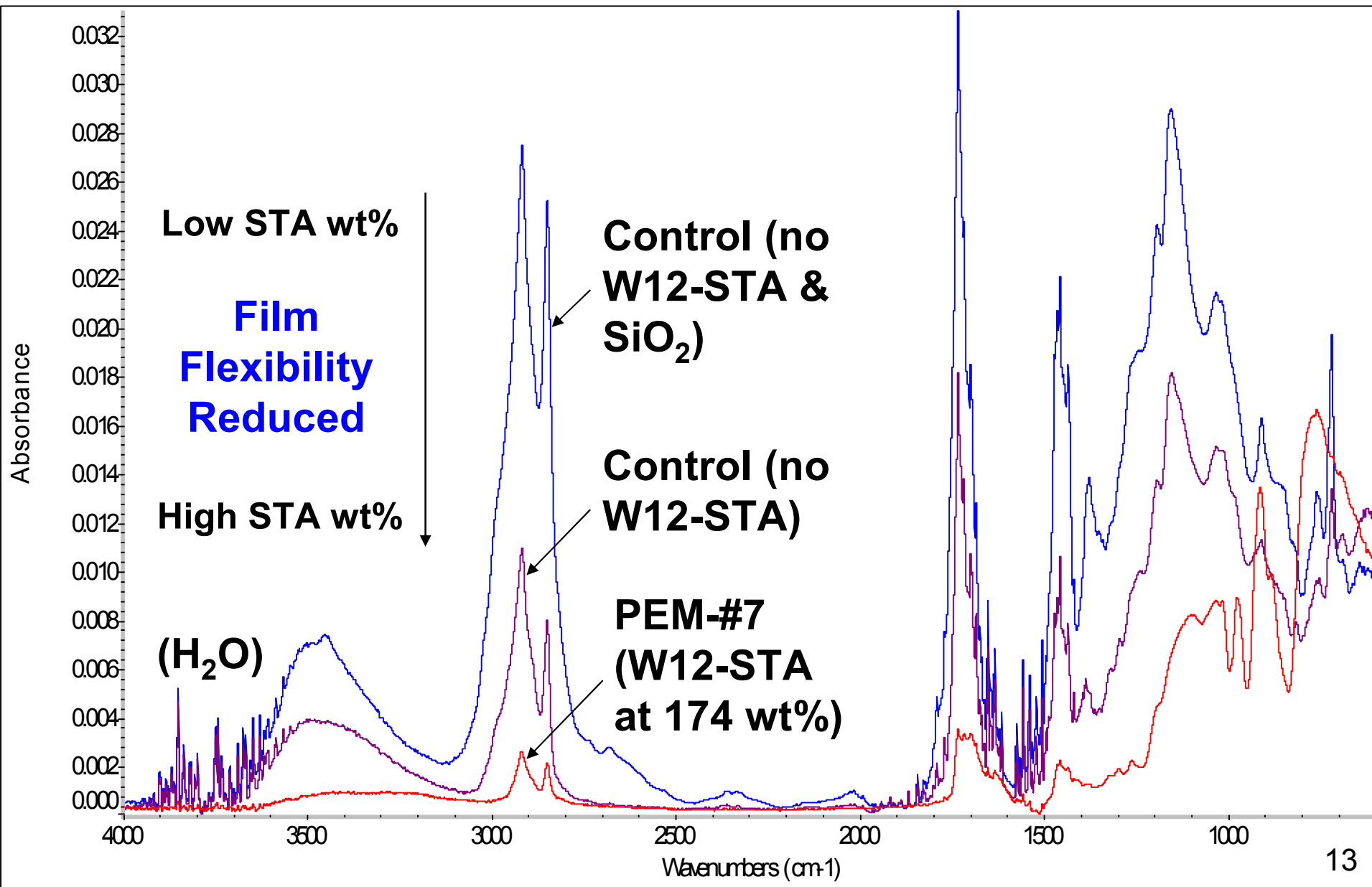


Chemical Stability of Membrane and Composite PEM



