High Temperature PEM Fuel Cells

Materials and fundamentals

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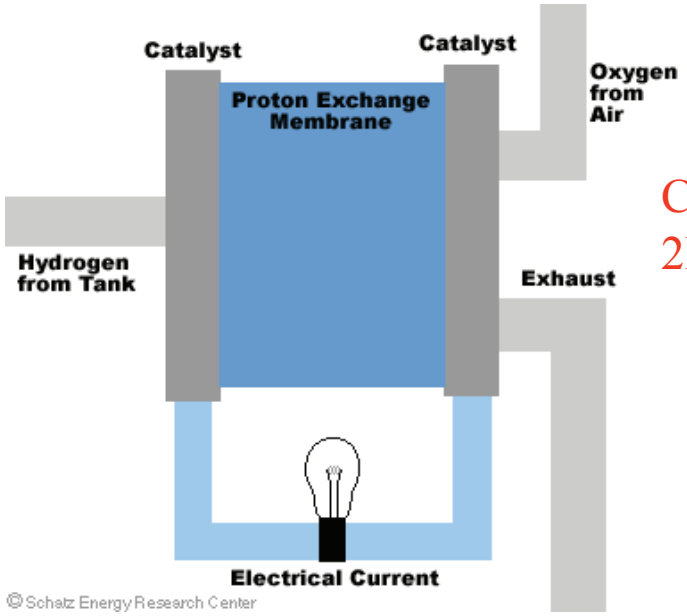
Outline

- Fuel cell fundamentals
- Fuel Cell types
- Low Temperature PEM Fuel cells
- High Temperature PEM Fuel cells
  - High temperature Polymer Electrolytes
  - Electrodes
  - MEA and Electrochemical interface
  - Performance

H_2 Fuel Cell

Anode
$H_2 \rightarrow 2H^+ + e^-$



Cathode
$2H^+ + 2e^- + \frac{1}{2}O_2 \rightarrow H_2O$

Why Hydrogen fuel cells?

CO_2 reduction

- Hydrogen can be produced from carbon free energy resources
- Hydrogen can be produced also from fossil fuels; through fuel cells, that provide higher efficiency the overall CO_2 emissions can be reduced
- In the future, CO_2 generated in producing hydrogen can be "sequestrated" and stored underground

Air Quality and health improvement

- Hydrogen offers the potential of zero emissions transport and stationary power generation

Hydrogen is currently the only practical fuel for use in present generation of Fuel cells, because of its **high electrochemical reactivity**, compared with that of the more common fuels from which it is derived, such as hydrocarbons, alcohols, or coal.

When **ordinary fuels** are **transformed into hydrogen**, **the energy density** of the product is always **less** than that of the original fuel.

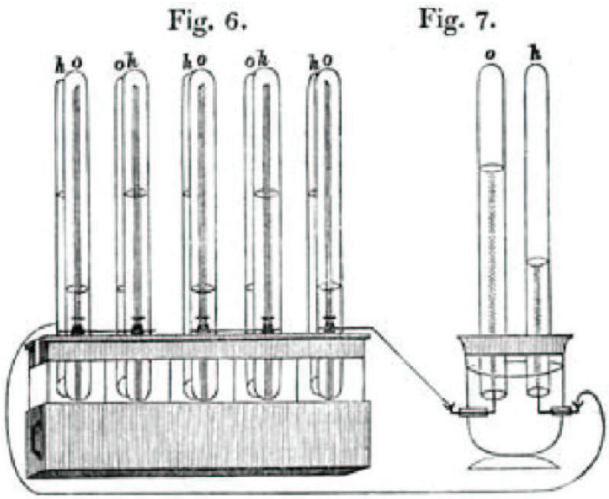
- Hydrogen has an energy density of about 20 kWh/kg
- Methane has a value of 10 kWh/kg
- Methanol-water mixture for use in FC has a value of only 2 kWh/kg

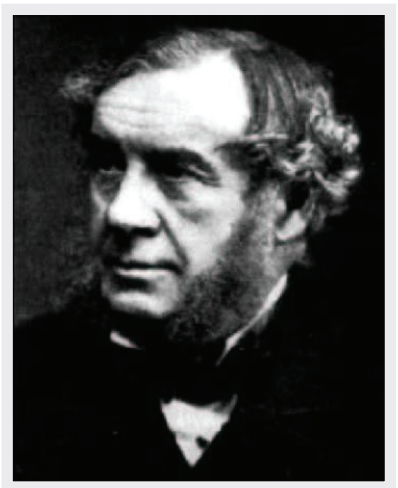
However, on a volume basis, gaseous or liquid hydrogen has:

- 1/3 of the energy density of gaseous or liquid methane
- 2/3 of the energy density of liquid methanol

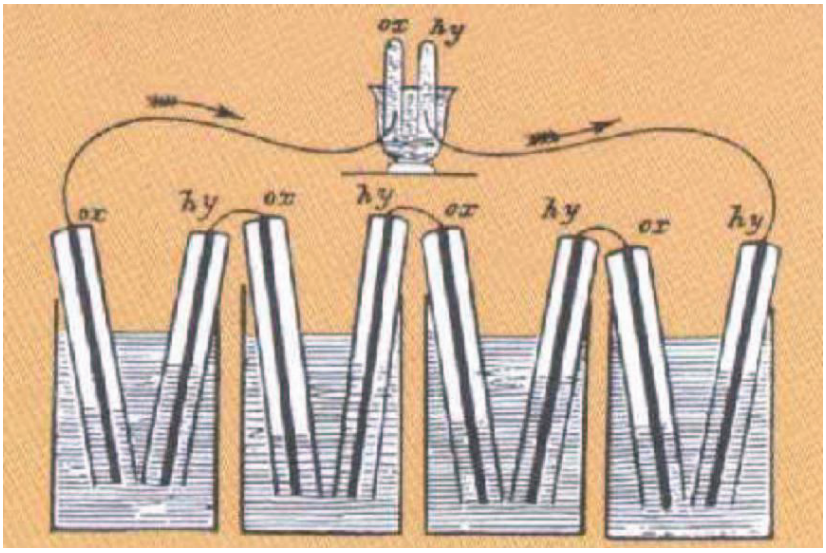
Fuel Cells -History

William Grove's drawing of an experimental "gas battery" from an **1843** letter Image from Proceedings of the Royal Society.





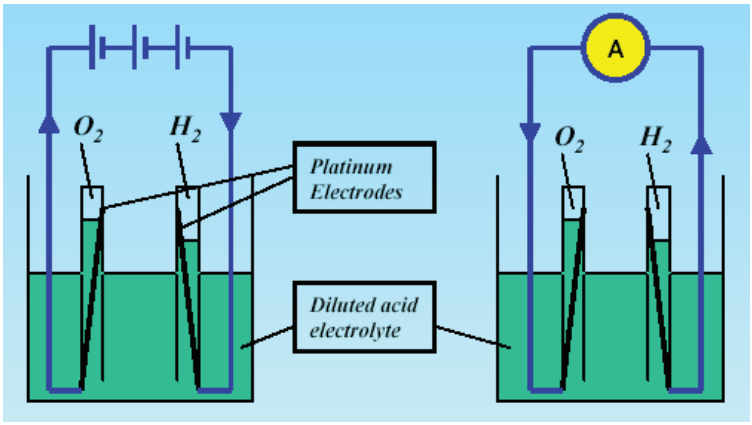
The invention of the fuel cell is attributed to **Sir William Robert Grove** when he published in **1839** a description of his experiment. He built a device, which contained up to 50 energy producing cells that was capable of electrolyzing water. This was nearly 200 years after the word electricity was devised by Sir Thomas Browne in 1646 and almost 50 years after the first battery built by the Italian scientist Count Alessandro Volta.



Grove's Device: *Oxygen and Hydrogen in the tubes over the lower resevoirs react in sulfuric acid solution to form water. That is the energy producing chemical reaction. The electrons produced electrolyze water to oxygen and hydrogen in the upper tube.*

Hydrogen Fuel Cells

- The basic operation of the hydrogen fuel cell is extremely simple
- Sir. William Grove's, experiment that can be summarized as depicted in the following figures:



Water is electrolyzed by the passage of an electric current, producing O_2 and H_2.

A small current is flowing in the opposite direction: O_2 and H_2 are recombining.

