
V.B.8 Advanced Fuel Cell Membranes Based on Heteropolyacids

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Objectives

- Develop the methodology for the fabrication of 3D cross-linked, hydrocarbon-based membranes using immobilized heteropolyacids (HPAs) as the proton conducting moiety.
- Develop immobilization technology based on covalent attachment of HPAs to oxide nanoparticles and the host polymer.
- Acquire an improved understanding of the property/structural relationship of HPAs and their salts made by custom synthesis.
- Conduct relevant characterizations of the membranes to better understand their structural, chemical, and thermal properties/stability and proton conductivity.
- Achieve a proton conductivity of ~0.1 S/cm at 120°C and <1.5 kPa H₂O.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4.4.2) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Durability
- (B) Cost
- (D) Thermal, Air and Water Management

Technical Targets

This project addresses the technical targets from Table 3.4.12 of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan.

- High temperature ($\leq 120^\circ\text{C}$), low humidity operation (25% relative humidity or 1.5 kPa).
- High conductivity 0.1 S/cm at operating temperature and 0.07 S/cm at room temperature.
- Cost of \$40/m².

Accomplishments

- A. Fabrication and performance of composite proton exchange membranes (PEMs):
 - By simple solution formulation with low-cost raw materials.
 - By simple solution casting method (also exploring doctor-blade method).
 - By direct copolymerization using brief thermal pressing process to form 3D cross-linked composite matrix with SiO₂ nanoparticles in the host polymer.
- B. Properties of HPA-based composite proton exchange membranes:
 - Effective binding of silicotungstic acids with variable tungsten content (Wn-STA, n = 10, 11, 12) with select functional silanes.
 - High Wn-STA loading.
 - High chemical stability.
 - Good thermal stability when embedded with highly reactive W12-STA.
 - Good mechanical flexibility.
 - Promising proton conductivity (25 mS/cm at 80°C/100% relative humidity).

Introduction

This project is focused on the development of low-cost, high-performance, novel proton exchange membranes (PEMs) based on heteropolyacids. The goal is to replace sulfonic acid (SFA)-based proton-conducting materials with HPAs as the proton-conducting moiety. A major problem in the use of SFA-based membranes is the limitation on operation temperatures to under 100°C and the requirement for 100% relative humidities (RHs). At higher temperatures, membranes based on SFAs cease to function because

of water loss from the clusters of sulfonic groups, resulting in a decrease of the proton transport through the membrane. Membranes that can operate at lower humidities and withstand higher temperature excursions will significantly advance fuel cell technology, hastening the implementation of a full hydrogen economy.

HPAs as a component in high-temperature PEMs have recently received considerable attention. They have structural diversity (Figure 1), high thermal stability at temperatures up to 250°C and are known to have high proton conductivity at low humidity. A major technical challenge in utilizing HPAs as the proton conductor in PEMs is their high solubility in aqueous environments, requiring an approach to effectively immobilize them. This project has developed a synthetic methodology that produces a 3D, cross-linked polymeric matrix with HPA immobilized by functional silanes along with *in situ* formed nano-oxide particles.

Approach

The three major technical challenges in realizing an HPA-based PEM that can operate at high temperature and low humidity (i.e., 120°C and 25% RH) are:

(1) substantial loading and immobilization of the highly water-soluble HPAs, (2) controlling the microstructure of the membrane to provide a mechanism and pathway for efficient proton conduction at low humidity, and (3) structural stability of the PEM under operational conditions.

We addressed these challenges by (i) identifying suitable polymer materials that are chemically stable against attack by the reactive HPAs and thermochemically stable under fuel cell operating conditions, (ii) composing formulations that allow the formation of a 3D cross-linked matrix for enhanced thermochemical stability and mechanical strength, (iii) immobilizing the HPA by select functional silanes and *in situ* formed SiO₂ nanoparticles in the matrix, and (iv) adjusting/modifying the formulations to achieve high weight loading of HPA to improve the proton conductivity. Additionally, through our academic partner, we have access to HPAs and their salts made by custom synthesis and we acquired an improved understanding of the structural/property relationships of HPAs, which we can apply to our PEM fabrications.

