Advanced Fuel Cell Membranes Based on Heteropolyacids

John A. Turner and John Pern
Hydrogen and Electricity, Systems and Infrastructure Group+
National Renewable Energy Laboratory
Golden, CO 80401-3393

Andrew M. Herring,* Steven F. Dec[x], Fanqin Meng,* Jennifer L. Malers,* and James Horan.[x]
Department of Chemical Engineering* and
Department of Chemistry and Geochemistry[x]
Colorado School of Mines
Golden, CO 80401-1887

May 24, 2005

Project ID #
FCP3

This presentation does not contain any proprietary or confidential information

NREL/PR-560-38191
Presented at the 2005 DOE Hydrogen, Fuel Cells & Infrastructure Technologies Program Review

Overview

Timeline

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

Budget

- Total project funding
  - DOE share: $150k

Barriers

- Barriers addressed
  - Thermal, Air and Water Management
  - Cost.
  - Durability

Partners

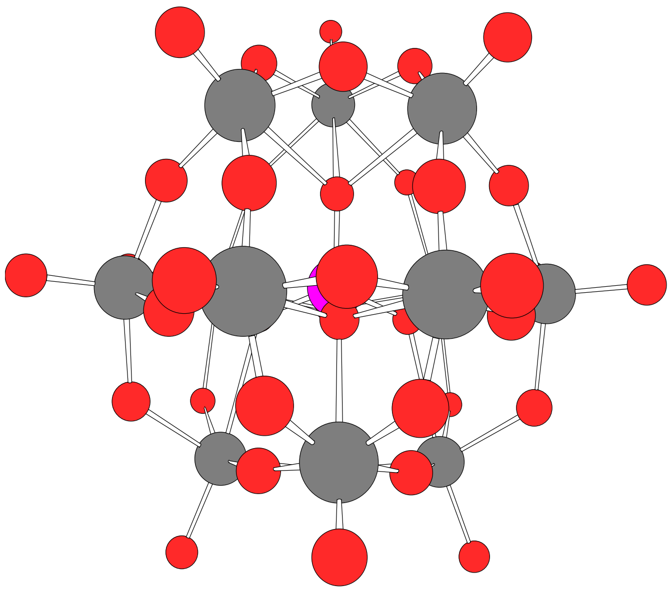
- 3M
- Colorado School of Mines.

Objectives and Approach

- To demonstrate dry inlet gas operation of HPA-based PEMs in FC at T ≥ 80°C.
- Synthesize and characterize selected "saturated" and lacunary heteropoly acids (HPA) that have high potential for the fabrication of FC membranes
- Fabricate heteropoly acid-based proton exchange membrane (PEM)
  - Mechanically strong
  - Stable operation
  - Low-cost
  - Higher temperature/low humidity operation.

Example Structures of Three HPAs

1. Keggin (saturated)

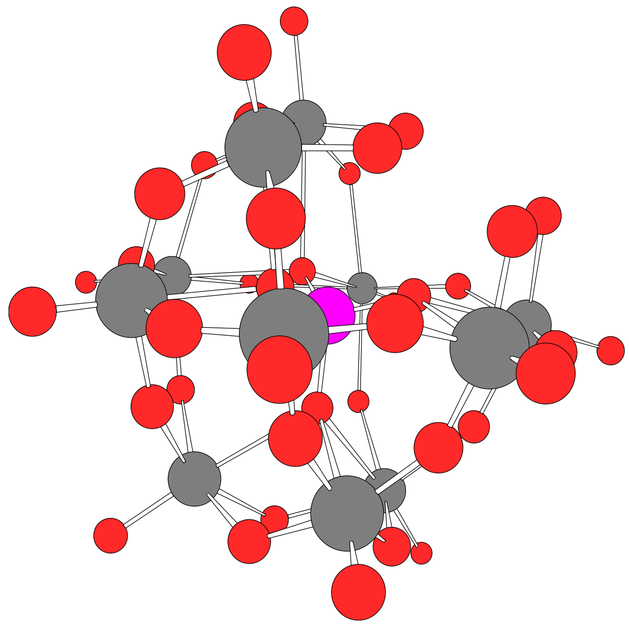


$[SiW_{12}O_{40}]^{4-}$

$H_4SiW_{12}O_{40}$-$22H_2O$

(12-HSiW)

2. Lacunary (vacant sites)

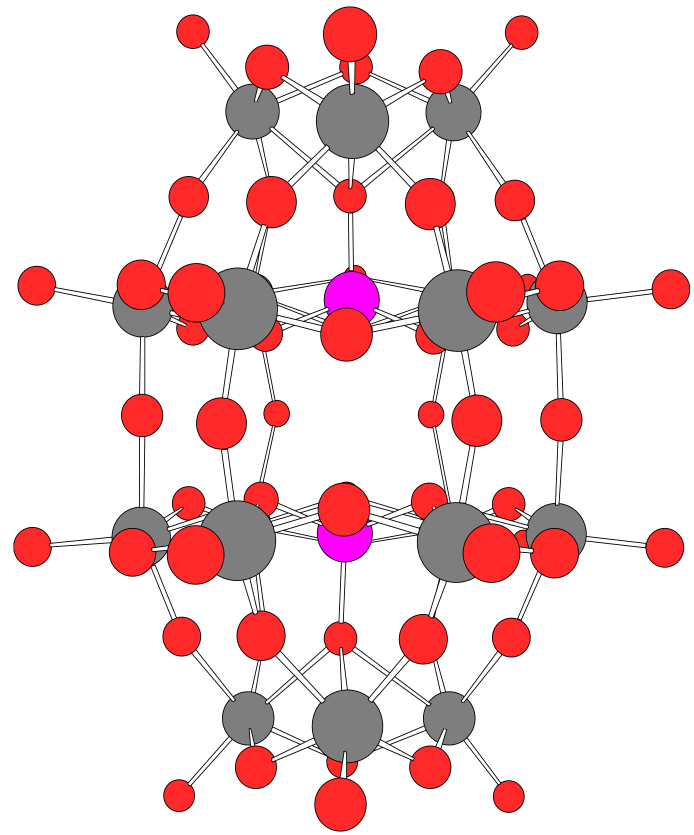


$[SiW_{11}O_{39}]^{8-}$

$H_8SiW_{11}O_{39}$-$26H_2O$

(11-HSiW)

3. Dawson



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

$H_6P2W_{18}O_{62}$-xH_2O

(18-HP2W)

