Polymer Electrolyte for Fuel Cells-an Overview

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What is a Fuel Cell?

An electrochemical device that converts chemical energy into electrical energy directly

Advantages

- More efficient than heat Engines
- Environment friendly
- Produces no noxious emissions
- Operates quietly (less sound)
- Fuel flexibility
- Compact design

Applications

- Automobiles
- Portable electronic devices
- Mobile & Stationary power stations

Fuel Cell Types

Fuel cell type/ Fuel used	Electrolyte/ Mobile ion	Operating temp. ºC	Efficiency %	Applications
Alkaline (AFC) H_2 & O_2	KOH/ OH^-	50-100 (low)	45-60	Space vehicles: ~10 kW
Proton exchange membrane (PEMFC)/DMFC H_2 / MeOH- O_2/air	PEM/ H^+	50-130 (low)	40-60	Small and mobile applications: 0.01-100 kW
Phosphoric acid (PAFC) H_2, Natural gas-air	H_3PO_4/ H^+	180-240 (medium)	35-40	Medium applications: 100-1000 kW
Molten carbonate (MCFC)/ Natural gas-air	Molten carbonate CO_3^{2-}	~650 (high)	45-60	Medium and large applications: 0.1-10 MW
Solid oxide (SOFC) Natural gas-air	Ceramic/ O^{2-}	500-1000 (high)	50-65	Wide scale applications: 1 kW-10 MW

Major Components of PEMFC

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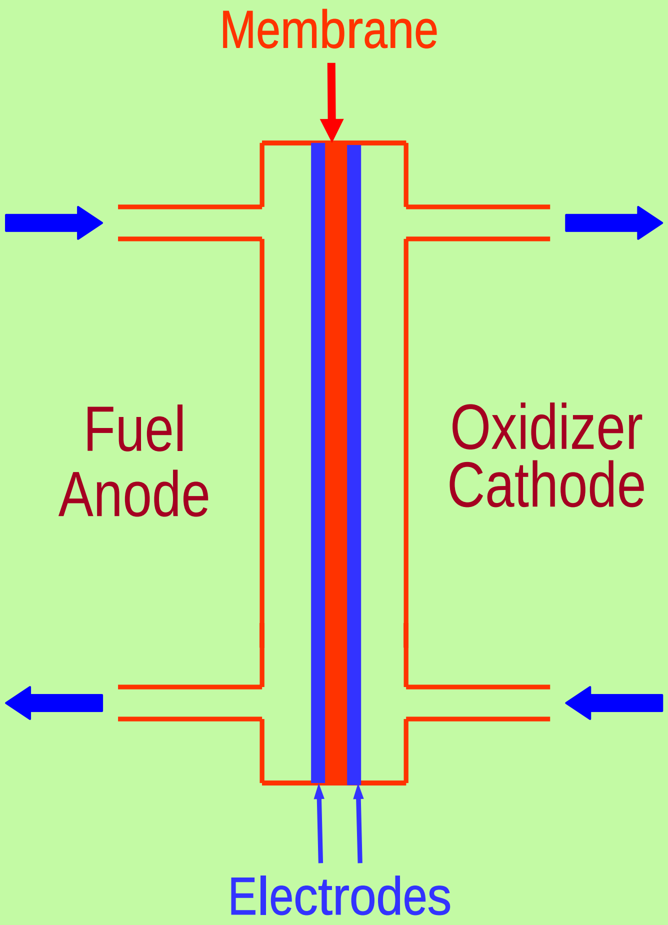
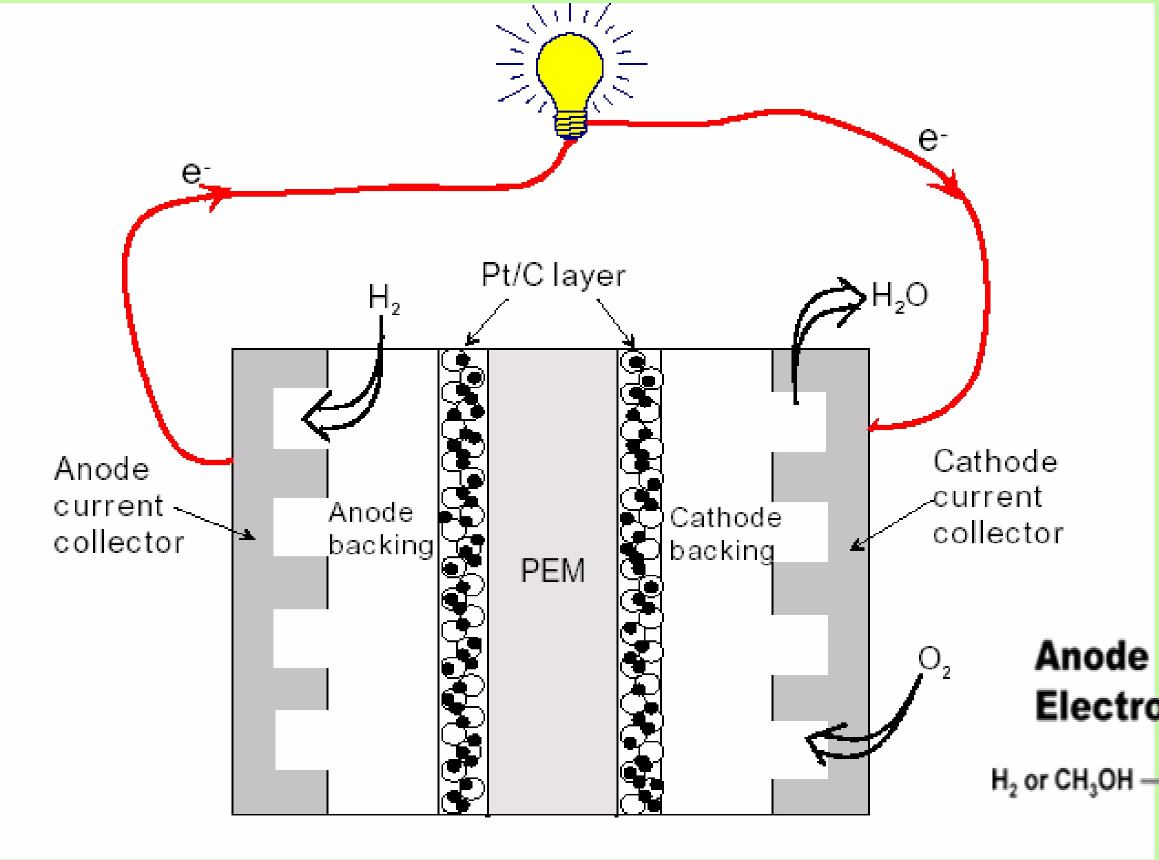
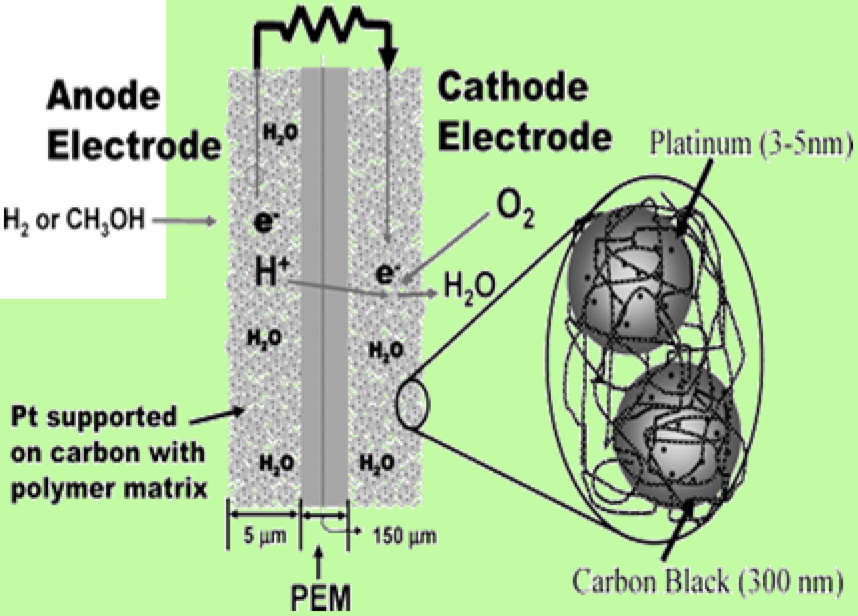
- Polymer Electrolyte Membrane
- Electrocatalyst (Pt)
- Bipolar plates (Graphite/ Polymer)