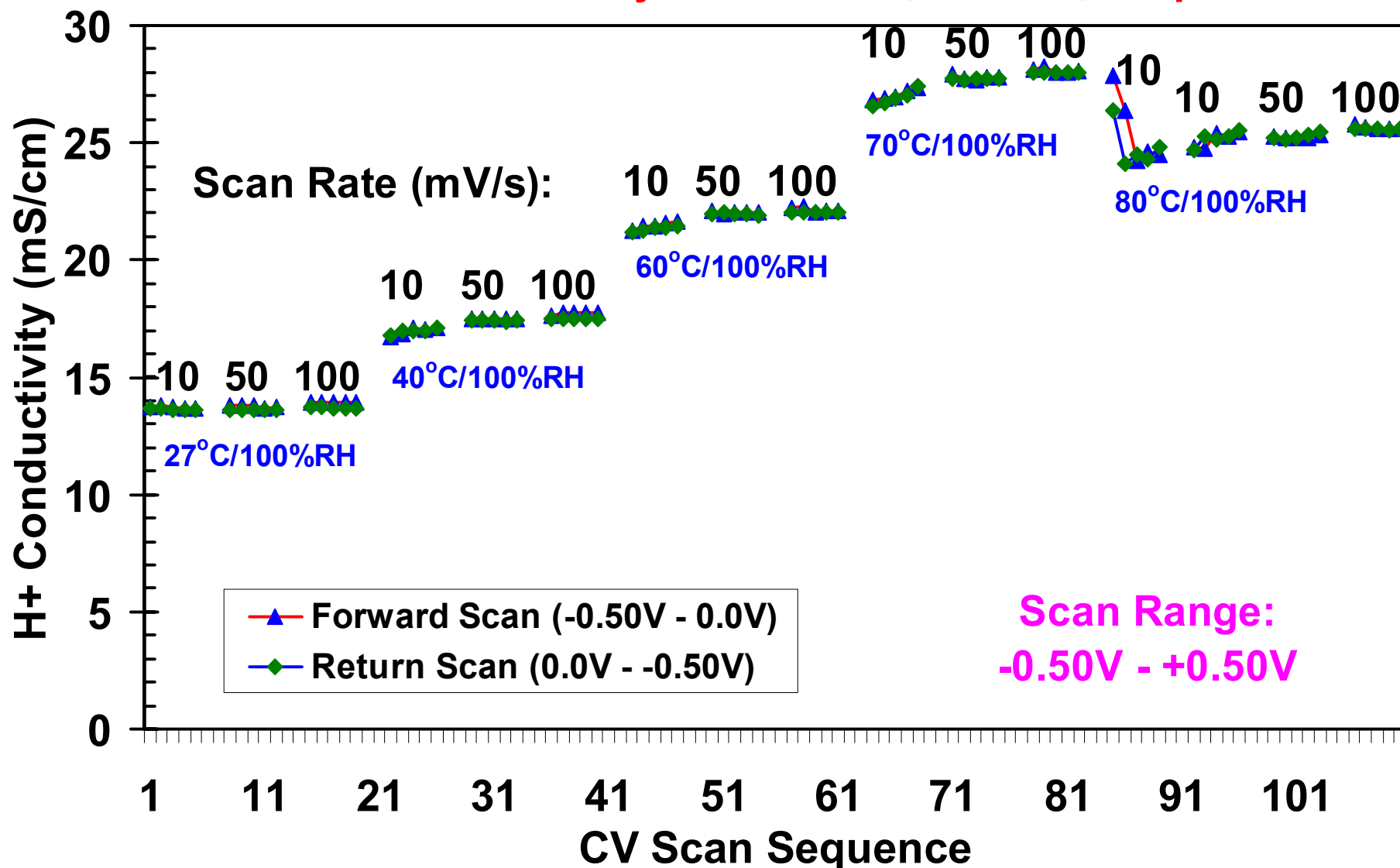
PEM Mechanical Strength and Flexibility Reduced by Increasing HPA Loading