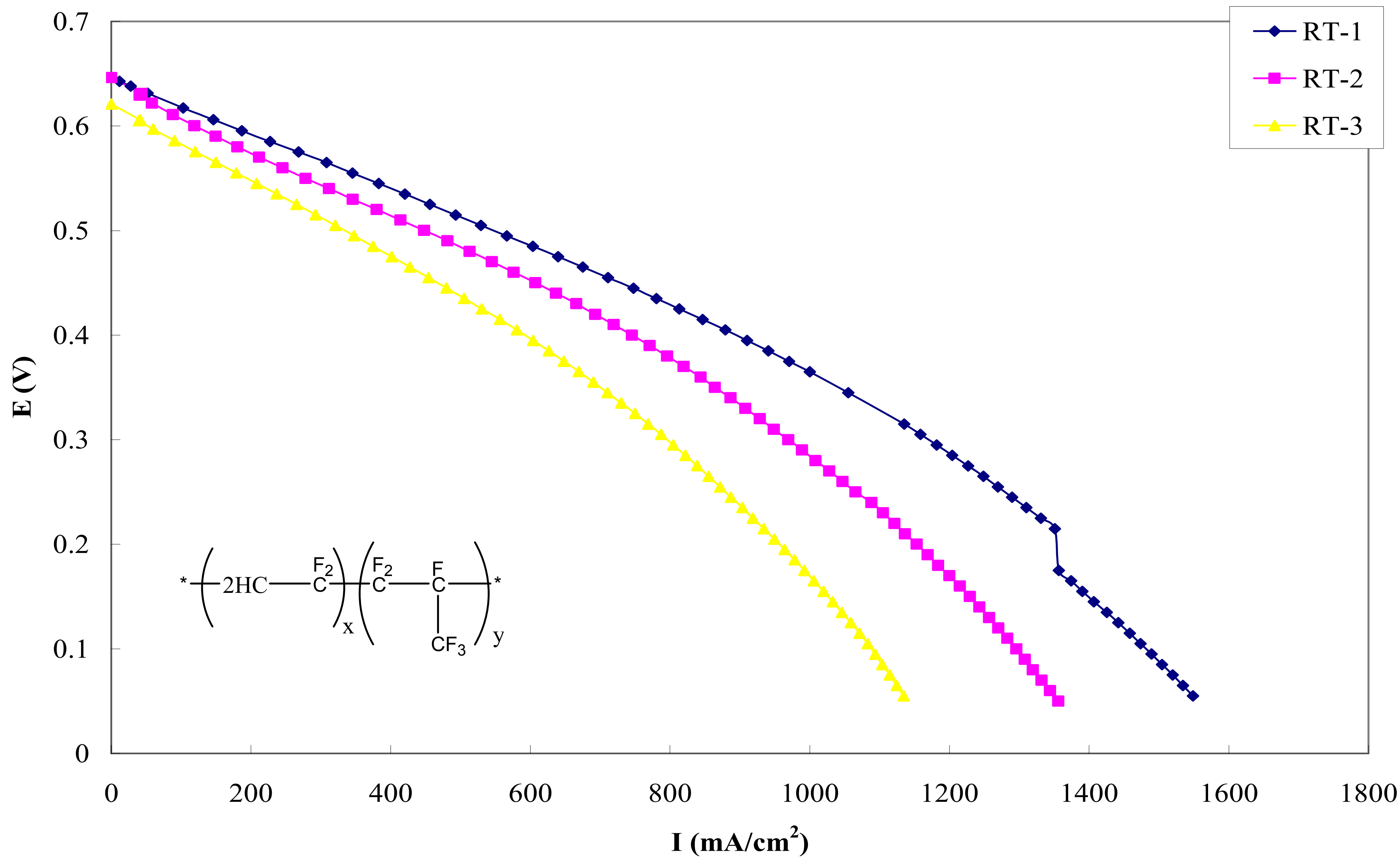
TGA for Various HPAs (after heating to 110 °C)

HPA	Water of crystallization		Secondary structure water		Neutralization		Decomp.
	Equiv. H_2O	Temp.° C	Equiv. H_2O	Temp.°C	Equiv. H_2O	Temp. °C	Temp.°C
$H_3PW_{12}O_{40}$	1	50	6	164	1	482	589
$H_8SiW_{11}O_{39}$	2	60	7	152	6	410	611
$H_6SiV_2W_{10}O_{40}$			6	129	2	250	471
$H_8SiV_3W_{10}O_{40}$			7	183			477
$H_6ZnW_{12}O_{40}$	10	90	10	160	2	480	
$H_6P_2W_{18}O_{62}$			4	114	3	290	>600
$Na_xH_y P_2W_{18}O_{62}$	7	60	5	114			597
$H_6As_2W_{21}O_{69}$			12	129	4	430	430
			2	316			
$H_6P_2W_{21}O_{71}$			4	170	3	350	590
$H_{21}B_3W_{39}O_{132}$	17	59	7	203	4	358	405

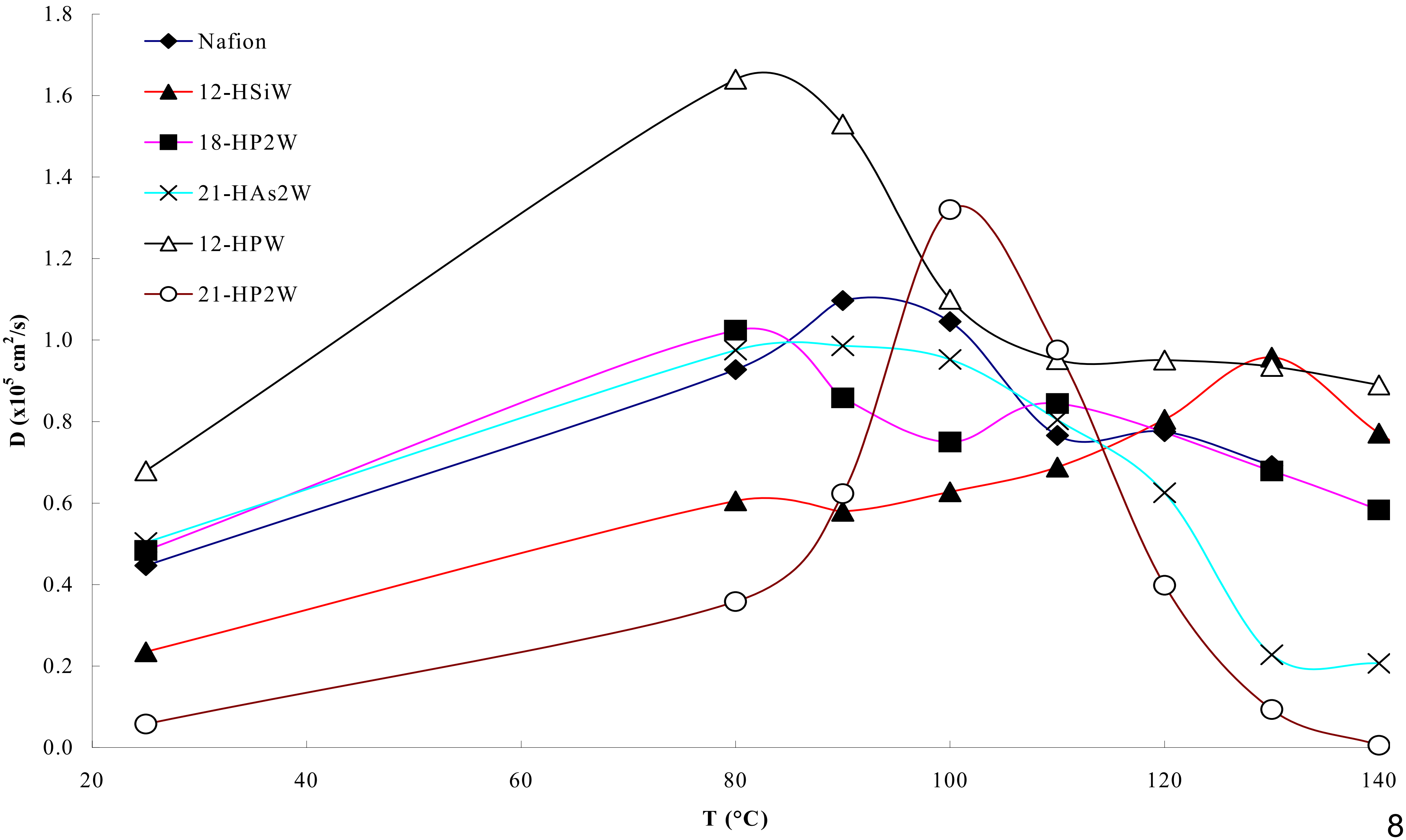
Proton Diffusion Coefficients of HPAs Determined by PF-NMR