Due to its commercial availability, we have been using the Keggin-type W12-silicotungstic acid (STA) (see Figure 1) for most of our experiments to test and confirm the feasibility and viability of our technical methodology. For the next generation HPAs needed for PEM fabrication in this project, the extensive experiences of our academic partner (the Fuel Cell Group at the Colorado School of Mines) in synthesizing and characterizing a large variety of HPA structures will be valuably employed.

Some HPA Structures

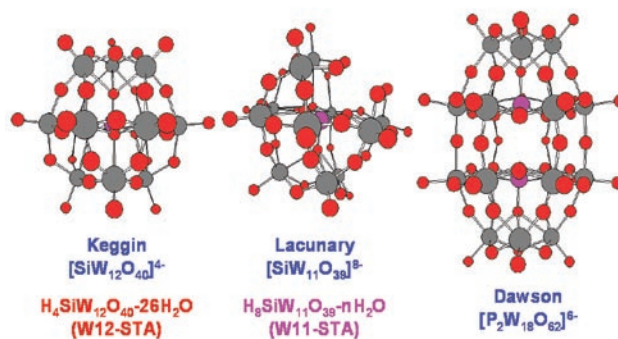


FIGURE 1. Examples of Relevant Heteropolyacid Structures: Keggin-type (W12-STA) and Lacunary (W11-STA)

Results

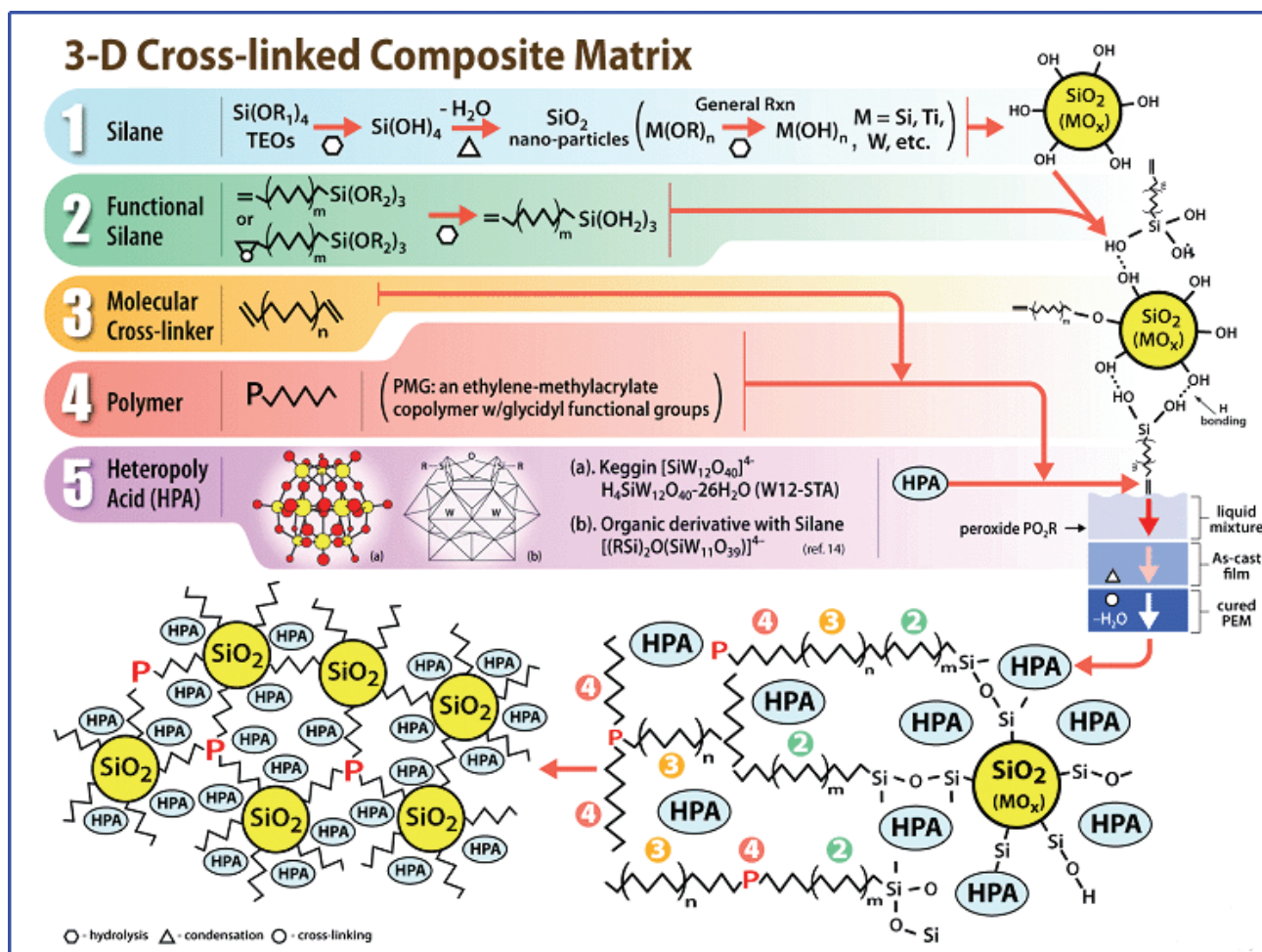
Table 1 demonstrates the effectiveness of the immobilization of W11- and W12-STA by three functional silanes at different molar concentration ratios, as determined by extracting the STA from the synthesized SiO₂-sol gel composite powders with deionized water. The retention of STA by the SiO₂-sol gel matrix was further confirmed by fourier transform infrared (FTIR) spectral analysis before and after water wash.

