

Strategies for the design and fabrication of membranes for fuel cells



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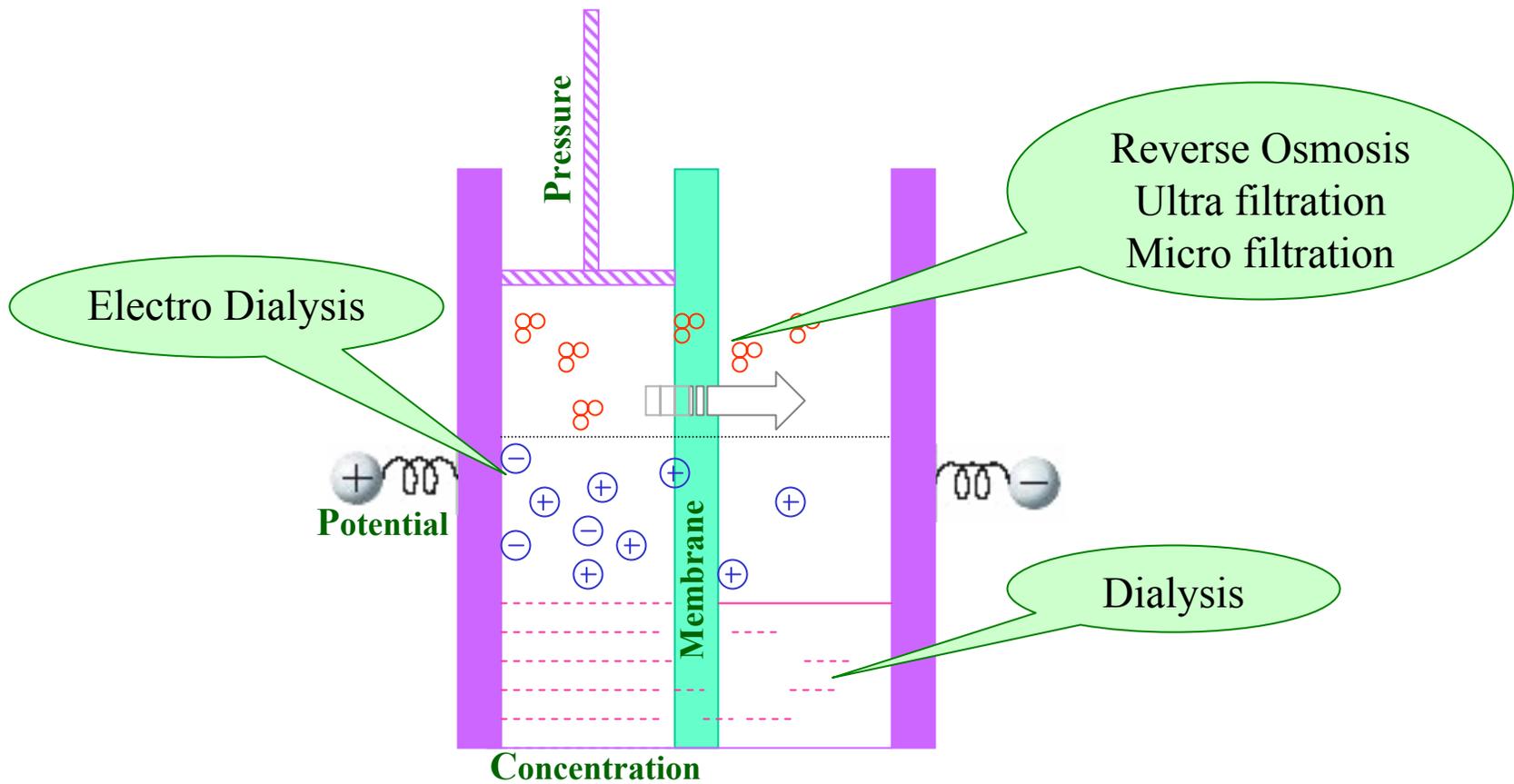


Why membranes are essential constituent of Fuel cells

- Separates the two electrodes
- Separates the two electrode reactions
- Prevents the mix up of reactants
- Allows the treatment of reactions as separate processes
 - no mixed kinetics



Schematic representation of membrane and processes therein



Pictorial representation of possible processes in a membrane



Role of membrane ?

In reverse osmosis, ultra filtration, micro filtration & dialysis

- To act as a molecular sieve

In electrochemical device

- To separate anode and cathode
- To prevent mixing of the fuel and oxidant
- To provide a conductive pathway



Membranes in electrochemical devices

- **Fuel cells** - Polymeric proton conducting membranes
- **Batteries** - Lithium ion cells - Amorphous polyethylene oxide (PEO)
- **Water electrolysis** - Bipolar ion exchange membranes
- **Sensor** - Polymeric membranes
- **Biosensors** – Lipid membranes, enzyme immobilized membranes

Role decides the type of membrane employed



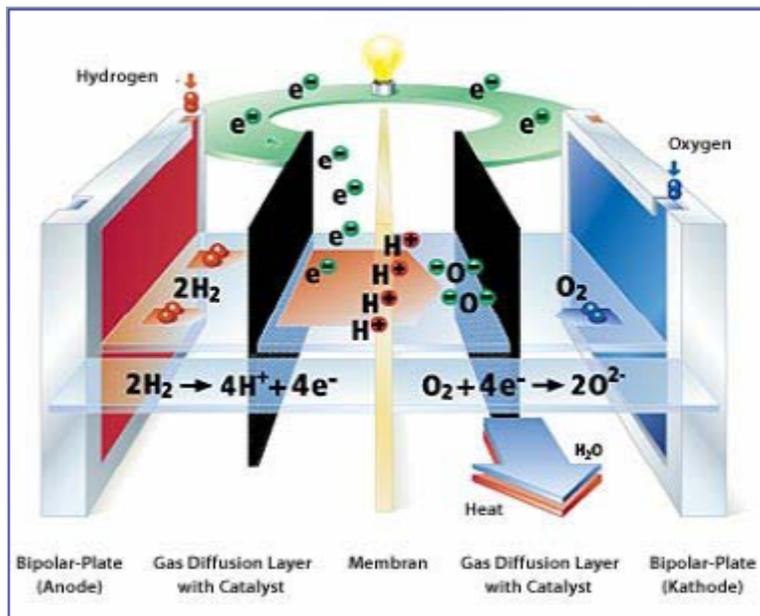
Required and desirable characteristics of membranes for fuel cell applications

- High ionic conductivity (and zero electronic conductivity)
- Long-term chemical stability at elevated temperatures in oxidizing and reducing environments
- Stable under the fuel cell potential window
- Good mechanical strength - resistance to swelling
- Low oxidant and fuel cross-over
- Low cost and ready availability



What Really Matters for Fuel Cell Commercialization?

Grand Challenges & Needed Breakthroughs for Fuel Cells



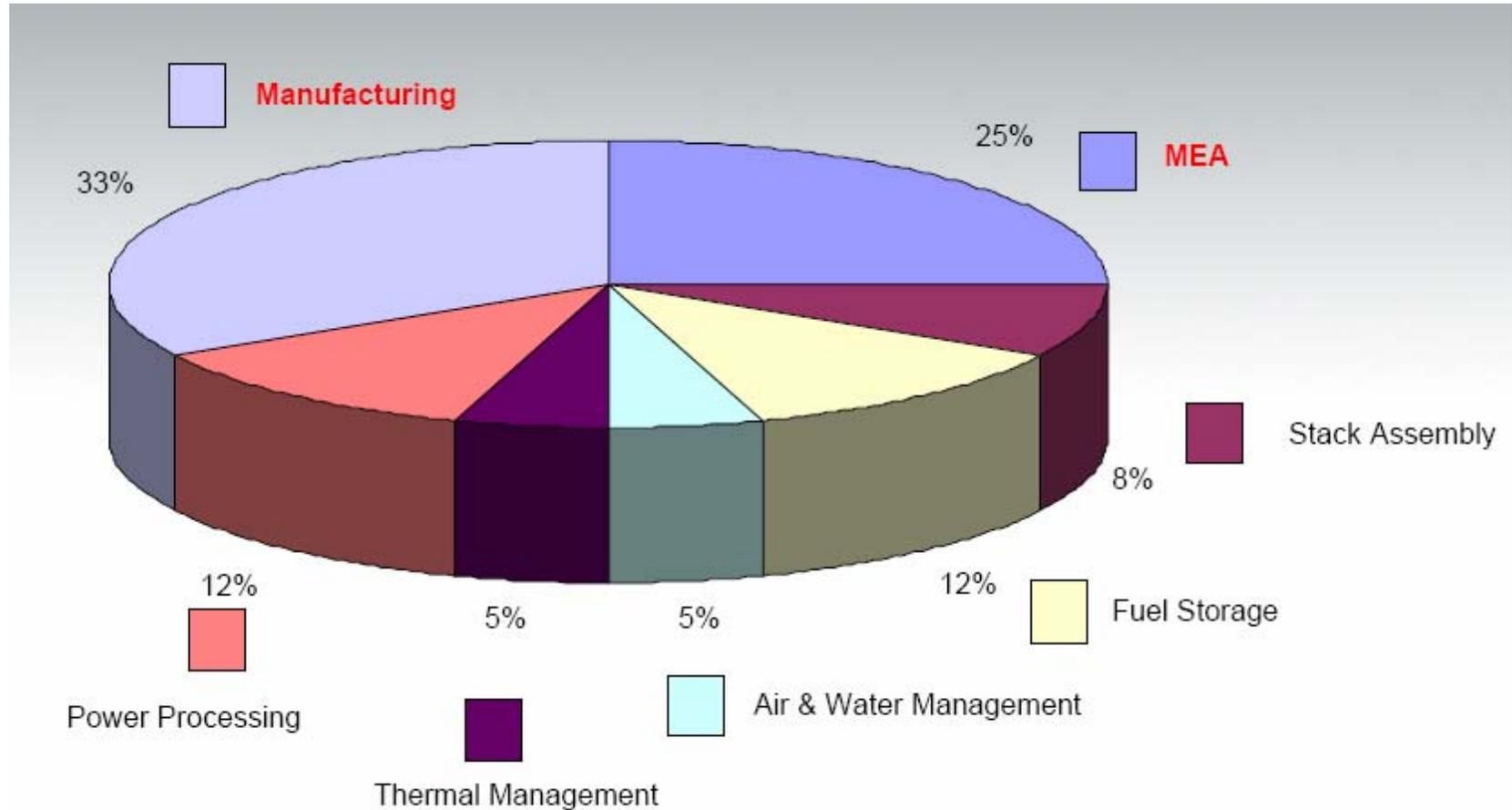
Grand Challenges

- Affordability (\$/kW)
- Durability (performance loss ~ time)

Needed Breakthroughs

- Adv. Catalysts
- Adv. PEM Material
- Innovative CCM/MEA mft.

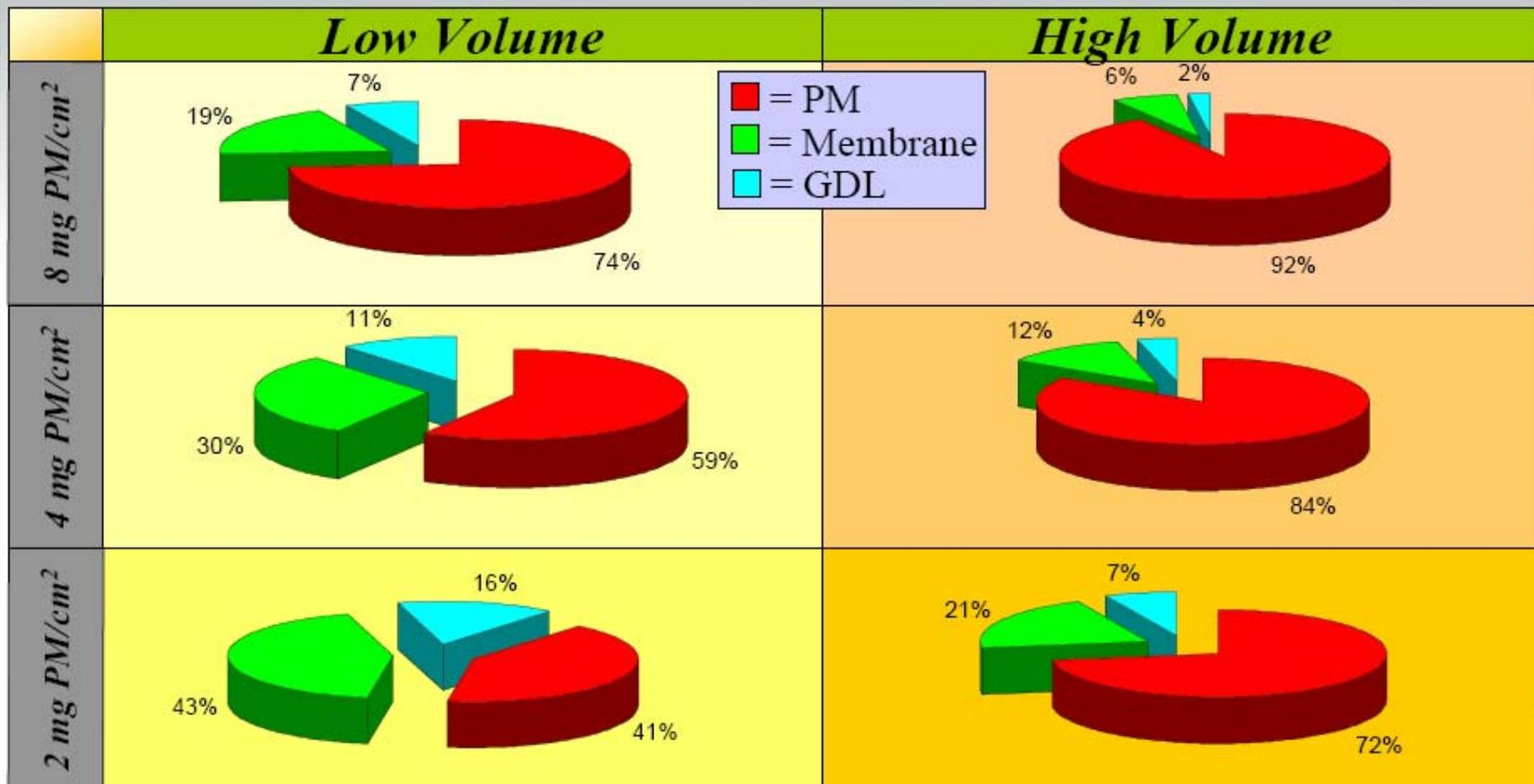
Cost breakdown for Automobile PEMFC Engine System