HPA	Max diffusion coefficent x 10^{-6} cm^2s^{-1}	Temperature of maximum D, ^oC	Ea before Max T, kJ mol^{-1}	IR H-bond strength	Secondary structure	
12-HPW	25	117	13	20	$H^+(H_2O)_x$	cubic
12-HSiW	30	130	20	40	$H^+(H_2O)_x$	cubic
12-HZnW	2	108	27	30	$H_5O_2^+$, OH	cubic
12-HGeW	0.7	90	35			cubic
11-SiW11	3	108	6	35	$H_5O_2^+$, OH	cubic
39-HB3W	7	128	8	18	$H^+(H_2O)_x$	sheets
18-HP2W	1.2	>150	20	20	H_3O^+	triclinic
21-HAs2W	3.7	>150	18	18	$H_5O_2^+$	
21-H_2Rb_4As2W	30	25	-		$H^+(H_2O)_x$	channels
21-HP2W	2.3	110	24	27	H_3O^+	

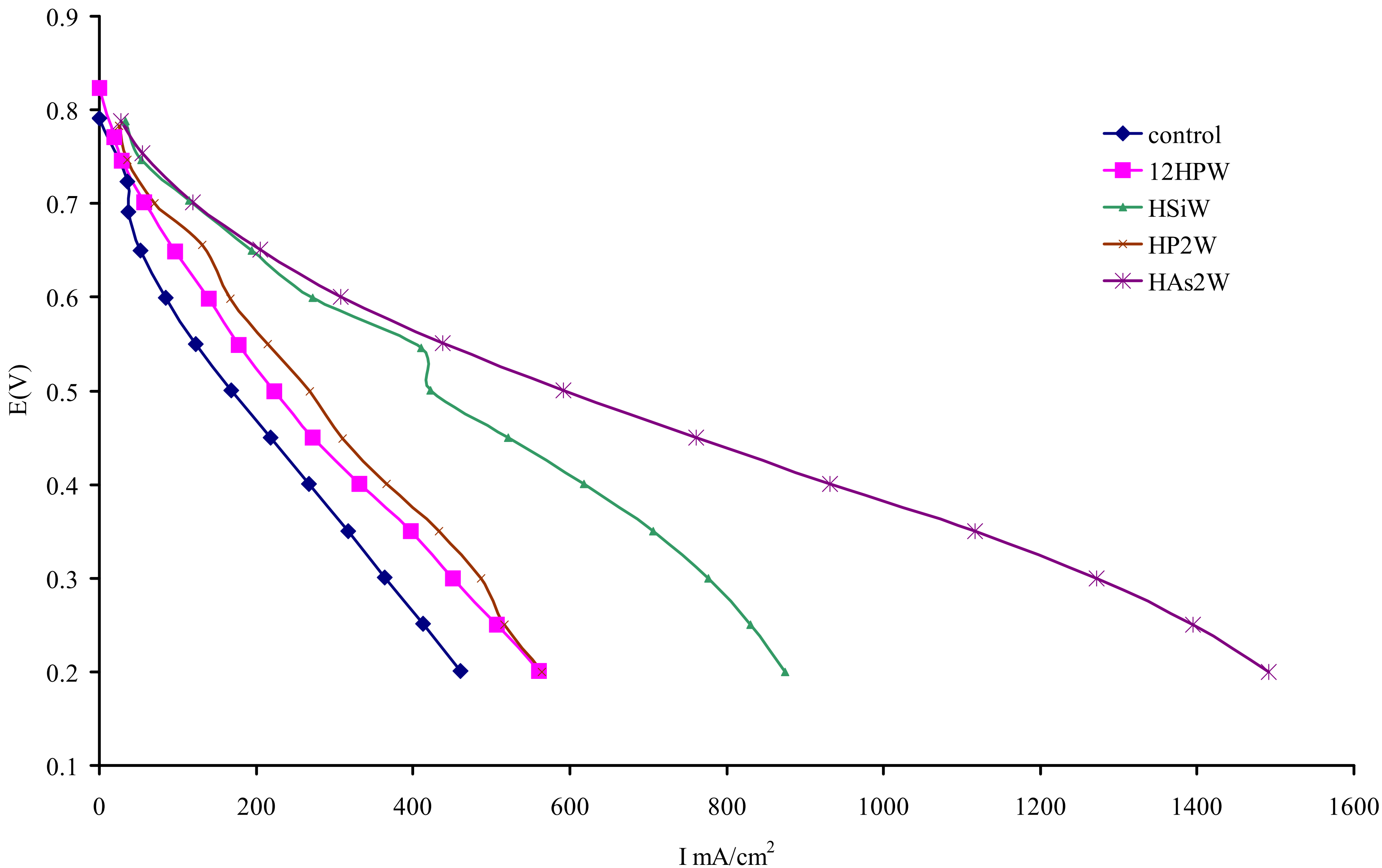
Polarization curves of PEM made of 12-HPW physically blended in PVDF-HFP



Diffusion coefficient data for HPA doped Nafion® 112 protons



Polarization curves comparing Nafion and HPA-doped Nafion®



120 ºC Nafion® 112, 25% RH, No ionomer in electrode (ELAT) 0.5 mg/cm² 20% Pt on carbon.

Strategies for Immobilizing HPAs

A. Bonding Approaches:

1. Covalent bonding directly to a polymeric matrix
2. Covalent bonding to oxide nanoparticles, which can further bond covalently to, or embed physically in a polymeric matrix
3. Direct embedding in a polymeric matrix