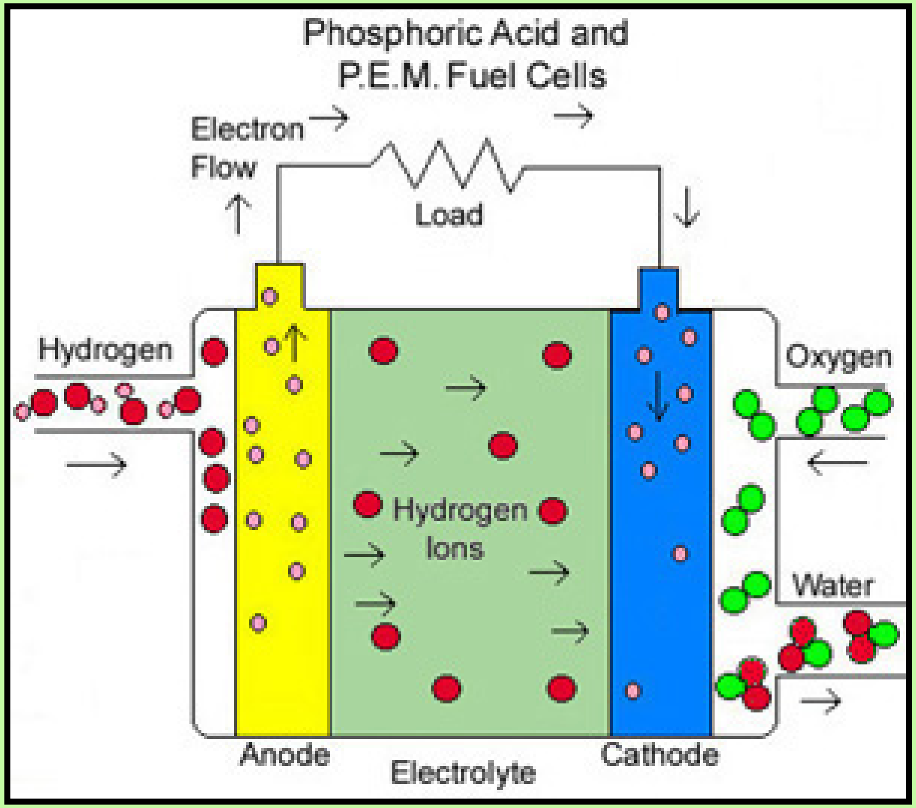
Basic Components of PEMFC

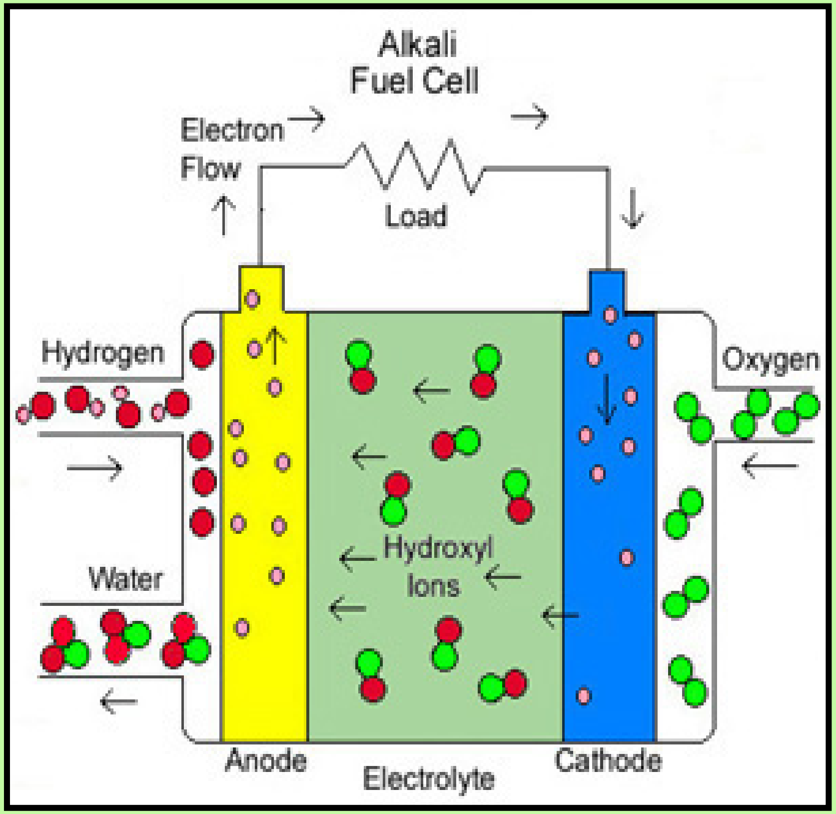
Membrane Electrode Assembly (MEA)





Electrochemical Reactions in PEMFC





Anode: $H_2 \longrightarrow 2H^+ + 2\,e^-$

Cathode: $1/2\ O_2 + 2H^+ + 2\,e^- \longrightarrow H_2O$

Overall: $H_2 + 1/2\ O_2 \longrightarrow H_2O$ + E. E + H. E

Cathode: $1/2O_2 + H_2O \longrightarrow 2OH^- + 2e$

Anode: $2OH^- + H_2 + 2e \longrightarrow H_2O$

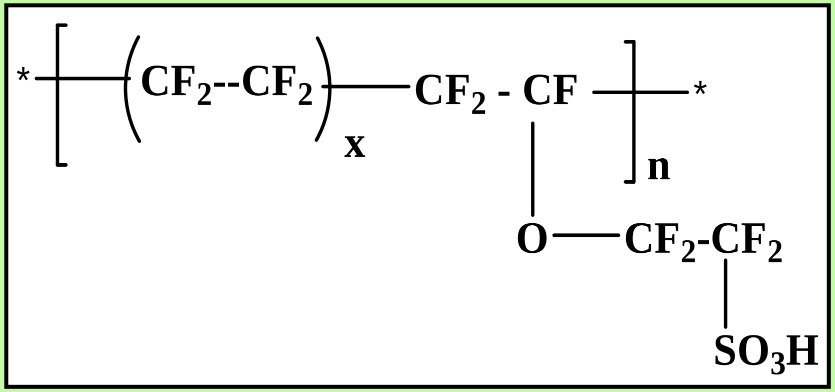
Overall: $H_2 + 1/2\ O_2 \longrightarrow H_2O$ + E. E + H. E

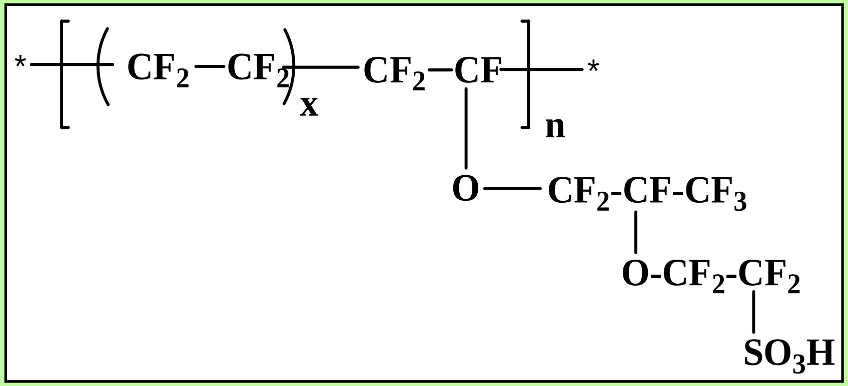
Polymer Electrolyte Membrane (MEA)

Desired Properties

- Good Mechanical strength (operating conditions)
- Good Thermal stability
- High Stability in oxidative & reductive environment
- Good Chemical & Electrochemical Stability
- Good Barrier property for reactant species
- Good Processability for MEA preparation
- Low electro-osmotic drag
- Zero Electronic conductivity
- High Proton conductivity (>0.1S/cm)
- Long life above 100^0C temperature (Operational conditions)
- Low Cost

NAFION





Advantages:

- Good mechanical strength
- High proton conductivity
- Good chemical resistance
- Low solvent solubility
- High water uptake
- Proven durability(>60,000h)
- Only material used in fuel cell today

Disadvantages:

- High cost
- Need to maintain humidity
- High electro-osmotic drag
- Poor mechanical strength at high water uptake
- High methanol crossover
- Catalyst poisoning in DMFC
- Low operating temperature (~80^0C)

Advantages of High temperature (> 100^0C) PEM

- Kinetics of both electrode reactions will be enhanced (especially) for DMFC
- Water is in single vapor phase (management easy)
- Cooling system will be simpler (larger temp. gradient between coolant & stack)
- Heat can be recovered as steam (can be used for reforming MeOH)
- CO tolerance can be enhanced (10-20 ppm at 80^0C; 1000 ppm at 130^0C; 100000 ppm at 200^0C.
- Pure H_2 is not required. H_2 from reformer can be used at 200^0C.

Development of prototype PEM fuel cell operating at high temp.(>100 ^{0}C)

Polymers used as Polymer Electrolytes

Fluorinated Polymers

- Sulfonated Ionomers (Nafion Type)
- Sulfonated Poly(trifluorostyrene)
- Graft fluorinated Polymers

Heterocyclic Polymers

- Polybenzimidazoles
- Polyoxadiazoles
- Polytriazoles

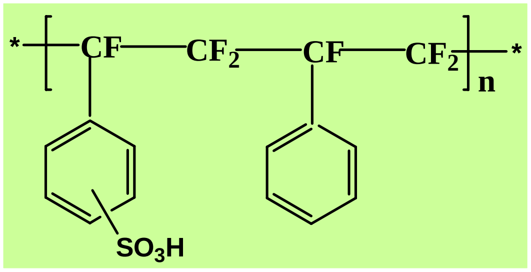
Sulfonated Aromatic Polymers

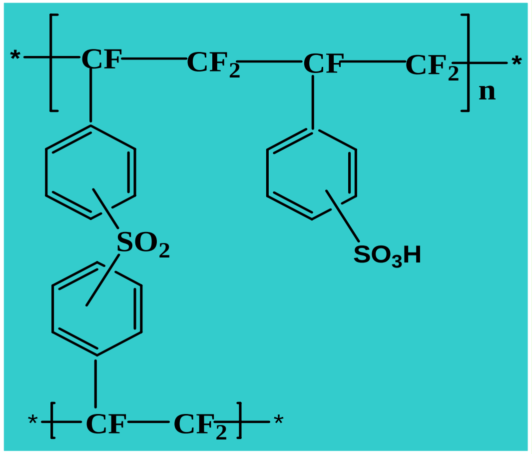
- Phenol Formaldehyde
- Polystyrenes
- Polyphosphazenes (PPZ)
- Polyphenylenequinoxaline (PPQ)
- Polyphenylene oxides (PPO)
- Polysulfones (PES)
- Polyetheretherketones (PEEK)
- Polyphenylenesulfides
- Polyimides (Polyimides)

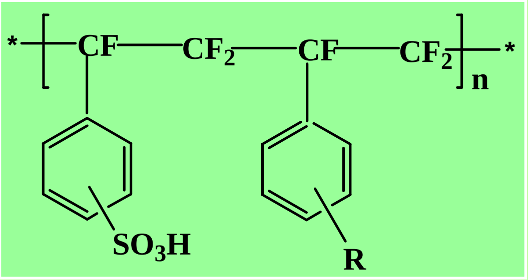
Sulfonated Hydrocarbon Polymers

- Styrene Propylene Block Copolymer
- Styrene Butadiene Block Copolymer
- Styrene Ethylene Propylene Triblock Polymer