DMFC MEA Raw Materials Cost Analysis

■ Cost of Raw Materials/cm² of MEA



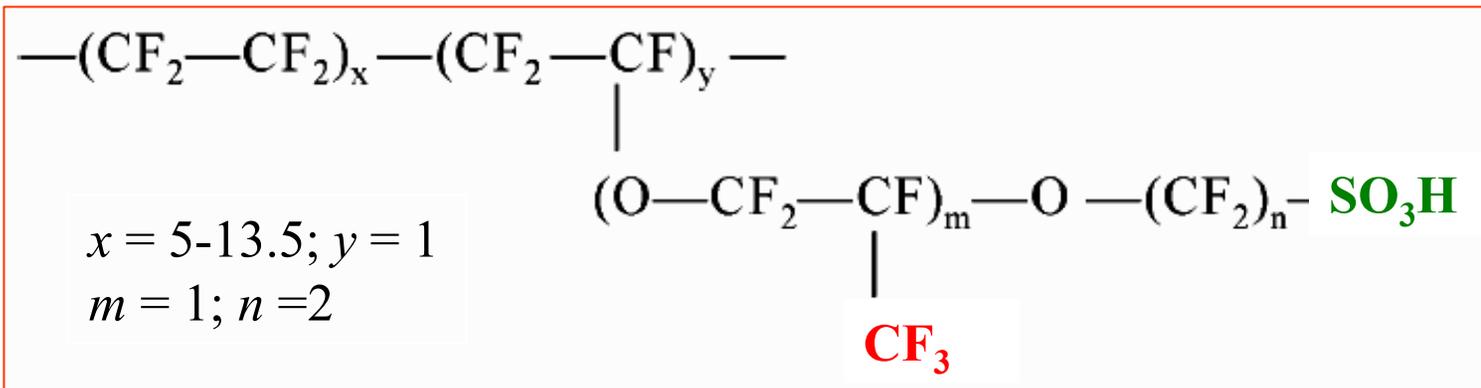
Challenges for Conventional CCM/MEA Technologies

- Non-uniformity of catalyst coating and limited catalyst utilization
- Random MEA hydrophobicity ~ hydrophilicity structure
 - *poor H^+ transportation*
 - *poor e^- transportation*
 - *poor water transportation*
 - *poor gas transportation*
- Limited FC performance
- High cost per kW





Nafion[®]

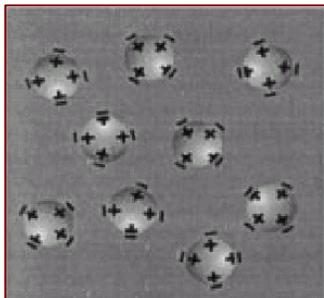


Advantages

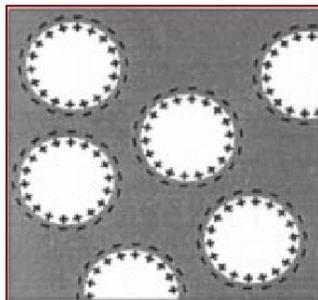
- Stable in both oxidative and reductive environments
- Excellent proton conductor (**0.07 - 0.23 S cm⁻¹ at 100 % RH**)
1M H₂SO₄ $\sigma = 0.08 \text{ S cm}^{-1}$
- Why Nafion[®] is so special as a membrane for fuel cells



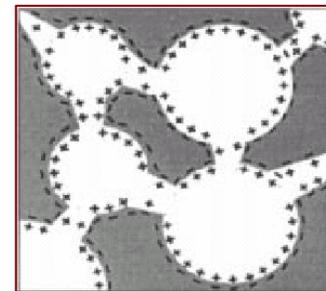
Simplified Nafion[®] structure according to water content



Dry state of PFSA



Water incorporated PFSA



Fully swollen PFSA

- Dry membrane is characterized by the presence of isolated spherical ionic clusters
- As water is absorbed in the membrane, its hydrophilic domain size increases – swells in water
- Swelling induces a modification of the cluster structure which become spherical water pools - in order to minimize the interfacial energy
- As more water is absorbed in the PFSA membrane, the cluster size is connected to each other through the water passage
- Water and hydrophilic solvents can penetrate the membrane through water channel and it can also provide the passage of protons - **Percolation**



Characteristics of Nafion[®] membranes

| Membrane | Dry thickness (μm) | Equivalent weight ($\text{gmol}^{-1}/\text{SO}_3^-$) | Area resistance ($\Omega\text{ cm}^2$) | Conductivity (Scm^{-1}) | Water content at 25°C |
|--------------------|------------------------------------|---|---|---------------------------------------|--------------------------|
| Nafion 105 | 125 | 1000 | - | - | - |
| Nafion 112 | 50 | 1100 | 0.07 | 0.165 | 20.7 ± 0.5 |
| Nafion 1135 | 89 | 1100 | 0.10 | 0.11 | 21.1 ± 0.6 |
| Nafion 115 | 125 | 1100 | 0.12 | 0.09 | 21.9 ± 0.6 |
| Nafion 117 | 175 | 1100 | 0.13 | 0.08 | 23.2 ± 0.4 |
| Nafion 1110 | 254 | 1100 | - | - | 38 |

Nafion *xyzz*'

xy - Equivalent weight/100

***zz*'** - Thickness x 25 μm



Characteristics of other commercial polymer membranes

| Membrane | Dry thickness (μm) | Equivalent weight ($\text{gmol}^{-1}/\text{SO}_3^-$) | Conductivity (Scm^{-1}) | Water content (wt %) | Manufacturer |
|--------------------|---------------------------------|--|------------------------------------|----------------------|----------------|
| Dow | 125 | 800 | 0.114 | 54 | Dow Chemical |
| Aciplex-S | 120 | 1000 | 0.108 | 43 | Asahi Chemical |
| Gore Select | 5-20 | 900-1100 | 0.028-0.096 | 32-43 | Gore |
| BAM 3G | 140(wet) | 375 -920 | N/A | 87 | Ballard |
| Flemion | 50 | 1000 | 0.14 | 38 | Asahi Glass |

General structure

A polymer containing anion groups(SO_3^-) on a polymer backbone or side chain (proton exchange membranes)

Why proton exchange membrane is essential ?



Limitations of Nafion®

- Dehydrates at $T > 80\text{ }^{\circ}\text{C}$ & $\text{RH} < 100\%$
- Diffusion of other species
- Lack of safety during its manufacturing and use (because of fluoro carbon)
- Expensive ($\sim 1000\text{ } \$/\text{m}^2$)



Modified PFSA membranes

- Thin and reinforced PFSA membranes
- Swelling with low volatile and non aqueous solvents
- Composites with hygroscopic oxides
- Composites with solid inorganic proton conductors like zirconium phosphates, heteropolyacids & metal hydrogen sulfate



Thin and reinforced PFSA membranes

- To decrease the internal resistance
- To reduce material cost

Nafion with porous polypropylene/polysulfone

- Thickness has been reduced to 5 - 30 μm
- Has good conductivity & mechanical properties
- Water management is improved

Drawback

- Reduced mechanical strength (under high temp & swelling)



Swelling with low volatile and non aqueous solvents

- Phosphoric acid (B.P: 158 °C) with Nafion achieved a conductivity of **0.05 S cm⁻¹** at **150 °C**
- Phosphoric acid acts as a Bronsted base & solvates the proton
- Allows high operational temperature >100 °C
- Imidazole (B.P: 255 °C) and benzimidazole (B.P: 360 °C) were also tried

Limitations

- No significant improvement in conductivity at low humidity
- Imidazole groups are not as water in solvating membrane acid groups



Composites with hygroscopic oxides

- SiO_2 and TiO_2
- Internal (self) humidification at low operational temperatures
- Water uptake:
 - Pristine Nafion - 27 wt %
 - Nafion containing 3 wt % SiO_2 - 43 wt %
- Conductivity in the range of **10^{-7} to $10^{-3} \text{ S cm}^{-1}$** at **$100^\circ\text{C}$**



Composites with solid inorganic proton conductors

- Bifunctional particles - both hydrophilic and proton conducting
- Inorganic proton conductors
 - Heteropolyacids
 - zirconium phosphates
- Decreases the **chemical potential** of water inside the membrane
- Provides H-bonding sites for water
 - Increase in hydration of the membrane
 - Decrease in water transport and evaporation



Nafion/HPA

Properties:

- Increased conductivity than Nafion : **$0.012 - 0.015 \text{ S cm}^{-1}$** at **35 % RH**
- Water uptake:
 - Pristine Nafion - 27 wt %
 - Nafion/HPA - 95 wt % (Due to increase in protonic sites of the membrane)

Drawbacks:

- HPA is highly water soluble eventually leaches out from PEM
- Decreased tensile strength ($\sim 14 \text{ kPa}$ whereas Pristine Nafion $\sim 40 \text{ MPa}$)



Nafion/ α -ZrP

Properties:

- Water insoluble
- Has intercalated hydronium ions with conductivity of **0.1 S cm⁻¹** at **100 °C** at **100% RH**
- Enhanced performance is due to increased water retention capability
 - Replacement of unassociated pore water with hydrophilic α -ZrP nanoparticles
 - Capillary condensation effects due to the smaller dimensions of the free spaces in α -ZrP filled pores

Drawbacks:

- H⁺ transport properties depend upon humidity
- Water management is difficult



Alternate sulfonated polymer membranes

Fluoropolymers

Polysiloxanes

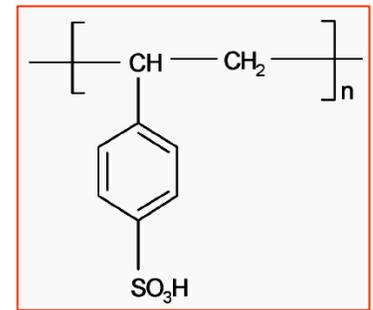
Aromatic polymers

Why?

- To lower the material cost
- To improve the operating temperature
- Polymers should have high chemical and thermal stability
- Alteration of conducting property
- Preferential transport characteristics



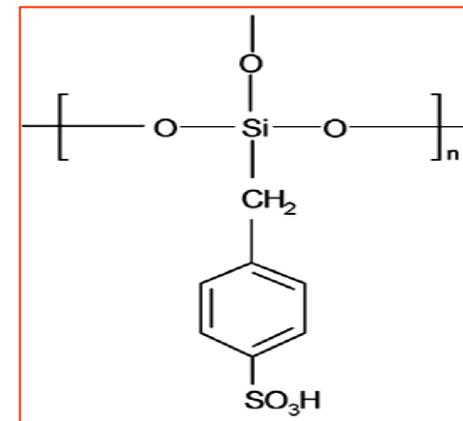
Fluoropolymers



- Sulfonated polystyrenes - first generation polymer electrolytes for fuel cells
- Suffers from a short lifetime – mechanical/chemical stability
- Partially fluorinated polymer
 - Poly(tetrafluoroethylene-hexafluoropropylene) (FEP)
 - Poly(vinylidene fluoride) (PVDF)
- Prepared by grafting and then sulfonating the styrene groups
- High water uptake & high proton conductivity



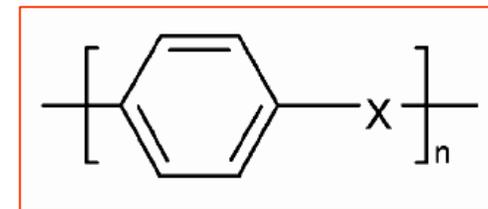
Polysiloxanes



- Organic modified silicate electrolyte (ORMOLYTE) by using arylsulfonic anions or alkylsulfonic anions grafted to the benzyl group were attempted
- Exhibit a proton conductivity of $10^{-2} \text{ S cm}^{-1}$ at **RT**
- Chemically and thermally stable up to 200 °C
- Water uptake alteration are possible



Aromatic polymers



- Cost effective and ready availability
- Good oxidation resistance of aromatic hydrocarbons
- Electrolyte for high temperature range ($> 100\text{ }^\circ\text{C}$)
- Investigated systems
 - polyetheretherketone (PEEK)
 - polysulfones (PSF) or Polyethersulfone (PES)
 - polybenzimidazoles (PBI)
 - polyimides (PI)
 - polyphenylenes (PP)
 - poly(4-phenoxybenzoyl-1,4-phenylene) (PPBP)