B. Modification of Lacunary HPAs:

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

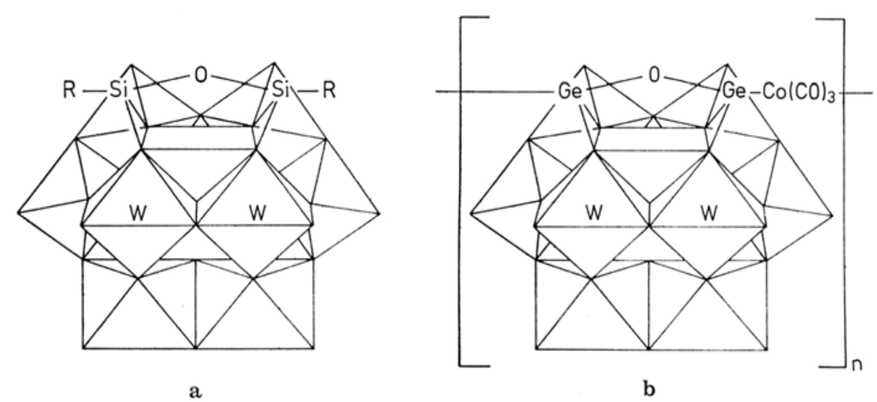
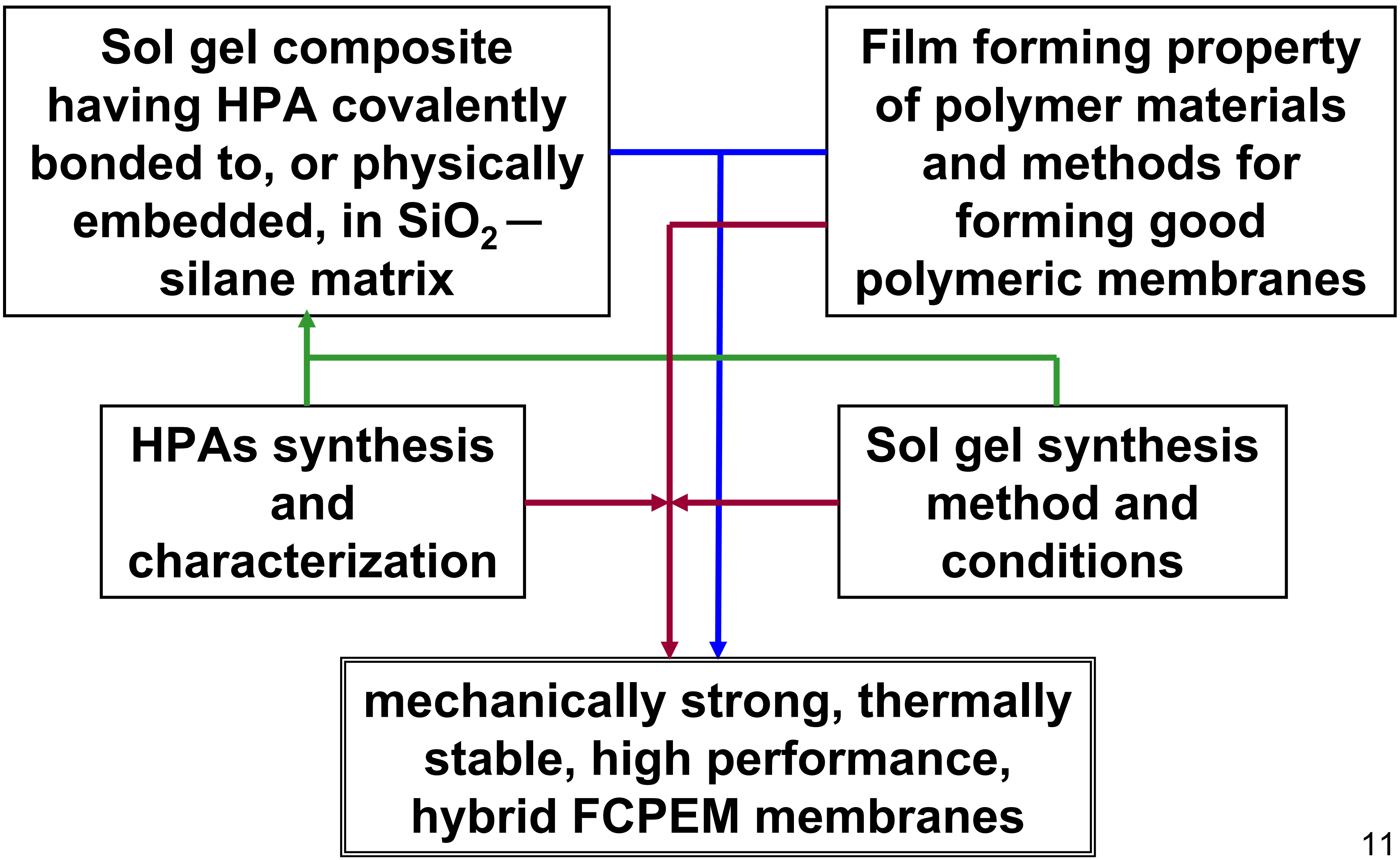


Fig. 7.8.
Proposed structures for (**a**) $[(RSi)_2O(SiW_{11}O_{39})]^{4-}$; (**b**) $\{[(OC)_3CoGeOGe(SiW_{11}O_{39})]^{5-}\}_n$

Multiple Approaches for Making HPA-based Hybrid PEM



Polymerization Methods for immobilizing H^+ Carrier/Transmitter Composites

1. Post-Polymerization:

(H^+): proton donor

$$C{=}C{-}{-}{-}Si{-}O{-}(H^+){-}O{-}Si{-} \longrightarrow C{-}C{-}{-}{-}Si{-}O{-}(H^+){-}O{-}Si{-}$$

2. Pre-Polymerization

$$C{-}C{-}{-}{-}Si(OR)_3 \xrightarrow{(+\ SiO_2)\ +\ (H^+)} C{-}C{-}{-}{-}Si{-}O{-}(H^+){-}O{-}Si{-}$$

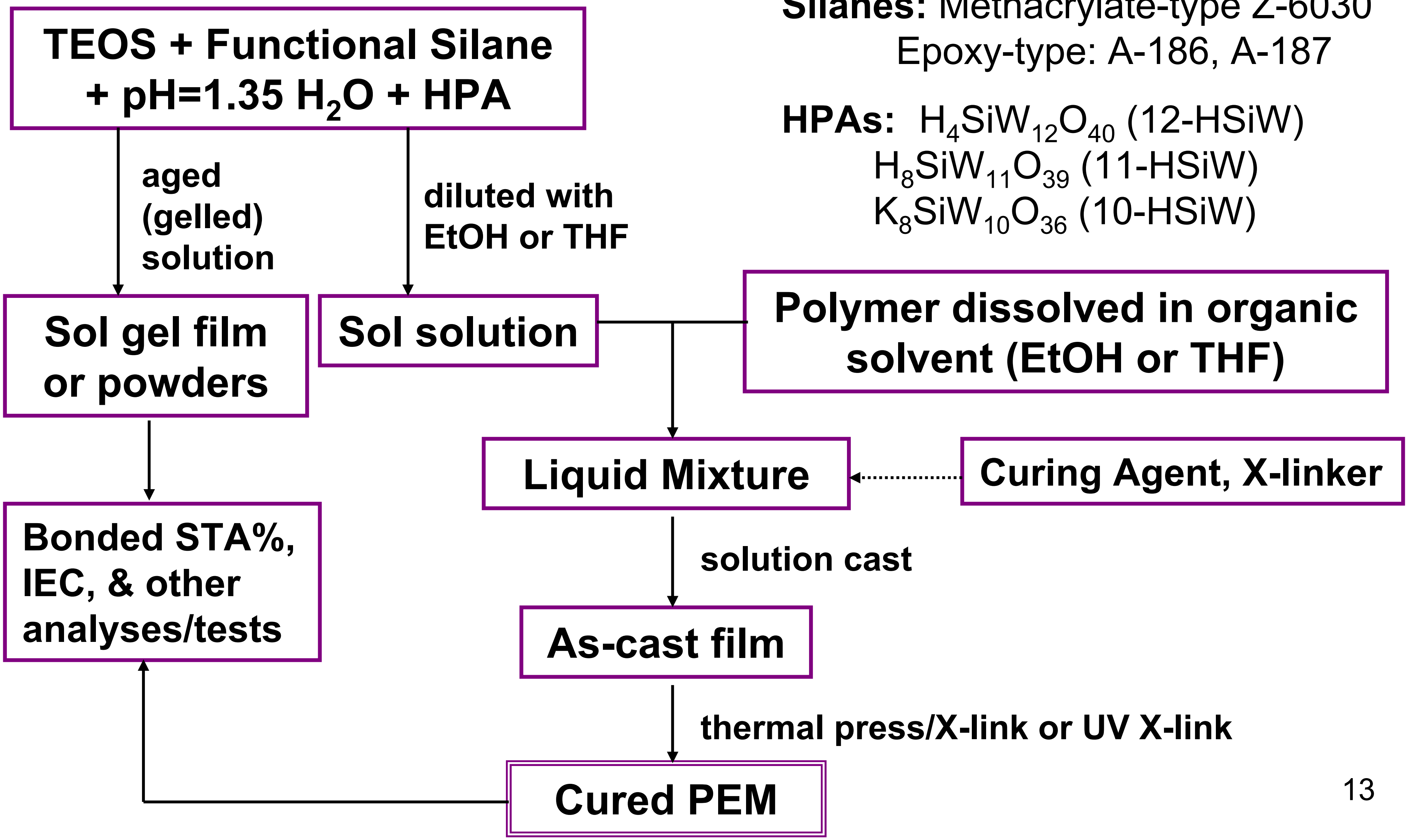
3. Co-Polymerization:

$$C{=}C{-}{-}{-}Si(OR)_3 + (H^+)\ (+\ SiO_2)\ (+\ Modifier) \longrightarrow C{-}C{-}{-}{-}Si{-}O{-}(H^+){-}O{-}Si{-}$$

