MEMBRANES FOR FUEL CELLS

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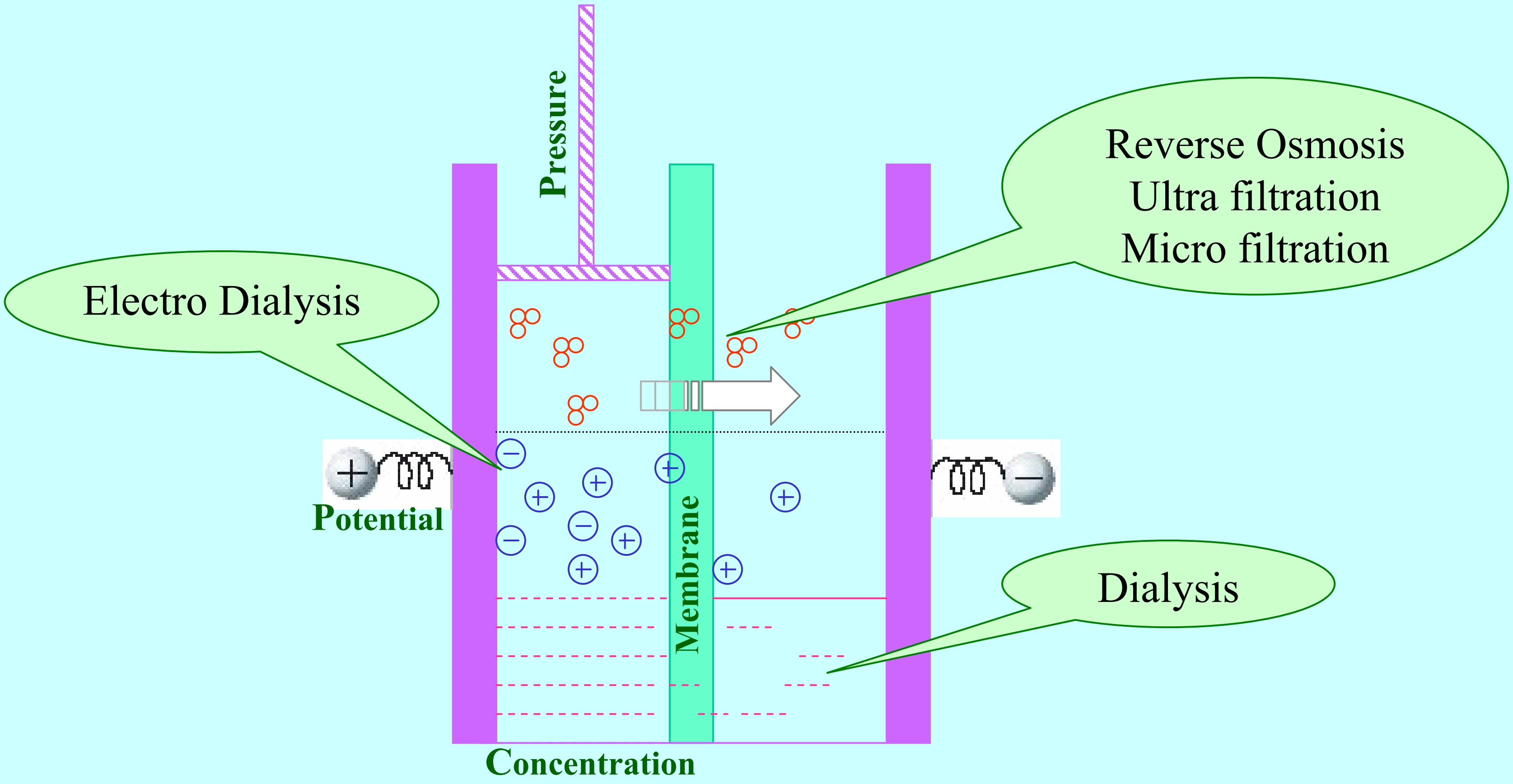
Why membranes are essential constituent of Fuel cells

- 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

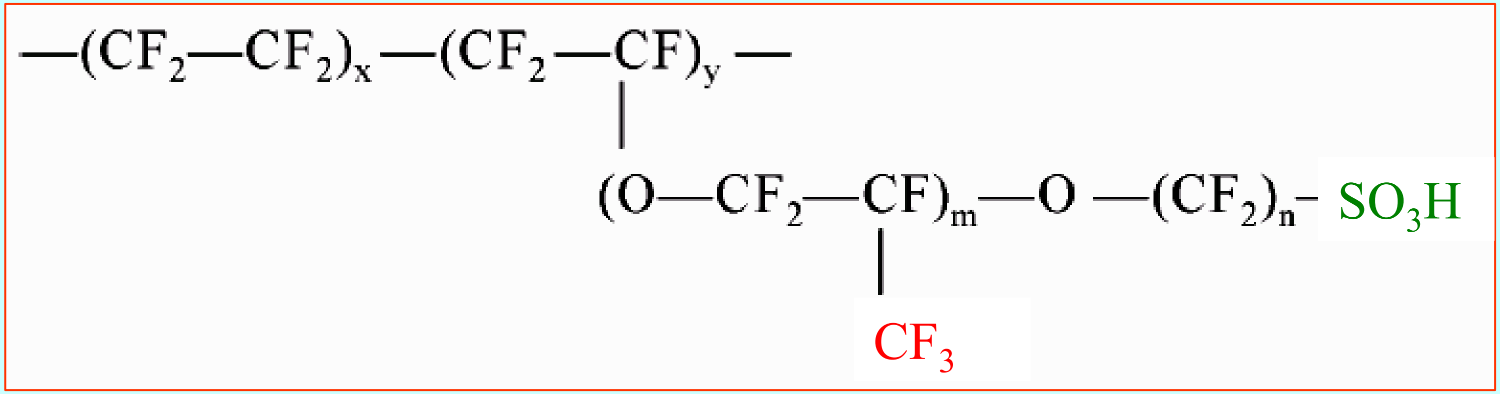
- Fuel cells - Polymeric proton conducting membranes
- Batteries - Lithium ion cells - Amorphous polyethylene oxide (PEO)
- Water electrolysis - Bipolar ion exchange membranes
- Sensor - Polymeric membranes
- Biosensors – Lipid membranes, enzyme immobilized membranes

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

Nafion®

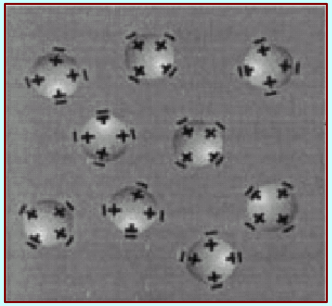


$$-(CF_2-CF_2)_x-(CF_2-\underset{\displaystyle (O-CF_2-\underset{\displaystyle CF_3}{CF})_m-O-(CF_2)_n-SO_3H}{CF})_y-$$

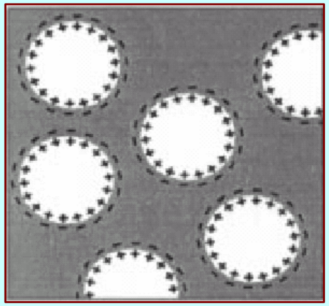
Advantages

- Stable in both oxidative and reductive environments
- Excellent proton conductor (**0.07 - 0.23 S cm^{-1}** **at** **100 % RH**)
  1M H_2SO_4 $\sigma = 0.08$ S cm^{-1}
- Why nafion is so special as a membrane for fuel cells

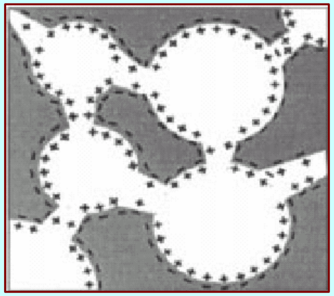
Simplified Nafion® structure according to water content



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**

G. Gebel, *Polymer* **41** (2000) 5829

Characteristics of Nafion® membranes

Membarne	Dry thickness (μm)	Equivalent weight ($gmol^{-1}/SO_3^-$)	Area resitance (Ωcm^2)	Conductiviy (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

S. Slade *et al., J. Electrochem. Soc.*, **149** (2002) A1556

Characteristics of other commercial polymer membranes

Membrane	Dry thickness (μm)	Equivalent weight ($gmol^{-1}/SO_3^-$)	Conductiviy (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)

Cont..

Membrane	Dry thickness (µm)	Conductivity (Scm^{-1})	IEC (meq g^{-1})	Methanol diffusion coefficient (cm^2 s^{-1} × 10^6)	Manufacturer
CRA[a]	160	0.045	1.4-2.2	0.58	Solvay
CRS[b]	160	0.05	1.7-2.2	0.92	Solvay
R1010[c]	40	0.07	1.2	0.6	IonClad
R4010	20	0.08	1.2	1.2	Pall Gelman Sciences

a. Polyethylene-Tetra-fluoroethylene radiochemically grafted sulphonyls-supliers
b. Fluorinated film - Tetra-fluoroethylene with poly(styrene sulfonic acid)
c. Tetra-fluoroethylene grafted poly(styrene sulfonic acid)

Limitations of Nafion®

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

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

Thin and reinforced PFSA membranes

- To decrease the internal resistance
- To reduce material cost
- To improve water management

Nafion with porous polypropylene/polysulfone

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

Drawback

- Reduced mechanical strength (under high temp & swelling)

B. Bae *et al.*, *J. Membr. Sci.*, **202** (2002) 245

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**
- 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

R. Savinell *et al.*, *J. Electrochem. Soc.*, **141** (1994) L46

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} S cm^{-1}** at **100°C**

M. Watanabe *et al.*, *J. Electrochem. Soc*. **143** (1996) 3847

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 S cm^{-1}** at **35 % RH**
- Water uptake:
  - Pristine Nafion - 27 wt %
  - Nafion/HPA - 95 wt %

Drawbacks:

- HPA is highly water soluble eventually leaches out from PEM
- Decreased tensile strength (~14 kPa whereas Pristine Nafion ~ 40 MPa)

S. Malhotra *et al.*, *J. Electrochem. Soc.* **144** (1997) L23

Nafion/α-ZrP

Properties:

- Water insoluble
- Has intercalated hydronium ions with conductivity of **0.1 S cm^{-1}** at **100 ºC** 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

P. Costamagna *et al.*, *Electrochim Acta* **47** (2002) 1023

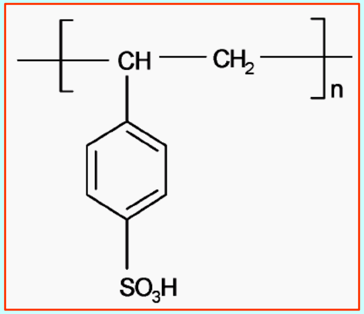
Alternate sulfonated polymer membranes

- 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

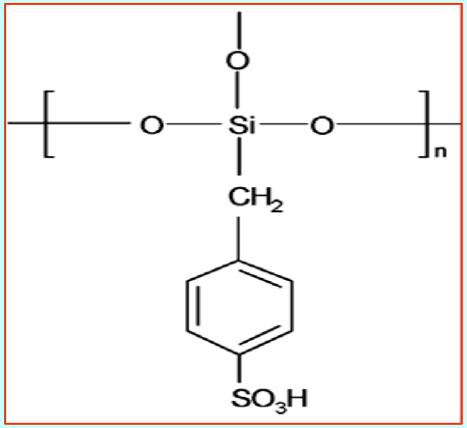
Fluoropolymers



- 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

S. Hietala *et al.*, *Mater. Chem.*, **8** (1998) 1127

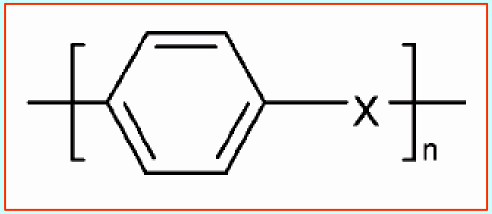
Polysiloxanes



- 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} S cm^{-1}** at **RT**
- Chemically and thermally stable up to 200 °C
- Water uptake alteration are possible

V. D. Noto *et al., Electrochimica Acta* **50** (2005) 4007

Aromatic polymers

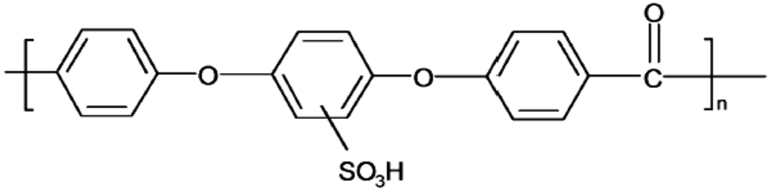


- Cost effective and ready availability
- Good oxidation resistance of aromatic hydrocarbons
- Electrolyte for high temperature range (> 100 ºC)
- Investigated systems
  - polyetheretherketone (PEEK)
  - polysulfones (PSF) or Polyethersulfone (PES)
  - polybenzimidazoles (PBI)
  - polyimides (PI)
  - 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, **$\sigma_{100^{o}C} = 8 \times 10^{-3}$ S cm^{-1}** at **100 % RH**

S-PEEK/SiO$_2$

- S-PEEK containing 10 wt% SiO$_2$ – Exhibited best mechanical and electrical characteristics (**$\sigma_{100^{o}C} = 9 \times 10^{-2}$ S cm^{-1}**)