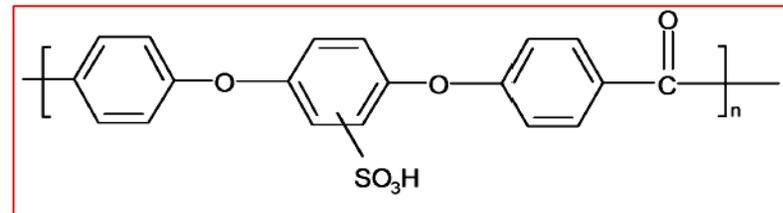


Sulfonation of polymers

- By direct sulfonation in concentrated sulfuric acid, chlorosulfonic acid or sulfur trioxide
- By lithiation-sulfonation-oxidation
- By chemically grafting a group containing a sulfonic acid onto a polymer
- By graft copolymerization using high energy radiation followed by sulfonation of the aromatic component
- By synthesis from monomers bearing sulfonic acid groups



Modification of S-PEEK



S-PEEK

- Has excellent thermal oxidation resistance with a glass transition temperature of 143 °C
- Conductivity, $\sigma_{100^\circ\text{C}} = 8 \times 10^{-3} \text{ S cm}^{-1}$ at 100 % RH

S-PEEK/SiO₂

- S-PEEK containing 10 wt% SiO₂ – Exhibited best mechanical and electrical characteristics ($\sigma_{100^\circ\text{C}} = 9 \times 10^{-2} \text{ S cm}^{-1}$)

S-PEEK/ZrO₂

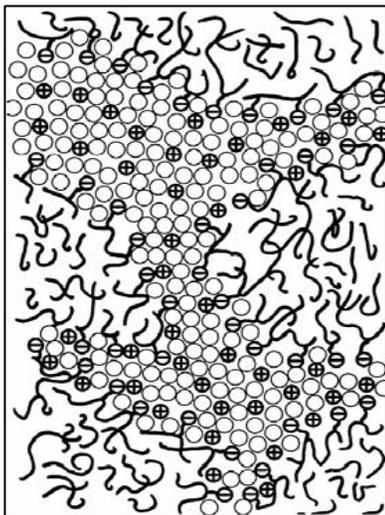
- S-PEEK containing 10 wt% ZrO₂ – Exhibited low permeability and good conductivity ($\sigma_{100^\circ\text{C}} = 4.5 \times 10^{-2} \text{ S cm}^{-1}$)

S-PEEK/HPA

- S-PEEK containing 60 wt% TPA – Increased glass transition temperature, humidity and conductivity ($\sigma_{120^\circ\text{C}} = 0.1 \text{ S cm}^{-1}$)

Microstructures

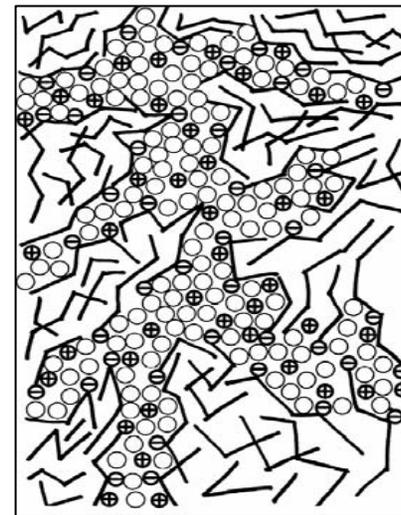
Nafion 117



\ominus : $-\text{SO}_3^-$
 \oplus : protonic charge carrier
 \circ : H_2O

- Wide channels
- More separated
- Less branched
- Small $-\text{SO}_3^- / -\text{SO}_3^-$ separation
- $\text{pK}_a \sim -6$
- $D_{\text{MeOH}} = 2.91 \times 10^{-6} \text{ cm}^2/\text{s}$

S-PEEK



- Narrow channels
- Less separated
- Highly branched
- Large $-\text{SO}_3^- / -\text{SO}_3^-$ separation
- $\text{pK}_a \sim -1$
- $D_{\text{MeOH}} = 6.57 \times 10^{-8} \text{ cm}^2/\text{s}$



Limitations of sulfonated polymers

- Highly deliquescent
- Hard to recover from solution
- Has a temperature limit at 200 °C
- H⁺ conductivity decays due to decomposition of the SO₃H groups
- High sulfonation results in high swelling and therefore poor mechanical properties



Acid-Base Polymer membranes

Two Approaches:

- Basic polymer with excess acid
- Acidic polymer with excess base (sulfonated polymer with absorbed imidazole, benzimidazole or another appropriate proton acceptor)

Basic polymers

Polybenzimidazole (PBI)

Poly-(ethylene oxide)s (PEO)

Polyvinyl alcohol (PVA)

Polyacrylamide (PAAM)

Polyethylenimine (PEI)

Nylon

Acids

H_3PO_4

H_2SO_4

HCl

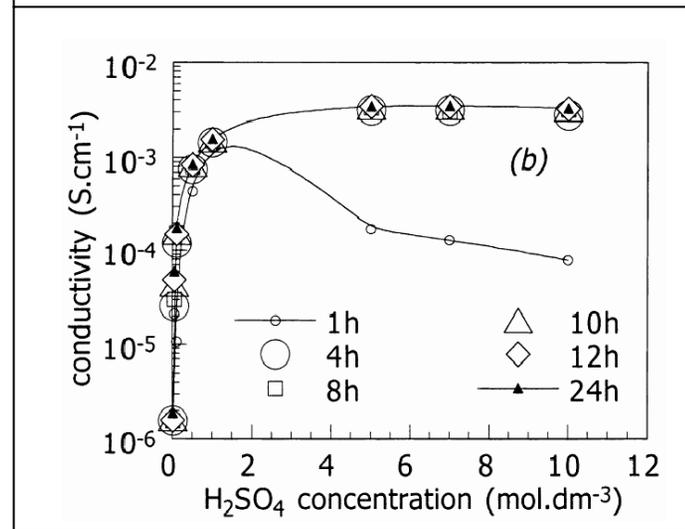
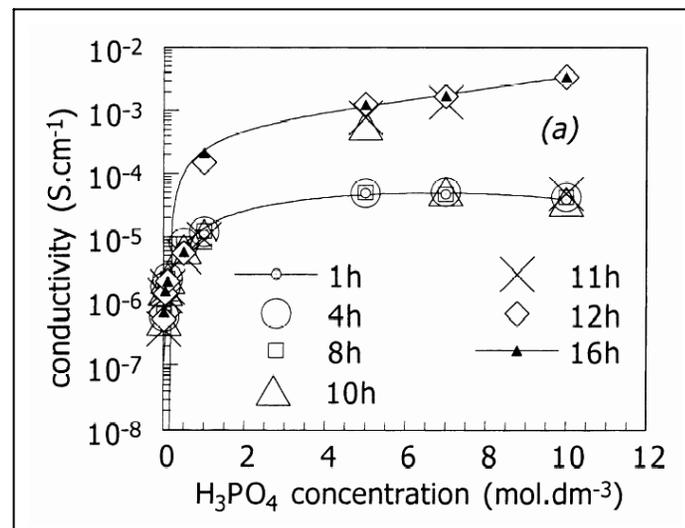
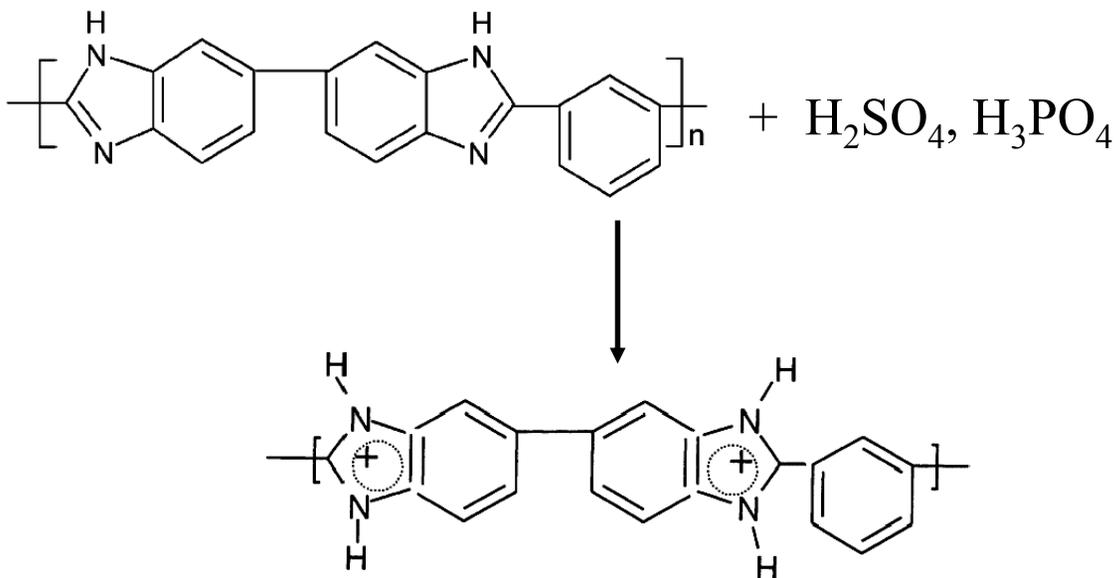
HNO_3

HClO_4



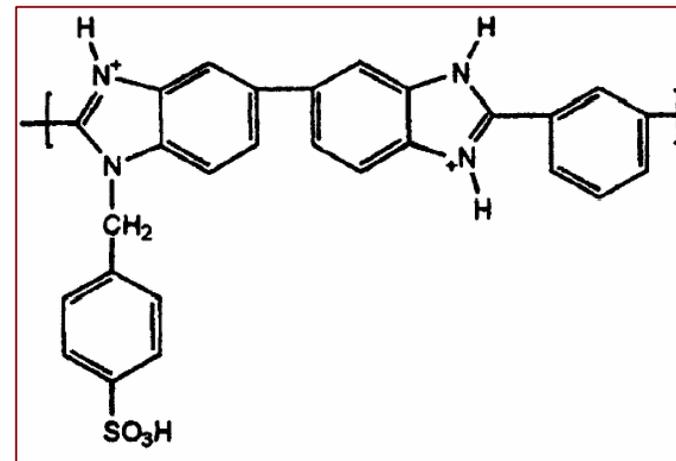
Acid doped polybenzimidazole (PBI)

- High thermal and mechanical stability
- Very low solvent permeability (electroosmotic drag ~ 0)





Doping with organic and inorganic bases



N-benzylsulfonate grafted PBI (PBI-S)

| Membrane | Conductivity (S cm ⁻¹) |
|--------------------------|------------------------------------|
| PBI-S | 4.2 x 10 ⁻⁴ |
| PBI-S/NH ₄ OH | 1.5 x 10 ⁻² |
| PBI-S/imidazole | 7.9 x 10 ⁻³ |
| PBI-S/LiOH | 1.2 x 10 ⁻² |
| PBI-S/NaOH | 1.2 x 10 ⁻² |
| PBI-S/KOH | 1.7 x 10 ⁻² |
| PBI-S/CsOH | 1.7 x 10 ⁻² |



Advantages

- High temperature oxidative stability of the blank PBI ($\sim 300\text{ }^{\circ}\text{C}$)
- Good chemical stability and mechanical properties of the blank PBI
- Exhibits good conductivity
- Ease of fabrication of the composite
- Less fuel (Hydrogen) cross-over than Nafion 117

Disadvantages

- Long-term stability and reliability based on composite PBI membranes must be proven
- Conductivity of PBI- H_3PO_4 is 10 times $<$ Nafion 117
- Diffusion of H_3PO_4 out of the PBI limit membrane performance



Inorganic Organic composite membranes

Justification:

- To improve self-humidification of the membrane
- To reduce the electro-osmotic drag
- To suppress fuel crossover
- To improve mechanical strength
- To improve thermal stability
- To enhance the proton conductivity



Organic component

Perfluorosulfonic acid (PFSA)

Poly-(ethylene oxide)s (PEO)

Polybenzimidazole (PBI)

Sulfonated polystyrene

Sulfonated polysulfone (SPSF)

Sulfonated polyetheretherketone (SPEEK)

Inorganic component

Oxides (Silica, titania & Zirconia)

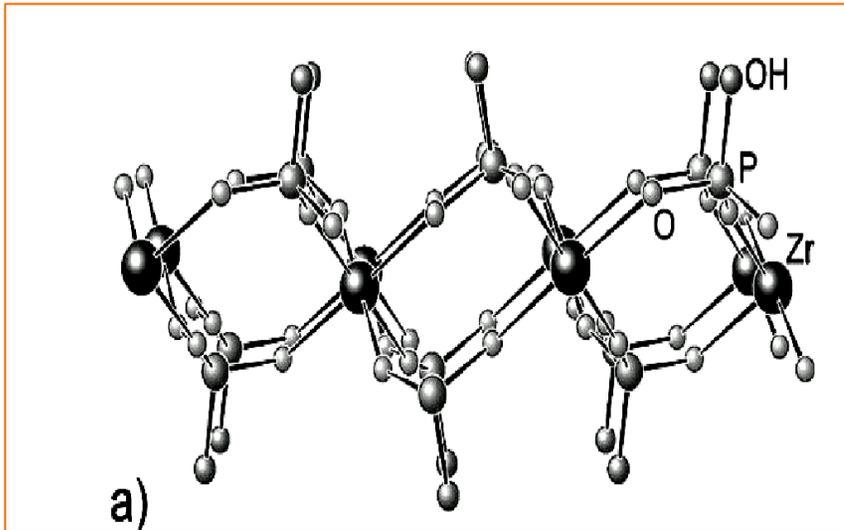
Inorganic proton conductors (zirconium phosphates, heteropolyacids, metal hydrogen sulfate)