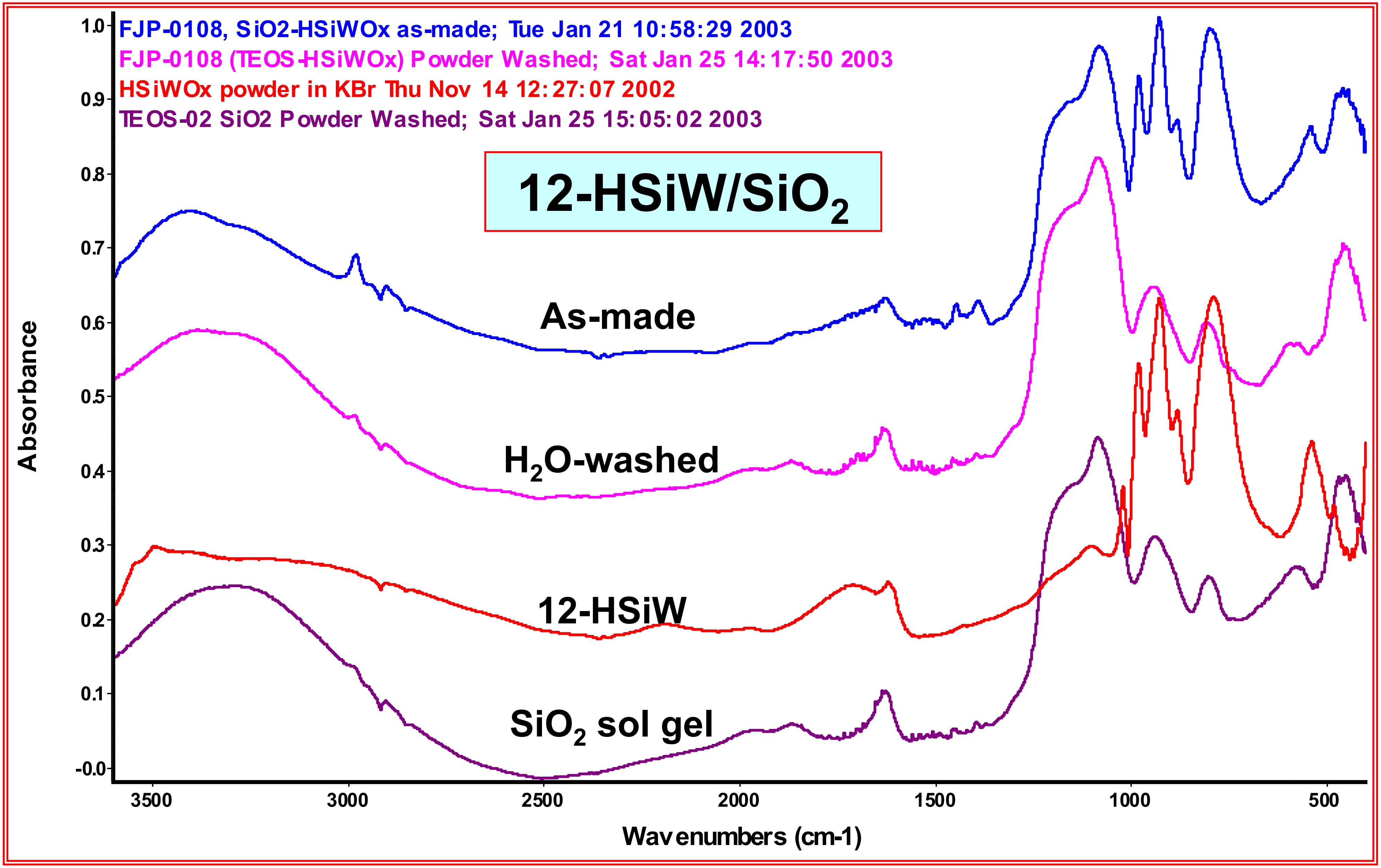
Procedure for Fabricating Hybrid Composite PEM Membranes

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

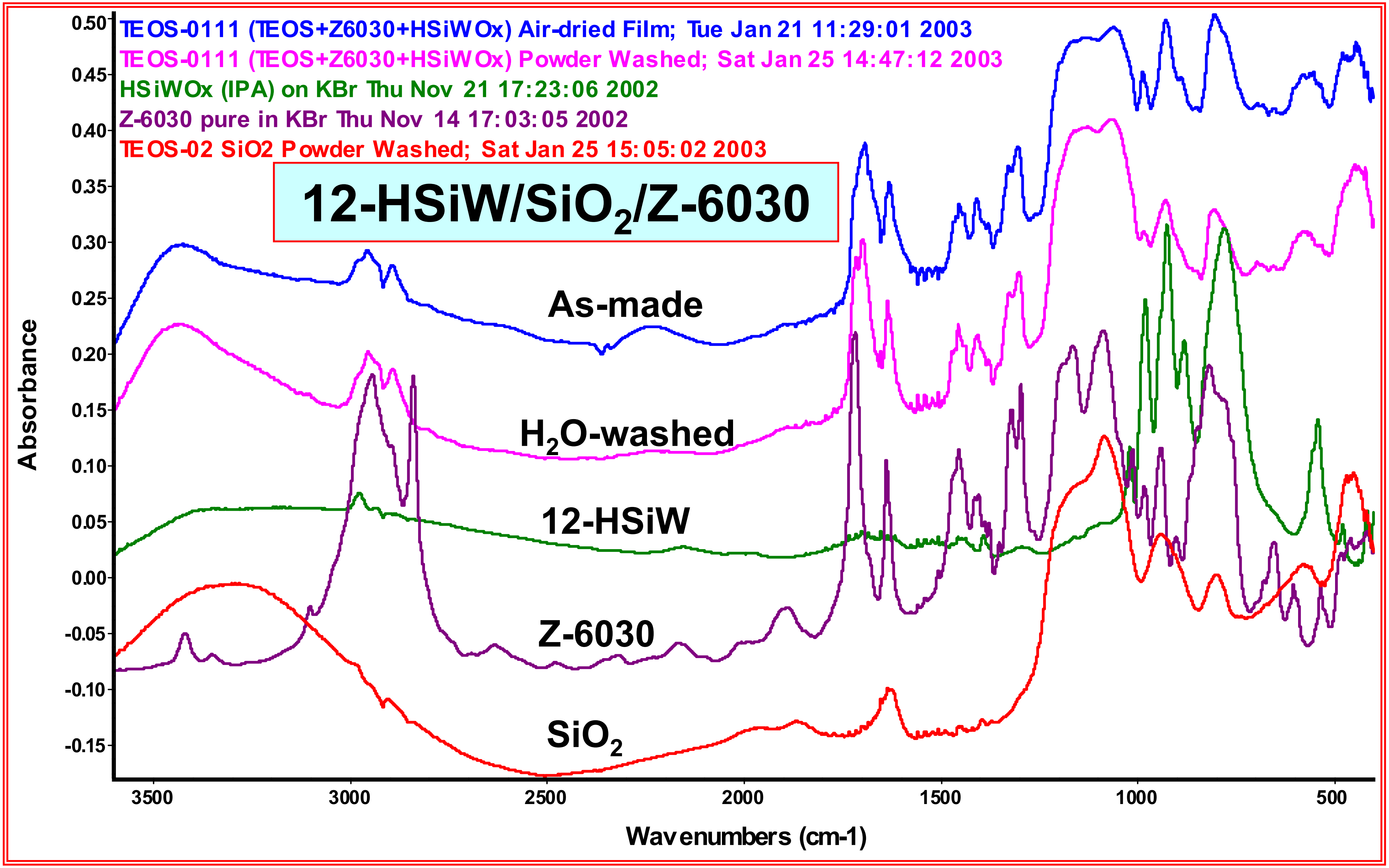
HPAs: $H_4SiW_{12}O_{40}$ (12-HSiW)
$H_8SiW_{11}O_{39}$ (11-HSiW)
$K_8SiW_{10}O_{36}$ (10-HSiW)