S-PEEK/ZrO$_2$

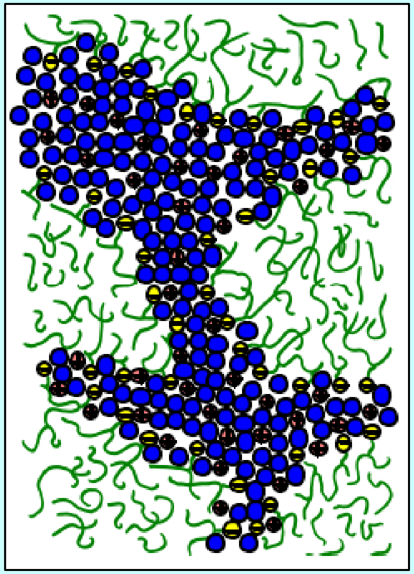
- S-PEEK containing 10 wt% ZrO$_2$ – Exhibited low permeability and good conductivity (**$\sigma_{100^{o}C} = 4.5 \times 10^{-2}$ S cm^{-1}**)

S-PEEK/HPA

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

Microstructures

Nafion 117

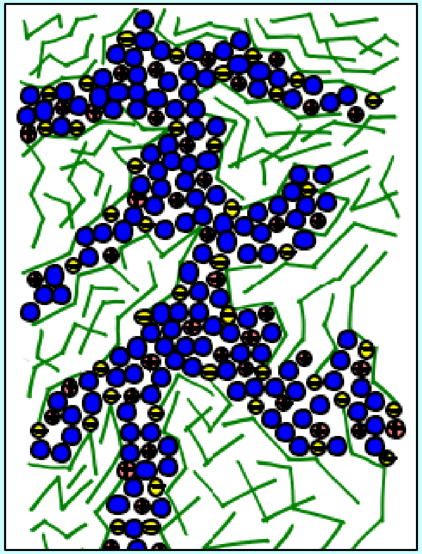


⊖ : $-SO_3^-$

⊕ : protonic charge carrier

● : H_2O

S-PEEK



- Wide channels
- More separated
- Less branched
- Small $-SO_3^-/-SO_3^-$ separation
- $pK_a \sim -6$
- $D_{MeOH} = 2.91 \times 10^{-6}\ cm^2/s$

- Narrow channels
- Less separated
- Highly branched
- Large $-SO_3^-/-SO_3^-$ separation
- $pK_a \sim -1$
- $D_{MeOH} = 6.57 \times 10^{-8}\ cm^2/s$

K. D. Kreuer, *J. Membr. Sci*. **185** (2001) 29

Limitations of sulfonated polymers

- Highly deliquescent
- Hard to recover from solution
- Has a temperature limit at 200 ºC
- H^+ conductivity decays due to decomposition of the SO_3H groups
- High sulfonation results in high swelling and therefore poor mechanical properties

Acid-Base Polymer membranes

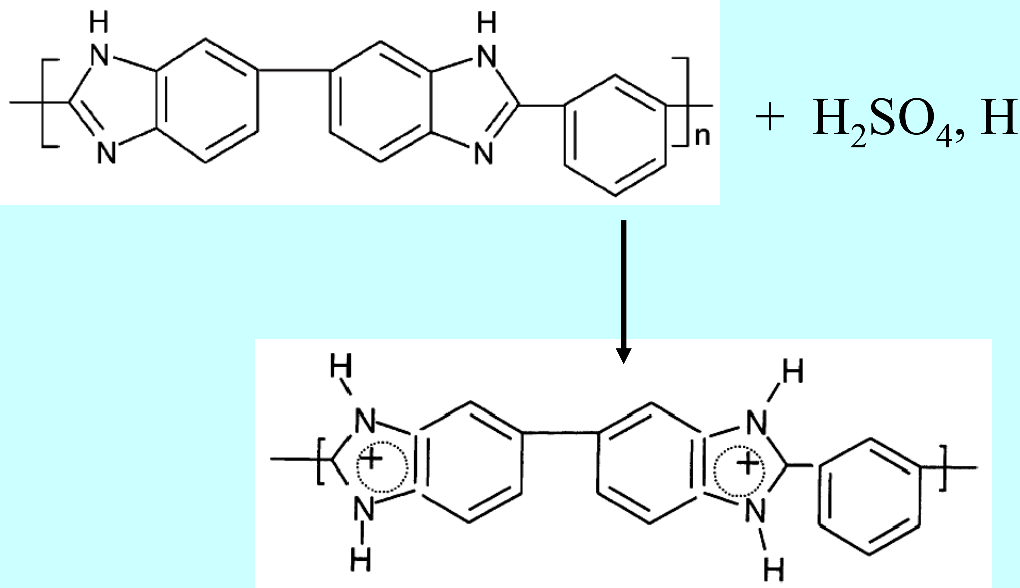
Two Approaches:

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

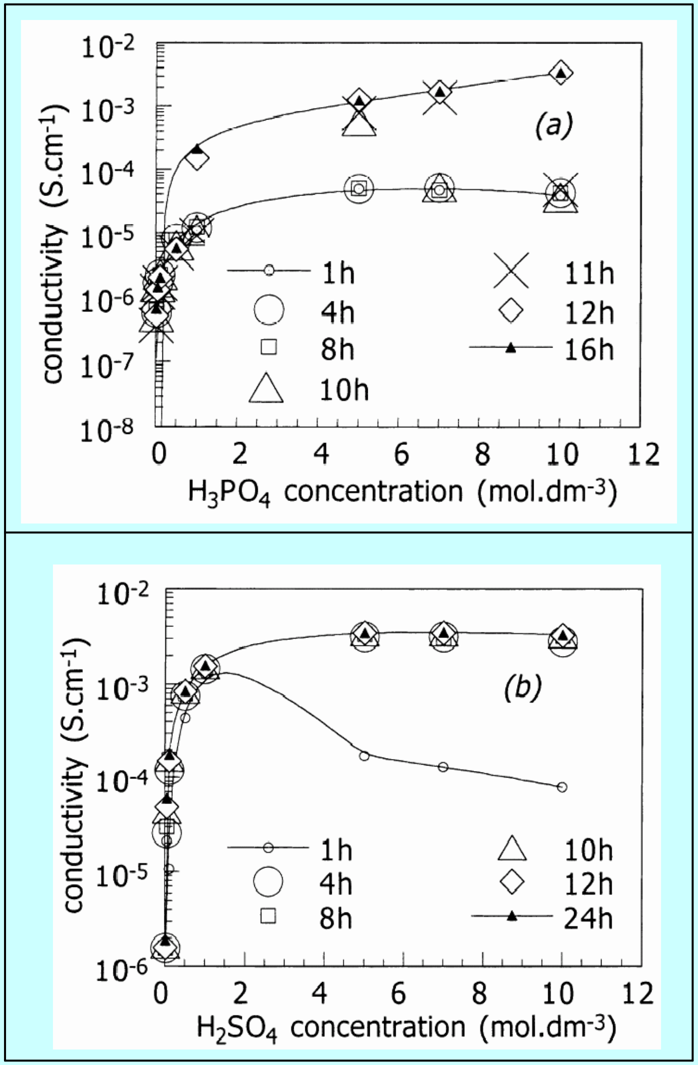
Basic polymers	Acids
Polybenzimidazole (PBI)	H_3PO_4
Poly-(ethylene oxide)s (PEO)	H_2SO_4
Polyvinyl alcohol (PVA)	HCl
Polyacrylamide (PAAM)	HNO_3
Polyethylenimine (PEI)	$HClO_4$
Nylon	

Acid doped polybenzimidazole

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

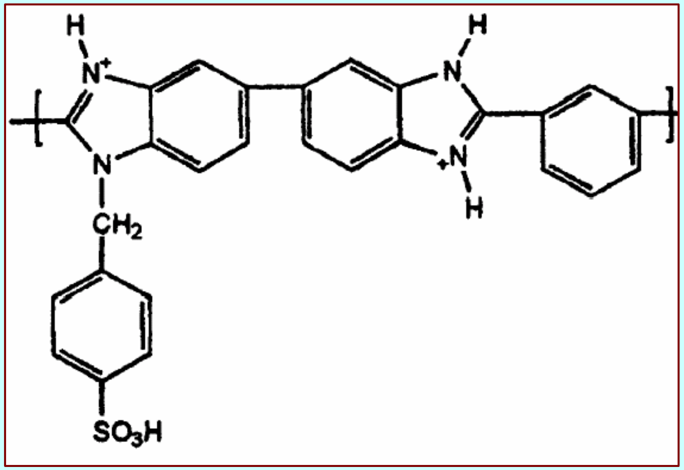


+ H_2SO_4, H_3PO_4



D. Jones *et al.*, *J. Membr. Sci.*, **185** (2001) 41

Doping with organic and inorganic bases



N-benzylsulfonate grafted PBI (PBI-S)

Membrane	Conductivity (S cm^{-1})
PBI-S	4.2×10^{-4}
PBI-S/NH_4OH	1.5×10^{-2}
PBI-S/imidazole	7.9×10^{-3}
PBI-S/LiOH	1.2×10^{-2}
PBI-S/NaOH	1.2×10^{-2}
PBI-S/KOH	1.7×10^{-2}
PBI-S/CsOH	1.7×10^{-2}

J. Roziere *et al*, *Solid State Ionics* **145** (2001) 61

Advantages

- High temperature oxidative stability of the blank PBI (~300 ºC)
- Good chemical stability and mechanical properties of the blank PBI
- Exhibits good conductivity
- Ease of fabrication of the composite
- Less fuel 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)

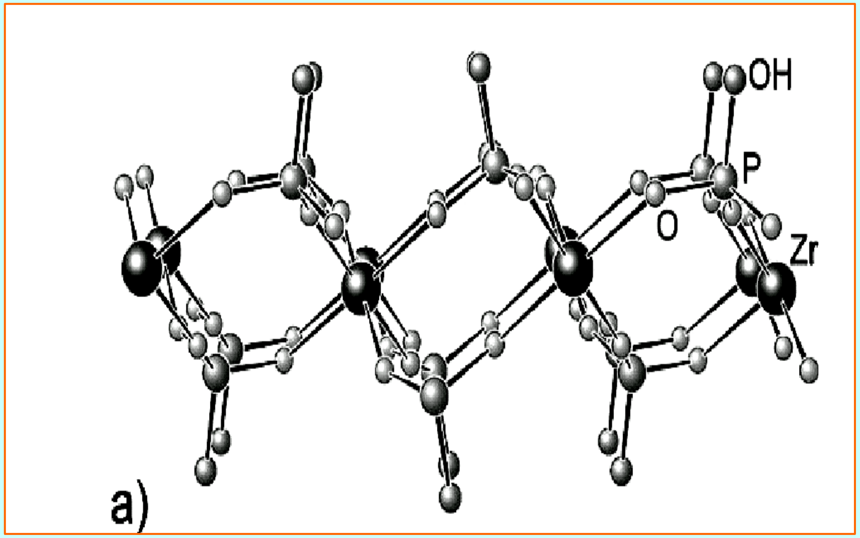
Inorganic proton conductors (zirconium phosphates, heteropolyacids, metal hydrogen sulfate)

Requirement - Stability under fuel cell operating conditions

Effect of adding an inorganic component to a polymer membrane

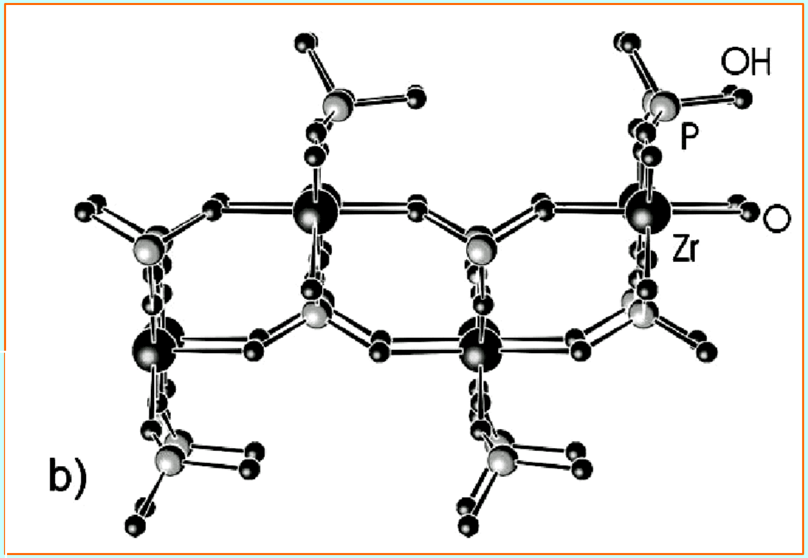
- Thermodynamic changes due to hygroscopic nature
- Changes in capillary forces and the vapour liquid equilibrium as a result of changes in the pore properties
- Surface charge interactions between the composite species
- Changes the morphology of the membrane
- Membrane architecture is possible
- Membrane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

Zirconium phosphates



α-$Zr(HPO_4)_2 \cdot H_2O$

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



γ $(ZrPO_4[O_2P(OH)_2] \cdot nH_2O)$

Attempts to enhance the proton conductivity

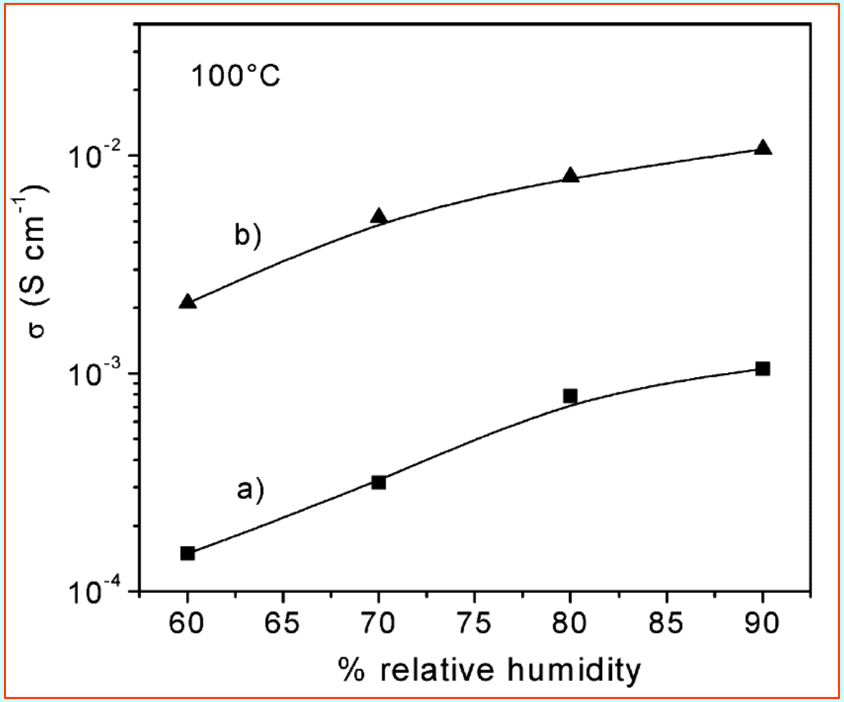
- Intercalation of functional groups
- Composites α-ZrP membranes
- External surface area maximization (mechanical and colloidal synthesis)
- Internal surface area maximization (sol–gel synthesis and pillaring)