The key concept in our PEM design was technically realized by the immobilization of a primary proton conductor within a 3D cross-linked matrix formed by the condensation of a nanoparticulate oxide from silanes and the cross-linking of a host polymer. Here the bridging polymerization was made via the bi-functional groups of a functional silane and, if needed, a molecular cross-linker serving as mechanical and structural modifier. Schematically illustrated in Figure 2, these elements involve the following:

- Oxide nanoparticles, such as SiO₂, TiO₂, WO₃, and V₂O₅, with large surface areas produced via hydrolysis and condensation, serving as immobilization site, moisture retainer as well as secondary proton donor or transmitter.
- A functional silane was employed as a bridging entity to bond to the oxide nanoparticles via the siloxy group on one end and to the polymer host via either a C=C double bond or epoxide group on the other.
- A cross-linkable polymer used as host for the primary proton conductor and the oxide nanoparticles, and a molecular cross-linker possibly added to facilitate/modify the polymerization and cross-linking.
- A primary proton donor/conductor such as heteropolyacid, which can be available in a large number of varieties, immobilized via the functional silane.

TABLE 1. Effect of Functional Silane Type and Molar Ratio on Immobilization of W11- and W12-STA

Sample ID	Composition SiO ₂ /Silane/HPA	Molar Ratio SiO ₂	Normalized Silane	To SiO ₂ HSiWO _x	Embedded/Total Ratio (%)
Sol Gel Approach					
W12-STA					
FJP-0108	TEOS/HSiWO _x	1.00	0.00	0.04	15.26
TEOS-0111	TEOS/Z-6030/HSiWO _x	1.00	0.63	0.04	36.80
TEOS-A186	TEOS/A-186/HSiWO _x	1.00	0.90	0.03	88.24
TEOS-A187	TEOS/A-187/HSiWO _x	1.00	1.01	0.03	79.20
TEOS-0303A	TEOS/Z-6030/HSiWO _x	1.00	1.88	0.06	95.17
TEOS-0304	TEOS/A-186/HSiWO _x	1.00	1.80	0.06	99.45
W11-STA					
TEOS-0403	TEOS/Z6030/HSiW11O _x	1.00	0.94	0.06	97.30
TEOS-0404	TEOS/A-186/HSiW11O _x	1.00	0.90	0.06	95.74

**FIGURE 2.** The Key Concept, Components, And Synthetic Approach in the Making of 3D Cross-Linked Composite PEM

- Final matrix condensation and structural cross-linking produced by thermal (or ultraviolet) curing at elevated temperatures under mild pressure, resulting in a 3D crosslinked matrix.