Fluorinated Polymers

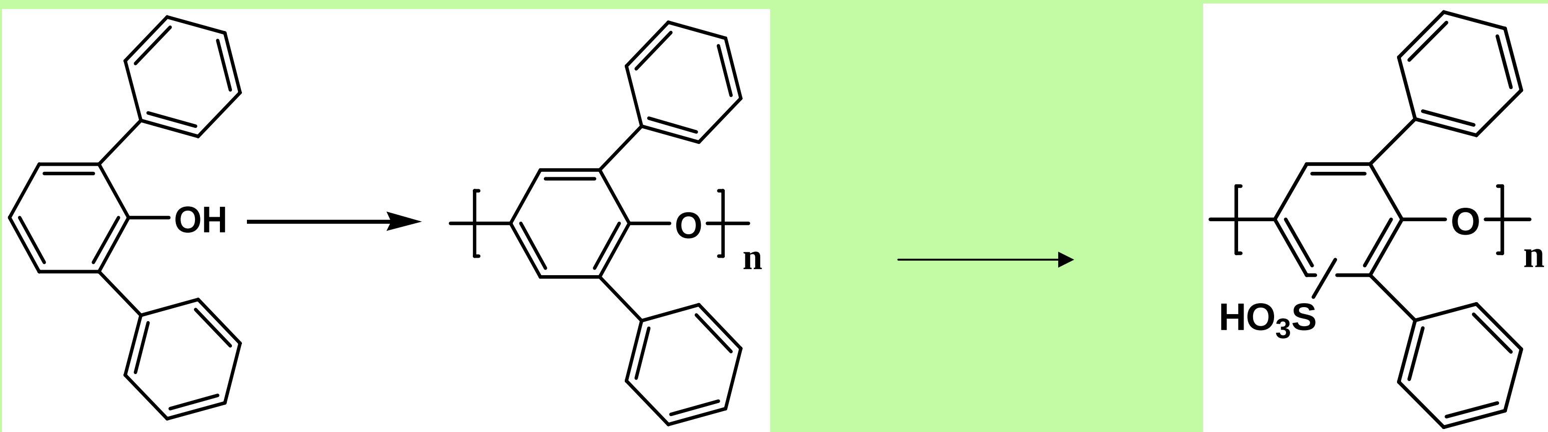






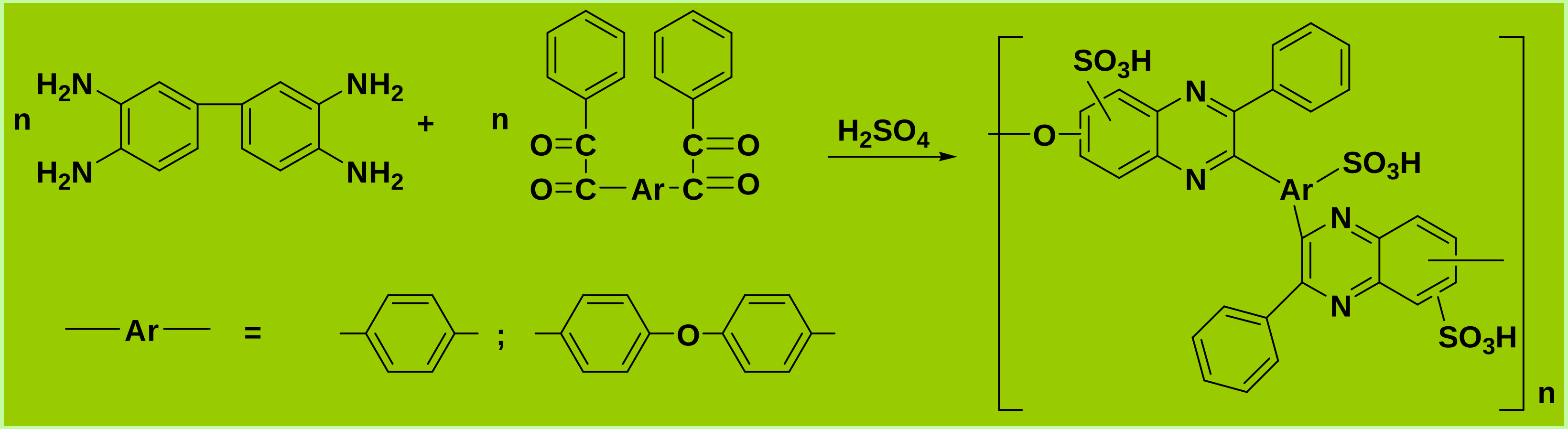
- High proton conductivity
- Resistant to oxidative degradation
- Cross-linking improves flexibility, dimensional stability and swelling
- Stable upto 15000 h at 50^{0}C (BAM3G)

Sulfonated Polyphenylene Oxides



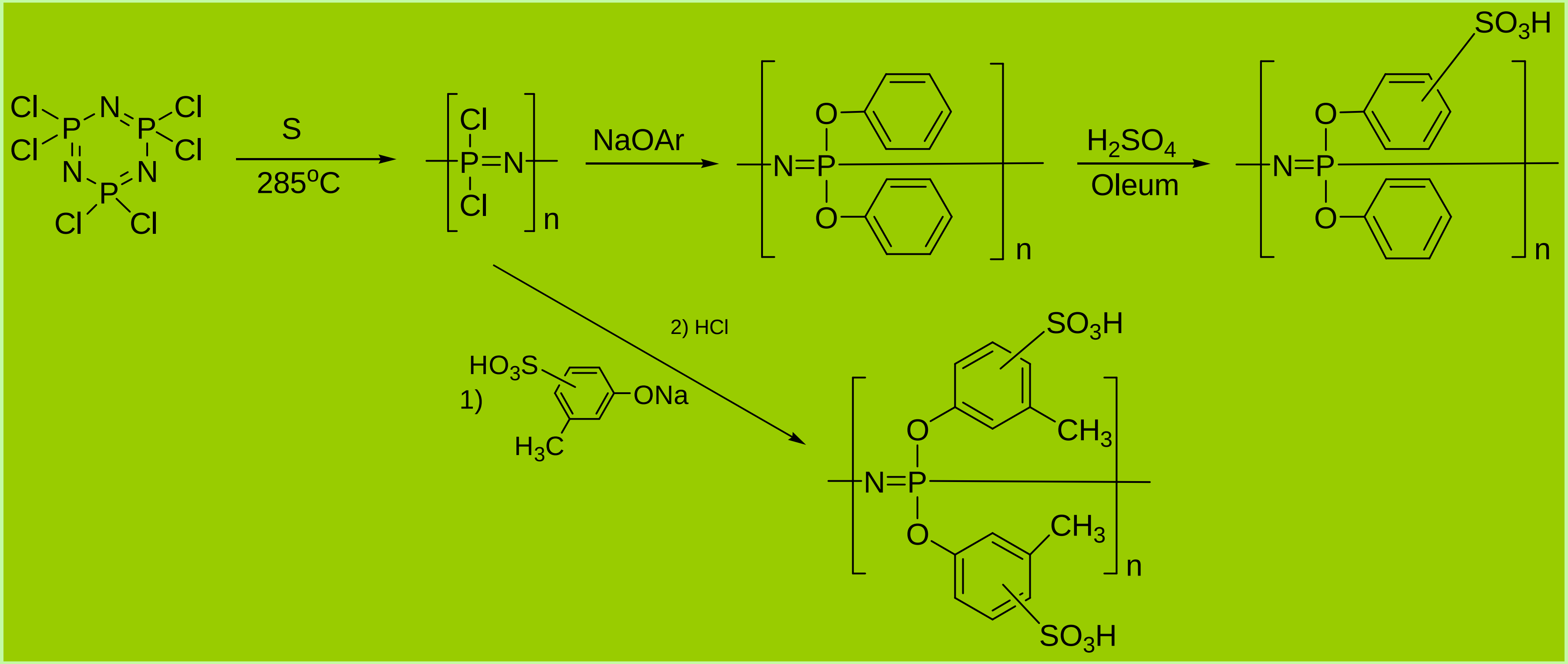
- Sulfonated by $ClSO_3H$ at back bone aryl group,
- Deactivation by Br gives sulfonation at peripheral phenyl ring
- Proton conductivity of sPPO (IEQ =2.63) is 0.012 S/cm at RT
- Life is 450 h

Sulfonated Polyphenylenequinoxaline



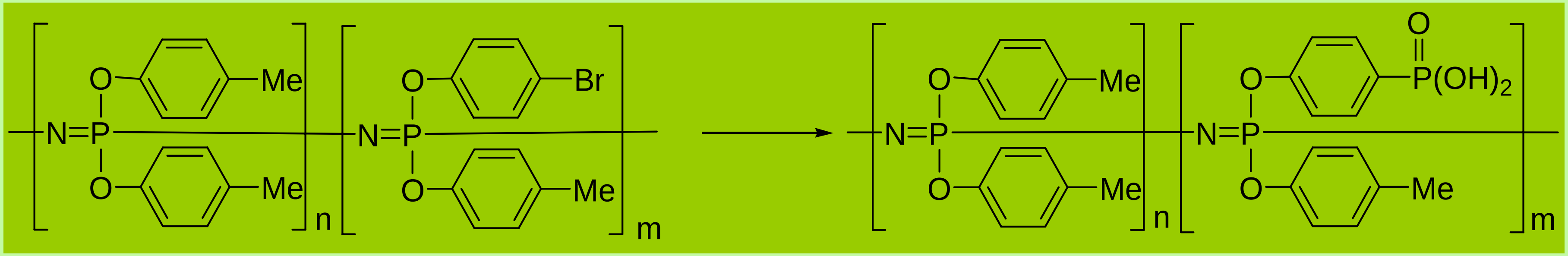
- It is sulfonated by H_2SO_4/oleum at 125^0C or by heating H_2SO_4 doped film at 300^0C
- It has high Tg of 220^0 C
- Stable upto 300^0C
- Proton conductivity is 0.1 S/cm at 80^0C (Nafion)
- It has limited life of 350 h at 70^0C for H_2/O_2 FC.

Sulfonated Polyphosphazenes



- **sPPZ prepared by condensing phenoxide with dichloroPZ followed by sulfonation**
- **By condensing sulfonated phenoxide with dichloroPZ**

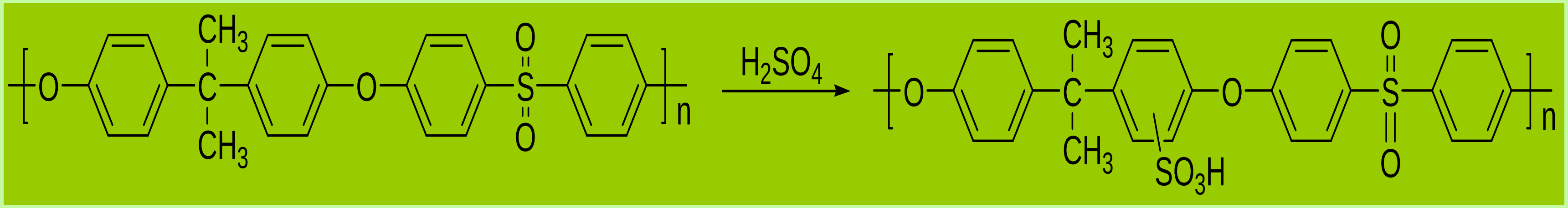
Sulfonated Polyphosphazenes (Cont.)