Intercalation of functional groups

Layered ZrP and phosphonates	**σ (S cm^{-1}) at 100^{o}C, 95% RH**
α-$Zr(O_3P\text{-}OH)_2 \,.\, H_2O$ *	1.8×10^{-5}
γ-$ZrPO_4[O_2P(OH)_2].\, 2H_2O$*	2×10^{-4}
$Zr(O_3P\text{-}OH)_2 \,.\, nH_2O$ ¶	$1–5 \text{ x } 10^{-3}$
$Zr(O_3P\text{-}OH)_{1.5}(O_3P\text{-}C_6H_4SO_3H)_{0.5}$ ¶	$0.9–1.1 \text{ x } 10^{-2}$
$Zr(O_3P\text{-}OH)(O_3P\text{-}C_6H_4SO_3H)\ nH_2O$ §	$0.8–1.1 \text{ x } 10^{-1}$

* Crystalline; § Semicrystal: ¶ Amorphous

Composites *α*-ZrP membranes



(a) s-PEK membrane (thickness 50 μm)

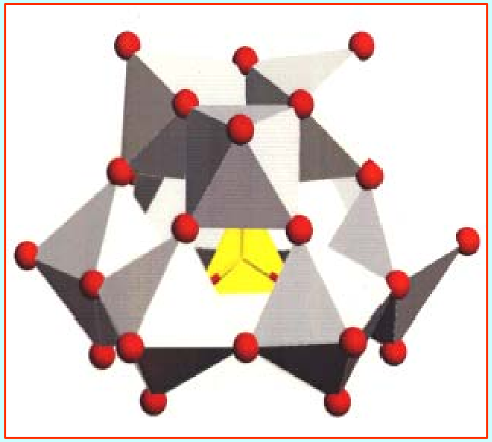
(b) s-PEK filled with 35 wt% of $Zr(O_3P\text{-}OH)(O_3P\text{-}C_6H_4SO_3H).nH_2O$

5th july 2007

P. Costamagna *et al.*, *Electrochimica Acta* **47** (2002) 1023

Heteropolyacids - $H_3PM_{12}O_{40}$

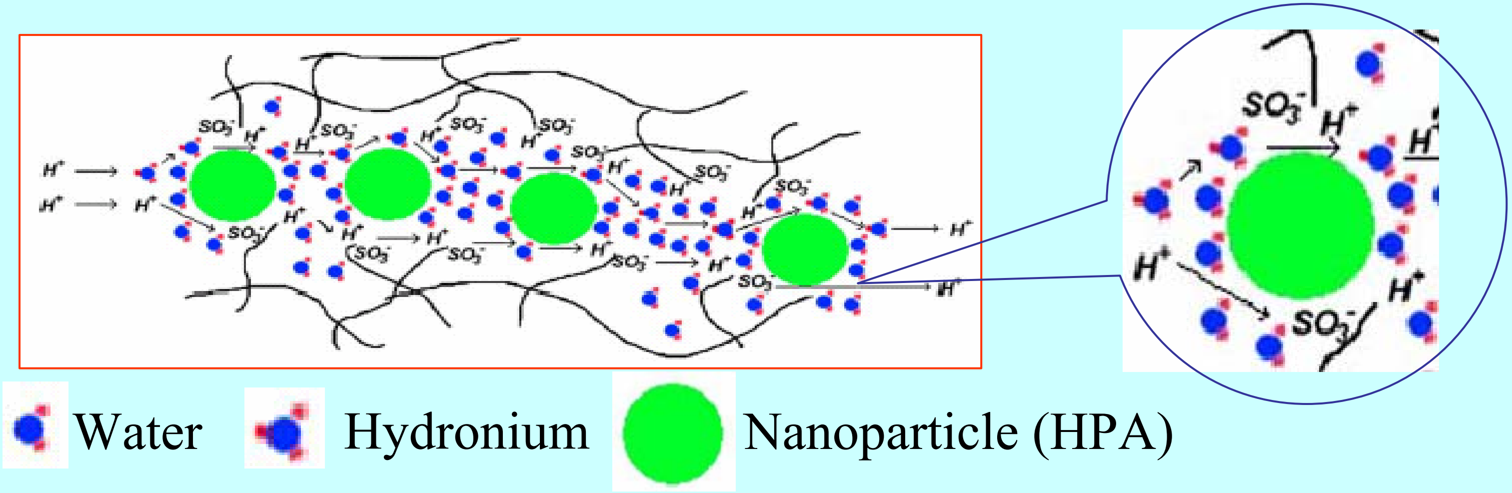
(cluster species)



- Exhibit high proton conductivities;
  - **0.18 S cm^{-1}** for $H_3PW_{12}O_{40}.29H_2O$
  - **0.17 S cm^{-1}** for $H_3PMo_{12}O_{40}.29H_2O$
- Thermally stable at temperatures of interest, < 200 °C
- Greater water uptake, but decreased tensile strength than Nafion 117
- Water soluble – need to be immobilized

S. Malhotra *et al.*, *J. Electrochem. Soc.* **144** (1997) L23

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, $MHSO_4$

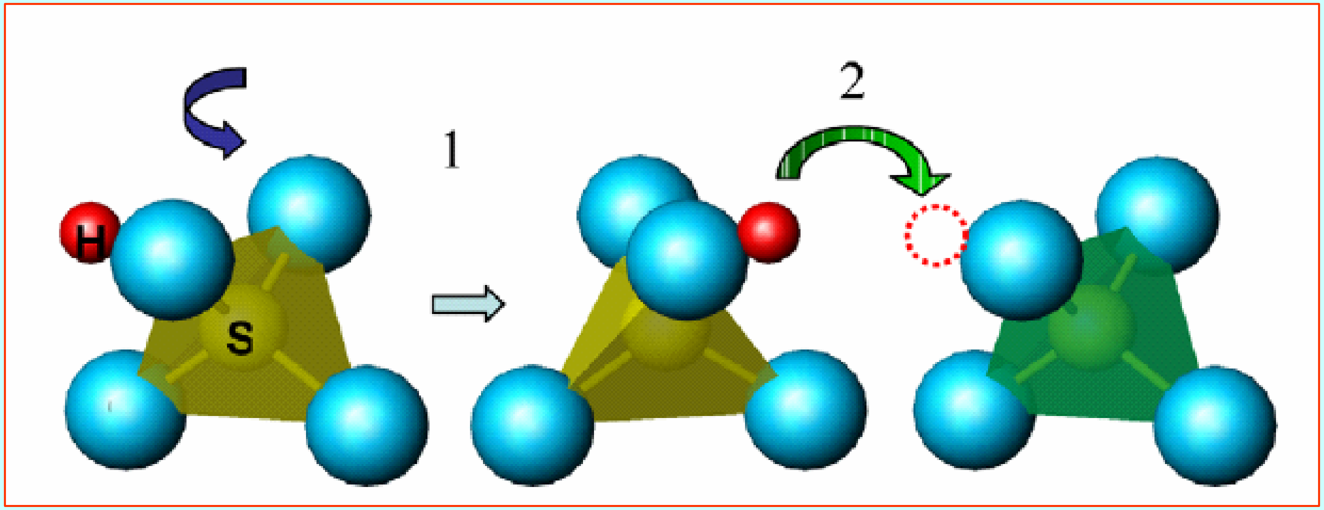
M - Rb, Cs, or NH_4^+

- 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

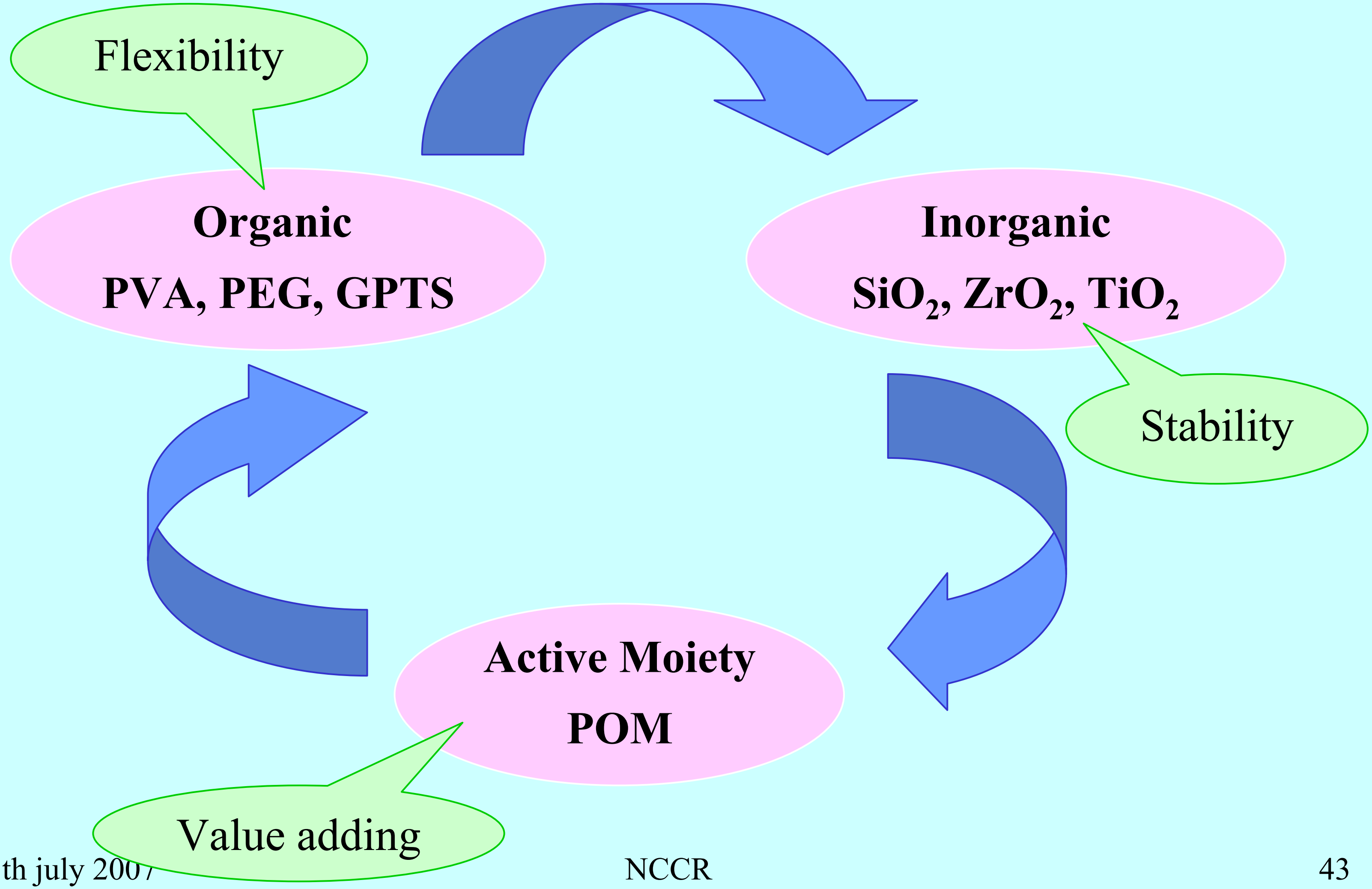
Proton transport mechanism in $CsHSO_4$



- $CsHSO_4$ consist of oxyanions, linked together through hydrogen bonds
- At 141ºC 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}**