"Bonding HPA": Sol Gel Composite (No Silane)➔ 12-HSiW Washed Off



"Bonding HPA": Sol Gel Composite (with Z-6030 silane) ➔ 12-HSiW Retained

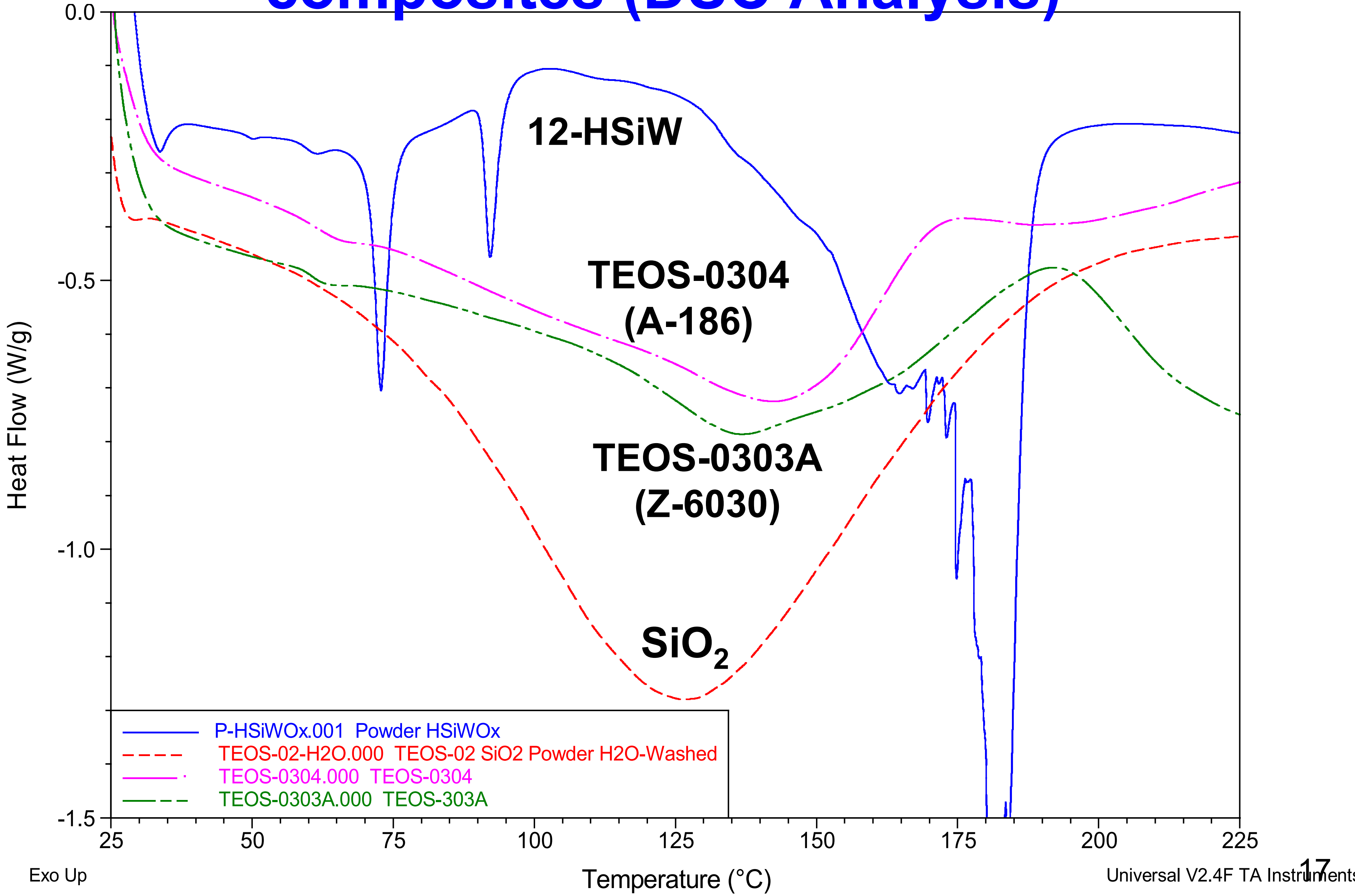


HSiWxOy Bonded/Embedded to Silica/Silane Network and IEC of Sol Gel Composites

Table 1. Molar Ratios vs. Weight% of Bonded HSiWOx and IEC of Composite Powders					
Sample ID	Composition SiO2/Silane/HPA	Molar Ratio Normaliz. to SiO2			Bonded/Total Ratio (%)
		COS/TEOS	Silane	HSiWOx	
Cab-O-Sil Approach					
	W12-STA				
FJP-1004	COS/Z-6030/HSiWOx	1.00	0.62	0.016	39.06
FJP-1012	COS/HSiWOx	1.00	0.00	0.016	6.72
FJP-1126*	COS/Z-6030/HSiWOx	1.00	0.33	0.04	0.89
Sol Gel Approach					
FJP-0108	TEOS/HSiWOx	1.00	0.00	0.04	15.26
TEOS-0111	TEOS/Z-6030/HSiWOx	1.00	0.63	0.04	36.80
TEOS-A186	TEOS/A-186/HSiWOx	1.00	0.90	0.03	88.24
TEOS-A187	TEOS/A-187/HSiWOx	1.00	1.01	0.03	79.20
TEOS-0303A	TEOS/Z-6030/HSiWOx	1.00	1.88	0.06	95.17
TEOS-0304	TEOS/A-186/HSiWOx	1.00	1.80	0.06	99.45
	W11-STA				
TEOS-0403	TEOS/Z6030/HSiW11Ox	1.00	0.94	0.06	97.30
TEOS-0404	TEOS/A-186/HSiW11Ox	1.00	0.90	0.06	95.74

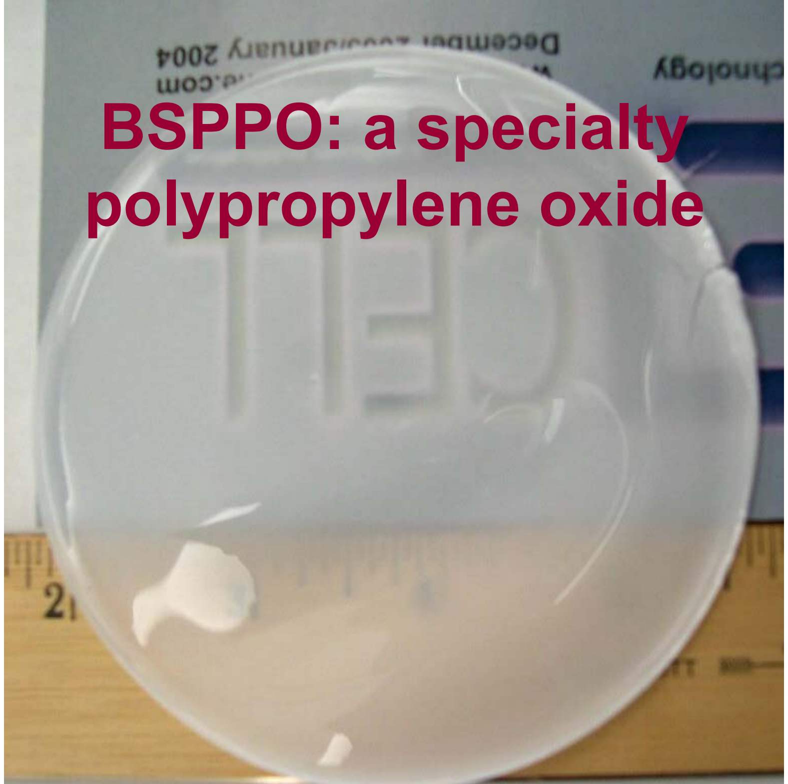
* Final solution pH~4.3; all others pH ≤ 1.0. **IEC are for H_2O-washed powders.**