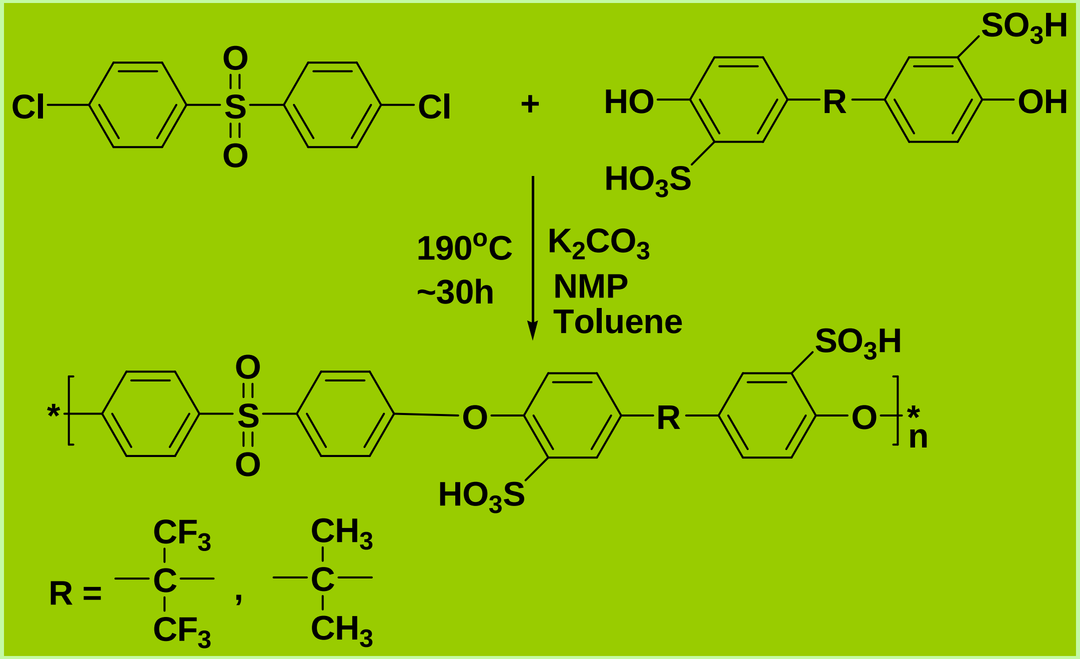


- Copolymers are prepared by condensing two different phenoxides
- 30% sulfonated polymer is soluble in water & S.P is 76^{0}C
- Photo cross-linking (Water uptake reduces 19 to 13)
- Proton conductivity is 0.04-0.08 S/cm at 30-60^{0}C & RH 100% (IEC 1.4 meq/g)
- Proton conductivity of phosphonic acid substituted (IEC 1.43 meq/g) PSZ is ~0.05 S/cm at RT (low MeOH permeability 12 times lower than Nafion)

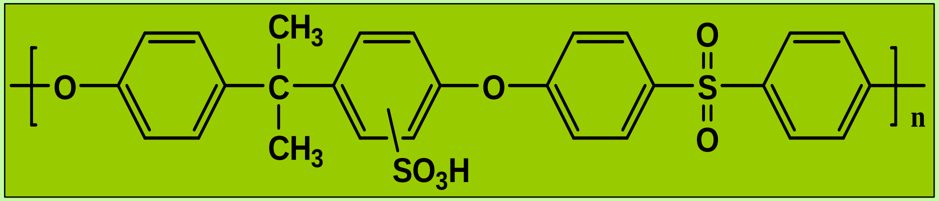
It may be useful for DMFC

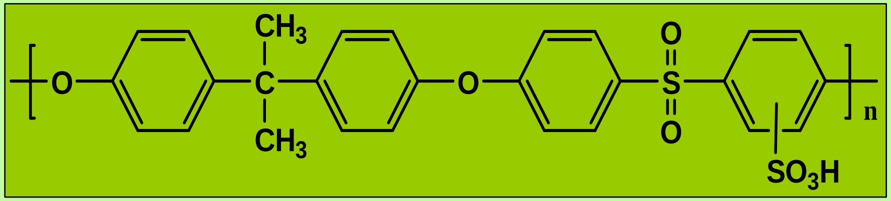
Sulfonated polysulfones





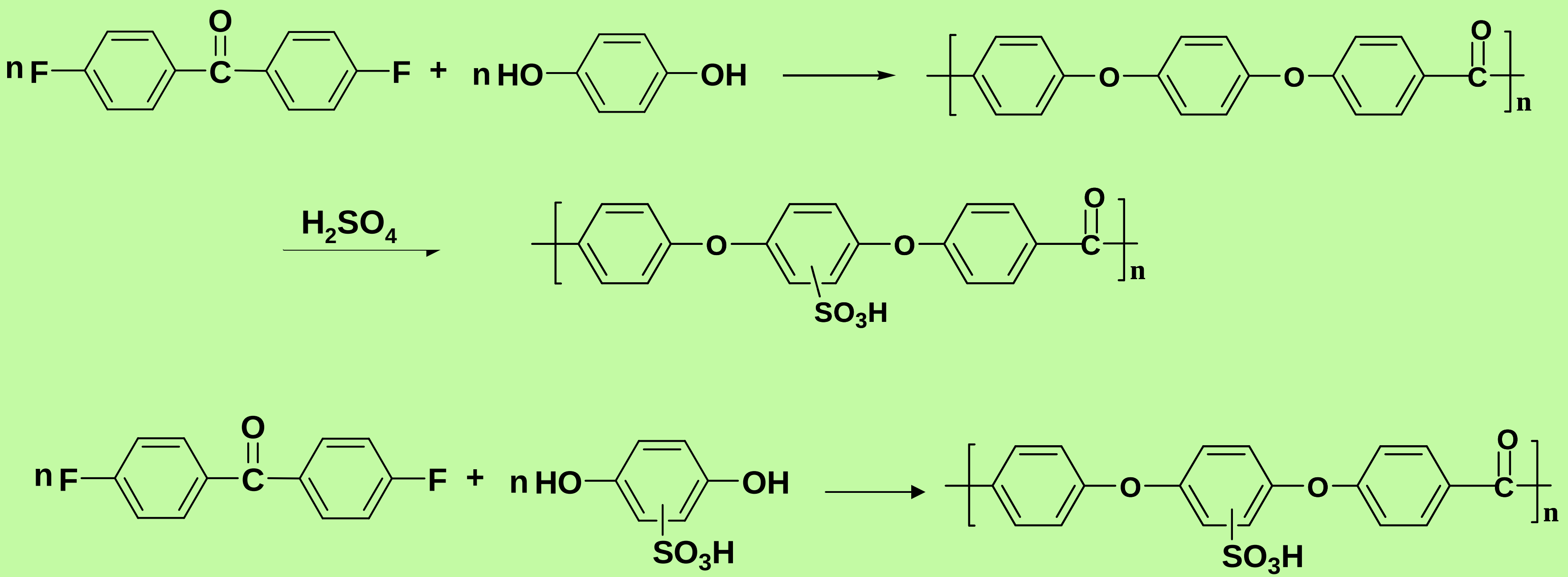
Sulfonated polysulfones (cont.)





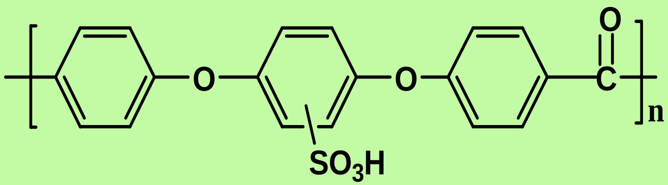
- Sulfonation by H_2SO_4 or $ClSO_3H$ leads to degradation SO_3 in DCM is preferred
- Sulfonation at o- phenol, (SO_3H group on sulfone moiety more stable)
- sPES with IEC- 2.5-3.0 has proton conductivity similar to Nafion, but high swelling.
- Cross-linked by diamine, reduces IEC
- Condensation polymers preferred. sPES with IEC 0.41-2.2 has 0.01-0.16 S/cm at 30^0C conductivity.

Sulfonated PEEK

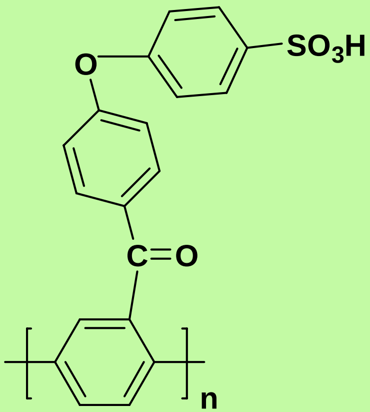


- PEEK is synthesized by condensing bisphenol with difluorobenzophenone

Sulfonated PEEK (cont.)



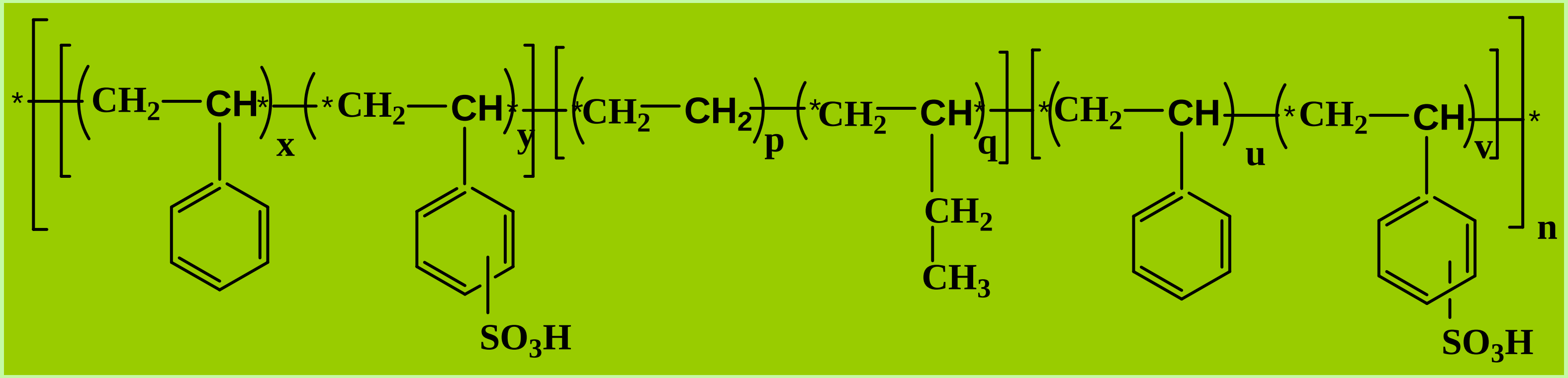
sPEEK



sPPBP

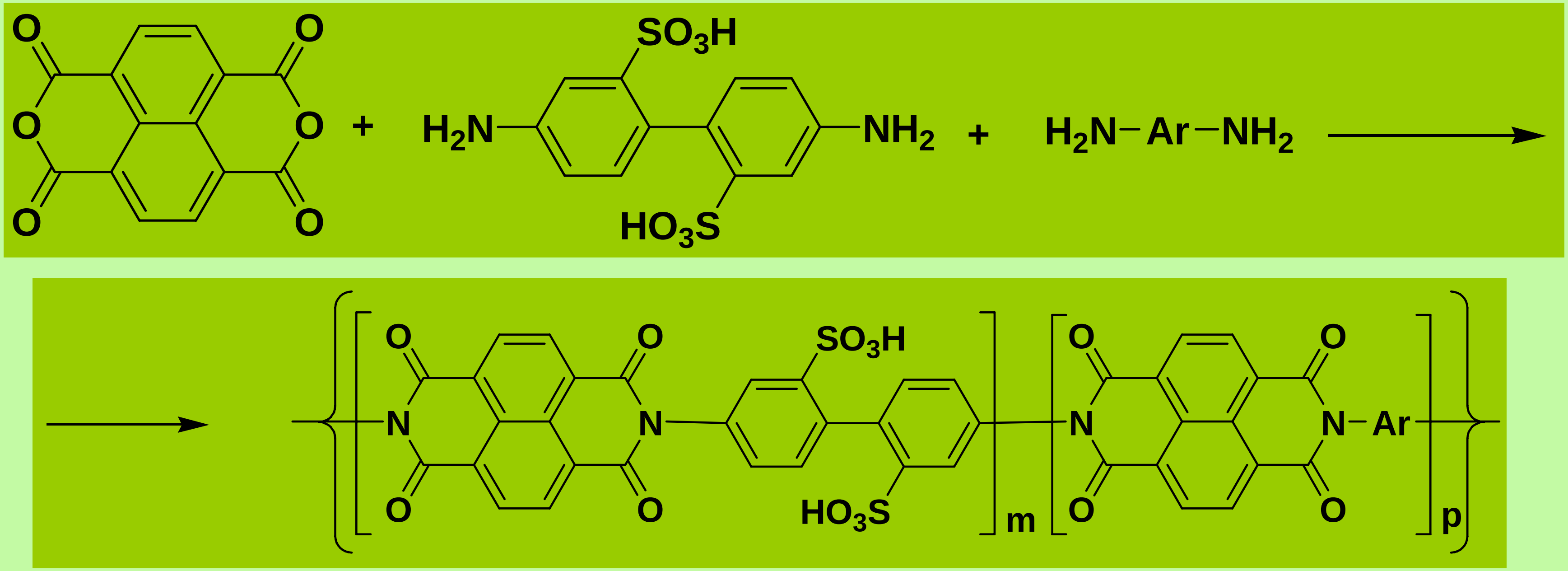
- PEEK is sulfonated by oleum/H_2SO_4 (o-ether group)
- Time & Temp decide extent of sulfonation
- 90% sulfonated-water soluble-proton conductivity Nafion
- Cross-linked by diamine or heating
- Solvent for film casting affects proton conductivity. (NMP-10^{-2}; DMF 10^{-5} S/cm
- Decompose at 240-300^{0}C
- Proton conductivity mechanism is similar to Nafion
- sPPBP has higher proton conductivity($9x10^{-2}$ S/cm) than sPEEK
- Life time of 5000 h