S. M. Haile *et al*, *Nature* **410** (2001) 1589

Hybrid Organic Inorganic Composite membranes



Flexibility

Organic

PVA, PEG, GPTS

Inorganic

SiO_2, ZrO_2, TiO_2

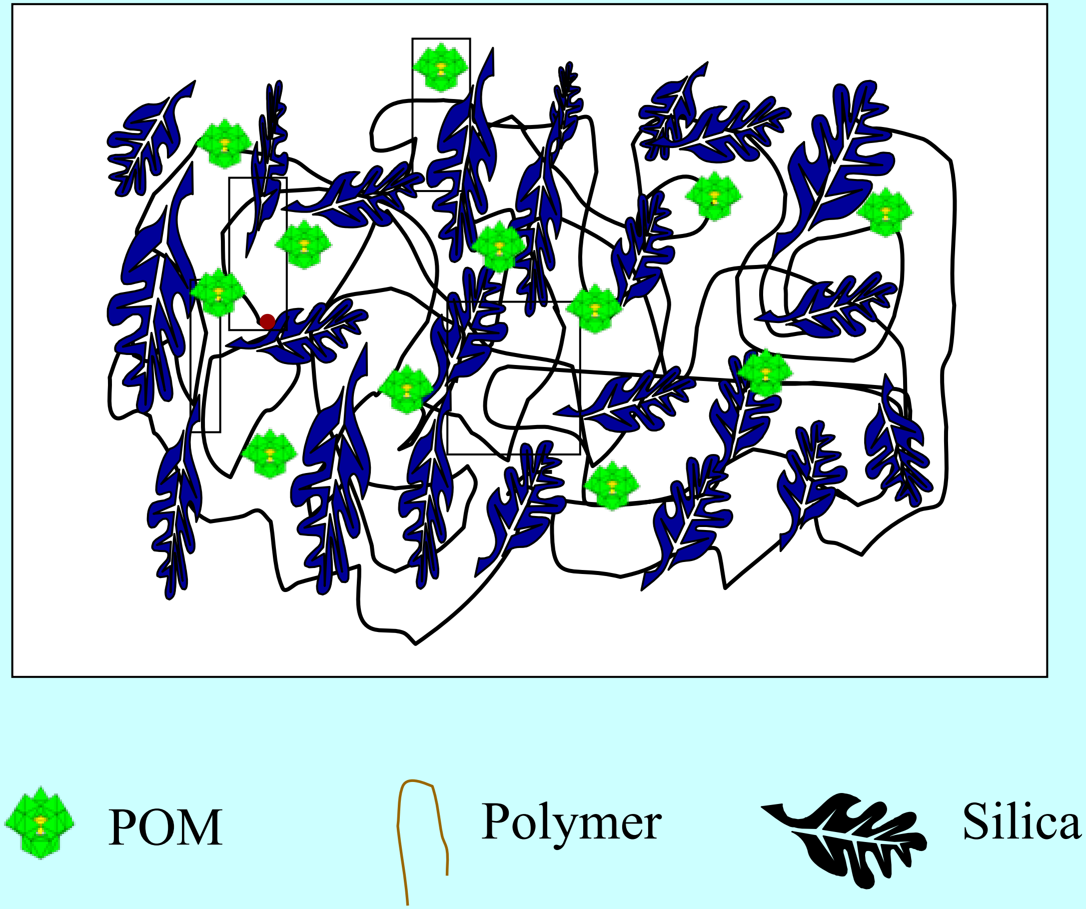
Stability

Active Moiety

POM

Value adding

Conceptual representation of Hybrid Composite



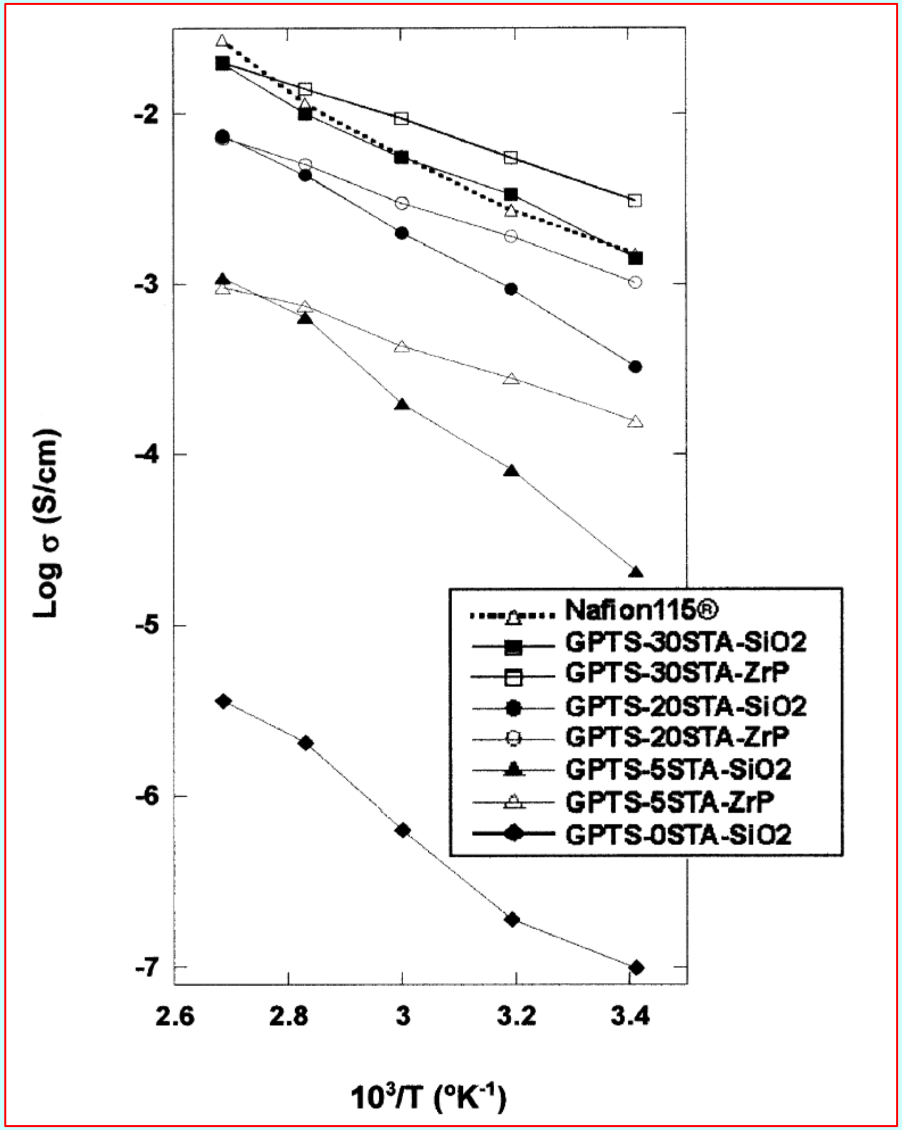
Characteristics of Hybrid Inorganic-Organic Composites

- 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$^{\#}$–SiO$_2$
- GPTS–STA–ZrP

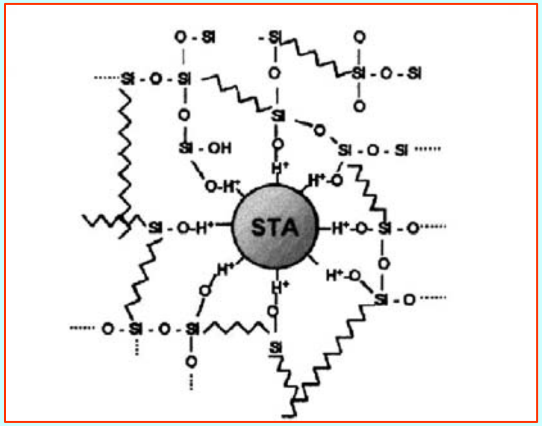
- GPTS–SiO$_2$, H$^+$ conductivity **1 x 10^{-7} - 3.6 x 10^{-6} S cm^{-1}** at **20 - 100°C**
- GPTS–SiO$_2$ with 30 wt% STA, H$^+$ conductivity **1.4 x 10^{-3} – 1.9 x 10^{-2} S cm^{-1}** at **20 – 100°C**
- GPTS–ZrP 30 wt% STA, H$^+$ conductivity **2 x 10^{-2} S cm^{-1}** at **100°C**

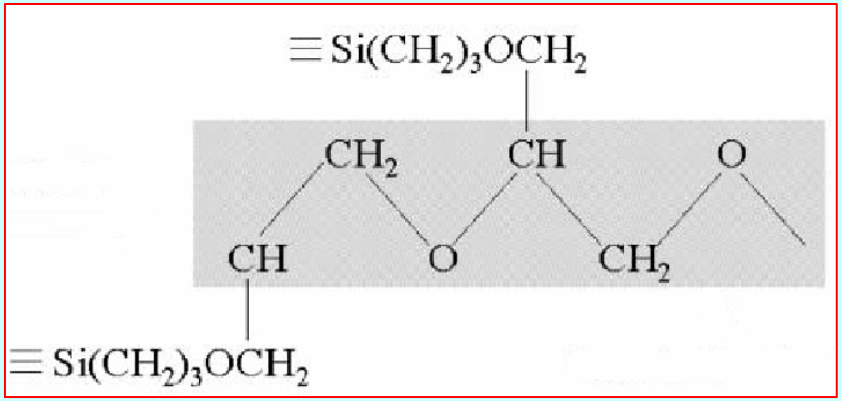


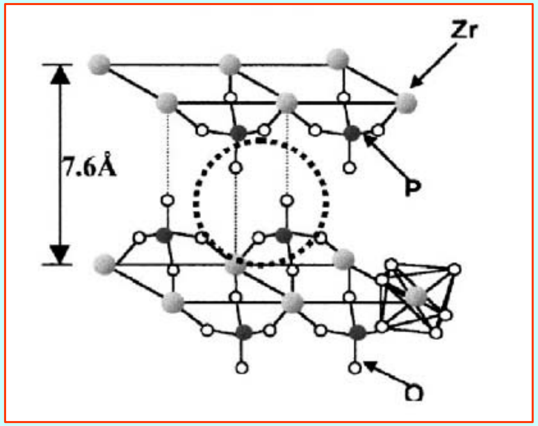
*3-glycidoxypropyltrimethoxysilane

silicotungstic acid

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







Y. Park *et al.*, *Solid State Ionics* **145** (2001) 149

Requirements for DMFC membranes

- Operation at high temperature and at low humid condition
- Low methanol crossover ($<10^{-6}$ mol min^{-1} cm^{-1}) or low methanol diffusion coefficient in the membrane ($<5.6 \times 10^{-6}$ cm^2 s^{-1} at $T = 25$ °C)
- High ionic conductivity (>80 mS cm^{-1})
- High chemical and mechanical durability especially at $T > 80$ °C (for increased CO tolerance)
- Low cost ($<\$10$ kW^{-1} based on a PEMFC)

Challenges ahead for the development of membranes for DMFC

- Membranes with controlled methanol permeability represents a primary goal
- Nafion - Instability at T > 80ºC & RH < 100%, diffusion of other species and cost (~ 1000 $\$/\mathrm{m}^2$)
- 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

Futuristic Outlook

- The search for alternate new membranes for fuel cell application should not start from **ionic conductivity**
- Alternate membranes can be superior to Nafion
  - stability in less humid conditions,
  - restricted or reduced swelling index as compared to Nafion &
  - showing improved activities against the limitations for fuel cross over from anode
- Composite or hybrid systems is desirable
  - to improve the durability
  - to exploit the electronegative environment provided by the matrices

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

✓ Inorganic fillers or proton conducting species can also function as catalysts for the fuel thus decomposing methanol

✓ This role of the components of membrane has not yet established or realized yet

✓ Salts of heteropoly anions can function as catalysts for the methanol decomposition and this could also result in the reduced cross over

✓ It is necessary that this role is identified and established so that new membrane development can have this additional criterion built in the search