The synthesized PEMs have shown good thermal/chemical stability (when embedded with the reactive W12-STA), high chemical stability against Fenton's reagent, and good mechanical flexibility (but still lack full flexibility). The PEMs also carried high Wn-STA loading [HPA/(PMG + X-Linker) > 150 wt%] and gave an encouraging proton conductivity of 25 mS/cm at 80°C/100% RH (Table 2).

Conclusions and Future Directions

We have shown the ability to immobilize HPAs into a polymer-composite matrix of our design. The HPA-based composite PEMs have shown:

- Effective binding of silicotungstic acids (Wn-STA, n = 10, 11, 12) with select functional silanes.
- High Wn-STA loading [HPA/(PMG + X-Linker) > 150 wt%].
- High chemical stability (Fenton's reagent test).
- Good thermal stability (with reactive W12-STA).
- Good mechanical flexibility.
- Promising proton conductivity (25 mS/cm at 80°C/100% RH).

Our future directions will focus on the following:

- Understand the binding mechanism of HPA, especially lacunary structures, with functional

silanes and SiO₂ nanoparticles in the polymer matrix.

- Understand the proton conduction mechanism for the 3D cross-linked composite membranes in order to further improve proton conductivity at low humidity and elevated temperatures.
- Continue to improve/modify/optimize the current PEM composite formulation, fabrication, and processing conditions. New HPAs with higher proton diffusion coefficients (as measured by PFG-NMR) will be tested.
- Enhance thermal stability of PEMs in the 90-120°C range.
- Improve mechanical strength and flexibility.
- Reduce membrane thickness and improve film uniformity.

FY 2006 Publications/Presentations

- F.J. John Pern, John A. Turner, Jane Meng, and Andy M. Herring, "Sol-Gel SiO₂-Polymer Hybrid Heteropoly Acid-Based Proton Exchange Membranes," Symposium Proceeding (in press), MRS 2005 Fall Meeting, Boston, MA, Nov. 28, 2005.
- F.J. John Pern, John A. Turner, and Andrew M. Herring, "Hybrid Proton Exchange Membranes Based on Heteropoly-Acid and Sulfonic-Acid Proton Conductors," Symposium Proceeding (in press), 209th ECS Meeting, Denver, CO, May 10, 2006.
- John A. Turner, F.J. John Pern, Andrew M. Herring, and Steven F. Dec, "Advanced Fuel Cell Membranes Based on Heteropolyacids," DOE Hydrogen Program Review Meeting, Project ID: FC4, May 18, 2006.

TABLE 2. Proton Conductivity Obtained for the PEMs Fabricated in this Work

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	HSiW ₁₂ O _x	BSPP0	No	0.56	0.15		
2	HSiW ₁₂ O _x	PMG	Yes	0.81	6.9		
3	HSiW ₁₂ O _x	PMG	Yes	1.09	6.4, 10.46	2.41	0.85
4	HSiW ₁₂ O _x	PMG	Yes	1.05	7.56, 13.3	1.66	0.25
5	HSiW ₁₂ O _x	PMG	Yes	1.50	8.8		
6	HSiW ₁₂ O _x	PMG	Yes	1.54	15.57		
7	HSiW ₁₂ O _x	PMG	Yes	1.74	14.55	2.1	
8	HSiW ₁₂ O _x	PMG	Yes	1.74	19.17	3.81	
9B	HSiW ₁₂ O _x	PMG	Yes	1.74	22.28		
9C	HSiW ₁₂ O _x	PMG	Yes	1.74	21.15		
9D	HSiW ₁₂ O _x	PMG	Yes	1.74	25.45	[28.25 at 70°C/100%RH]	
Nafion 112	SO ₃ H				149.9	99.99	49.25

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