Sulfonated Block Copolymer SEBS



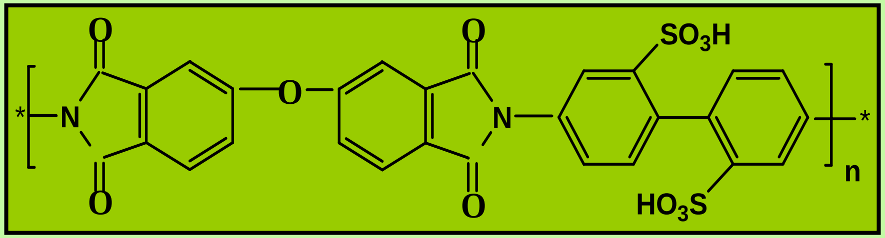
- Sulfonation is by acetyl sulfate or SO_3 in DCM
- Polymer with 60% sulfonated phenyl group has proton conductivity more than Nafion
- Polymer degrade at higher temp.
- Life time 2500 h at 60^0C and 4000h at RT

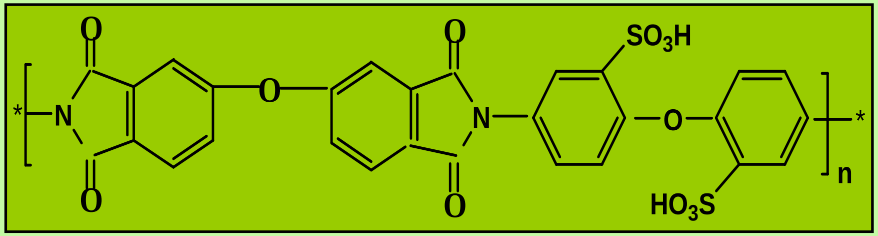
Sulfonated polyimides

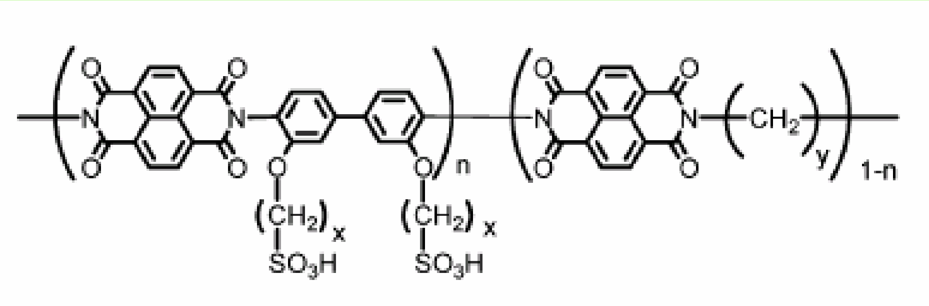


- sPI are synthesized by condensing dianhydride with sulfonated diamine
- Properties can be adjusted by copolymerization
- Length of ionic block in copolymer has significant effect on proton conductivity
- 5 membered imide ring is hydrolytically unstable. Six membered imide ring is stable.

Sulfonated Polyimide (cont.)

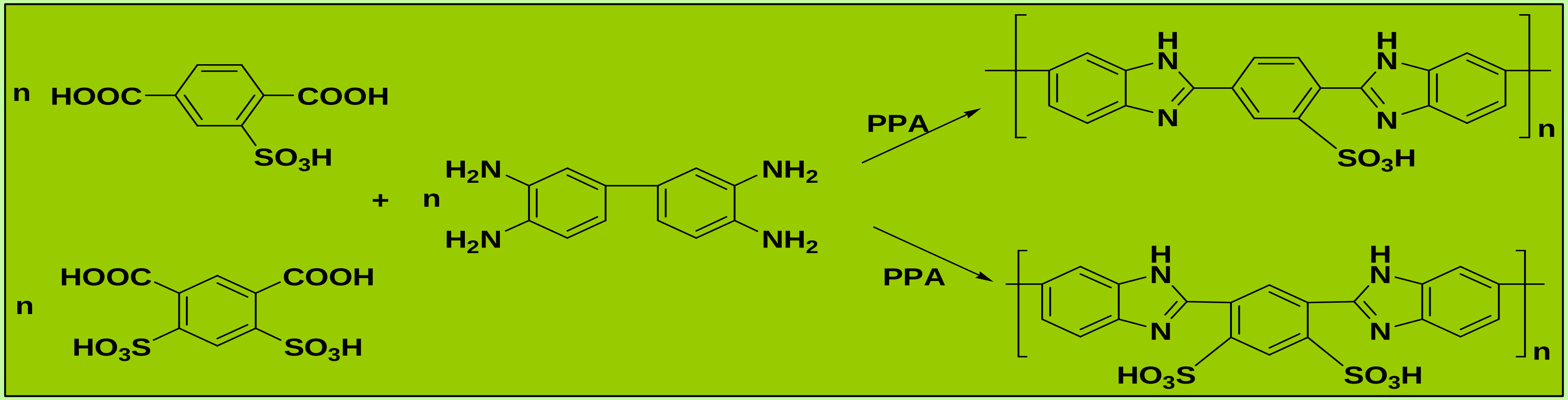


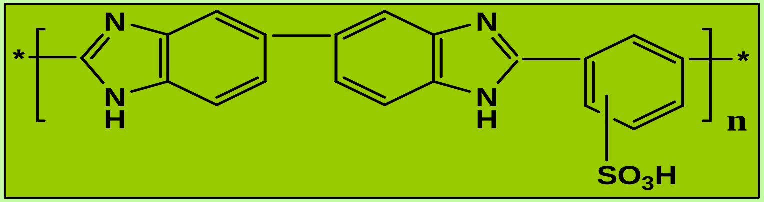




- PI bearing alkyl sulfonic acid group in side chain has good thermal and mechanical stability.
- Low O_2 & H_2 permeability (10 times < Nafion)
- High water absorption (22% for IEC 1.9 meq/g)
- Proton conductivity of sPI (NTDA) of IEC 1.9 is 0.21S/cm at 120^0C 90% RH

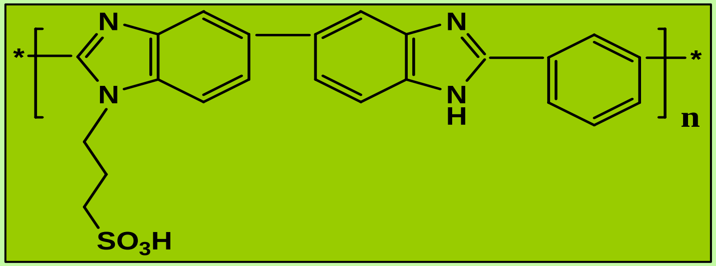
Sulfonated Polybenzimidazole

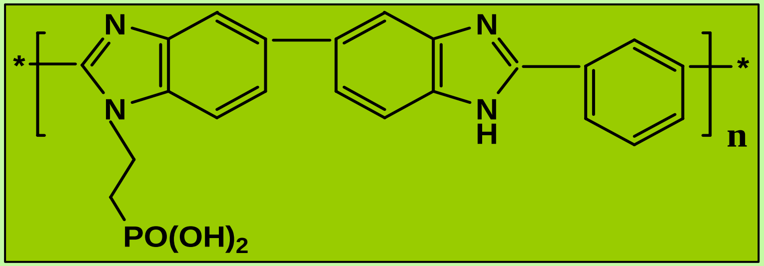


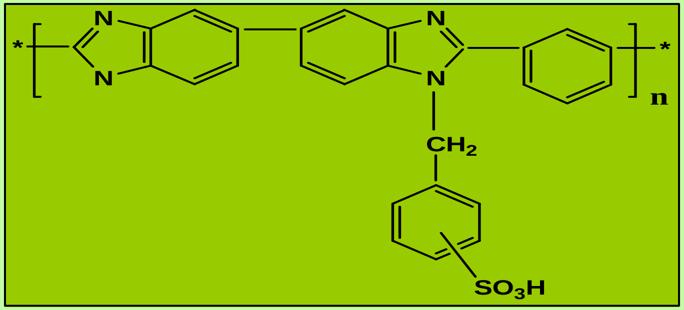


- PBI can be sulfonated by heating PBI film doped with H_2SO_4 at 400^0C
- It can be prepared by condensing sulfonated diacids with tetraamine
- They have poor solvent solubility

Alkyl sulfonate substituted Polybenzimidazole (sPBI)







- sPBI are synthesized by condensing propylsultone with lithiated PBI
- Akylsulfonate group induces water absorption. Water absorption more for higher alkyl group.(73.155 substituted PS-PBI take up 11.3 mole H_2O/SO_3H at RT (Nafion 11 mole). Methyl propyl sulfonated PBI take up 27 moles water
- Proton cond. Of PB-PBI is 10^{-3} S/cm at RT (similar for Nafion).
- Methyl benzene sulfonated derivative has conductivity of 10^{-3} S/cm at 40^0C
- Life time stability is not available

Acid doped Polybenzimidazole Alternative Polymer Electrolyte to Nafion

Advantages

- Low cost.
- High thermal stability (>500^{0}C)
- Good mechanical strength.
- Low hydrogen, oxygen and methanol permeability.
- No humidification is required
- Zero electro-osmotic drag co-efficient.
- Greater dimensional stability after doping.
- Can be operated at higher temperature (200^{0}C)
- Reformed H_2 can be used
- Life time of 5000h at 150^{0}C at cell voltage 0.5 V
- Most suitable for DMFC

Disadvantages

- 10 times less conductivity than Nafion
- Efficiency may be affected by leaching of H_3PO_4