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

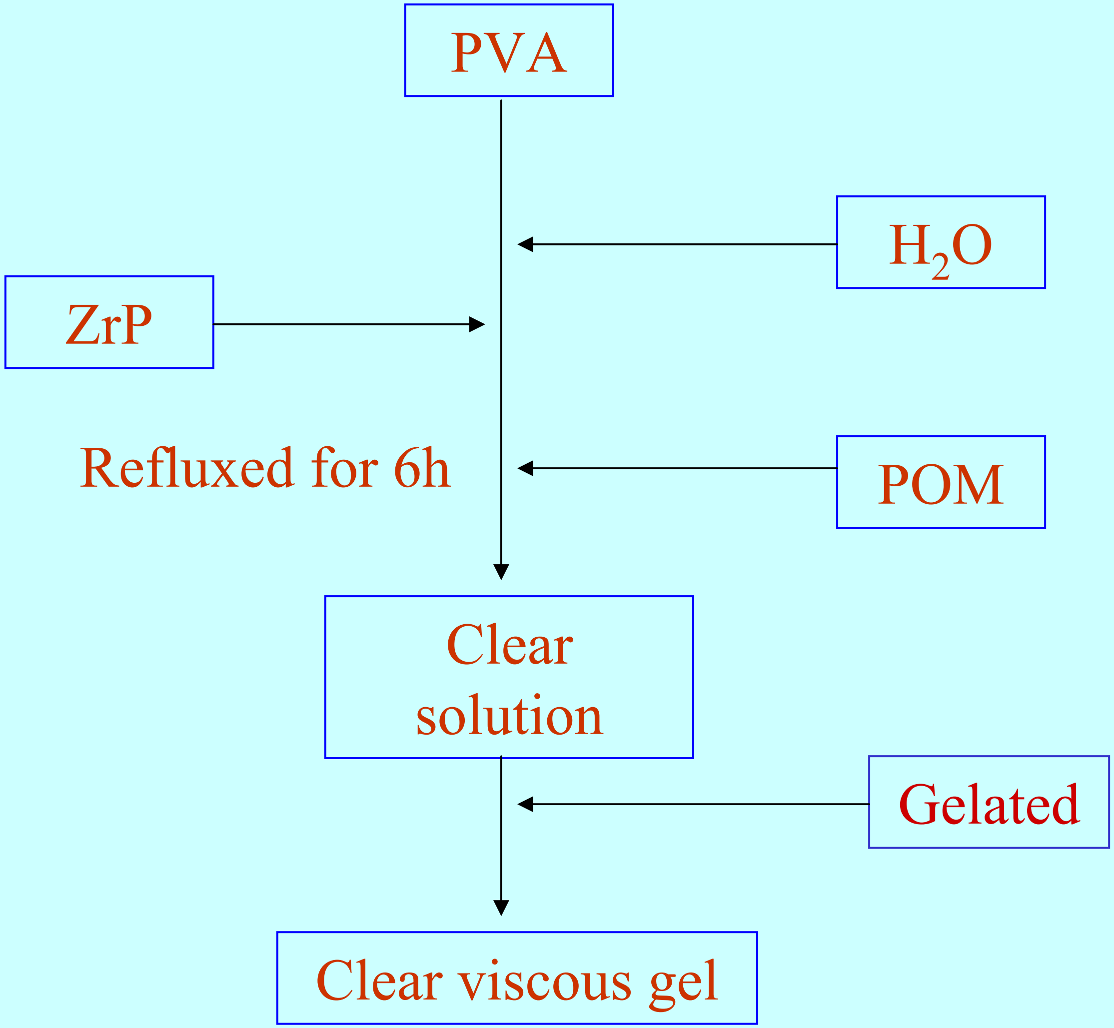
1M $ZrOCl_2.8H_2O$

Stirred for 3 h

α - $Zr(HPO_4)_2$. H_20

Dried at 95ºC for 2 h and stored at 100 % RH

Preparation of PVA–ZrP–SWA composite



PVA

H_2O

ZrP

Refluxed for 6h

POM

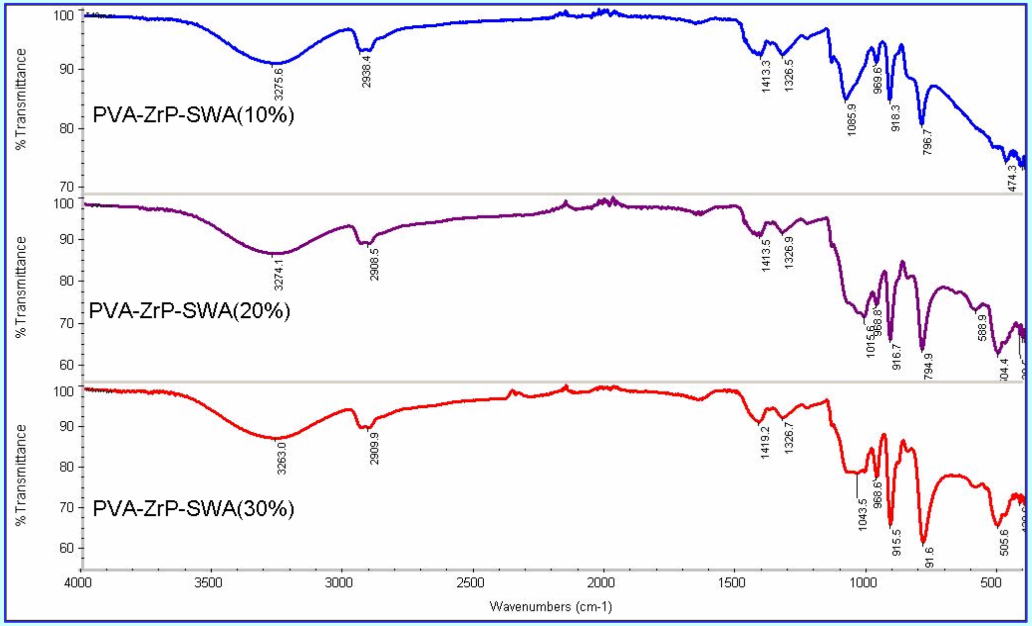
Clear solution

Gelated

Clear viscous gel

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 $-CH_2$ stretching; 1420 cm^{-1} is for $-CH_3$ bending
- Characteristics of ZrP - 500 cm^{-1} and 1050 cm^{-1} are due to Zr-O and P-O_4 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 ºC

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

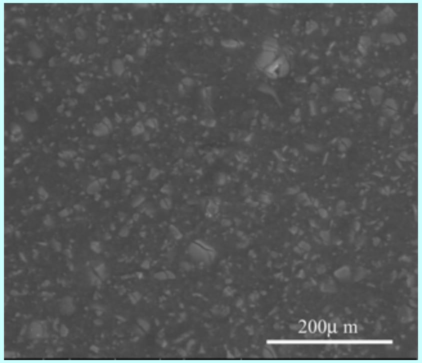
Water uptake, swelling and IEC values for different hybrid membranes with a 250 μm thickness

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

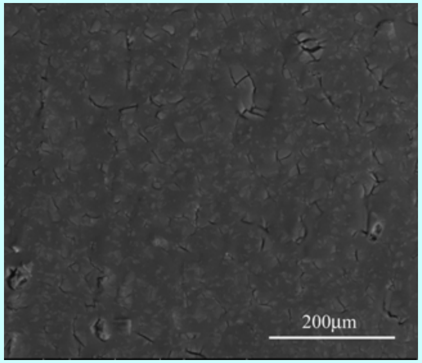
$$\mathbf{IEC} = \frac{\mathbf{V \times M}}{\mathbf{W_{dry}}}$$

IEC - ion-exchange capacity (meq g^{-1}),
V - Added titrant volume at the equivalent point (ml),
M - Molar concentration of the titrant and
W_{dry} -The dry mass of the sample (g)

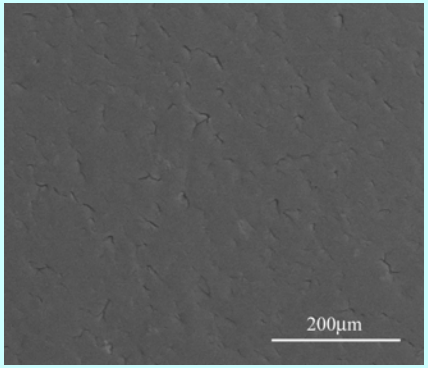
Surface morphology



PVA-ZrP-SWA(10%)



PVA-ZrP-SWA(20%)

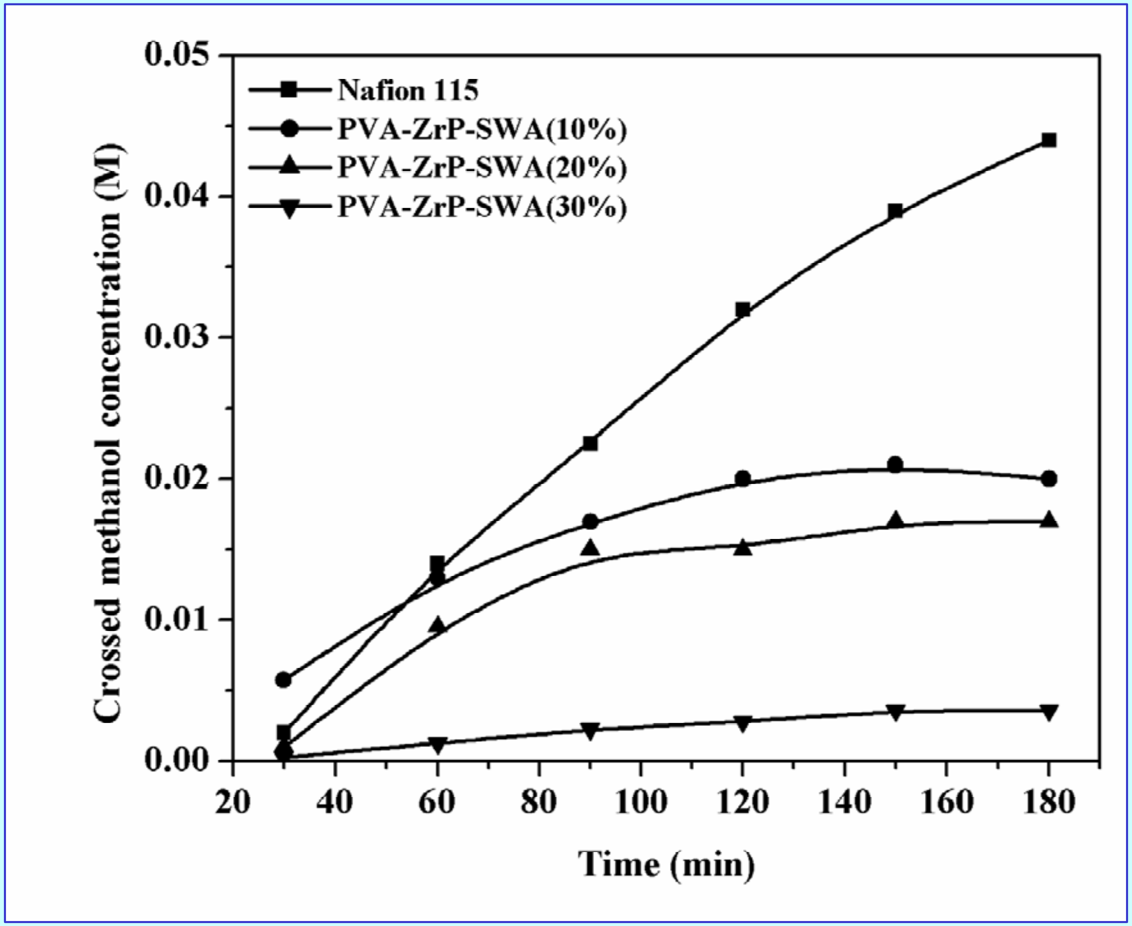


PVA-ZrP-SWA(30%)

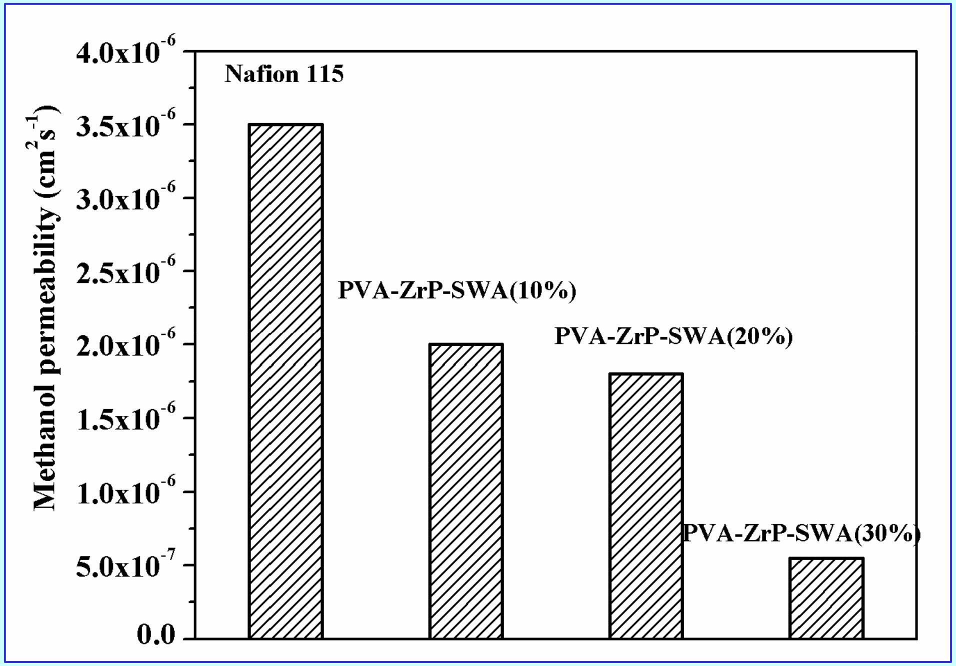
Proton conductivity at 60 % RH as a function of temperature

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-Cs_1SWA and PVA-ZrP-Cs_2SWA hybrid membranes with a 180 μm thickness compared with Nafion 115

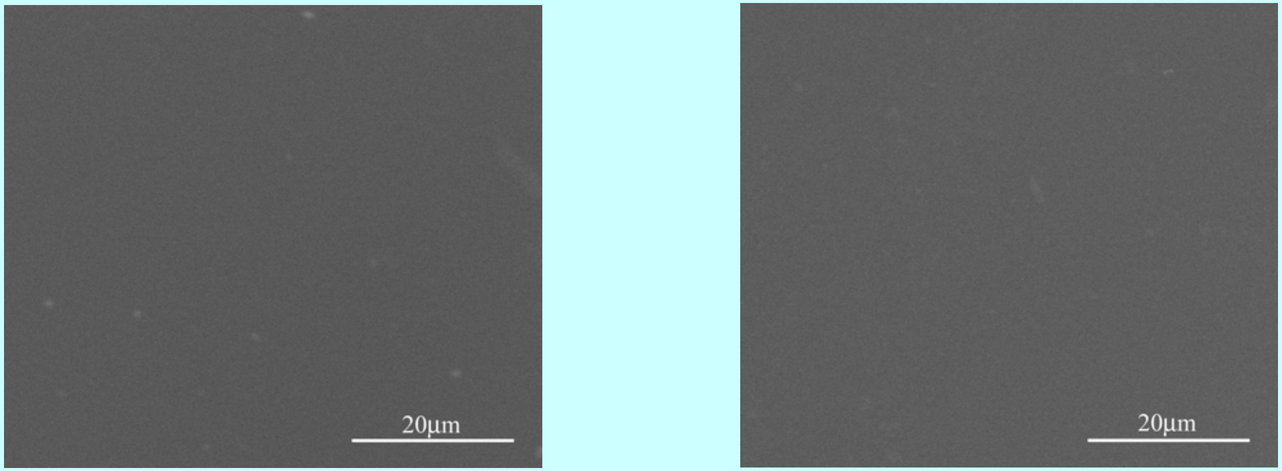
Membrane	**Water uptake (%)**	**Swelling (%)**	**IEC (meq/g)**
PVA-ZrP-Cs_1SWA	260	100	3.2
PVA-ZrP-Cs_2SWA	140	85	3
Nafion®115	22	12	0.9