Requirement - Stability under fuel cell operating conditions



Effect of adding an inorganic component to a polymer membrane

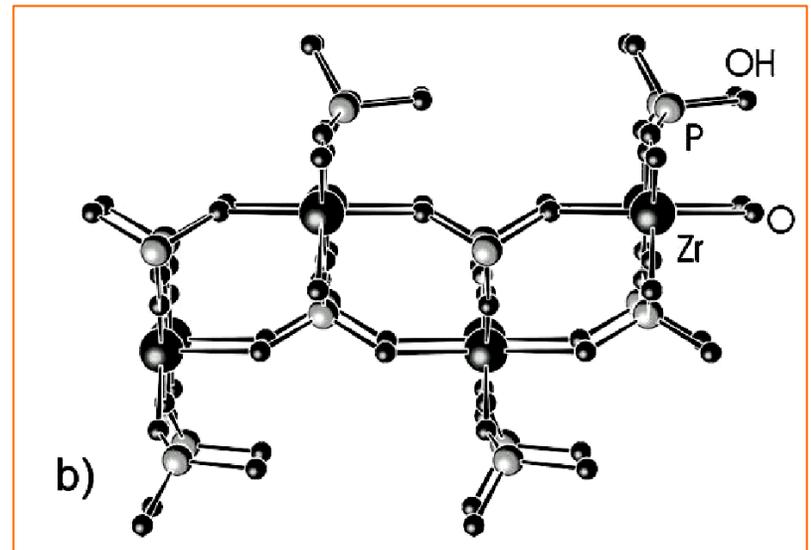
- Thermodynamic changes due to hygroscopic nature
- Changes in capillary forces and the vapour liquid equilibrium as a result of changes in the pore properties
- Surface charge interactions between the composite species
- Changes the morphology of the membrane
- Membrane architecture is possible
- Membrane casting conditions allowed



$\alpha\text{-Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$

- Exhibits H^+ conductivity upto 300 °C
- Transport mechanism is dominated by surface transport than bulk

Zirconium phosphates



$\gamma (\text{ZrPO}_4[\text{O}_2\text{P}(\text{OH})_2] \cdot n\text{H}_2\text{O})$



Attempts to enhance the proton conductivity

- Intercalation of functional groups (zirconium phosphate sulfophenylenphosphonate)
 - ✓ HPO_4 groups of the α -type $\text{Zr}(\text{HPO}_4)_2 \cdot n\text{H}_2\text{O}$ and the $\text{O}_2\text{P}(\text{OH})_2$ groups of γ -type $\text{ZrPO}_4\text{O}_3\text{P}(\text{OH})_2 \cdot n\text{H}_2\text{O}$ are replaced with O_3POR or $\text{O}_2\text{PR}'\text{R}$ - groups
 - ✓ R and R' are organic moieties containing a proton-generating function such as $-\text{COOH}$, $-\text{PO}_3\text{H}$, $-\text{SO}_3\text{H}$, or NH_3
- Composites α -ZrP membranes
- External surface area maximization (mechanical and colloidal synthesis)
- Internal surface area maximization (sol–gel synthesis and pillaring)



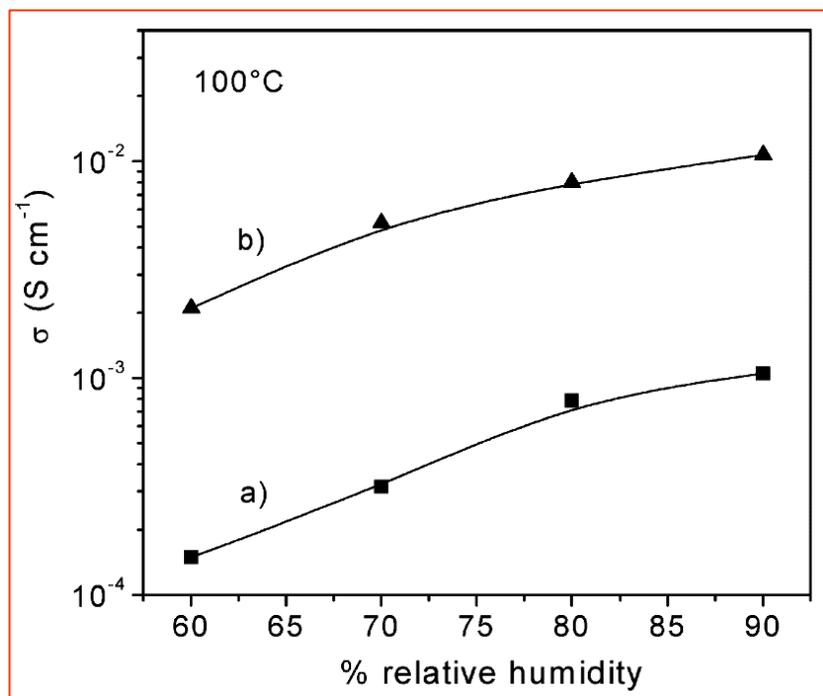
Intercalation of functional groups

| Layered ZrP and phosphonates | σ (S cm ⁻¹) at 100°C, 95% RH |
|--|---|
| α -Zr(O ₃ P-OH) ₂ · H ₂ O * | 1.8×10^{-5} |
| γ -ZrPO ₄ [O ₂ P(OH) ₂]. 2H ₂ O* | 2×10^{-4} |
| Zr(O ₃ P-OH) ₂ · nH ₂ O ¶ | $1-5 \times 10^{-3}$ |
| Zr(O ₃ P-OH) _{1.5} (O ₃ P-C ₆ H ₄ SO ₃ H) _{0.5} ¶ | $0.9-1.1 \times 10^{-2}$ |
| Zr(O ₃ P-OH)(O ₃ P-C ₆ H ₄ SO ₃ H) nH ₂ O § | $0.8-1.1 \times 10^{-1}$ |

* Crystalline; § Semicrystal: ¶ Amorphous



Composites α -ZrP membranes

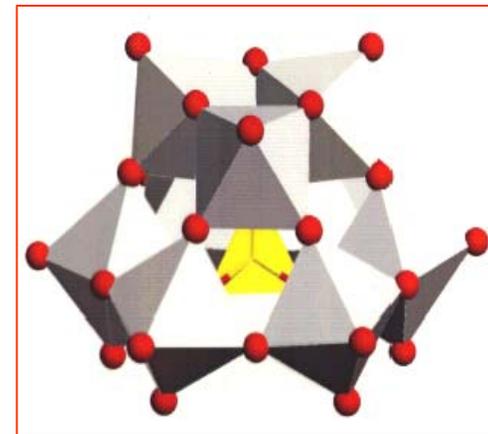


(a) s-PEK membrane (thickness 50 μm)

(b) s-PEK filled with 35 wt% of $\text{Zr}(\text{O}_3\text{P-OH})(\text{O}_3\text{P-C}_6\text{H}_4\text{SO}_3\text{H}).n\text{H}_2\text{O}$



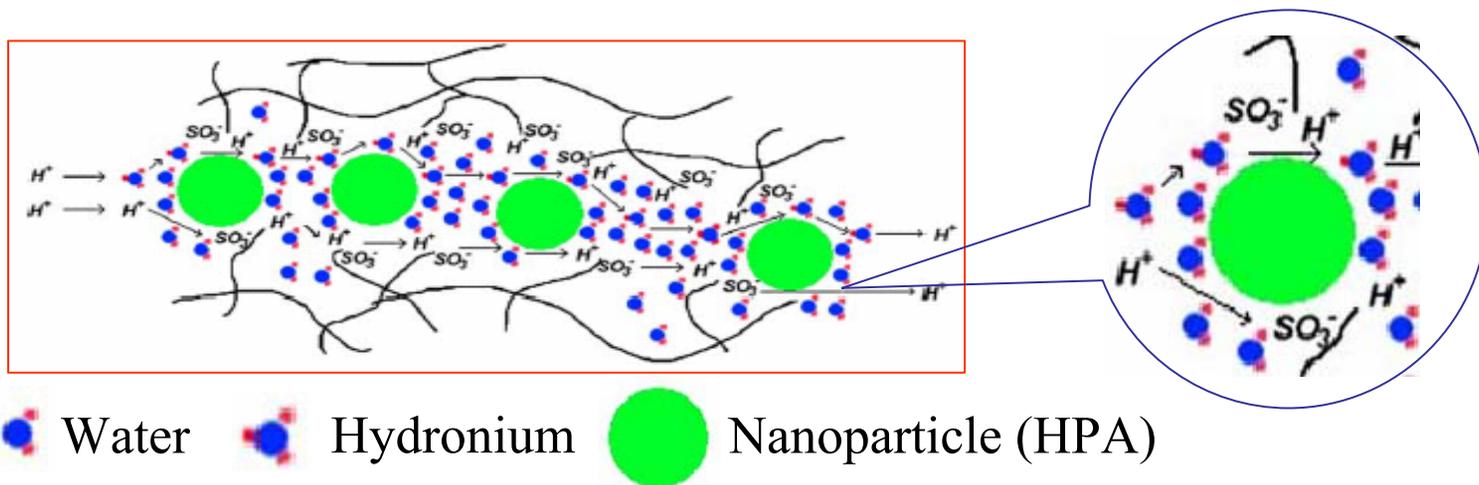
Heteropolyacids - $\text{H}_3\text{PM}_{12}\text{O}_{40}$ (cluster species)



- Exhibit high proton conductivities;
 - **0.18 S cm^{-1}** for $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 29\text{H}_2\text{O}$
 - **0.17 S cm^{-1}** for $\text{H}_3\text{PMo}_{12}\text{O}_{40} \cdot 29\text{H}_2\text{O}$
- Thermally stable at temperatures of interest, $< 200 \text{ }^\circ\text{C}$
- Greater water uptake, but decreased tensile strength than Nafion 117
- **Water soluble – need to be immobilized**



Proton transport in polymer/nano particle composite membranes



- Increases the swelling of the membranes at lower relative humidity
- Increases the resistance to fuel crossover
- Increases the proton transport through the water phase and reduces methanol permeability



Hydrogen sulphates, $MHSO_4$

M - Rb, Cs, or NH_4^+

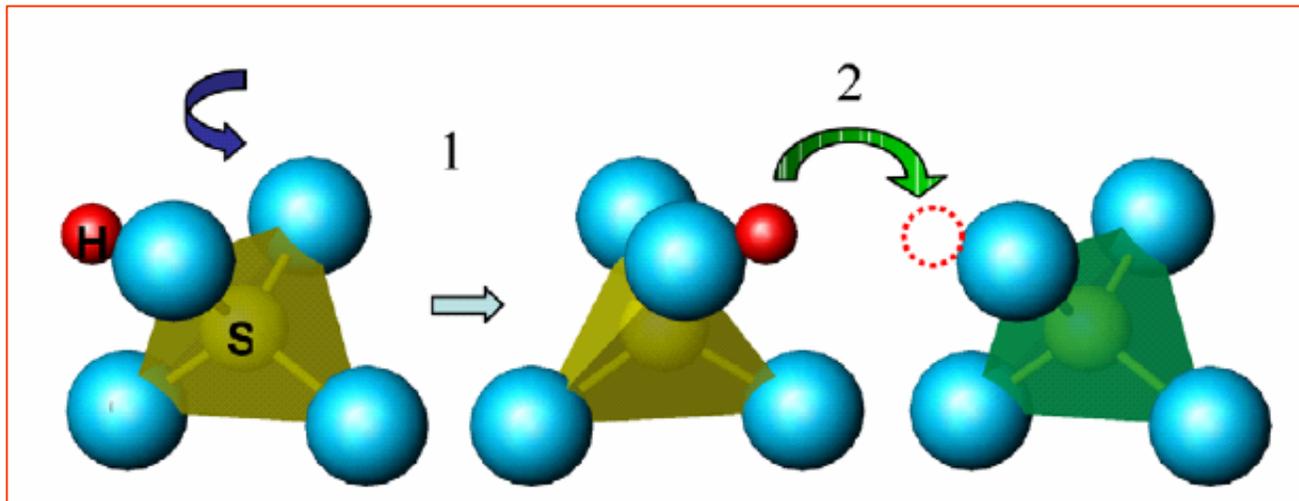
- H-bonded solid acids with disordered phases show high conductivity
- Upon slight heating changes to disordered structure
- Proton transport is due to reorientation of SO_4 groups in the disordered structure

Drawbacks

- Water soluble
- Poor mechanical strength
- Volume expansion at raised temperatures
- SO_4 reduced under H_2 atm