Polymer Blends

- Acid-Base blends are prepared by blending acidic polymer with basic polymer.
- sPEEK and sPS is blended with PBI
- These blends are miscible due to ionicinteraction
- Tg of blends is higher than the individual polymer components
- Solubility and swelling in water decreases by blending
- Above 70ºc ionic bonds break sdepending on polymer blends
- Low MeOH permeability (10-20 times lower than Nafion)
- Doping of these blends with H_3PO_4 improves proton conductivity

Composites

Hygroscopic Composite (Silica):

- Materials used hold water
- Resist fuel crossover
- Increases proton conductivity
- Can be used >100^0C

Conductive composites(ZrP):

- Increase proton conductivity
- Reduce MeOH & H_2O Permeability
- Can be used >100^0C

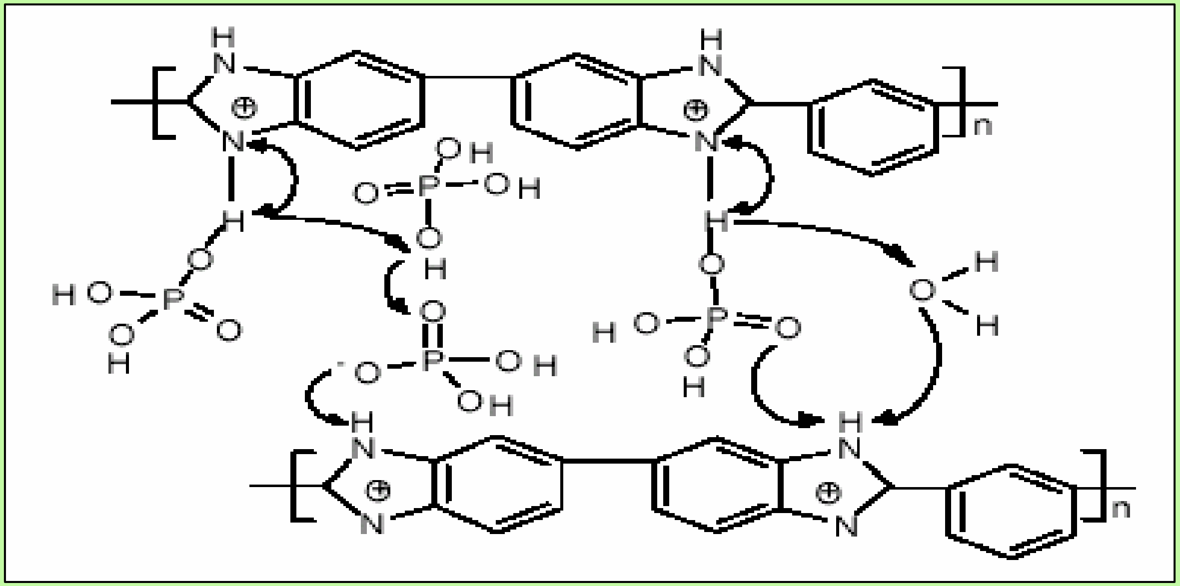
Water substituted Composites:

- Alternate proton conductor (imidazole):
- Low electro-osmotic drag
- Proton conductivity is independent of water
- Can be used > 100^0C

Proton Conductivity of Composites

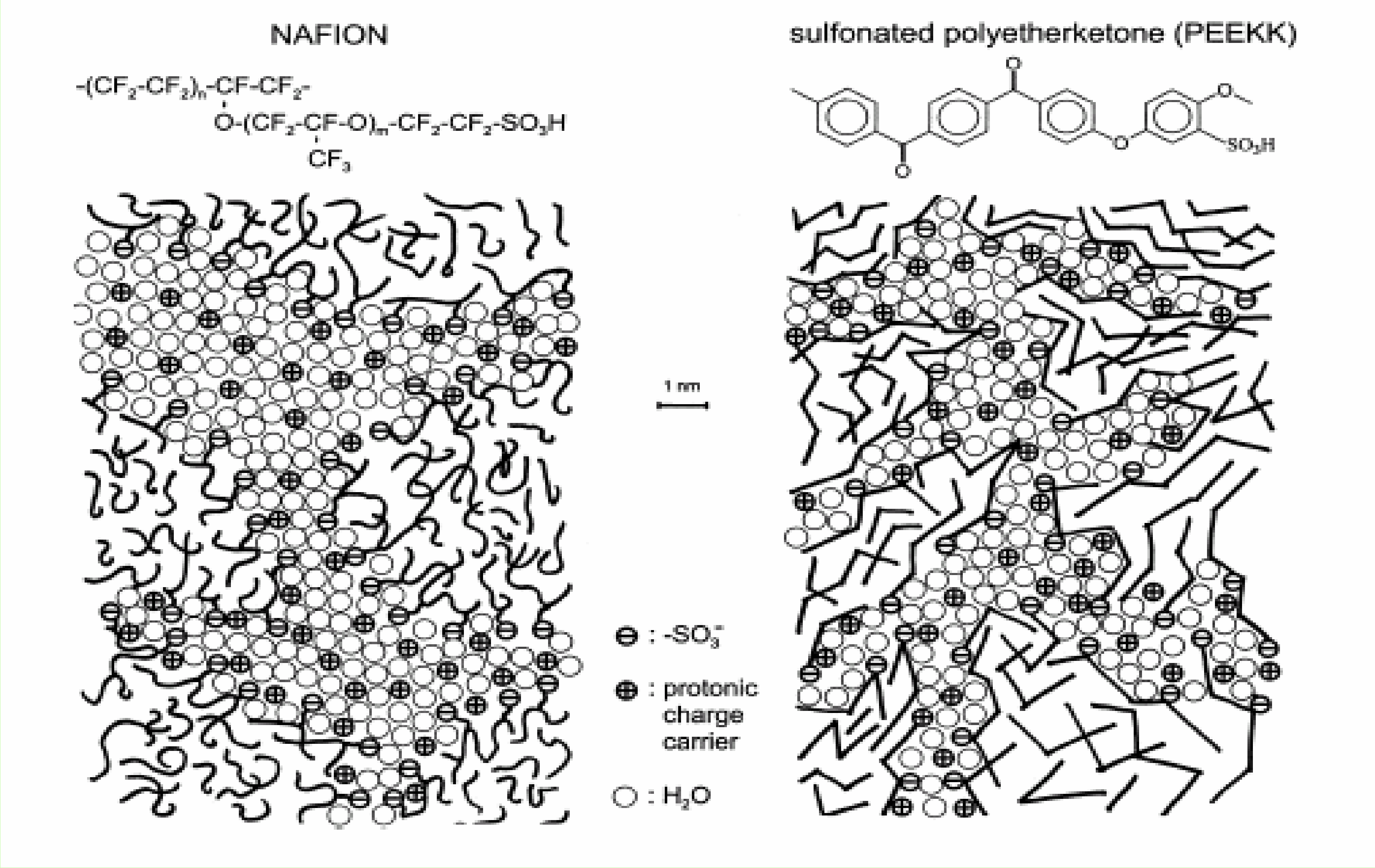
Organic component	Inorganic component	Comments
sPEK, sPEEK	ZrP + (SiO_2, TiO_2, ZrO_2)	Reduced methanol crossover
sPEEK	SiO2, ZrP, Zr-SPP	0.09 S/cm at 100°C, 100% RH H_2/O_2 fuel cell test at 95°C
sPEEK	HPA	10^{-1} S·cm^{-1} above 100°C
sPEEK	BPO_4	5×10^{-1} S·cm^{-1}, 160ºC, fully hydrated
sPEEK	SiO2	3-4×10^{-2} S/cm at 100°C, 100%RH
sPSF	PWA	0.15 S/cm at 130°C, 100%RH
sPSF	PAA	0.135 S·cm^{-1} at 50°C, 100% RH
sPSF	PAA	2×10^{-2} S·cm^{-1}, 80°C, 98% RH
PBI	ZrP + H_3PO_4 PWA/SiWA + H_3PO_4	9×10^{-2} S·cm^{-1} at 200°C, 5% RH 3 - 4×10^{-2} S·cm^{-1}at 200°C, 5% RH
PBI	SiWA + SiO_2	2.2×10^{-3} S·cm^{-1} at 160°C, 100% RH
PBI	PWA + SiO_2 + H_3PO_4	Td > 400°C; 1.5×10^{-3} S·cm^{-1} at 150°C, 100% RH

Mechanism of proton conductivity in doped PBI



- Proton hopping from one N site to another: (little proton conductivity)
- Proton hopping from the N-H site to a phosphoric acid anion: significant conductivity (1:2 mole doping < 10^{-2} S/cm at 200^{0}C)
- Proton hopping along the $H_2PO_4^-$ anion chain: At doping level of 5.7 mole (4.6x 10^{-3} at RT: 7.9x10^{-2} at 200^{0}C) Major contribution
- Proton hopping via water molecules: Conductivity increases with humidity: At 200^{0}C increase in humidity from 0.15% to 5.0% RH increases conductivity from 0.03 S/cm to 0.07 S/cm