Cu K_α XRD patterns of PVA-ZrP-Cs_1SWA and PVA-ZrP-Cs_2SWA hybrid membranes

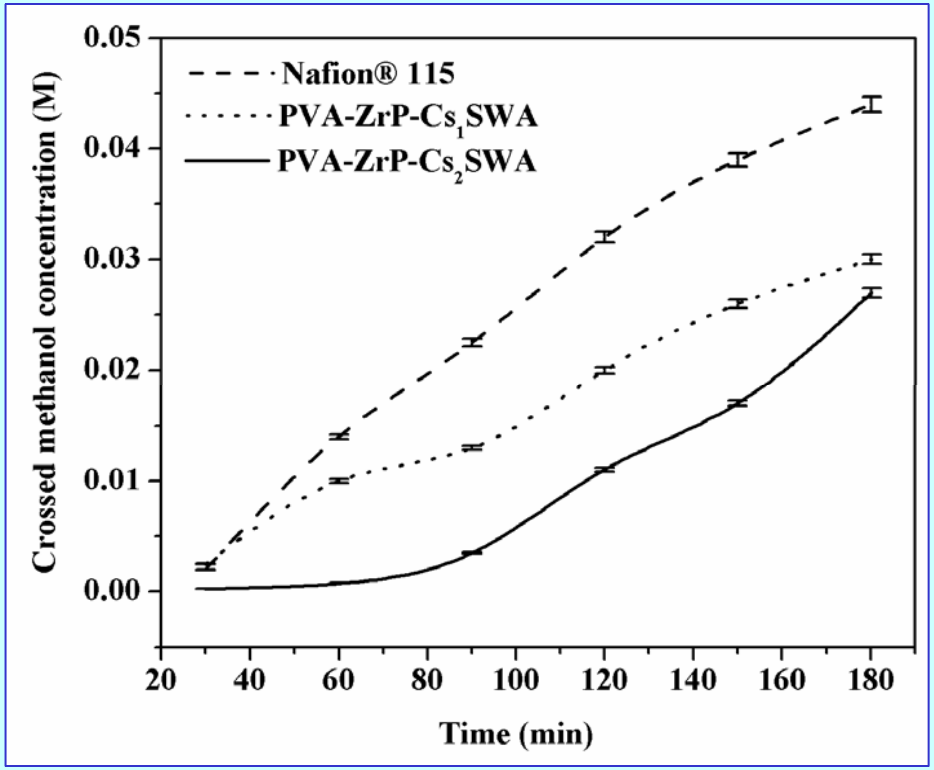
- The broad hump in the 2θ range 20 to 35 is due to the presence of PVA and zirconium phosphate

Assignments of main absorption bands for PVA-ZrP-Cs_1SWA and PVA-ZrP-Cs_2SWA hybrid membranes

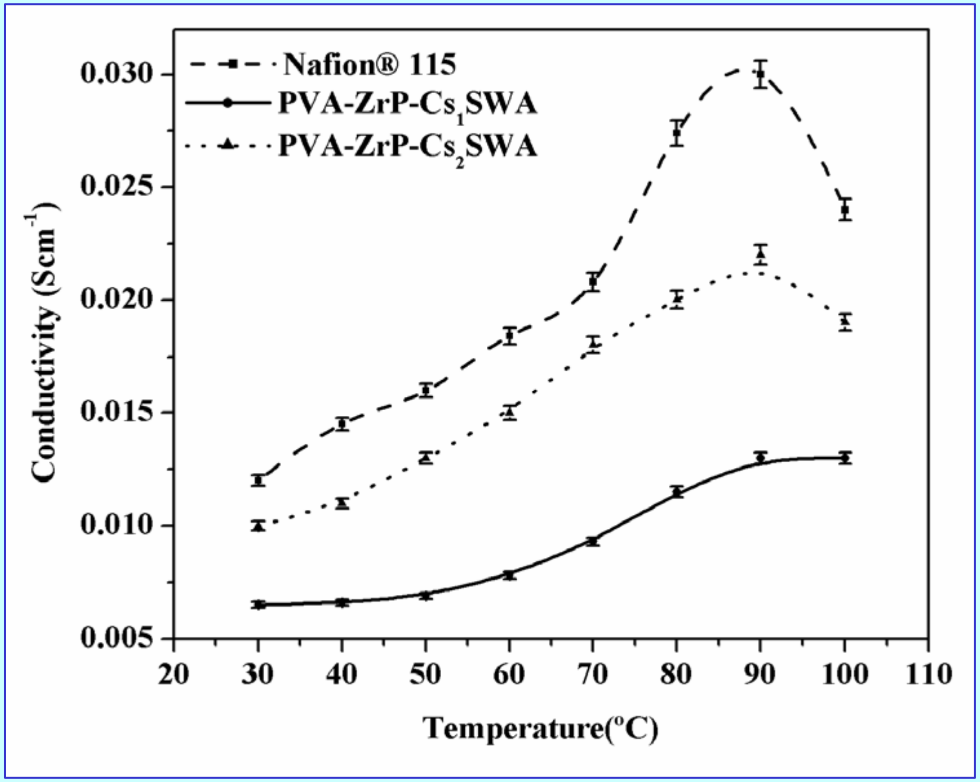
Vibration frequency (cm^{-1})		Bond Assignment
PVA-ZrP-Cs_1SWA	PVA-ZrP-Cs_2SWA	
981 cm^{-1}	969 cm^{-1}	$W=O_t$ stretching
917 cm^{-1}	916 cm^{-1}	X-O stretching
876 cm^{-1}	-	corner sharing $W-O_b-W$
744 cm^{-1}	793 cm^{-1}	edge sharing $W-O_b-W$
3274 cm^{-1}	3257 cm^{-1}	O–H stretching
2906 cm^{-1}	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



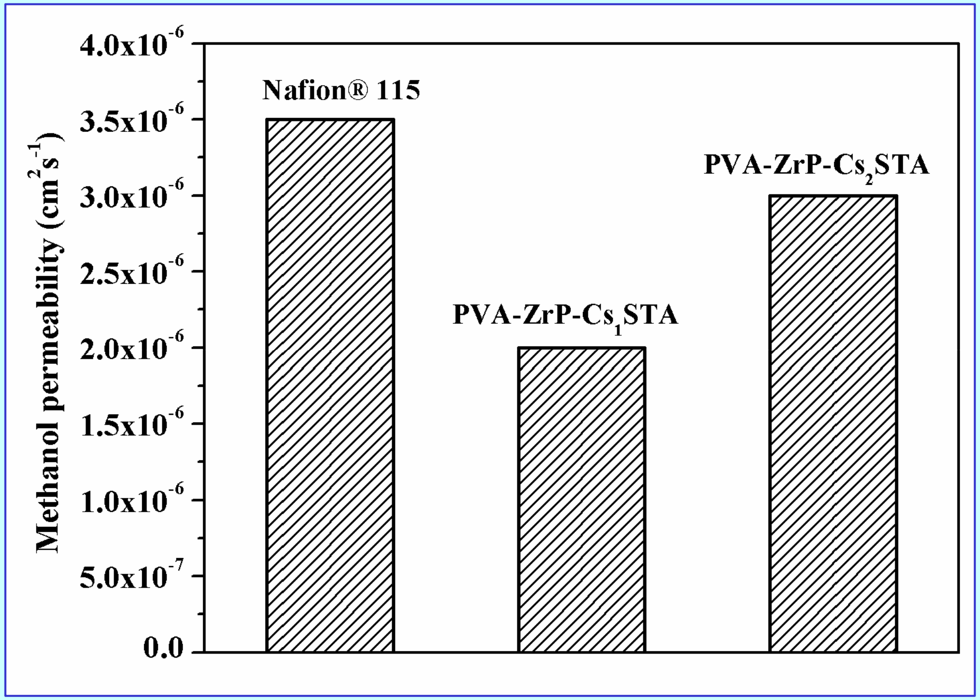
Scanning electron micrographs of PVA-ZrP-Cs_1SWA and PVA-ZrP-Cs_2SWA hybrid membranes



Concentration of crossed methanol as a function of crossover time



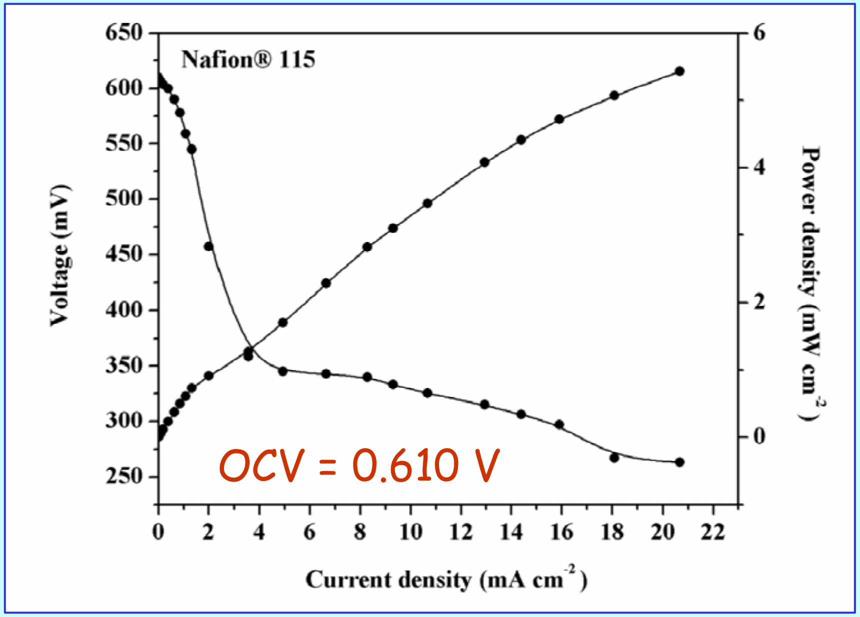
Proton conductivity at 50 % RH as a function of temperature for PVA-ZrP-Cs$_1$SWA and PVA-ZrP-Cs$_2$SWA membranes compared with Nafion® 115 at 100% RH

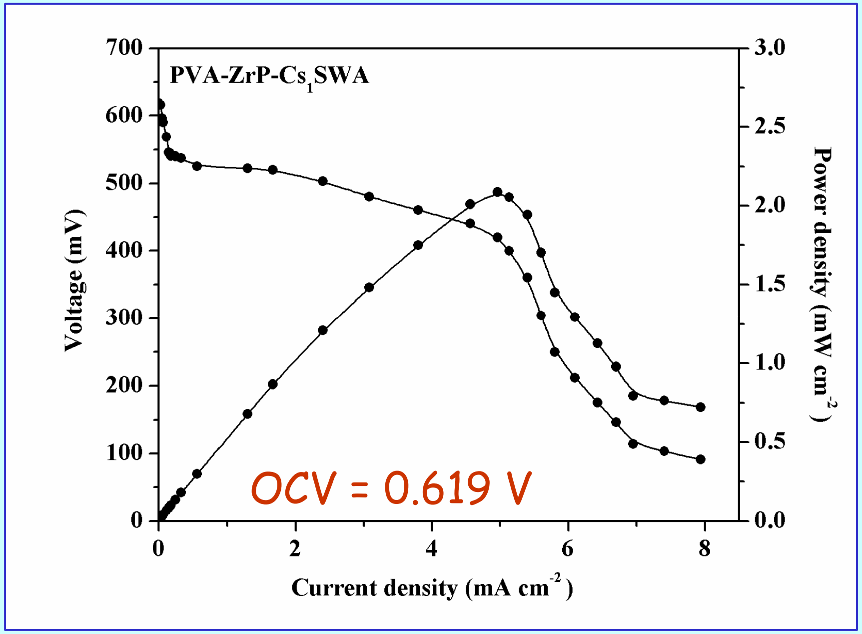


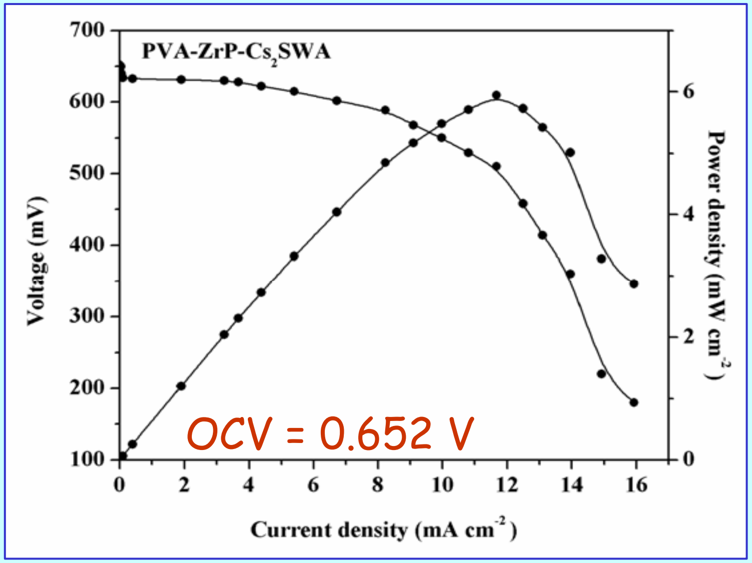
Methanol permeability of PVA-ZrP-Cs_1SWA and PVA-ZrP-Cs_2SWA hybrid membranes compared with Nafion® 115

Comparison of conductivity and permeability for various membranes

Membrane	RH (%)	Temperature (°C)	Conductivity (Scm^{-1})	Permeability (cm^2s^{-1})	References
PVA-ZrP-Cs_1SWA	50	100	0.013	2 x 10^{-6}	*J. Power Sources 163* (2006) 433
PVA-ZrP-Cs_2SWA	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	-	J. Membr. Sci., 217 (2003) 5
SPEK/ZP/ZrO_2 (70/20/10 wt %)	100	70	2.3 x 10^{-3}	-	Solid State Ionics, 162–163 (2003) 269-275.
PVA/PWA/SiO_2	-	-	0.004-0.017	10^{-7} to 10^{-8}	Solid State Ionics, 171 (2004) 121-127
PEG/SiO_2/SWA	100	80	0.01	10^{-5} to10^{-6}	J. Power Sources, 139 (2005) 141-151
PEG/SiO_2/PWA	-	-	10^{-5} to 10^{-3}	10^{-6} to10^{-7}	J. Membr. Sci., 254 (2005) 197-205
PVA–SiO_2–SWA	100	100	4.13 x 10^{-3}	-	J. Membr. Sci., 275 (2006) 105-109
SPEEK/PWA	100	100	1.7 x 10^{-2}	-	J. Membr. Sci., 254 (2005) 197-205