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



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

Proton Conductivity of PEM-#9D, Film #1, Strip#3



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

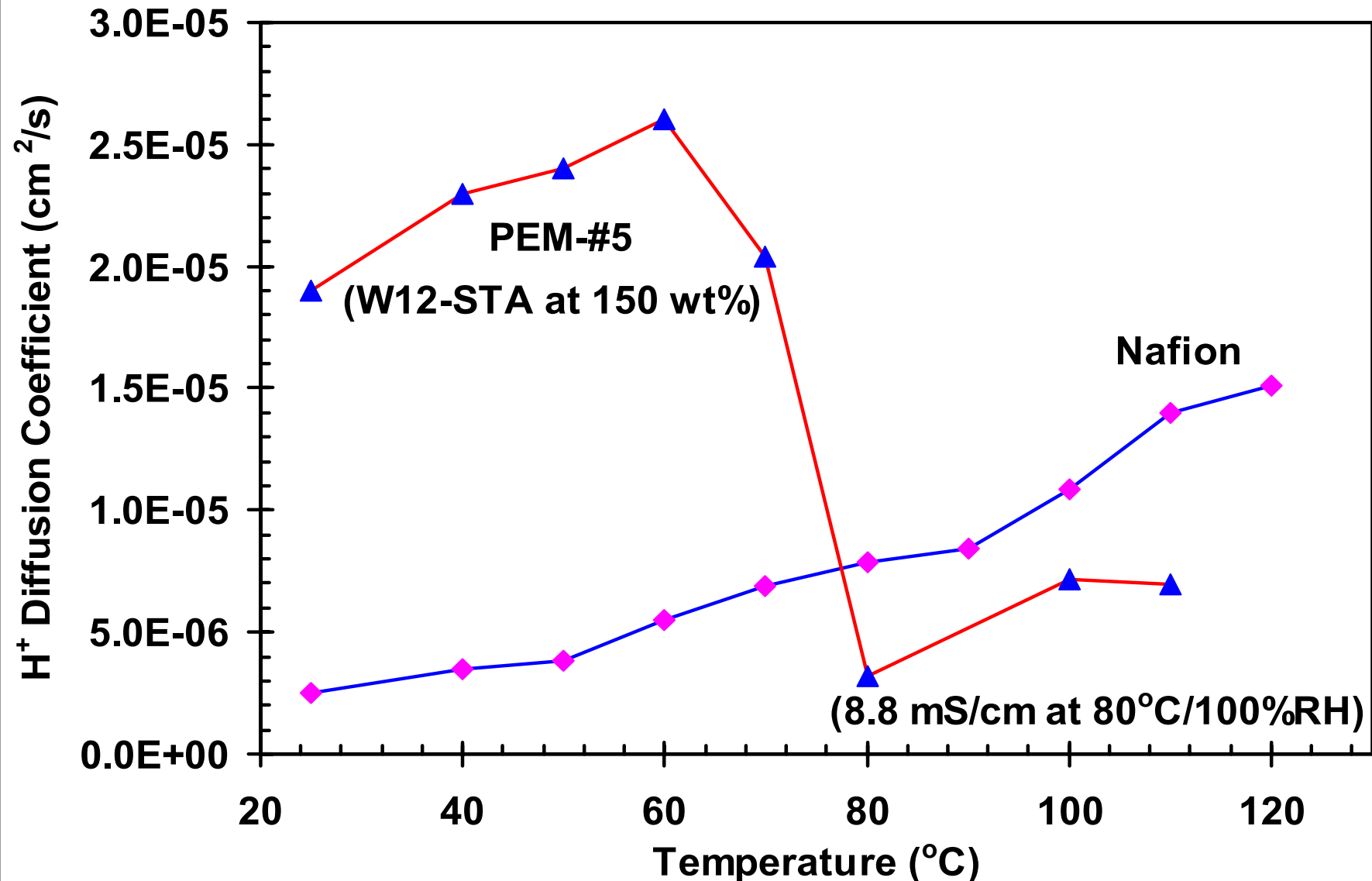
Table 1. PEM Compositions vs Proton Conductivity Derived from I-V Curves of CV Scans

PEM ID	HPA	Components		Weight Ratio HPA/(PMG + X-Linker)	Best Proton Conductivity (mS/cm)		
		Host Polymer	X-Linker		80°C/100%RH	100°C/46%RH	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