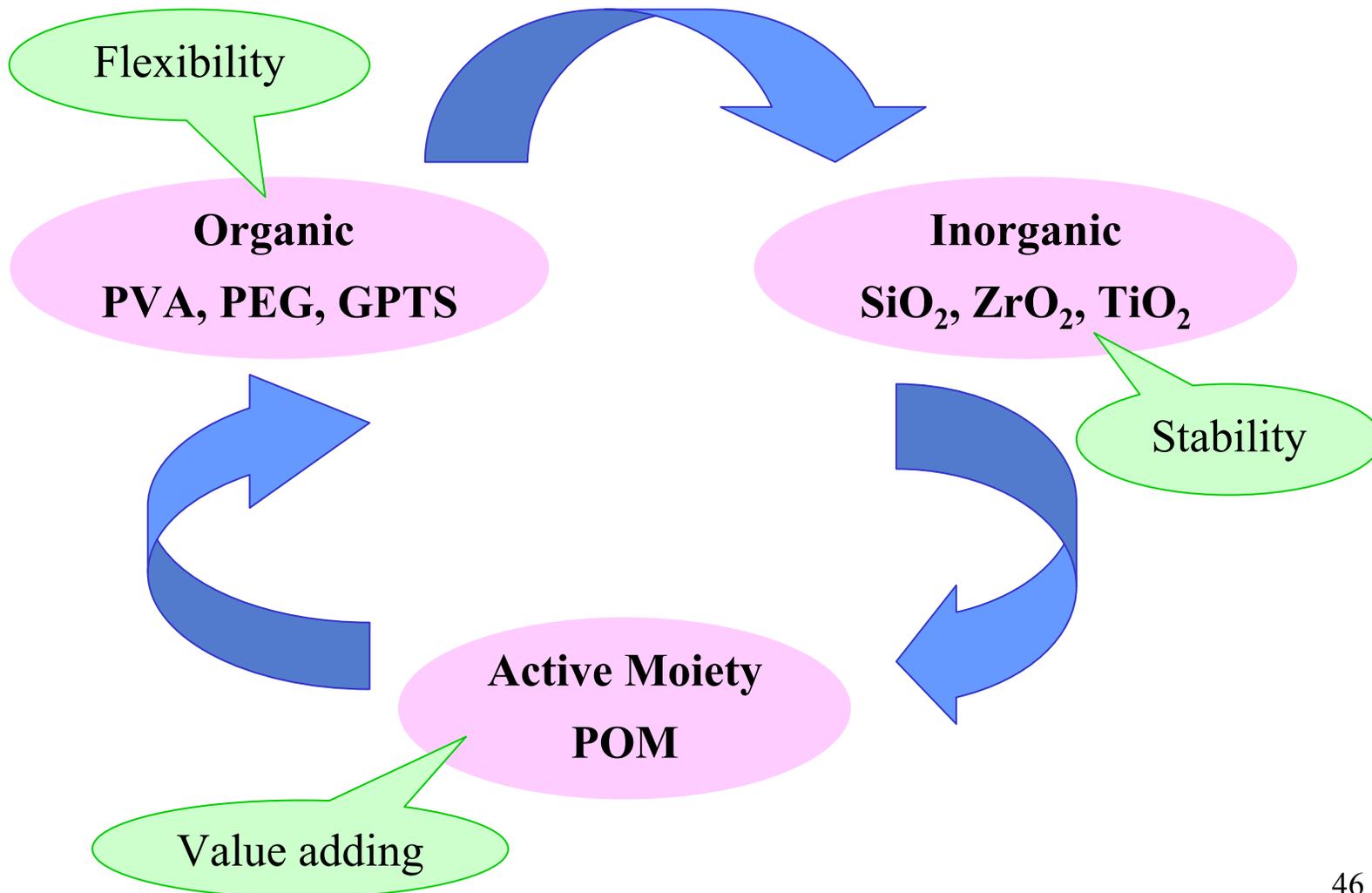
Proton transport mechanism in CsHSO₄



- CsHSO₄ consist of oxyanions, linked together through hydrogen bonds
- At 141°C it undergoes a “superprotonic” phase change (from monoclinic to tetragonal structure)
- Undergoes rapid reorientation - time scale 10^{-11} sec
- Proton conductivity **10^{-2} S cm⁻¹**

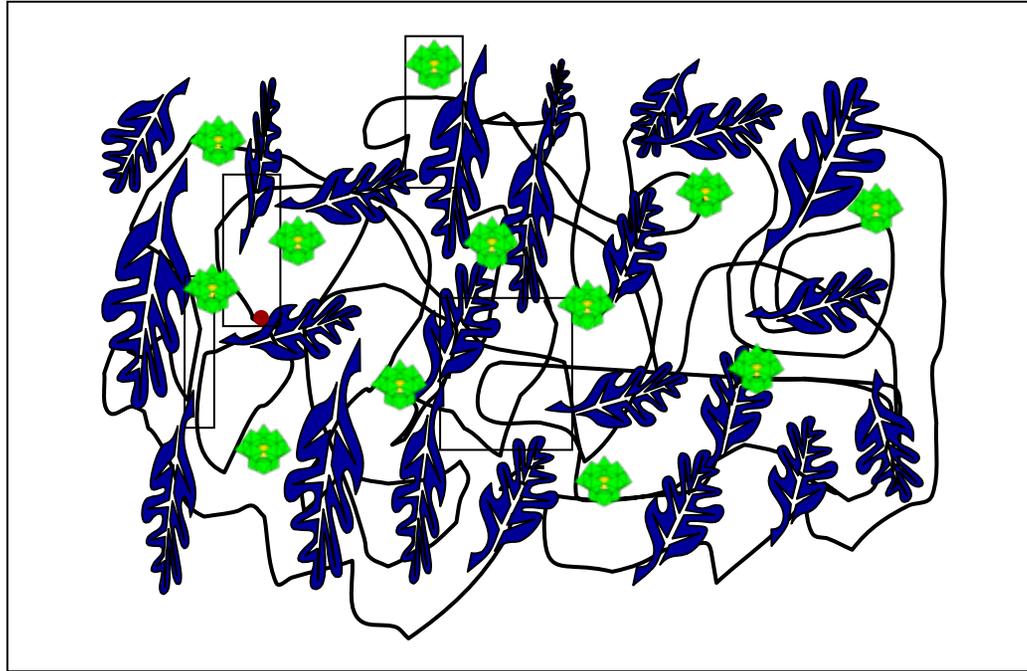


Hybrid Organic Inorganic Composite membranes





Conceptual representation of Hybrid Composite



POM



Polymer



Silica



Characteristics of Hybrid Inorganic-Organic Composites

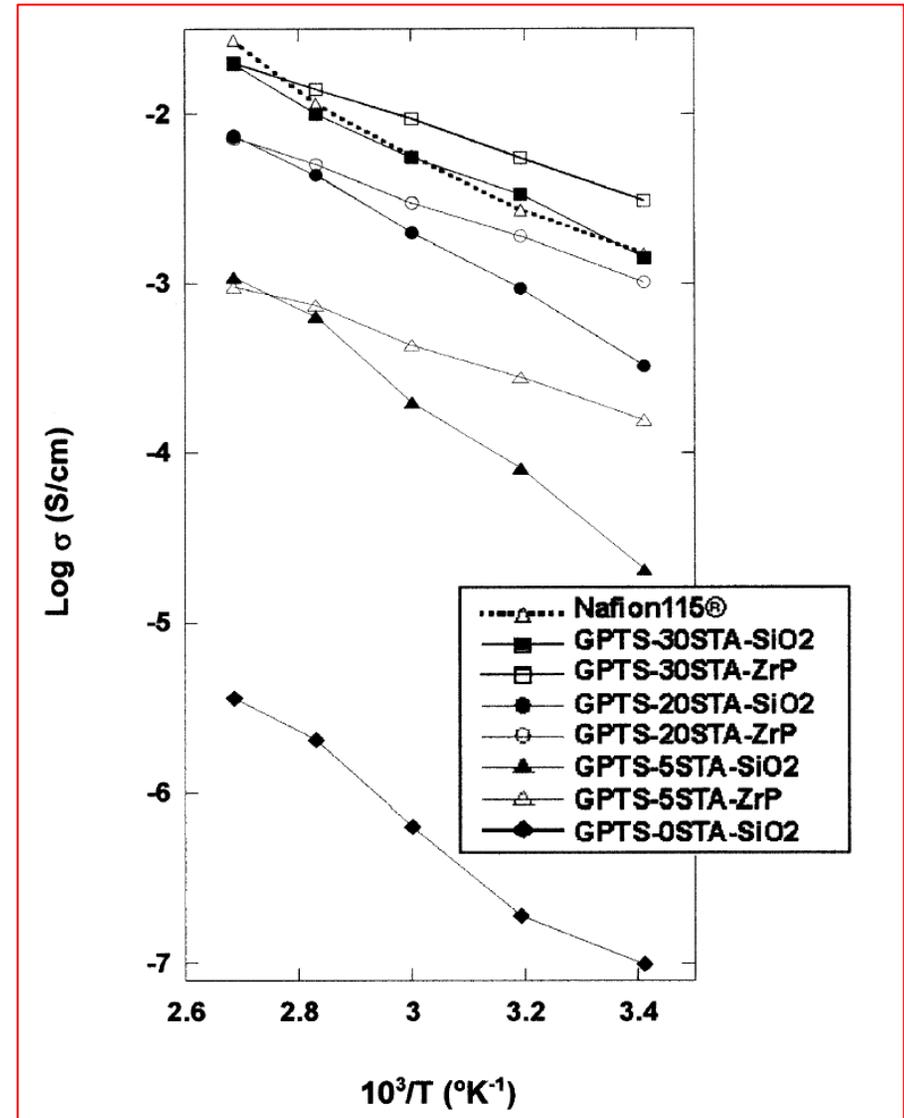
- Hybrid membranes – Isotropic, flexible, amorphous nanocomposite materials
- Material properties can be widely controlled
- Thermal stability can be improved
- The composite is flexible and homogeneous

Systems investigated

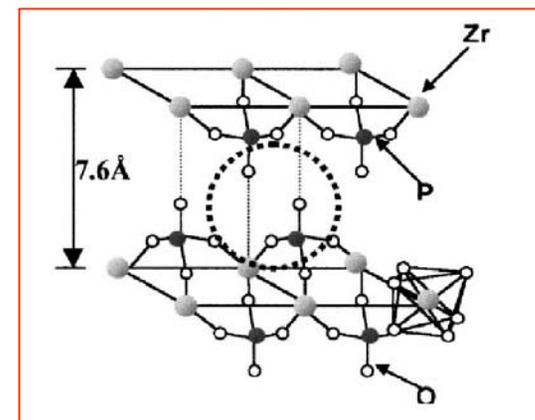
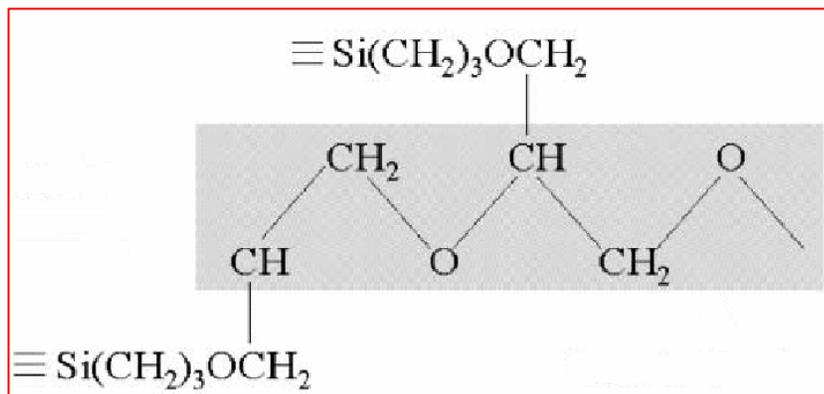
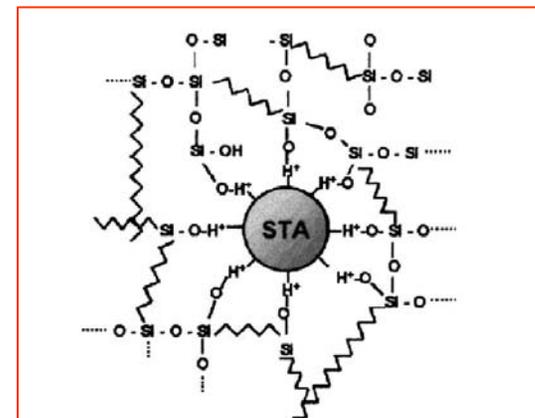
- GPTS*-STA[#]-SiO₂
- GPTS-SiO₂-ZrP
- GPTS-SiO₂, H⁺ conductivity **$1 \times 10^{-7} - 3.6 \times 10^{-6} \text{ S cm}^{-1}$** at **20 - 100°C**
- GPTS-SiO₂ with 30 wt% STA, H⁺ conductivity **$1.4 \times 10^{-3} - 1.9 \times 10^{-2} \text{ S cm}^{-1}$** at **20 - 100°C**
- GPTS-ZrP 30 wt% STA, H⁺ conductivity **$2 \times 10^{-2} \text{ S cm}^{-1}$** at **100°C**

*3-glycidoxypropyltrimethoxysilane

silicotungstic acid



- Inorganic additives enhanced **thermal stability and water uptake**
- The proton conducting path is through the pseudo-polyethylene oxide network



Challenges ahead for the development of membranes for DMFC

- Membranes with controlled methanol permeability represents a primary goal
- Nafion - Instability at $T > 80^{\circ}\text{C}$ & $\text{RH} < 100\%$, diffusion of other species and cost ($\sim 1000 \text{ \$/m}^2$)
- Alternative membranes - sulfonated polysulfones (PSU), polybenzimidazole (PBI), sulfonated polyetherketones (SPEK), & sulfonated polyetheretherketones (SPEEK)
- Sulfonation of these polymers leads to the formation of water-soluble polymers at high sulfonation levels
- **The procedure and the reaction conditions are sometimes extreme**
- Compromise needs to balance the hydrophilicity and the hydrophobicity



Why Hybrid Organic–Inorganic Composites?