Passive cell DMFC

Electrode area = 2 x 3 cm^2
catalyst loading = 6 mg/cm^2
4 M CH_3OH

Polarization and power density curves for passive DMFC cell with Nafion® 115, PVA-ZrP-Cs$_1$SWA and PVA-ZrP-Cs$_2$SWA hybrid membranes as proton conducting electrolyte at 273 K and at atmospheric pressure

Characteristic of commercial and composite membranes for DMFCs

Membrane	Water uptake (%)	IEC meq g^{-1}	Methanol diffusion coefficient $cm^2\ s^{-1}$	DMFC performance	Proton conductivity
Nafion 117	28-31	0.9	1.72×10^{-6}	OCV=0.65 V and current density 100 $mAcm^{-2}$ (0.5 V, 70°C, 2 bar air, 2 M)	95 mS cm^{-1} (25°C)
CRA-08 [a]	33.7	1.4-2.2	0.58×10^{-6}	-	45 mS cm^{-1} (60°C)
IonClad® R1010 [b]	-	1.2	0.6×10^{-6}	-	146 mS cm^{-1} (60°C)
SPEEK	30 (SD=87 %)	1.7	17.5×10^{-7}	current density 25 $mAcm^{-2}$ (0.5 V, 80°C, 2M)	13 mS cm^{-1} (60°C)
Composite membrane	40-80	2-3	10^{-8}	OCV=0.75 V and current density 160 mA/cm^2 (0.35 V)	0.1-0.93 S cm^{-1}(90°C)

a- Polyethylene-Tetra-fluoroethylene with sulphonyls in divinyl benzene matrix

b- Tetra-fluoroethylene with poly(styrene sulfonic acid)

Summary of Inorganic-Organic Composite Membranes

Membranes	**(Water uptake in %)** **[Swelling %]** **{IEC}**	**Conductivity σ (S/cm)** **(Temp in ºC))** **[RH %]**	**Diffusion coefficient/ permeability**	**Fuel cell performance**
Silica as filler				
Nafion–SiO_2			10^{-5} cm^2 s^{-1}	DMFC performance- current density of 0.6 A/cm^2 at a cell potential of 0.4 V at 130 °C
Nafion®/Aerosil (SiO_2)	(30-40)	0.1 – 0.4 (90)	0.1 mol m^{-2} s^{-1} Selectivity 4 - 6	
sulfonated polysulfone/ SiO_2		5 x 10^{-2} (25-90)		Power density in 2M methanol/oxygen fuel cell 0.18 W/cm^2 at 120 °C
PEO/SiO_2		10^{-3} (80)		
PTFE /amorphous fumed SiO_2		0.22		DMFC (OCV) was 0.56 and 0.65 V with 50 and 130 mW cm^{-2} at 80 and 130 °C, respectively.
PTFE/SiO_2 (commercial SiO_2 sol)		0.1 (RT)		
Nafion/polyaniline/ SiO_2	(20)	9.1 x 10^{-3} (50) [100]	methanol crossover of the composite membrane is reduced by over two orders of magnitude	The MEA performance of polyaniline modified membranes reaches 8 mW cm^{-2} at 40 °C in a cell operating on 2 M methanol solution and air. This performance is about two-fold lower than for MEAs with Nafion,
Nafion/PTFE/ SiO_2		3.25 × 10^{-3}		OCV of 0.564 V for DMFCs operated at 70 °C, with methanol feed concentration of 2M with maximum power density of 70 mA cm^{-2}

Membranes	**(Water uptake in %) [Swelling %] {IEC}**	**Conductivity σ (S/cm) (Temp in °C)) [RH %]**	**Diffusion coefficient/ permeability**	**Fuel cell performance**
Poly(vinylidene) fluoride-chloro tetrafluoro ethylene, (PVdF-CTFE), copolymer/SiO_2		10^{-2} (RT)		DMFC- power density of about 1.4 mW cm^{-2} and currents of the order of 10–20 mA cm^{-2}
PEG / DBSA(4-dodecylbenzene sulfonic acid) /SiO_2	(30-60) {0.5 - 1 m mol g^{-1}}	4 – 7 x 10^{-3} (RT) [100]	(0.78 - 2.1) x 10^{-8} cm^2 s^{-1} Selectivity = 5.09 x 10^3 – 1.87 x 10^5	
Sulfonated styrene-(ethylene-butylene)-sulfonated styrene (SEBSS)/ SiO_2			8-14 µ mol cm^2 s^{-1}	DMFC- highest current densities are 74, 229, and 442 mA/cm^2 at temperatures 30, 60, and 90°C at a potential of 0.3.
PVA/functionalized SiO_2/ Glutaraldehyde		10^{-1}		
Krytox- SiO_2–Nafion®	(42)	10^{-4} (130)		
Nafion®/Diphenylsilicate		2.39 x 10^{-2}		DMFC performance shows OCV of 0.65 V with 1.0 M methanol
Nafion / diphenyldimethoxysilicate	[30]	10^{-2} (RT)		DMFC-performance is comparable to that of Nafion.
Nafion/Organic SiO_2 with thiol group		1.57 x 10^{-2} (RT) [100]		The DMFC performance at 75°C with 0.2 MPa O_2 & 1M methanol - Nafion 117 membrane> Nafion/Organic silica with thiol group> Nafion/ silica(unmodified)

Membranes	**(Water uptake in %) [Swelling %] {IEC}**	**Conductivity σ (S/cm) (Temp in °C)) [RH %]**	**Diffusion coefficient/ permeability**	**Fuel cell performance**
Sulfonation of poly(ether sulfone)/ SiO_2 with phosphonic acid functionality	(28.73) {0.961mequiv. g^{-1}}	6.36 x 10^{-2}	4.89 x 10^{-7} cm^2 s^{-1}	Performance of DMFC reaches 30W/cm^2 at 70 °C in a cell operating in air mode with 10 psi pressure
PVDF/ SiO_2 with surface-anchored sulfonic acid		3.6 x 10^{-3} (75)		DMFC- OCV value of the cell was 0.66 V & power density 32 mW cm^{-2} at 70 °C
$Cs_{2.5}H_{0.5}PWO_{40}/SiO_2$/Nafion® NRE-212 membrane				H2/O2 fuel cells with Cs2.5H0.5PWO40-SiO2/Nafion showed better performance than Nafion® NRE-212 membranes at 60 °C and 80 °C.
Alumina as filler				
Nafion/Al_2O_3				DMFC performance- current density of 0.4 A/cm^2 at a cell potential of 0.4 V at 130 °C
PVDF-g-PSSA/Al_2O_3	(68)	4.5 × 10^{-2}	6.6 × 10^{-8} cm^2 s^{-1} Selectivity 6.8 × 10^5 S s cm^{-3}	The maximum peak power density DMFC is about 12 mW cm^{-2} with 2.5 M methanol.
poly-vinylidene fluoride/poly-acrylonitrile (PVdF/PAN)/ Al_2O_3		0.10		
poly(vinylidene) fluoride /alumina/ dodecatungstophosphoric acid		10^{-3} (< 50)		

Membranes	**(Water uptake in %) [Swelling %] {IEC}**	**Conductivity σ (S/cm) (Temp in ºC)) [RH %]**	**Diffusion coefficient/ permeability**	**Fuel cell performance**
Zirconia as filler				
Nafion/ ZrO_2	(24) {0.85 meq g^{-1}}			H_2/air fuel cell - Power density values of 604 mW cm^{-2} and of 387 mW cm^{-2} were obtained at 0.6 V and at $T = 110$ °C (100% of RH) and $T = 130$ °C (85% RH), respectively
Sulfonated poly(ether ether ketone) (SPEEK)/ ZrO_2		34×10^{-3} (25)	60-fold reduction of the methanol flux.	
Nafion / sulfated zirconia	(27) {0.9-1.1 meq g^{-1}}			H_2/O_2- 1.35 W/cm^2 at 80 °C and 0.99 W/cm^2 at 120 °C was better than that of Nafion under same condition (e.g. 1.28 W/cm^2 at 80 °C, 0.75 W/cm^2 at 120 °C).
Titania as filler				
Nafion/TiO_2	(29) {0.93 meq g^{-1}}	0.15–0.18 (85) [100]		PEMFC- Power density values of 0.514 and 0.256 W cm^{-2} at 0.56 V were obtained at 110 and 130 °C, respectively,
PVA/TiO_2	(89)	10^{-2} (30)		The maximum peak power density of the alkaline DMFC is about 7.54 mW cm^{-2} at 60 °C
Nafion®/sulfonated titanate		0.16 (75)	Permeability of methanol reduced by 38 %, relative to Nafion 115	DMFC-57% higher power density (73.0 mW cm^{-2}) than Nafion

Membranes	**(Water uptake in %) [Swelling %] {IEC}**	**Conductivity σ (S/cm) (Temp in ºC)) [RH %]**	**Diffusion coefficient/ permeability**	**Fuel cell performance**
Titania as filler				
Nafion/TiO_2	(29) {0.93 meq g^{-1}}	0.15–0.18 (85) [100]		PEMFC- Power density values of 0.514 and 0.256 W cm^{-2} at 0.56 V were obtained at 110 and 130 °C, respectively,
PVA/TiO_2	(89)	10^{-2} (30)		The maximum peak power density of the alkaline DMFC is about 7.54 mW cm^{-2} at 60 °C
Nafion®/sulfonated titanate		0.16 (75)	Permeability of methanol reduced by 38 %, relative to Nafion 115	DMFC-57% higher power density (73.0 mW cm^{-2}) than Nafion
Tungten trioxide as filler				
Nafion/ WO_3	(37)	10^{-2} (100)		PEMFC- operated at 110 °C- current densities of 300 and 540 mA/cm^2 at 0.4 V
PEO/$WO_3{\cdot}2H_2O$		10^{-2}–10^{-3} (R.T. to 120)		

Membranes	(Water uptake in %) [Swelling %] {IEC}	Conductivity σ (S/cm) (Temp in °C)) [RH %]	Diffusion coefficient/ permeability	Fuel cell performance
Heteropolyacids as filler				
Nafion/PTA, PMA, STA, SMA	(8)	0.06-0.08 (70) [100]		H_2/air- current density of 0.1-0.9 A/cm^2 at a cell potential of 0.6 V at 80 °C and at 75 %RH
Sulfonated poly(arylene ether sulfone)/PTA	(15-40) {1.4 meq g^{-1}}	0.09 - 0.15 (30-100) [100]		
Poly(vinyl alcohol)/ PTA	(157) {0.794 m mol g^{-1}}	10^{-4}	6.16×10^{-7} to 8.31×10^{-10} $cm^2\ s^{-1}$	H_2/O_2 current density of 46 mA cm^{-2} DMFC current density of 80 mA cm^{-2} at 80 °C.
s-Polyether ether ketone (PEEK)/Heteropolyacids(tungstophosphoric acid, $H_3PW_{12}O_{40}\ 29H_2O$ (TPA), molybdo-phosphoric acid, $H_3PMo_{12}O_{40}\ 29H_2O$ (MPA) and the disodium salt of tungstophosphoric acid, $Na_2HPW_{12}O_{40}$ (Na-TPA)	sPEEK -TPA (600) sPEEK – MPA (320) sPEEK - Na-TPA (400)	sPEEK -TPA 9.5×10^{-3} sPEEK - MPA 3.0×10^{-3} sPEEK - Na-TPA 5.8×10^{-3} (100)		
Sulfonated polyethersulfone Cardo/ PTA	(52)	6.7×10^{-2} (110)		
Nafion/polyphenylene oxide (PPO)/phosphomolybdic acid (PMA)		0.03	2.01×10^{-6} $cm^2\ s^{-1}$	DMFC - OCV=0.75 V and current density 160 mA/cm^2 0.35 V.
polyethylene glycol/silica/lacunary heteropolyacid ($H_8SiW_{11}O_{39}$)	{2–2.5 meq g^{-1}}		1.2×10^{-6} $cm^2\ s^{-1}$	
Nafion®/ Sulfonic-functionalized heteropolyacid/silica nanoparticles				DMFC- The power density was 33 mW cm^{-2} at 80 °C, 39 mW cm^{-2} at 160 °C and 44 mW cm^{-2} at 200 °C, respectively.