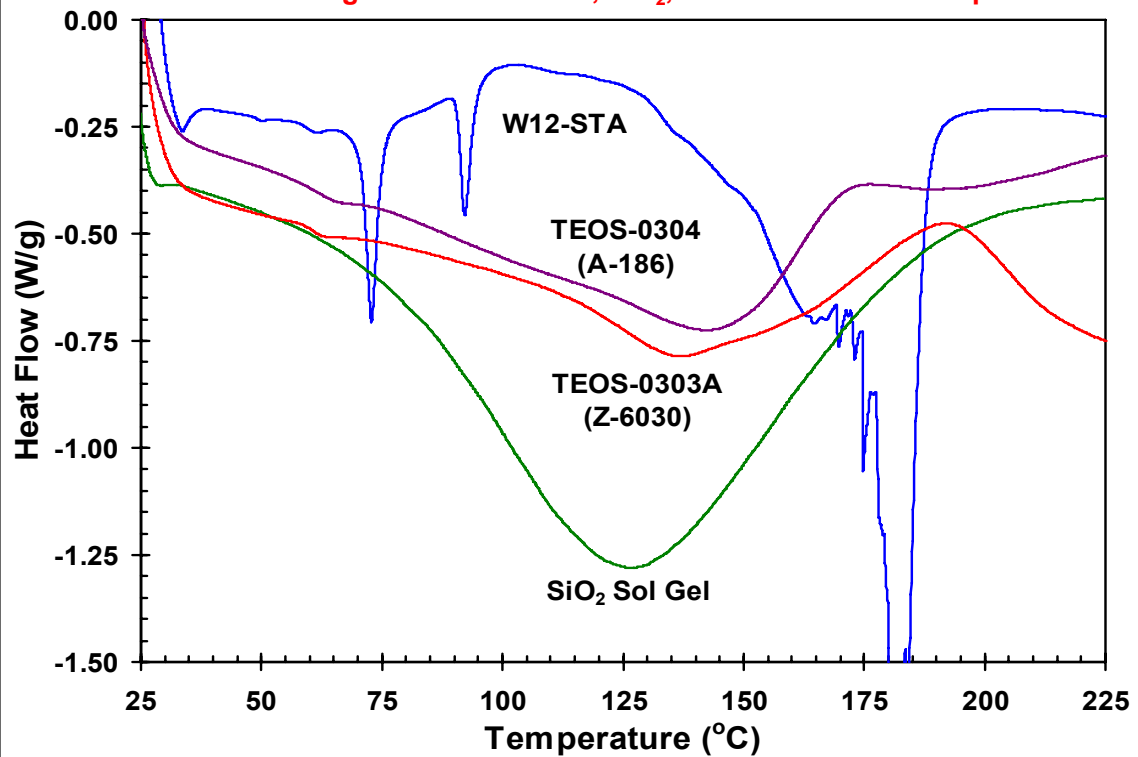
¹ Values of the proton conductivity at 120°C/23%RH are with large uncertainty because of rapidly lost linearity on I-V curves

High H⁺ Diffusion Coefficients for Composite Membrane

Proton Diffusion Data from PFG-NMR Measurements



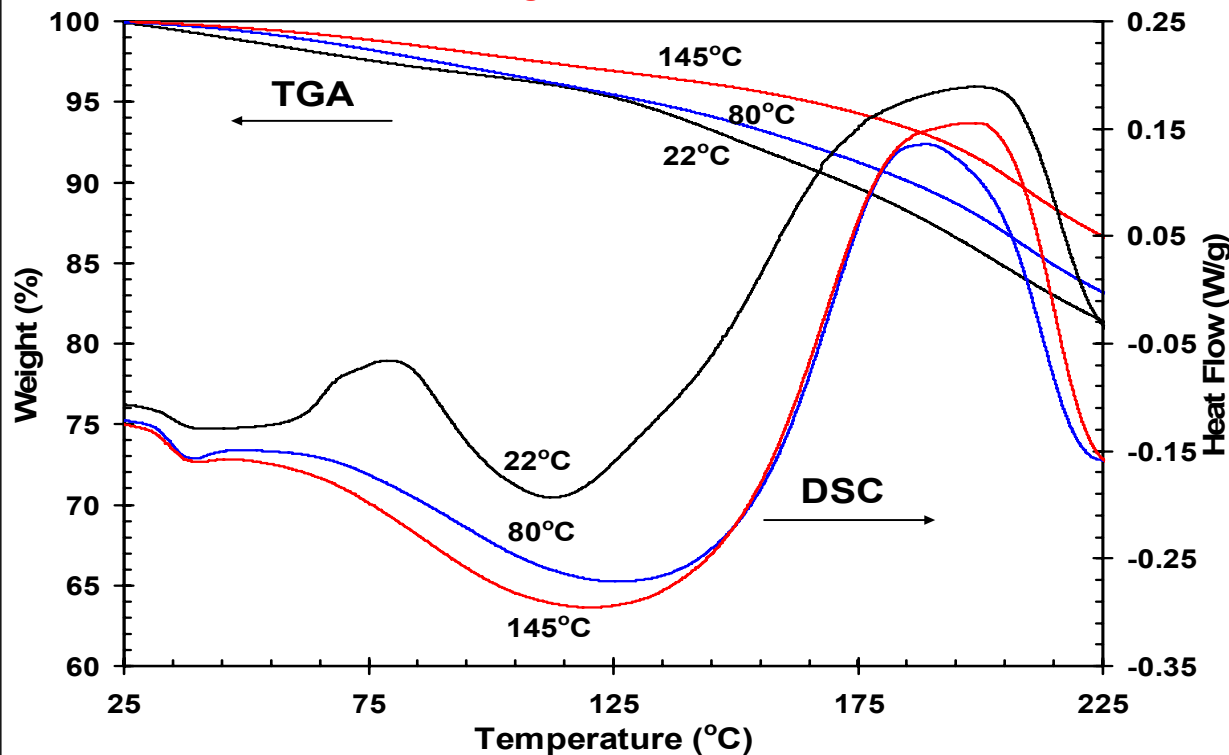
DSC Thermograms of W12-STA, SiO₂, and Two Sol Gel Composites