- Hybrid organic–inorganic composites show **controllable physical properties** (thermal & mechanical) by combining the properties of both organic polymers and inorganic compounds
- Composite membranes - Proton conductivity of polymer electrolyte membranes can be considerably improved by incorporating fast proton conductors
- Fast proton conductors - Zirconium phosphate, Titanium phosphate, Calcium phosphate, Heteropolyacids, Boron phosphate (BPO_4)
- The strong interaction between the organic polymer and inorganic mineral is expected to result in a hybrid with markedly improved properties



Objective

- To develop a simple and controllable fabrication method
- To develop self-humidifying membrane
- To develop cost effective membrane with appreciable conductivity and thermal and mechanical stability



PVA-ZrP-SWA (10,20 & 30%) composite membranes

- PVA is cost effective polymer
- HPAs are generally water-soluble
- Composite matrix reduces the leaching of HPA
- Zirconium phosphate
 - suppress crack formation
 - mitigates HPA solubility
 - contributes to protonic conduction



Preparation of Zirconium phosphate

10 M H_3PO_4



1M $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$



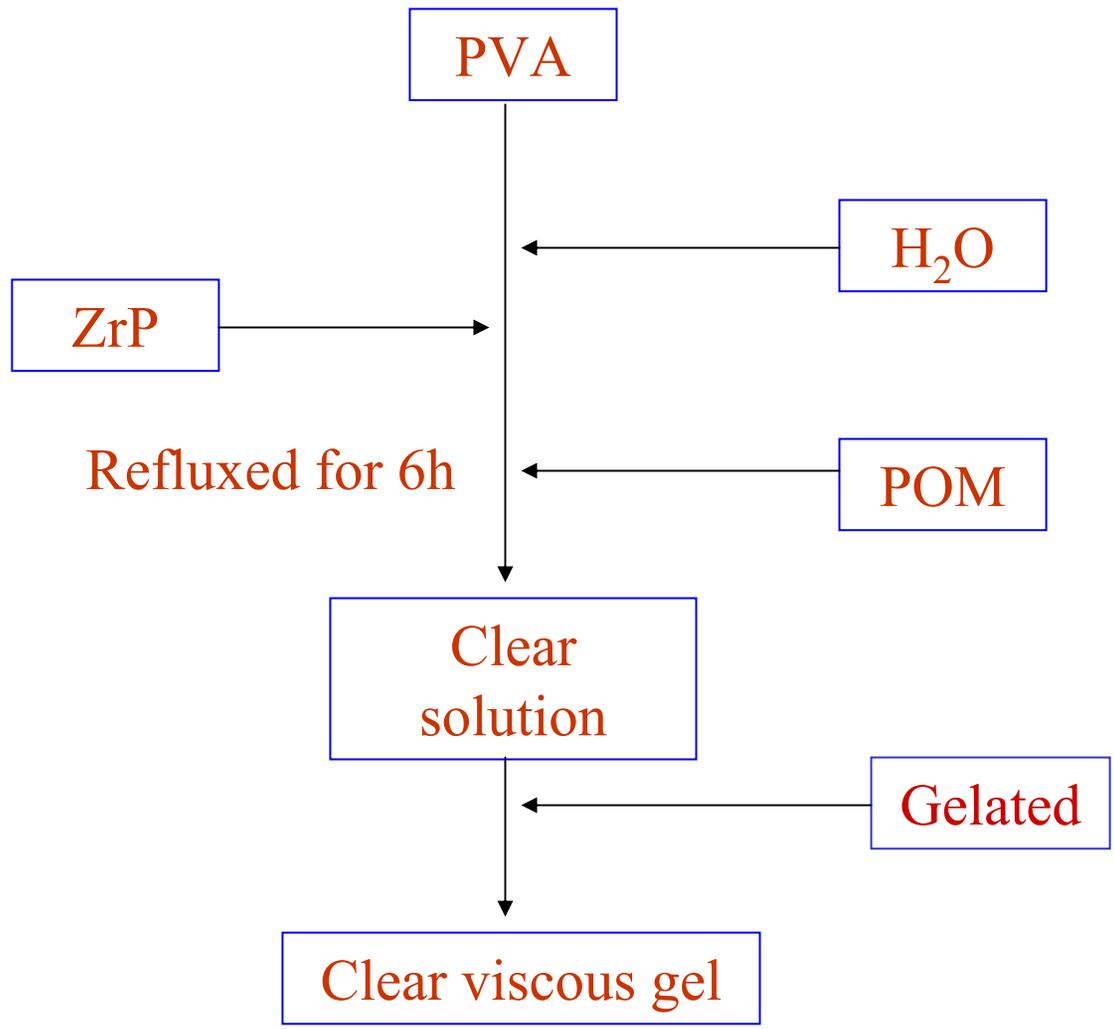
Stirred for 3 h

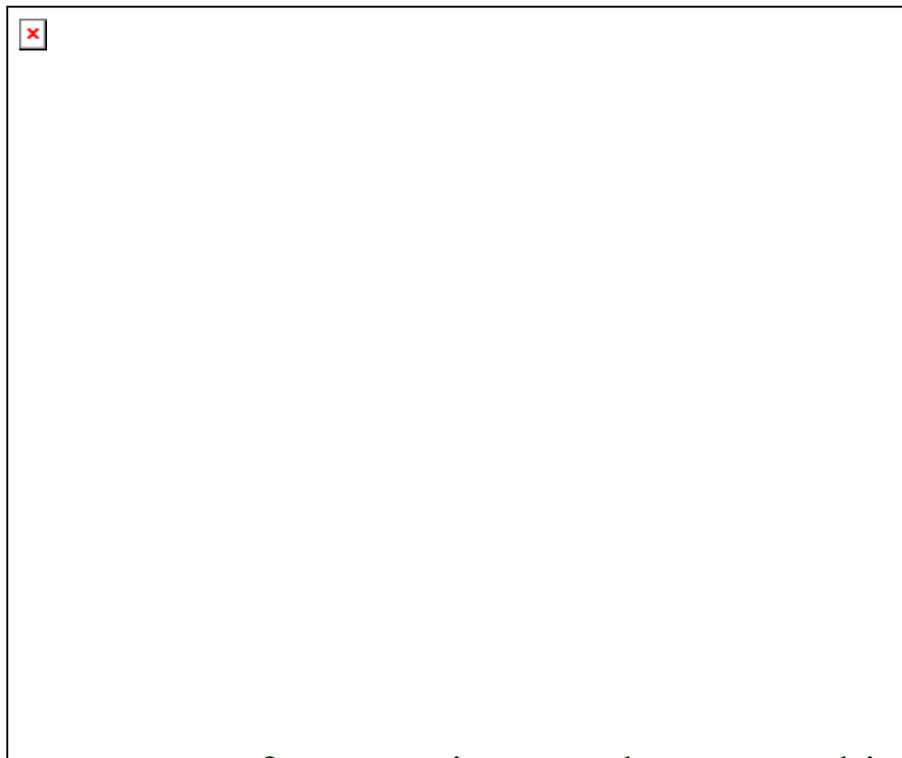
$\alpha - \text{Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$

Dried at 95°C for 2 h and stored at 100 % RH



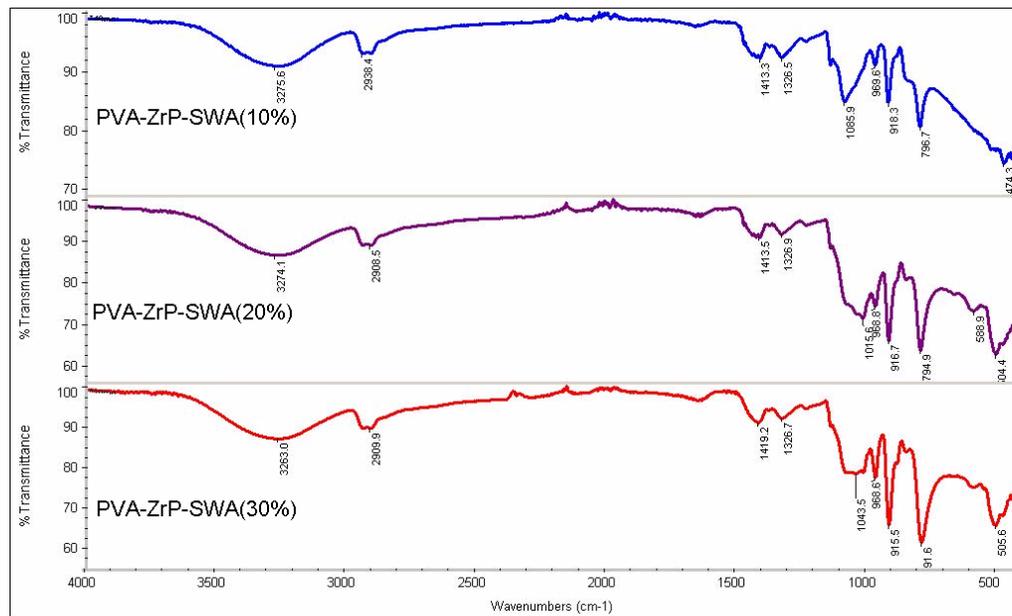
Preparation of PVA-ZrP-SWA composite





Cu K_α XRD patterns of composite membranes and its components for comparison

- $2\theta = 20^\circ$ corresponds to the (101) plane of PVA
- $2\theta = 20$ to 40° - overlap of the diffraction lines of ZrP and SWA
- **Absence of any sharp diffraction line - uniform distribution.**



FT-IR spectra of composite membranes

- Characteristic bands of PVA - 3260 cm^{-1} and 2900 cm^{-1} represent O-H stretching and -CH₂ stretching; 1420 cm^{-1} is for -CH₃ bending
- Characteristics of ZrP - 500 cm^{-1} and 1050 cm^{-1} are due to Zr-O and P-O₄ asymmetric stretching; 969 cm^{-1} is due to P-OH asymmetric stretching
- Band of W-Ob-W blue shift from 779 to 790 cm^{-1} ; W-O_t bond red shifted from 926 to 918 cm^{-1}



TGA analysis of composite membranes in a temperature range from 50 to 800 °C

- At 100 °C - loss of absorbed water molecules
- At 200-300 °C - decomposition of polyvinyl alcohol
- >300 °C - decomposition of silicotungstic acid to respective metal oxides combined with loss due to phase transition



Water uptake, swelling and IEC values for different hybrid membranes with a 250 μm thickness

| Membrane | Water uptake (wt %) | Swelling (%) | IEC(meq/g) |
|------------------|---------------------|--------------|------------|
| PVA-ZrP-SWA(10%) | 204 | 90 | 0.902 |
| PVA-ZrP-SWA(20%) | 388 | 170 | 0.958 |
| PVA-ZrP-SWA(30%) | 482 | 230 | 1.07 |

$$\text{IEC} = \frac{V \times M}{W_{\text{dry}}}$$

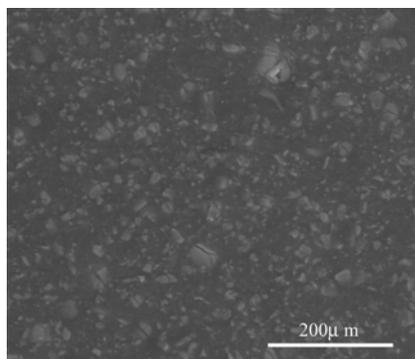
IEC - Ion-exchange capacity (meq g^{-1}),

V - Added titrant volume at the equivalent point (ml),

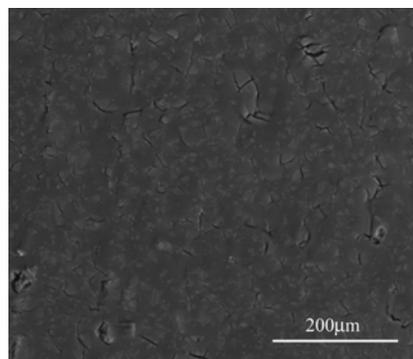
M - Molar concentration of the titrant &

W_{dry} -The dry mass of the sample (g)

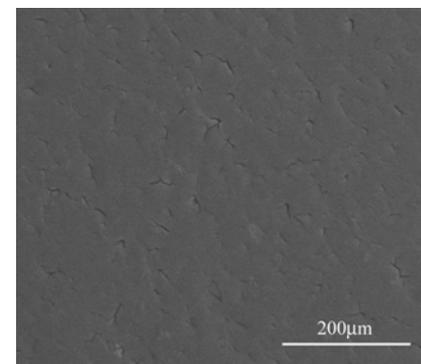
Surface morphology



PVA-ZrP-SWA(10%)



PVA-ZrP-SWA(20%)



PVA-ZrP-SWA(30%)