Mechanism of proton conductivity in Nafion

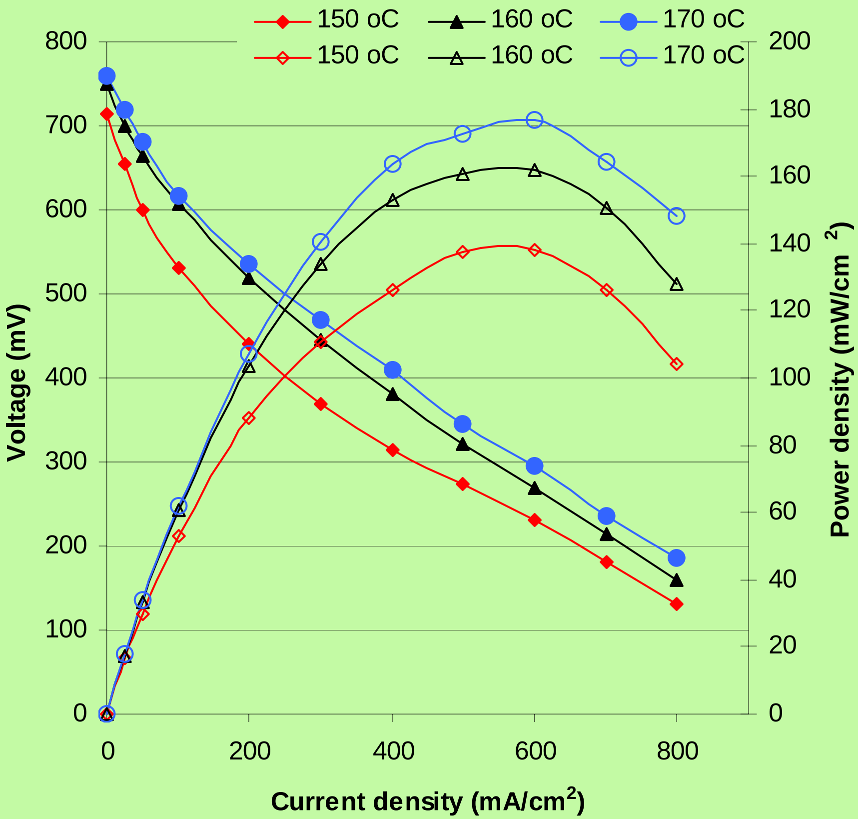


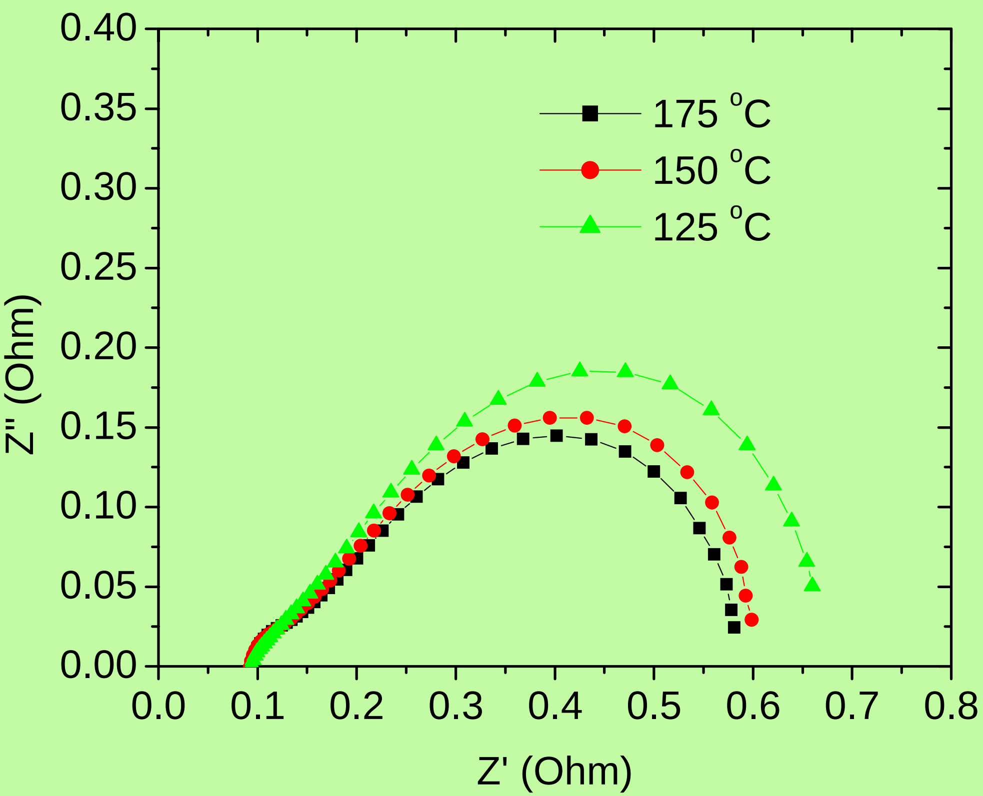
Work at NCL on Polymer electrolytes

- Development a process for the synthesis of PBI by solution polymerization in polyphosphoric acid
- Development of a process for the synthesis of tetraamine
- Synthesis of new PBI
- Evaluation of PBI membranes for PEMFC

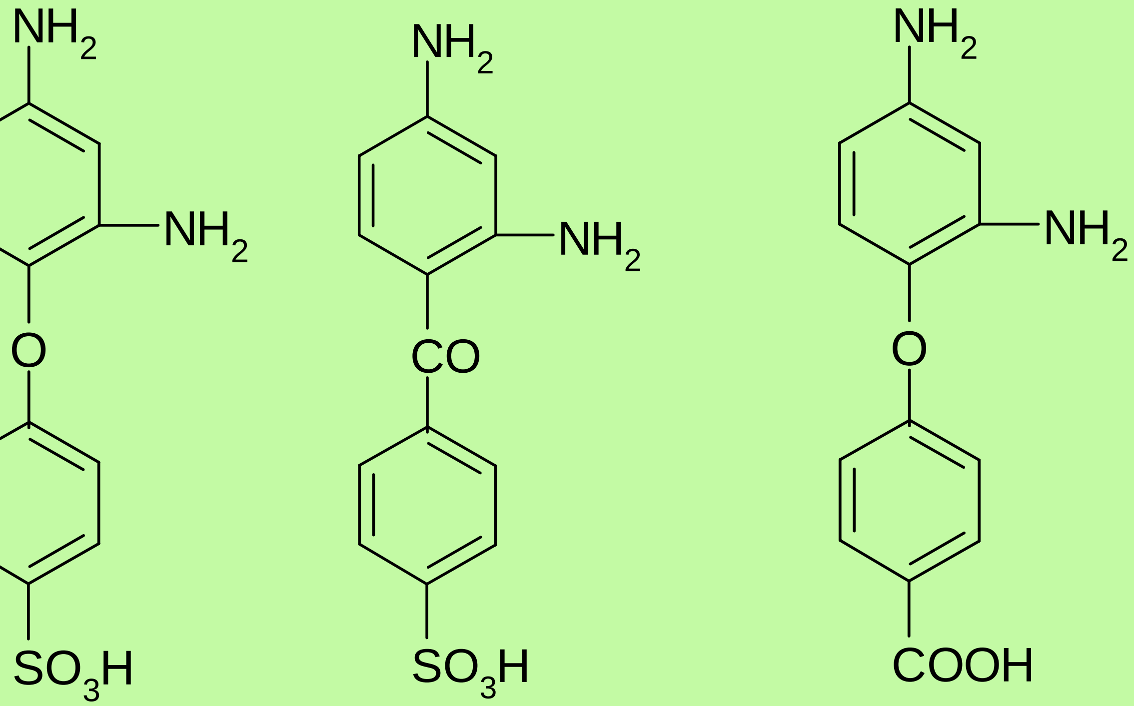
Synthesis of Polyibenzimidazol

The conductivity of Doped PBI was tested by impedance method
Polarisation curve was estimated
Results are similar to reported values
Process for DAB synthesis was developed





Synthesis of Polyimides



Several Polyimides and copolyimides were synthesized
High thermal stability Tg above 220 C IDT above 400 C


THANK YOU

Fuel Flexibility and Pollution

Hydrogen – The most efficient fuel for all types of fuel cell, but a lot of storage and transport problems. No pollution.

Methanol, ethanol, biogas – Good fuel, but lower efficiency. Low CO_2 pollution.

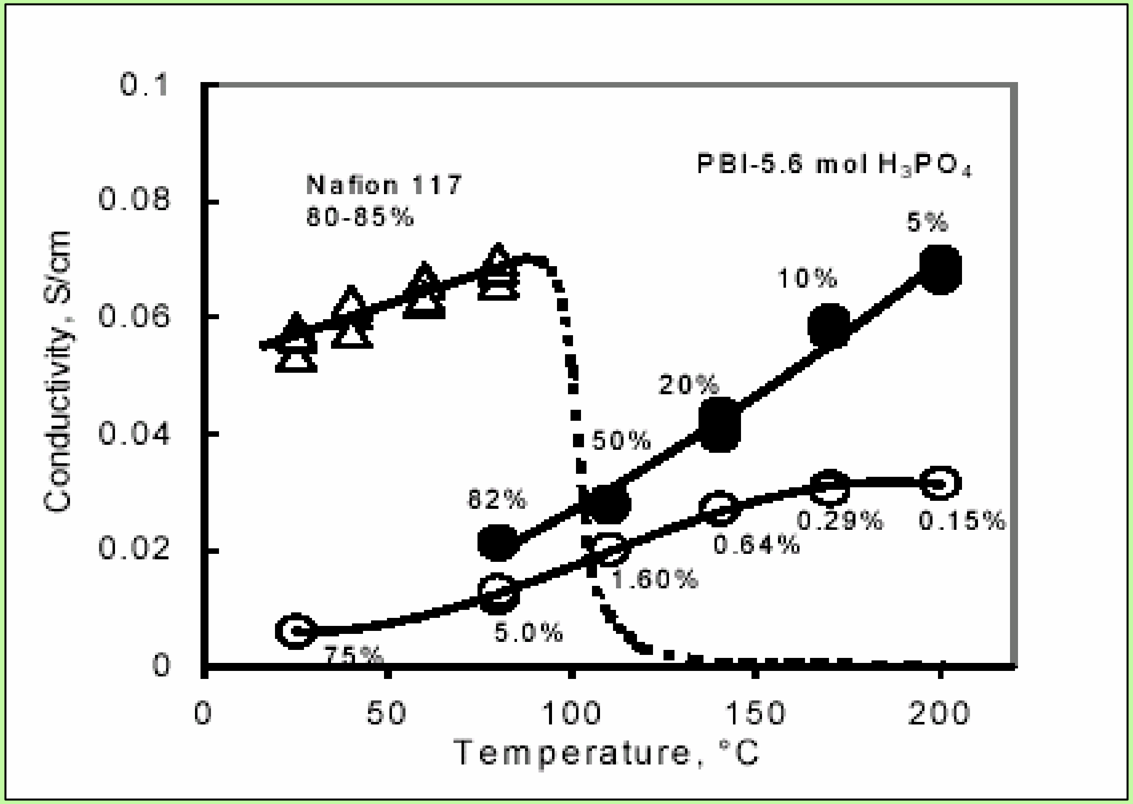
Natural oil or gas – Not so good fuel, usually need some kind of preprocessing before fuel cell (e.g. sulphur elimination, etc). CO_2 pollution, very low NxOy or SxOy pollution.

Construction materials for fuel cells – Some bad components (e.g. fluorine, heavy metals, etc), but many possibilities for reproduction.