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

W12-STA/SiO₂/Z-6030
W12-STA/SiO₂/A-186

TGA and DSC Thermograms for PEM-20050823 Membrane



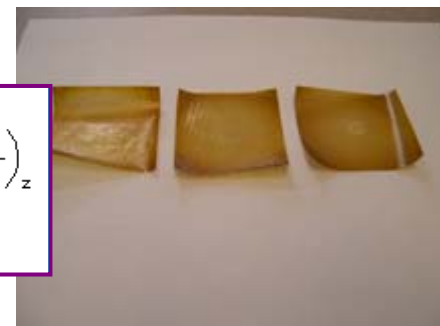
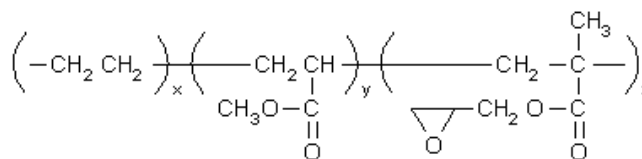
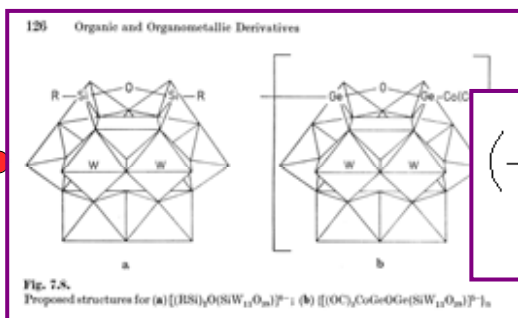
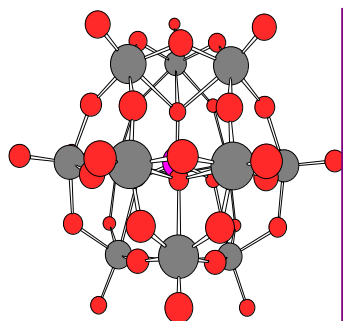
TGA and DSC of as-cast, 80°C-pressed, and 145°C-cured PEM

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 (W_n-STA) with select functional silanes (n = 10, 11, 12)
 - high W_n-STA loading [HPA/(PMG + X-Linker) > 150 wt%]
 - moderate proton conductivity (25 mS/cm at 80°C/100%RH)
- **Clear progress towards meeting the DOE targets**



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°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 SiO₂ 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

Presentations and Publications

1. A. M. Herring, J. A. Turner, S. F. Dec, M. A. Sweikart, J. L. Malers, F. Meng, F. J. Pern, J. Horan, and D. Vernon; "The Use of Heteropoly Acids in Composite Membranes for Elevated Temperature PEM Fuel Cell Operation; Lessons Learnt from Three Different Approaches," 2004 Joint International Meeting, W1 - Fourth International Symposium on Proton Conducting Membrane Fuel Cells, 206th ECS Meeting, October 3-8, 2004, Honolulu, HI.
2. F. J. Pern, J. A. Turner, and A. M. Herring; "Hybrid Proton-Carrier Polymer Composites for High-Temperature FCPEM Applications," in *Nanostructured Materials in Alternative Energy Devices*, edited by Erik M. Kelder, Edson Roberto Leite, Jean-Marie Tarascon, and Yet-Ming Chiang (Mater. Res. Soc. Symp. Proc. 822, Warrendale, PA, 2004), pp. S.8.6.1 – S.8.6.6.
3. A. M. Herring, J. A. Turner, S. F. Dec, M. A. Sweikart, J. Malers, F. Meng, J. Pern, J. Horan, and D. Vernon; "The Use Of Heteropoly Acids In Composite Membranes for Elevated Temperature PEM Fuel Cell Operation; Lessons Learnt from Three Different Approaches." Fuel Cell Seminar, 2004.
4. F. J. Pern, J. A. Turner, Fanqin Meng, and A. M. Herring; "Sol-Gel SiO₂-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.
5. 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)
6. 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
7. 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
8. 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
9. 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