Hybrid inorganic-organic polymer composites for polymer-electrolyte fuel cells

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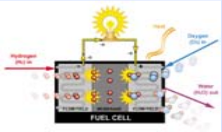
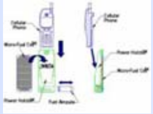
INTRODUCTION

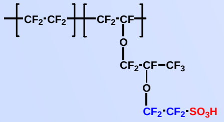
Polymer Electrolyte Membrane (PEM) Fuel Cells

PEM fuel cells are currently the leading candidates for battery replacement in portable electronics and energy converters for automotive and stationary applications. One of the primary technical deficiencies of PEMs is their poor performance at low relative humidities, due to poor proton transport in the polymeric membrane. Because of these humidity limitations, fuel cells utilizing organic polymer membranes can operate only at temperatures <100 ºC. The development of polymer electrolytes that can operate between 120-150 ºC and at lower relative humidities will result in more efficient fuel cell systems.





Current State of the Art Membranes: Nafion



Current Shortcomings:

- Proton conductivity is water dependent
- Polymer must remain hydrated
- Material cost ($700/m²)

Hydration requirements result in:

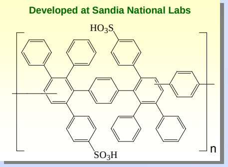
- Need for constant water supply
- More complicated cooling systems
- Operating temperature ≤ 100 °C
- Low catalyst efficiency

Advantages

- High proton conductivity
- Good mechanical properties
- Long fuel cell lifetime

Sulfonated Diels-Alder Poly(Phenylene) (SDAPP)

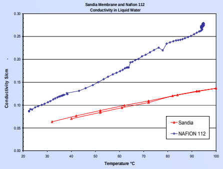
Fujimoto, C.H, Hickner, M.A., Cornelius, C.J., Loy, D.A.*Macromolecules* **2005**, 38(12), 5010-5016.



SDAPP polymers are:

- Thermal and chemically stable
- Less expensive than Nafion
- Chemically diverse
- Exhibit compositional control

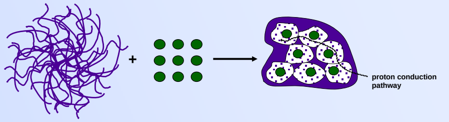
But their ionic conductivities are currently lower than those of Nafion



HYBRID ORGANIC-INORGANIC COMPOSITES

Approach

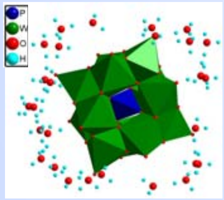
Combine the facile processability of organic polymers with the high temperature stability, functionality and structural reinforcement attributes of inorganic materials.



Benefits over current membranes:

Increased temperature stability | Improved conductivity
Improved water retention | Greater mechanical strength

Heteropolyacids (HPA)



- Inorganic "superacids" that conduct protons
- Consist of $[XM_{12}O_{40}]^{-y}$ "Keggin" clusters (X = P, Si; M = Mo, W, V; 3≤y≤6) balanced by monovalent cations, including H^+
- Proton conductors: σ (rt) = 170 mS/cm for $H_3PW_{12}O_{40}$[1]
- In hydrated form, can be coordinated to up to 29 H_2O molecules, some of which they can retain at temperatures above 200 °C
- Can be functionalized

(1) Honma, I.; Nomura, S.; Nakajima, H., J. Membrane Sci. 2001, 185, 83.

Phosphotungstic Acid (PWA)	$H_3[PW_{12}O_{40}]\cdot nH_2O$
Phosphomolybdic Acid (PMA)	$H_3[PMo_{12}O_{40}]\cdot nH_2O$
Silicotungstic Acid (SWA)	$H_4[SiW_{12}O_{40}]\cdot nH_2O$
Silicomolybdic Acid (SMA)	$H_4[SiMo_{12}O_{40}]\cdot nH_2O$

Hybrid Film Synthesis

Co-cast: HPA and protonated SDAPP were dissolved individually in dimethylacetamide solvent. The solutions were mixed together, stirred for several hours, cast, and dried in a vacuum oven at 40 °C/12 h and 60 °C/12 h. Cast films were stored in a Ziploc bag with a small amount of DI H_2O to keep the film hydrated.

SDAPP film

Imbibed: Protonated SDAPP films were soaked in H_2O/HPA solutions of various weight % for 48 hours at room temperature. Films were stored in a Ziploc bag with some of the HPA/H_2O mother solution.

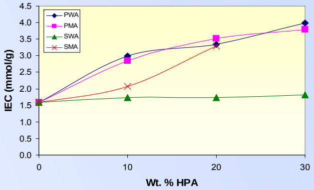
CHARACTERIZATION

Ion Exchange Capacity (IEC)

IEC was determined by titration of acidified films. Films were soaked in 1.0 M Na_2SO_4 for 24 h.The solutions were then titrated to an end point of pH 7 with 0.005 M NaOH. The IEC of the film was computed by

$$IEC = V_{base}[NaOH] / m_{dry}*0.001$$

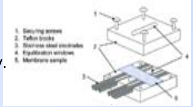
where V_{base} is the volume of base required to reach the endpoint, [NaOH] is the concentration of the base, and m_{dry} is the mass of the dry polymer.



IECs of co-cast films doped with various HPAs.

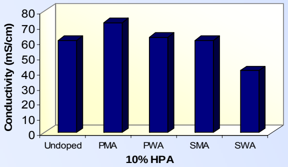
Conductivity

The ionic conductivity of fully-hydrated membranes was measured in water at room temperature by two-probe electrochemical impedance spectroscopy. Proton conductivity is computed by:

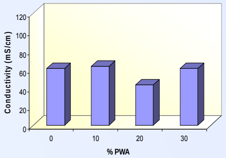


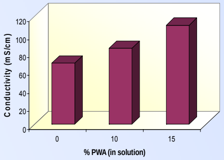
$$\sigma = L / Z' A$$

where L is the length between the sense electrodes, Z ' is the real part of the impedance response (extrapolated to Z" = 0), and A is the area available for proton conduction (width x thickness).



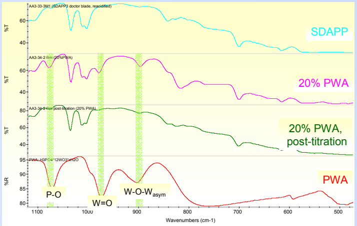
Above: Conductivity of films co-cast with various HPAs (10 weight %).
Bottom Left: Conductivity of films co-cast with various amounts of PWA.
Bottom Right: Conductivity of films imbibed in various solutions of PWA/H_2O.





CHARACTERIZATION (continued)

IR Spectroscopy



IR shows PWA present in the co-cast film, but much less is present after titration. This implies that some of the water-soluble HPA is leaching out of the film.

CONCLUSIONS

Summary

- SDAPP films doped with inorganic acids have the potential to act as PEM materials with higher conductivities at lower relative humidities
- IR shows that HPAs are most likely being leached from the film when soaked in water. This may account for increasing IEC values, but lower corresponding conductivities.
- Conductivities of films imbibed in HPA solutions have higher conductivities than films co-cast with SDAPP.

Future Work

- Determination of actual concentrations of HPAs in hybrid films (XRF)
- Temperature-stability measurements of doped films (TGA)
- Continued structural characterization (SEM, AFM)
- Covalent attachment of HPAs to SDAPP backbone in order to prevent leaching

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