Membranes	**(Water uptake in %) [Swelling %] {IEC}**	**Conductivity σ (S/cm) (Temp in ºC)) [RH %]**	**Diffusion coefficient/ permeability**	**Fuel cell performance**
SPEEK/silica/divacant tungstosilicate $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$		13×10^{-3} (110) [100]	$0.8 \times 10^{-16}\ \text{m}^{2}\ \text{s}^{-1}\ \text{Pa}^{-1}$	
Nafion /SiO_2/phosphotungstic acid (PWA)	(38)	0.01 (100) [40]		PEMFC- operated at 110 °C- current densities of 540 mA/cm^2 at 0.4 V
PBI /PWA/SiO_2		3.0×10^{-3} (100) [100]		
PVA/PWA/SiO_2	[10-30]	0.017 (RT)	10^{-7} to 10^{-8} cm^2/s. Selectivity 0.02×10^{7}	
PVA/silica/silicotungstic acid		$(4.13–8.31) \times 10^{-3}$ (80 to 100) [100]		
PEG/SiO_2/PWA	(44.7)	10^{-3}	$1.05\times10^{-7}\ cm^2\ s^{-1}$	H_2/O_2FC OCV=900 mV DMFC OCV=650 mV
Nafion®/PTA supported on SiO_2, ZrO_2 and TiO_2			low crossover compared to recast Nafion®	The MEAs, at 120 ◦C and 35% RH indicated that the composite membranes had 15% superior conductivity when compared to recast Nafion®
SPEEK/heteropolyacids loaded MCM-41	(74-83)	$6.7\text{-}8.1 \times 10^{-3}$ (140)		

Membranes	**(Water uptake in %) [Swelling %] {IEC}**	**Conductivity σ (S/cm) (Temp in ºC)) [RH %]**	**Diffusion coefficient/ permeability**	**Fuel cell performance**
Polyethyleneimine (PEI)/Tungstosilicate mesoporous materials(Si-MCM-41)		6.1×10^{-2} (100) [100]		Performance at 100 °C and 100% RH OCV= 0.93 V current density= 42.9 mA/cm^2 power density=18.3mW/cm^2
Sulfonated polyether ether ketone (SPEEK) /heteropolyacid-loaded Y-zeolite	(70-98)	$7.8\ x10^{-3}$ (140)		
PVA/zirconium phosphate/silicotungstic acid	[90] {0.9 meq g^{-1}}	10^{-2} (100) [60]	5×10^{-7} ($cm^2\ s^{-1}$)	
Zirconium phosphate or Zirconium sulphophenyl phosphate (ZrSPP) as filler				
Nafion/ zirconium phosphates		0.025 [92]		The power output of Nafion 117 was higher than that of the composite under the same conditions.
Disulfonated poly(arylene ether sulfone)/ Zirconium hydrogen phosphate	(40-60)	0.027 (80) [100]	7.5×10^{-7}	
Nafion®/Teflon®/$Zr(HPO_4)_2$				H_2/O_2 - demonstrated high performance - The cell voltages achieved at 400 mA/cm^2 current density were 0.73 and 0.59V, at 80 and 120 ◦C, respectively under ambient pressure.

Membranes	**(Water uptake in %) [Swelling %] {IEC}**	**Conductivity σ (S/cm) (Temp in ºC)) [RH %]**	**Diffusion coefficient/ permeability**	**Fuel cell performance**
Nafion/PTFE/zirconium phosphate		2.38 x10^{-3} (70-80)	1.64x10^{-4} for composite membranes 8.77x10^{-4} Nafion-117 (wt% cm hr^{-1})	Decreased fuel cell performane compared to Nafion
zirconium phosphate/ divinylbenzene (DVB) crosslinked, sulfonated, polystyrene grafted poly(ethylene-alt-tetrafluoroethylene)/poly(vinyl difluoride)	{1.8–2 meq g^{-1}}	40 x10^{-3} (130) [90]		
Nafion/ZrSPP		10^{-1} (110) [98]		H_2/O_2 -current density of Nafion/ZrSPP 20 wt% was 700 mA/cm^2 at 100 °C, it was four times higher than that of Nafion at the same voltage of 0.4 V.
Polybenzimidazole/ zirconium tricarboxybutylphosphonate		3.82 × 10^{-3} (200)		
PVDF/Zirconium sulfophenylenphosphonate,Zr(SPP), $Zr(HPO_4)_{1.0}(O_3PC_6H_4SO_3H)_{1.0}$	(46)	2 x10^{-3} (120) [90]		
SPEEK/zirconium phosphate sulfophenylenphosphonate		0.03 (60) [100]		

Membranes	**(Water uptake in %) [Swelling %] {IEC}**	**Conductivity σ (S/cm) (Temp in ºC)) [RH %]**	**Diffusion coefficient/ permeability**	**Fuel cell performance**
Sulfonated poly(etheretherketone) cardo/ zirconium phosphate sulfophenylenphosphonate	(10-40)	10^{-2} (22) [100]	45 × 10^8 (cm^2 s^{-1}) reduced by one order of magnitude compared to Nafion	
Poly (fluorinated arylene ether)s/ Zirconium phosphate sulfonated	(85.6)	1.63 × 10^{-2} (RT)		PEMFC- current densities 760 mA/cm^2 and 470 mA/cm^2 at 0.6 V
sPEEK/ZrPh/PBI	[0.6]	11.5 x10^{-3} (25)	4.0 × 10^3 barrier (1 barrer = 10^{-10} cm^3 [STP] cm/(cm^2 s cmHg))	DMFC at 110 °C and 138% RH - power density value of 14.7 mW/cm^2 for 58.8 mA/cm^2
PVA/zirconium phosphate/ Cesium salt of silicotungstic acid	(100) [85] {3 meq g^{-1}}	10^{-2} (100) [50]	2×10^{-6}(cm2 s−1)	DMFC- maximum power density of 6mWcm^{-2} OCV (0.652 V) is higher compared to Nafion® 115 (0.610 V)
SPEK/ZrP/ZrO_2	(21.5) [100]	0.8 (25)	9.75 × 10^3 barrer 8247 g h^{-1} m^{-2}	DMFC- exhibits lower performance compared to Nafion

Layered silicate nanoparticles (e.g., montmorillonite, Laponite, and modified montmorillonite) as fillers				
Nafion 115/sulfonated montmorillonite	(93)	0.93	1.14×10^{-6} $cm^2\ s^{-1}$	DMFC - 30 mW cm^{-2} for composite and for Nafion 115 membrane (25 mW cm^{-1}) at a cell voltage of 0.35 V
SPEEK/MCM-41		$8\text{-}16\times 10^{-3}$	3×10^{-17} ($m^2\ s^{-1}$ Pa $^{-1}$)	
SPEEK/laponite		$3\text{-}10\times 10^{-3}$ (90)	3×10^{-17} ($m^2\ s^{-1}$ Pa $^{-1}$)	
SPEEK/organic-montmorillonite (OMMT)	(150)	1.2×10^{-2} (90) [100]	10^{-8} $cm^2\ s^{-1}$	
Nafion®/poly(oxyproplene)/ montmorillonite (MMT)	(32) {0.89 mmol g^{-1}}	$60\text{-}90 \times 10^{-3}$	0.4 x 10^{-8} $cm^2\ s^{-1}$ Selectivity =5500	DMFC - maximum power density of 13.3 mW cm^{-2} at 0.2 V
Nafion/organic sultones and perfluorinated sultone grafted montmorillonite (MMT)	{0.8-1.1 mmol g^{-1}}	0.13 (50) [98]	Reduced by 40% compared to Nafion	passive single cell DMFC - current densities 140 mA cm^{-2}, at 0.3 V
Polyimide (PI), polyamideimide (PAI), polyvinylidene fluoride PVDF/ styrene–ethylene–butylenes–styrene elastomer (SEBS)/phosphosilicate (P_2O_5–SiO_2)		PI/ (P_2O_5–SiO_2) - 1.6×10^{-2} (150) [18] PAI /(P_2O_5–SiO_2) - 1.5×10^{-3} (150) [18] PVdF/(P_2O_5–SiO_2) - 8.1×10^{-4} (130) [25] SEBS/ (P_2O_5–SiO_2) - 6.9×10^{-3} (130) [25]		PI/ (P_2O_5–SiO_2) OCV of 0.9 V 25– and power density of 20 mW cm^{-2} at 150 °C under 4% RH. PAI /(P_2O_5–SiO_2) OCV of 0.95 V and power density of 52 mW cm^{-2} at 30 °C under 60% RH . PVdF/(P_2O_5–SiO_2) OCV of 0.79 V at 130 and 150 °C. Power density of 29 mW cm^{-2} at 130 °C under 25% RH 10^{-2} - SEBS/ (P_2O_5–SiO_2) OCV of 0.72 V at 150 °C 14% RH. Power density of 34 mW cm^{-2} at 110 °C under 30% RH

Membranes	**(Water uptake in %) [Swelling %] {IEC}**	**Conductivity σ (S/cm) (Temp in ºC)) [RH %]**	**Diffusion coefficient/ permeability**	**Fuel cell performance**
Phosphatoantimonic acid				
Sulfonated polysulfone/ Phosphatoantimonic acid		10^{-2} (80) [92]		
Noble metals (Pt,Ru)				
($Pt-SiO_2$)nafion coated /SPEEK/PTFE				H_2/O_2 fuel cell - OCV = 0.98 V and maximum power density value of 0.8 W cm^{-2} than 0.94 V, 0.33 W cm^{-2}
Pt/SiO_2/ Nafion/PTFE	(54) [6.7]		10^{-3} cm^2/s	PEMFC -80 °C (1.65 W cm^{-2}). The cell performance with the Pt–SiO_2 /Nafion/PTFE- was better than that with the NRE-212
Pt–ZrP–Nafion		0.06 [RT]		PEMFC performance - 275 mA/cm^2 at cell voltage of 0.620 V
PtRu/Nafion		0.18 (90) [100]		DMFC single cell test - the performance of the composite membrane was approximately 28% and 31% higher at an operating temperature of 30 and 45 °C than the pure Nafion membrane, respectively
$Ag-SiO_2$/sulfonated poly(biphenyl ether sulfone	(60-100)			H_2/O_2 single PEMFCs -exhibits better performance compared to parent polymer

Membranes	**(Water uptake in %) [Swelling %] {IEC}**	**Conductivity σ (S/cm) (Temp in ºC)) [RH %]**	**Diffusion coefficient/ permeability**	**Fuel cell performance**
Zeolite				
Nafion /Zeolite (ZSM-5)	(30)	0.14 (RT)	1.4×10^{-6} cm^2 s^{-1}	
Nafion /chabazite and clinoptilolite				DMFC- Maximum power densities of 350–370 mW cm^{-2} and 200–210 mW cm^{-2} were recorded at 140 °C
Poly(tetrafluoroethylene) (PTFE)/zeolite	(60-80)	0.01 (RT)		DMFC at 70°C - Maximum current and power densities obtained were ~ 50 mA/cm^2 and 4 mW/cm^2
Pt/zeolite–Nafion (PZN)	(38.6)			With dry H_2 and O_2 at 50 °C, 0.65 wt.% of Pt/zeolite shows 75% of the performance obtained at 0.6 V with humidified reactants at 75 °C
Nafion/mordenite		0.01 (70) [100]		H_2/O_2- current densities 400 mA cm^{-2}, at a potential of 0.5 V at 100°C
Phosphates				
Nafion/calcium phosphate composite			1.8×10^{-6} cm^2 s^{-1}	
Nafion/CHP (calcium hydroxyphosphate)	(34)		0.6×10^{-7} cm^2/s	
Sulfonated poly(ether ether ketone)/boron phosphate	(50-130)	0.065 (70) [100]		
SPEEK/PBI/boron phosphate	(25)	5.9×10^{-3}		

✓ 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

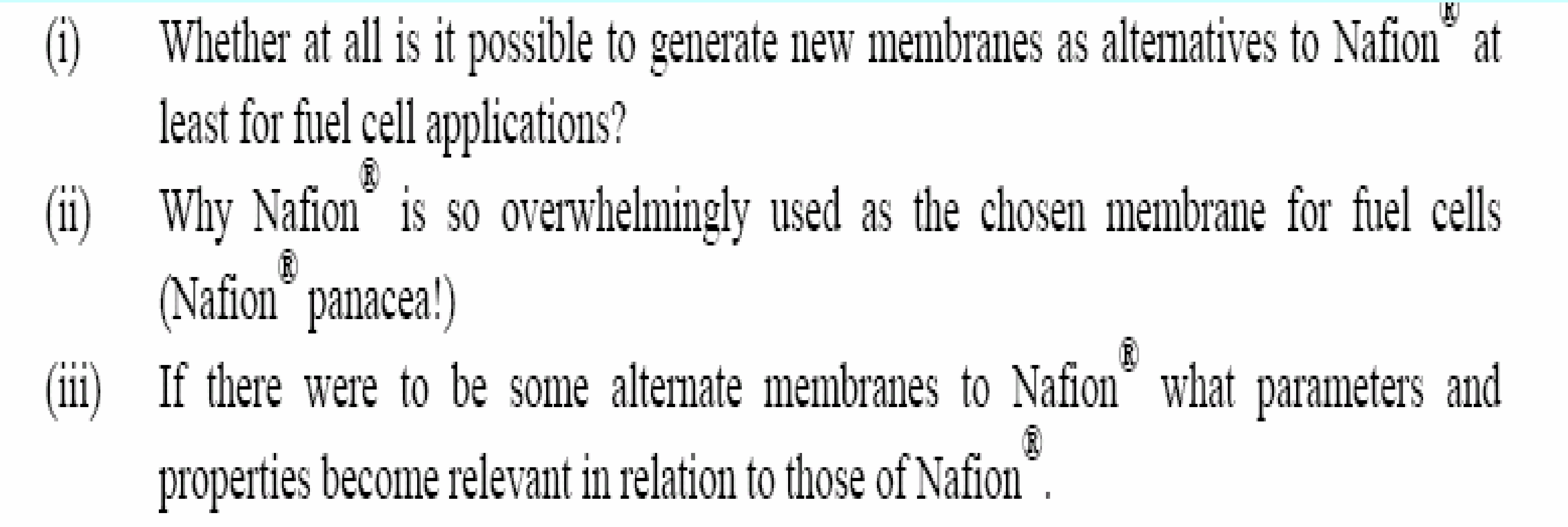
✓ At 50 % RH, the protonic conductivity of the hybrid membranes was in the range of 10^{-3} to 10^{-2} S cm^{-1}

✓ The open circuit voltage (OCV) for the cell with PVA–ZrP–Cs$_2$STA hybrid membrane is 0.652 V and that for PVA–ZrP–Cs$_1$STA 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

SUMMARY

This presentation aimed to answer the following three questions



(i) Whether at all is it possible to generate new membranes as alternatives to Nafion® at least for fuel cell applications?

(ii) Why Nafion® is so overwhelmingly used as the chosen membrane for fuel cells (Nafion® panacea!)

(iii) If there were to be some alternate membranes to Nafion® what parameters and properties become relevant in relation to those of Nafion®.

Thank you