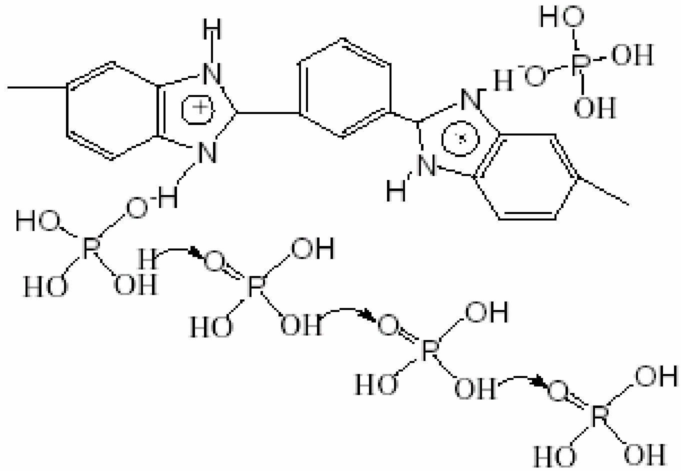
PBI doped with H_3PO_4

- PBI is a basic polymer
- Good mechanical strength and high thermal stability (IDT 600^0C)
- Forms complex with acids
- H_3PO_4 doped PBI has good proton conductivity 0.079 S/cm (at 200^0C) 0.0046 at RT
- Low CO poisoning (direct reformed MeOH fuel can be used)
- Zero electro-osmotic drag

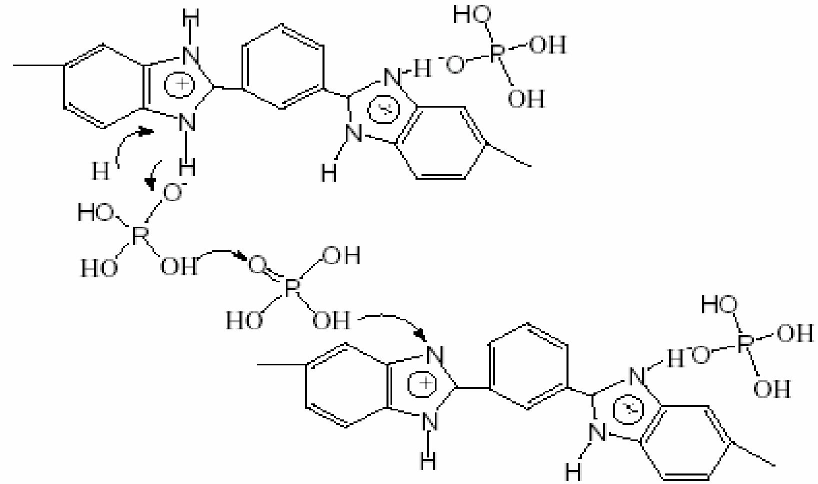
Proton Conductivity of NAFION & PBI Doped with H_3PO_4

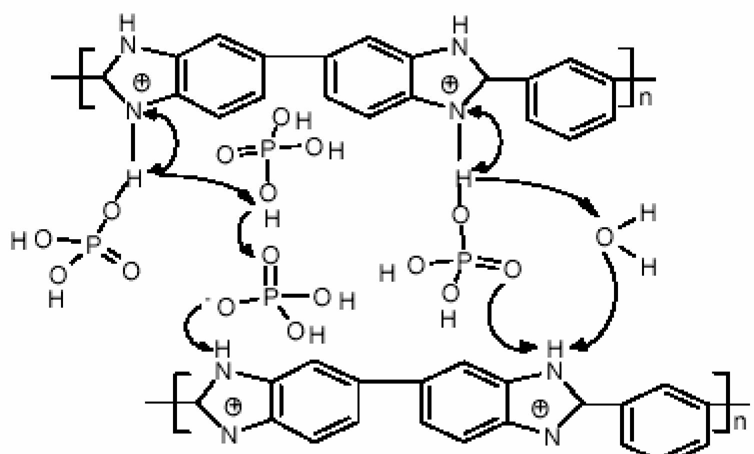


ACID - ACID

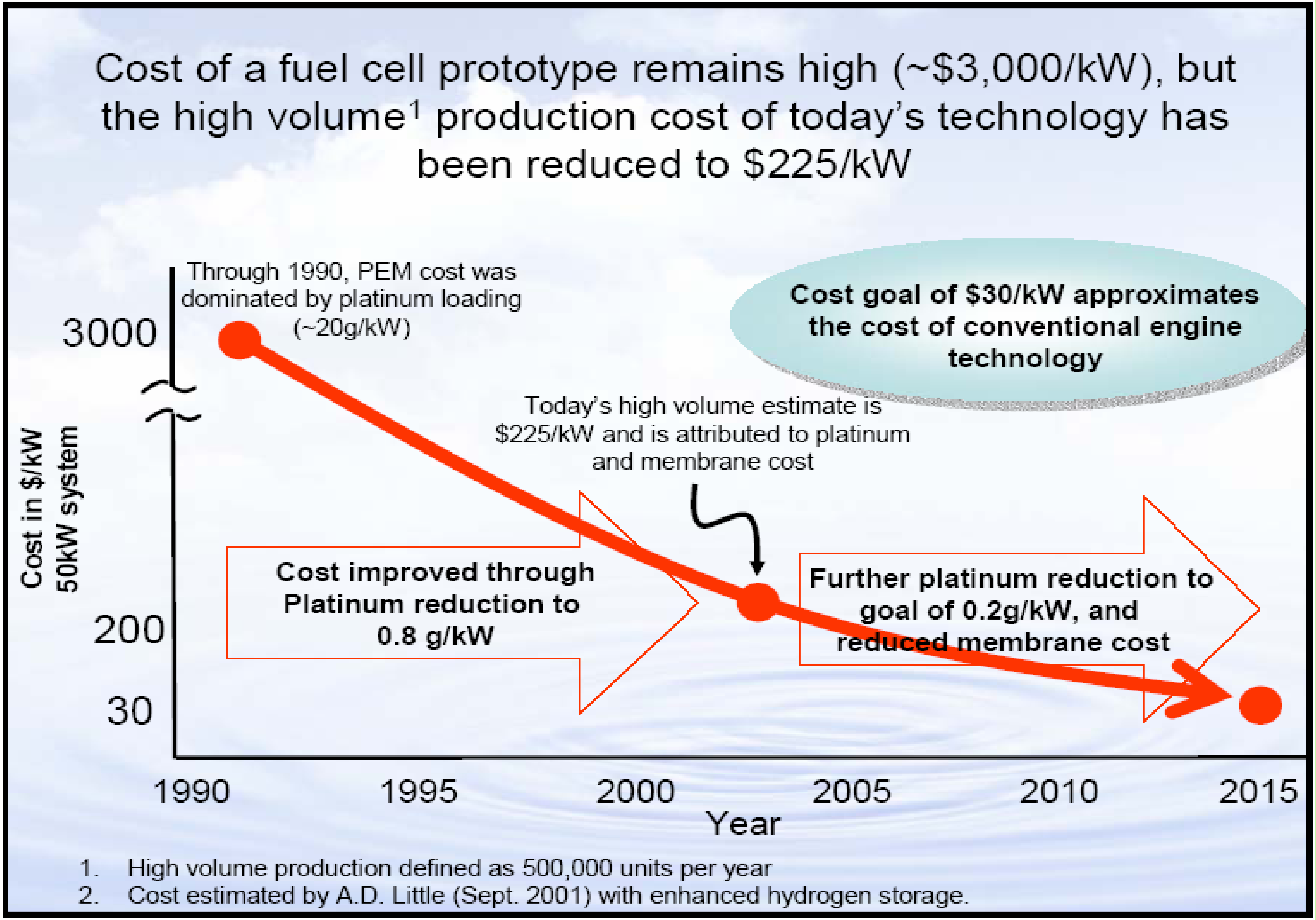


ACID-BI-ACID

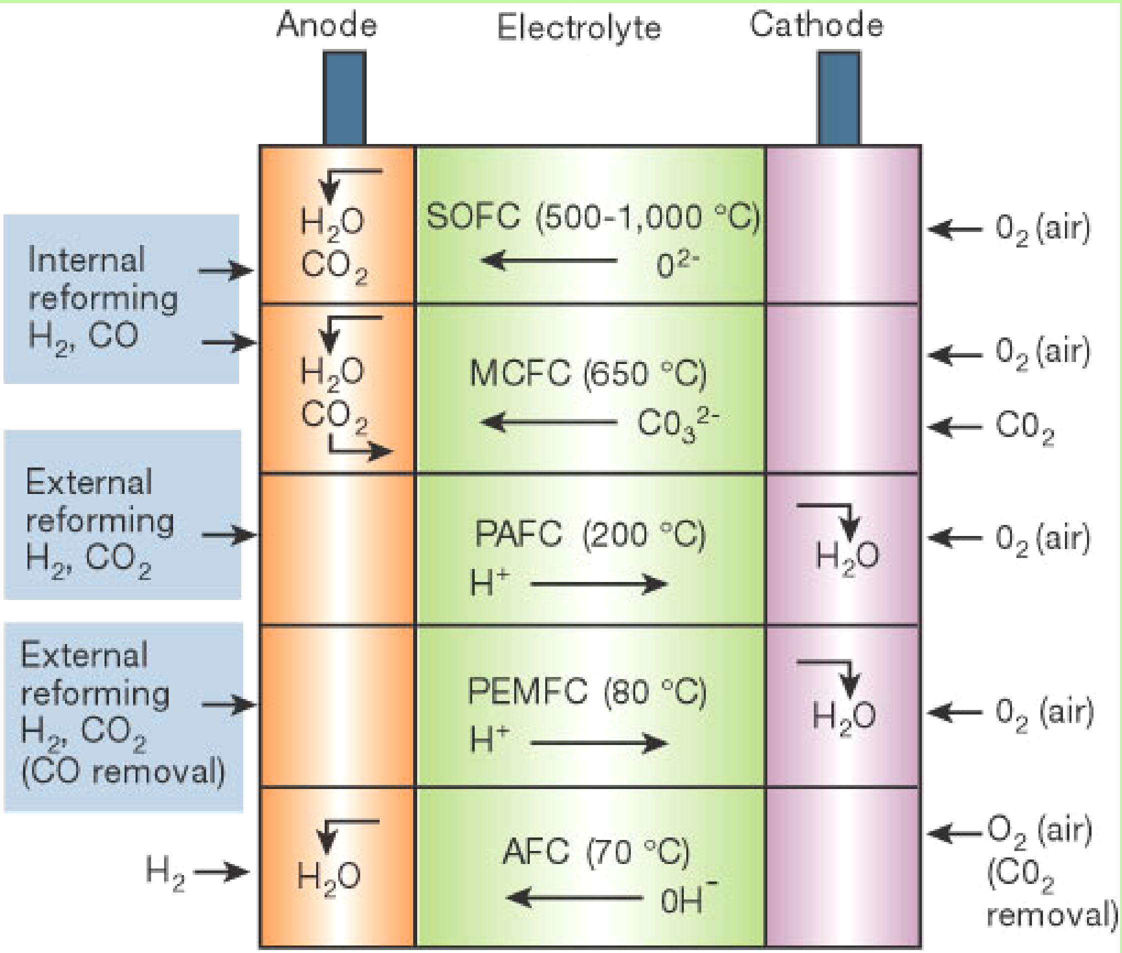




Cost of Power by PEMFC



Source: US DOE



Anode
Electrolyte
Cathode
Internal reforming H2, CO
External reforming H2, CO2
External reforming H2, CO2 (CO removal)
H2
H2O CO2
SOFC (500-1,000 °C)
02-
02 (air)
MCFC (650 °C)
C03 2-
C02
PAFC (200 °C)
H+
H2O
PEMFC (80 °C)
AFC (70 °C)
0H-
O2 (air) (C02 removal)

Characterization of Polymer Electrolytes

- Proton conductivity- (AC impedence measurement)
- Water uptake
- Dopant uptake
- Thermal stability
- Microstructure
- Polarization studies
- Open circuit voltage (OCV) determination

Characteristics of sulfonated polymer electrolytes

- High proton conductivity
- Proton conductivity depends on extent of sulfonation
- Water solubility increases with extent of sulfonation
- Proton conductivity depends on water uptake
- Excessive swelling due to water uptake affects mechanical properties
- Degradation due to desulfonation above 250^0C