Water-retention capability of SiO_2, 12-HSiW, and two 12-HSiW/SiO_2/Silane sol gel composites (DSC Analysis)



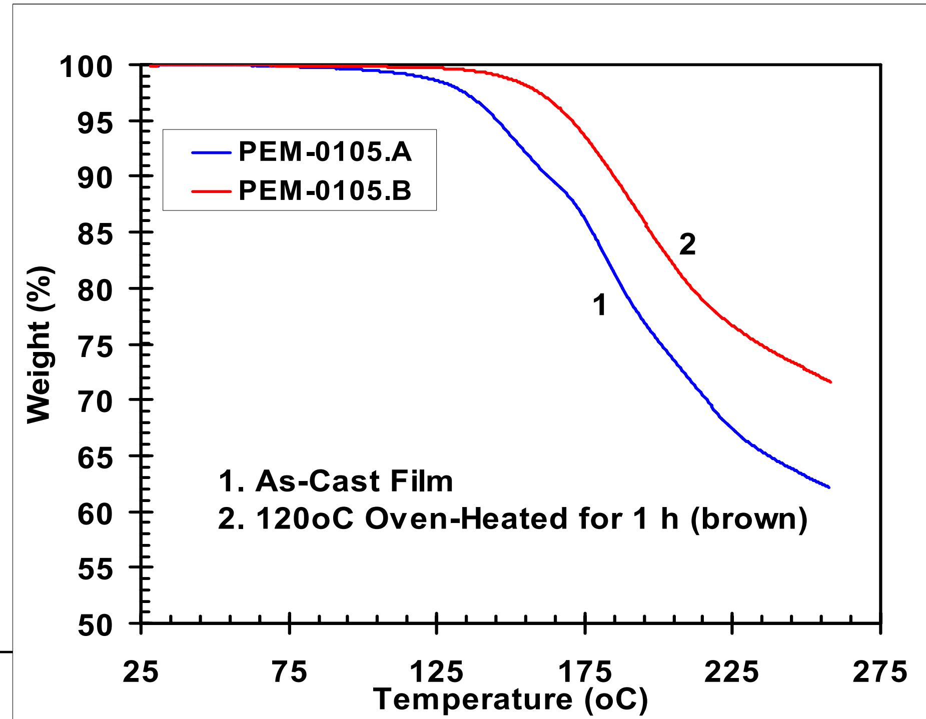
12-HSiW Sol Gel Composite/ BSPPO Hybrid PEM