Proton conductivity at 60 % RH as a function of temperature

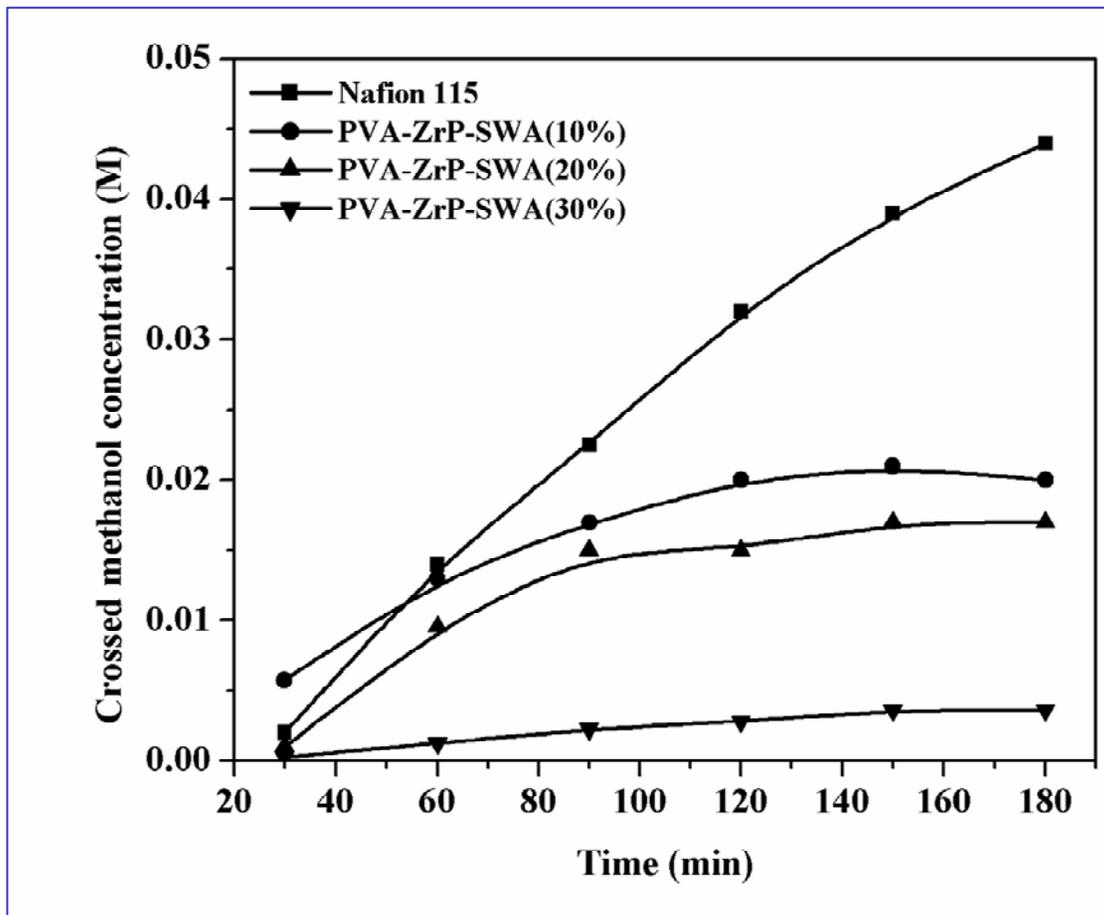
Frequency: 10 Hz to 1 MHz

Amplitude: 5 mV

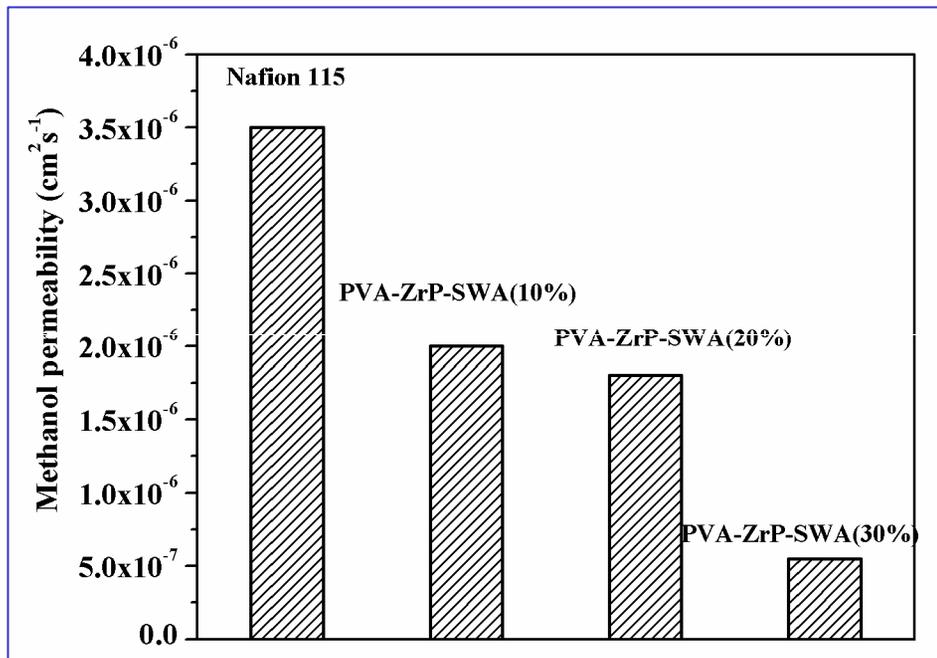
at 60 % RH



Methanol cross over studies



Concentration of crossed methanol as a function of crossover time



Methanol permeability of hybrid membranes compared with Nafion 115



PVA-ZrP-CsHPA (Cs salt of SWA) composite membranes

HPA solubility

- ✓ forming composites
- ✓ ion exchanging protons of HPA with larger cations like Cs^+ , NH_4^+ , Rb^+ and Tl^+



Preparation of salts of silicotungstic acid

Silicotungstic acid solution

Neutralized with cesium carbonate

Salts of silicotungstic acid

Dried at RT

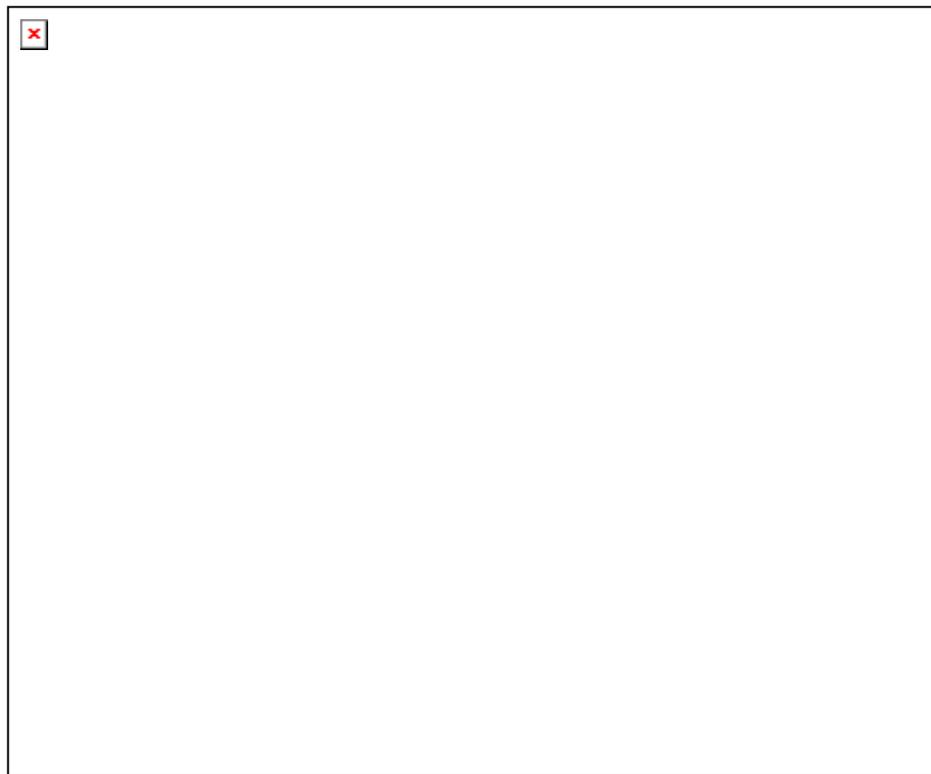
Crystal of Cs-SWA

Kept in constant-humidity air until constant mass was attained



Water uptake, swelling and IEC values for PVA-ZrP-Cs₁SWA and PVA-ZrP-Cs₂SWA hybrid membranes with a 180 μ m thickness compared with Nafion 115

| Membrane | Water uptake (%) | Swelling (%) | IEC (meq/g) |
|-----------------------------|-------------------------|---------------------|--------------------|
| PVA-ZrP-Cs ₁ SWA | 260 | 100 | 3.2 |
| PVA-ZrP-Cs ₂ SWA | 140 | 85 | 3 |
| Nafion [®] 115 | 22 | 12 | 0.9 |



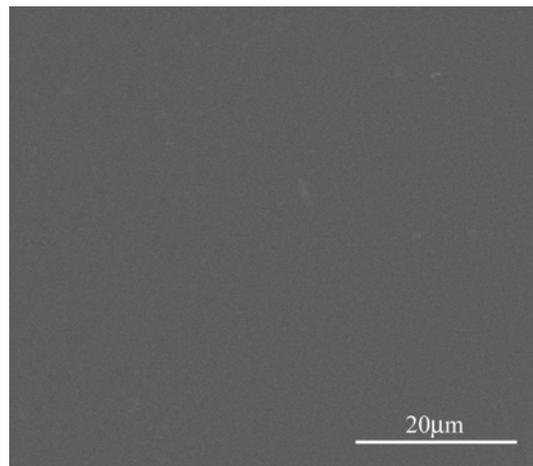
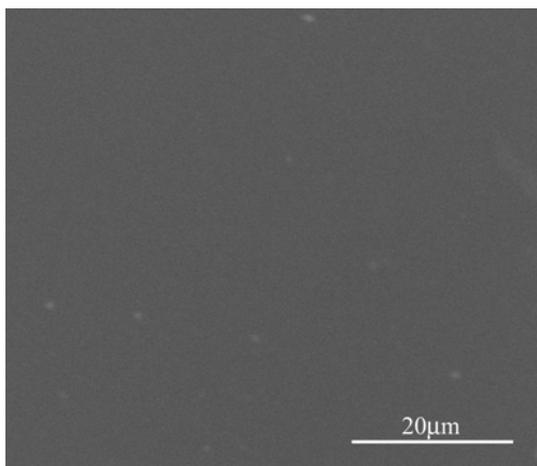
Cu K_α XRD patterns of PVA-ZrP-Cs₁SWA and PVA-ZrP-Cs₂SWA hybrid membranes

- The broad hump in the 2θ range 20 to 35 is due to the presence of PVA and zirconium phosphate

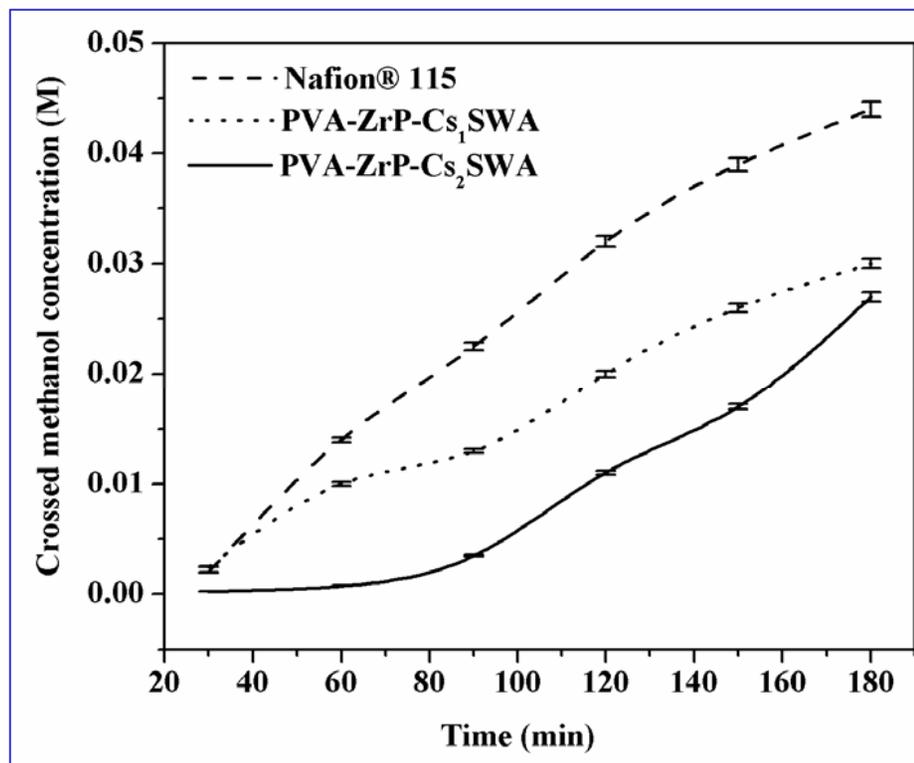


Assignments of main absorption bands for PVA-ZrP-Cs₁SWA and PVA-ZrP-Cs₂SWA hybrid membranes