BSPPO: a specialty polypropylene oxide

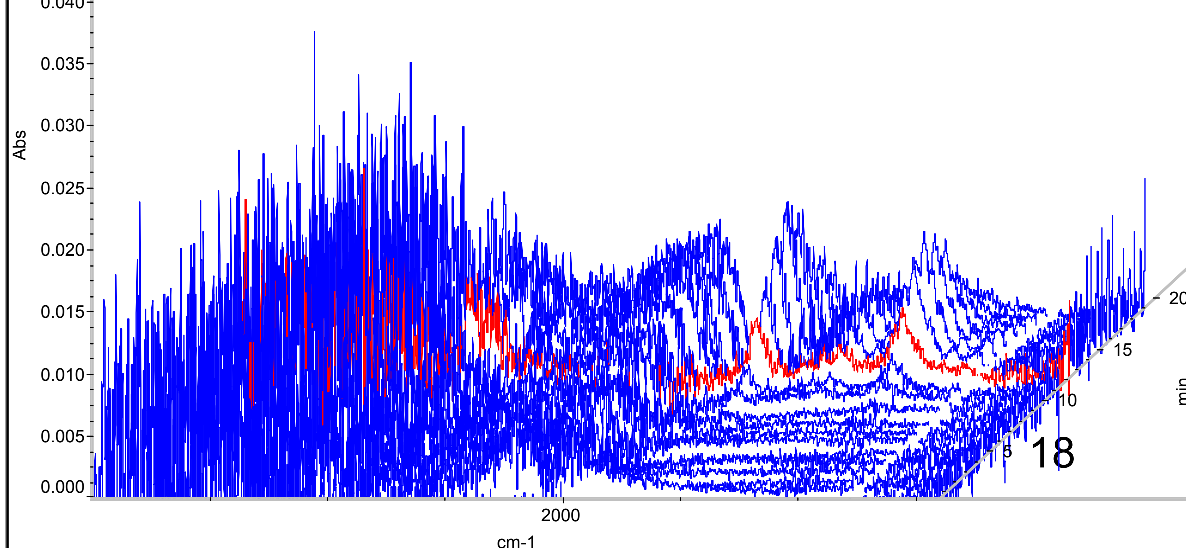


12-HSiW/BSPPO = 44 wt%
SiO_2/BSPPO = 13.5 wt%

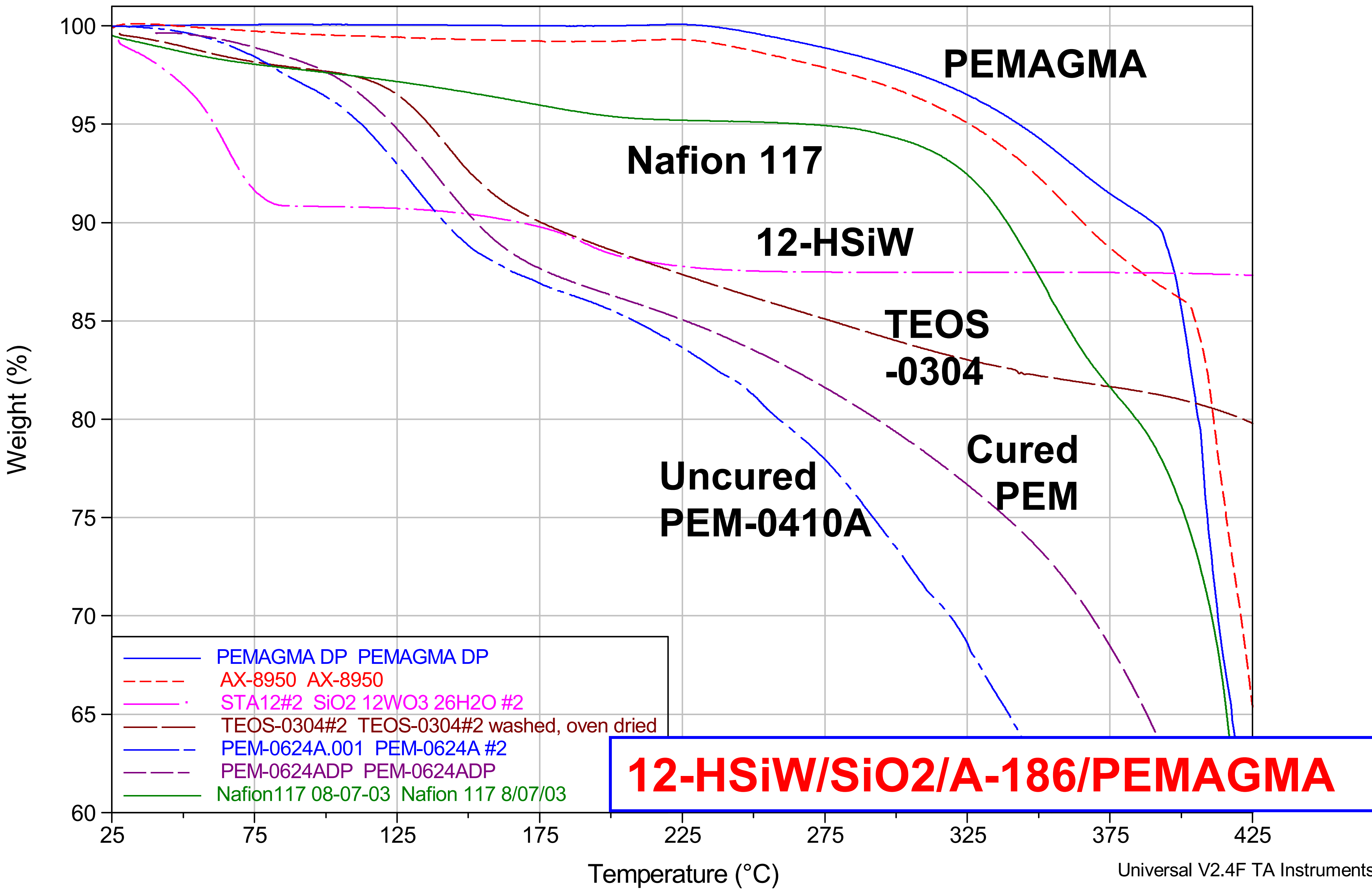
PEM-0105 Cured/Pressed Film



TGA-FTIR Analysis:
PEM-0105 Oven-heated at 120°C for 1h

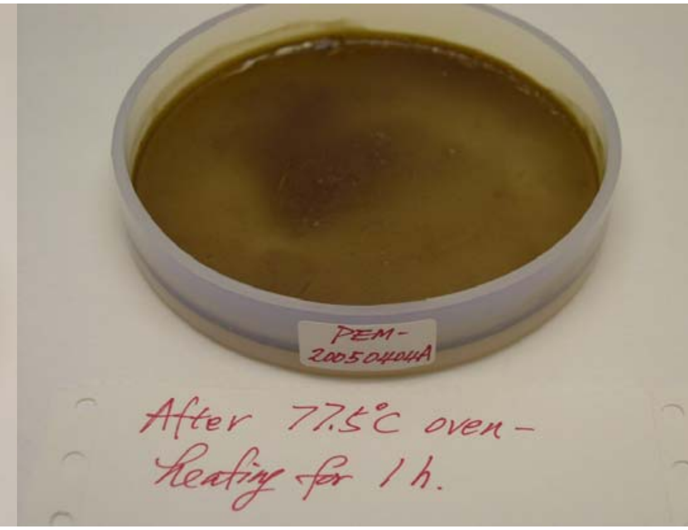


TGA Analysis of a Hybrid Membrane and its Key Components



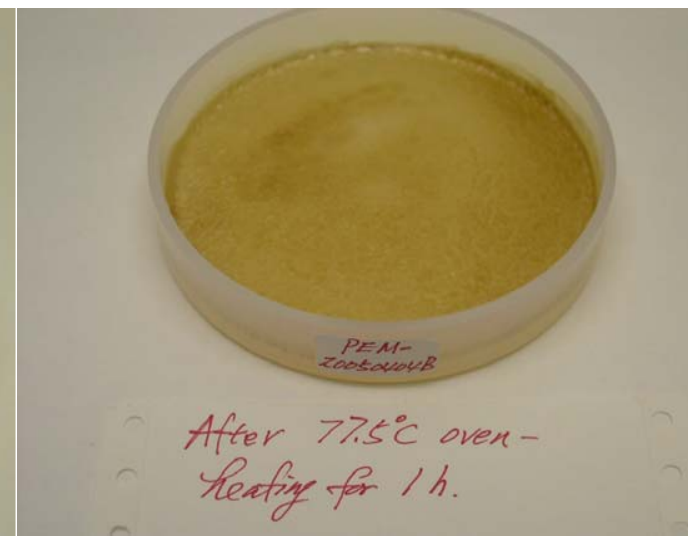
12-HSiW/SiO2/A-186/PEMAGMA

Flexible, high-HSiW-loading hybrid PEMs are obtained for the first time



PEM-20050404A: 11-HSiW/TEOS/Z6030/PEMAGMA, STA/Polym=109 wt%

PEM-20050404B: 12-HSiW/TEOS/Z6030/PEMAGMA, STA/Polym=114 wt%



Accomplishments/Progress - 1 – HPA and Doped Nafion®

- **HPAs:** A large number of HPAs based on the Keggin, Dawson, and more complex skeletons have been synthesized and their structural properties relevant to proton conduction elucidated by IR, NMR. Thermal stability of all proton conducting phases determined by TGA.
- Proton diffusion properties are characterized by pulse field gradient spin echo NMR. Many HPA have high diffusion coefficients and low activation energies for diffusion.
- **HPA /PVDF:** HPA high proton conduction under dry conditions was demonstrated in a PVDF matrix.
- **HPA Doped Nafion®:** Nafion® was doped with various HPA which interact strongly with the $-SO_3H$ groups and in some cases dramatically improved proton diffusion.
- These doped Nafion® membranes were incorporated in MEAs and tested in a fuel cell, showing dramatic improvements at 120°C, but as the HPA in these systems are not immobilized this may be a result of improvements to the membrane/electrode interface.

Accomplishments/Progress – 2 -- PEM Fabrication and Performance

- **SiO_2 Sol Gel Composite-Polymer Hybrids:**
  - **by simple mixing method**
  - **by "Two-Step" method**
  - **by direct copolymerization method**
  - **various host polymers**
  - **on-going work**
- **Sol-gel synthetic methods:** Several are established for making HPA-containing sol gel composites with the functional silanes
- **HPA-containing hybrid PEM membranes:** Physical blending, two-step and direct copolymerization methods are developed.
- **Analytical procedures** are established for IEC, bleaching, structural, thermal stability analysis, electrical (conductivity), and fuel cell performance tests.

Summary

- **A variety of HPAs have been successfully synthesized, characterized, and used for PEM fabrications.**
- **A variety of methods for immobilizing HPAs in different polymer matrices have been successfully demonstrated:**
  - **Physical blending/embedding**
  - **Sol gel composite-polymer hybrid**
  - **Flexible, cross-linked, high-STA-loading hybrid PEMs are obtained for the first time**
- **FC performance test results indicate the HPA-based PEMs are very promising for high-temp operations without the need of humidification.**

Future Work

- Understand the synergistic interaction of HPA with ionomers in terms of improving proton conduction at low humidity/elevated temperatures
- Continue to develop immobilization strategies and optimize hybrid HPA for proton conduction

Hydrogen Safety

The most significant, potential hydrogen hazard associated with this project is fire and/or explosion due to either leak, ignition, or strong impact of the highly pressurized H_2 gas cylinders, resulting in personnel injuries and/or loss of equipment in the laboratory.

Hydrogen Safety

Our approach to deal with the potential hazard:

- A Standard Operating Procedure (SOP) has been implemented.
- All personnel involved in the use of compressed H_2 cylinders are required to take pertinent ES&H training at NREL and familiar with the SOP prior to being authorized for work.
- Personnel protective equipment (PPE) such as safety goggles or glasses are required when present in the lab. Wearing a face shield is required when changing the pressure regulator.
- The H_2 cylinders are well secured and properly capped when not in use. NFPA warning labels (e.g., High Pressure Gas, Flammable Compressed H_2) are attached to the cylinders. Valves are only opened to the necessary pressure.
- No hot work, open fire, and compressed O_2 cylinders are allowed nearby the H_2 cylinders or fuel cell test station.
- Regular check of leaking is conducted with soapy water solution.
- Fire extinguishers are available in the laboratory.
- Emergency response and exit are clearly stated in the SOP and also marked in the lab.