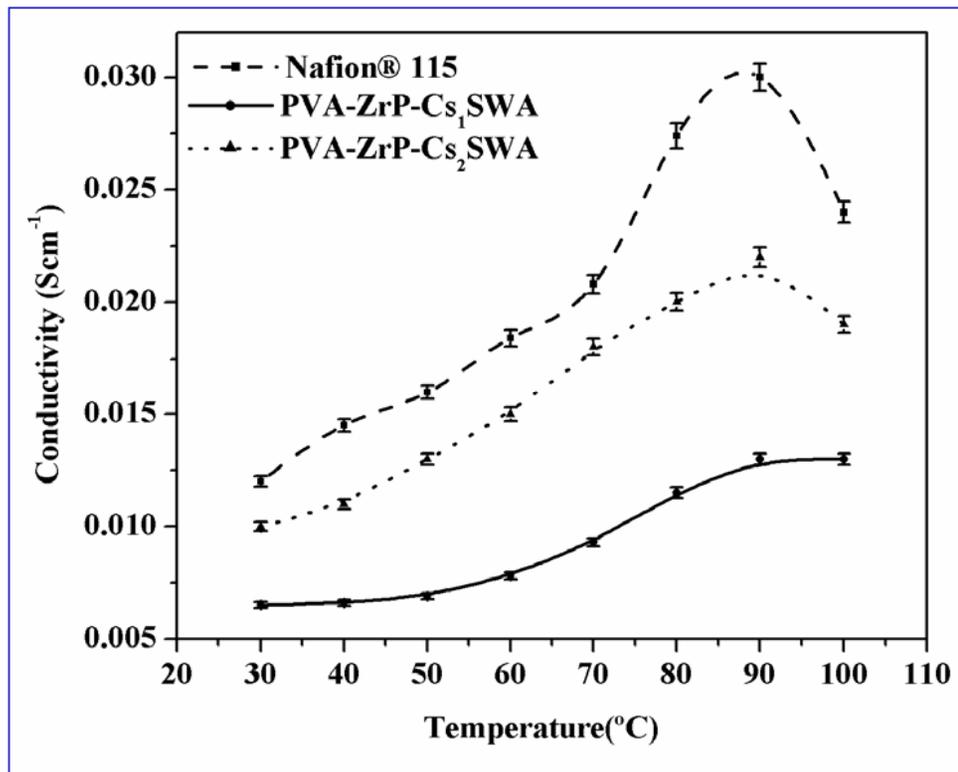
| Vibration frequency (cm ⁻¹) | | Bond Assignment |
|---|-----------------------------|---------------------------------------|
| PVA-ZrP-Cs ₁ SWA | PVA-ZrP-Cs ₂ SWA | |
| 981 cm ⁻¹ | 969 cm ⁻¹ | W=O ₊ stretching |
| 917 cm ⁻¹ | 916 cm ⁻¹ | X-O stretching |
| 876 cm ⁻¹ | - | corner sharing W-O _b -W |
| 744 cm ⁻¹ | 793 cm ⁻¹ | edge sharing W-O _b -W |
| 3274 cm ⁻¹ | 3257 cm ⁻¹ | O-H stretching |
| 2906 cm ⁻¹ | 2907 cm ⁻¹ | -CH ₂ stretching |
| 1426 cm ⁻¹ | 1413 cm ⁻¹ | -CH ₃ bending |
| 504 cm ⁻¹ | 525 cm ⁻¹ | Zr-O symmetric stretching |
| 1018 cm ⁻¹ | 1085 cm ⁻¹ | P-O ₄ symmetric stretching |



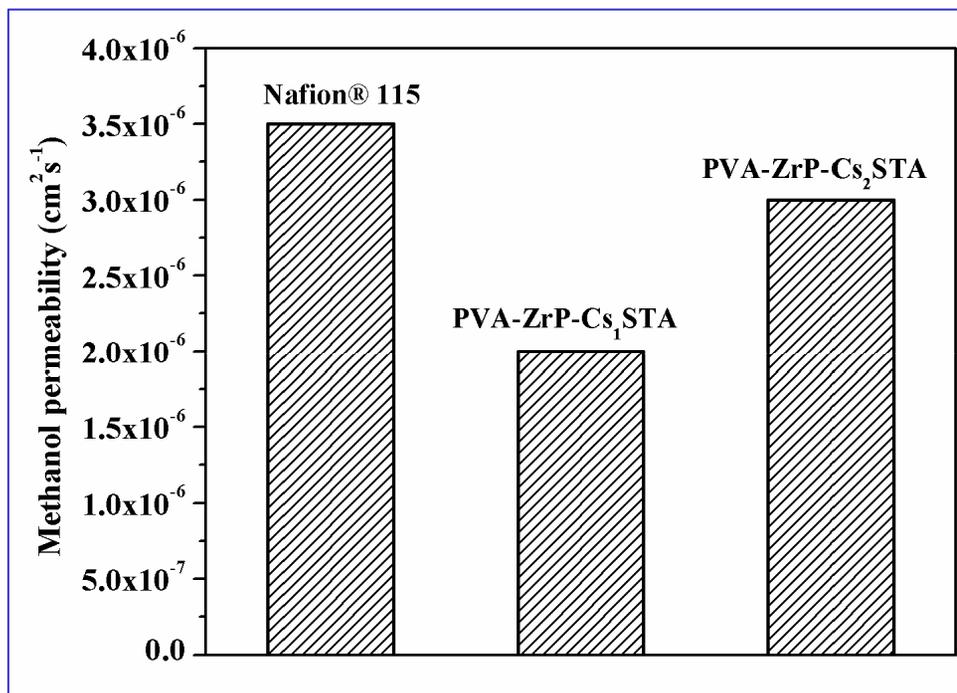
Scanning electron micrographs of PVA-ZrP-Cs₁SWA and PVA-ZrP-Cs₂SWA hybrid membranes



Concentration of crossed methanol as a function of crossover time



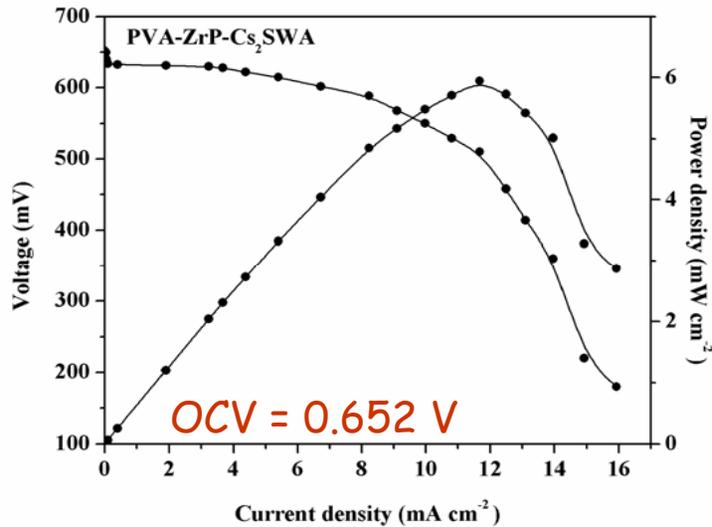
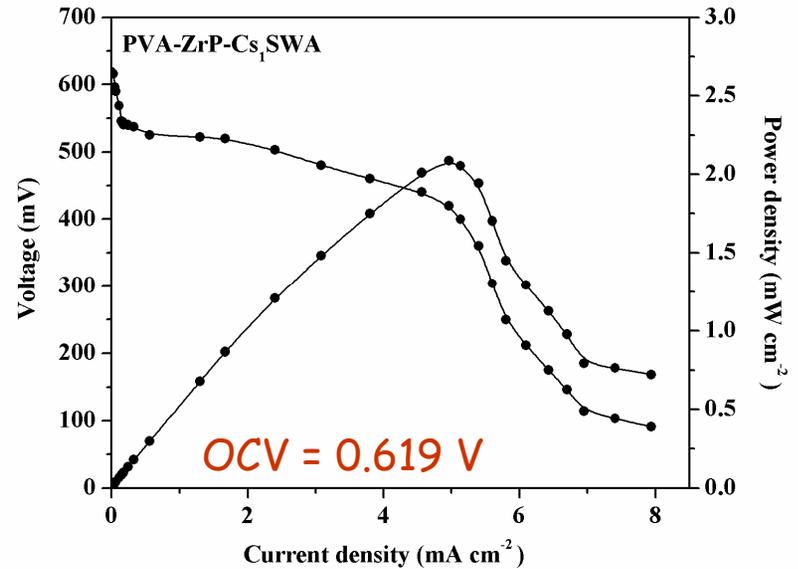
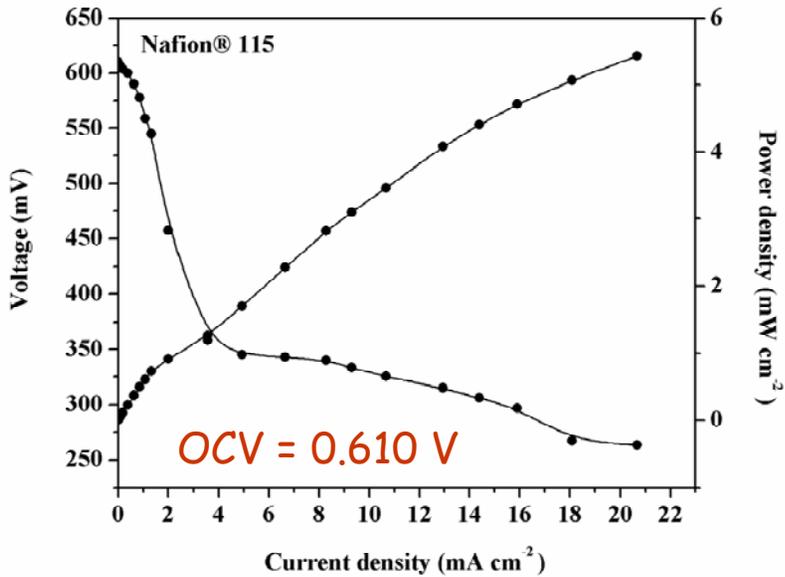
Proton conductivity at 50 % RH as a function of temperature for PVA-ZrP-Cs₁SWA and PVA-ZrP-Cs₂SWA membranes compared with Nafion® 115 at 100% RH



Methanol permeability of PVA-ZrP-Cs₁SWA and PVA-ZrP-Cs₂SWA hybrid membranes compared with Nafion® 115

Comparison of conductivity and permeability for various membranes

| Membrane | RH (%) | Temperature (°C) | Conductivity (Scm ⁻¹) | Permeability (cm ² s ⁻¹) | References |
|--|--------|------------------|--------------------------------------|---|---|
| PVA-ZrP-Cs₁SWA | 50 | 100 | 0.013 | 2 x 10 ⁻⁶ | <i>J. Power Sources</i> (2006, Inpress) |
| PVA-ZrP-Cs₂SWA | 50 | 100 | 0.02 | 3 x 10 ⁻⁶ | " |
| Nafion[®] 115 | 100 | 90 | 0.03 | 3.5 x 10 ⁻⁶ | " |
| Nafion[®]115/Cs⁺,NH₄⁺, Rb⁺ and Tl⁺ modified PTA | 35 | 120 | 0.016 | - | <i>J. Membr. Sci.</i> , 217 (2003) 5 |
| SPEK/ZP/ZrO₂ (70/20/10 wt %) | 100 | 70 | 2.3 x 10 ⁻³ | - | <i>Solid State Ionics</i> , 162–163 (2003) 269-275. |
| PVA/PWA/SiO₂ | - | - | 0.004-0.017 | 10 ⁻⁷ to 10 ⁻⁸ | <i>Solid State Ionics</i> , 171 (2004) 121-127 |
| PEG/SiO₂/SWA | 100 | 80 | 0.01 | 10 ⁻⁵ to 10 ⁻⁶ | <i>J. Power Sources</i> , 139 (2005) 141-151 |
| PEG/SiO₂/PWA | - | - | 10 ⁻⁵ to 10 ⁻³ | 10 ⁻⁶ to 10 ⁻⁷ | <i>J. Membr. Sci.</i> , 254 (2005) 197-205 |
| PVA–SiO₂–SWA | 100 | 100 | 4.13 x 10 ⁻³ | - | <i>J. Membr. Sci.</i> , 275 (2006) 105-109 |
| SPEEK/PWA | 100 | 100 | 1.7 x 10 ⁻² | - | <i>J. Membr. Sci.</i> , 254 (2005) 197-205 |



Passive cell DMFC

Electrode area = 2 x 3 cm²
 catalyst loading = 6 mg/cm²
 4 M CH₃OH

Polarization and power density curves for passive DMFC cell with Nafion® 115, PVA-ZrP-Cs₁SWA and PVA-ZrP-Cs₂SWA hybrid membranes as proton conducting electrolyte at 273 K and at atmospheric pressure



Conclusions

- ✓ Composite membranes with polyvinyl alcohol as organic matrix and zirconium phosphate and silicotungstic acid as inorganic components were prepared by a **simple method**
- ✓ Water uptake, IEC and proton conductivity **increased with silicotungstic acid content.**
- ✓ Though number of reports are available in literature on stabilizing the HPA in membrane matrix, a combined approach of **composite formation with salts of HPA was investigated.**
- ✓ These composite membranes exhibited **reduced methanol crossover** compared to Nafion 115
- ✓ At **50 % RH**, the protonic conductivity of the hybrid membranes was in the range of **10^{-3} to 10^{-2} S cm⁻¹**
- ✓ The open circuit voltage (OCV) for the cell with **PVA–ZrP–Cs₂STA** hybrid membrane is **0.652 V** and that for **PVA–ZrP–Cs₁STA** hybrid membrane is **0.619 V** which is higher compared to the cell with **Nafion® 115 (0.610 V)** indicating reduced methanol crossover.
- ✓ Though they exhibit little lower proton conductivity it appears as promising materials due to its reduced methanol crossover.



**Thank you all for
your kind attention**