- Another way of looking at the fuel cell is to say that **Hydrogen fuel is being "burnt" or combusted** in the reaction:

$$2\ H_2 + O_2 \rightarrow 2\ H_2O$$

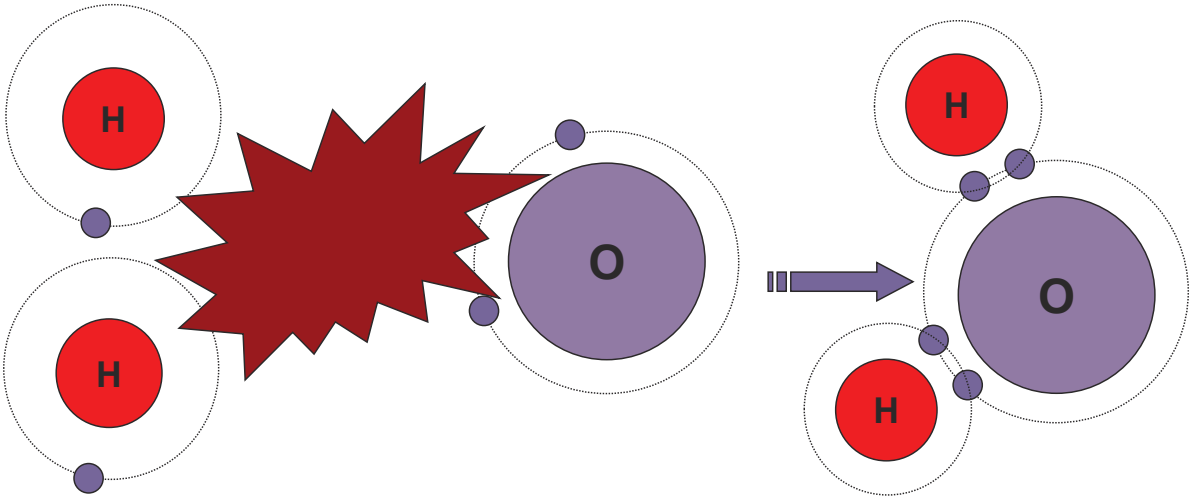
- The important fact is that, with the arrangement shown, instead of liberating energy under the form of heat, **electrical energy is produced**. This is clearly understood if we take into consideration the separate reactions taking place at each electrode:

Anode: $2\ H_2 \rightarrow 4\ H^+ + 4\ e +$ ***energy***

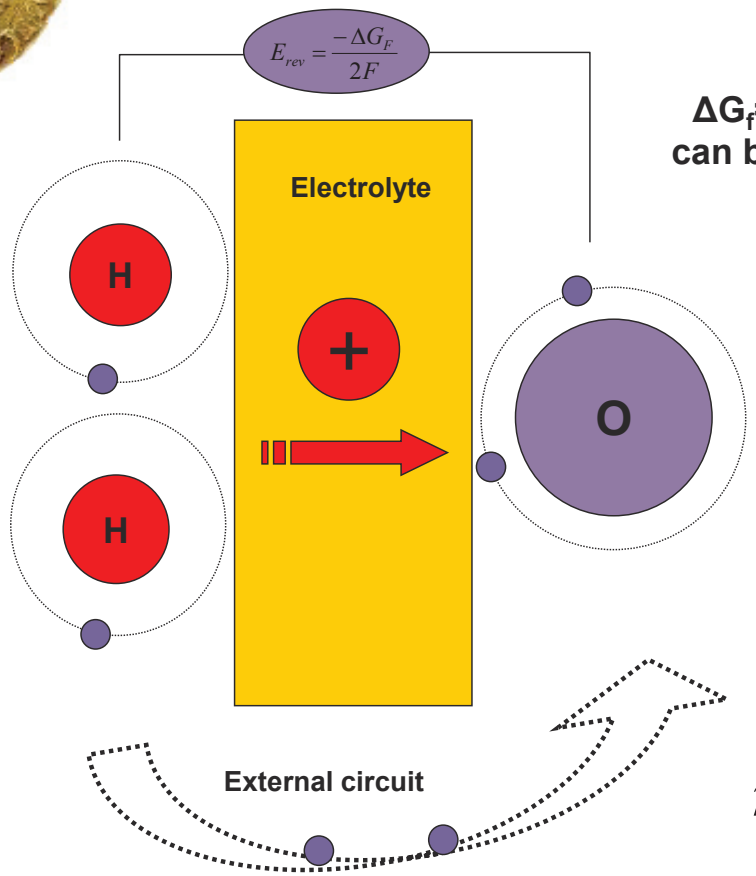
Cathode: $O_2 + 4e + 4\ H^+ \rightarrow 2\ H_2O$

- For both these reactions to proceed continuously, electrons produced at the anode must pass through an electrical circuit to the cathode.

Chemical reaction of Oxygen and H_2
Non controlable charge transfer and
Enthalpy/heat release



The energy change during water formation is equal to the Gibbs Free energy (ΔG) of the reaction. The charge is beingtransferred in a controlable way through the external circuit.



E_{rev}=1.23 V

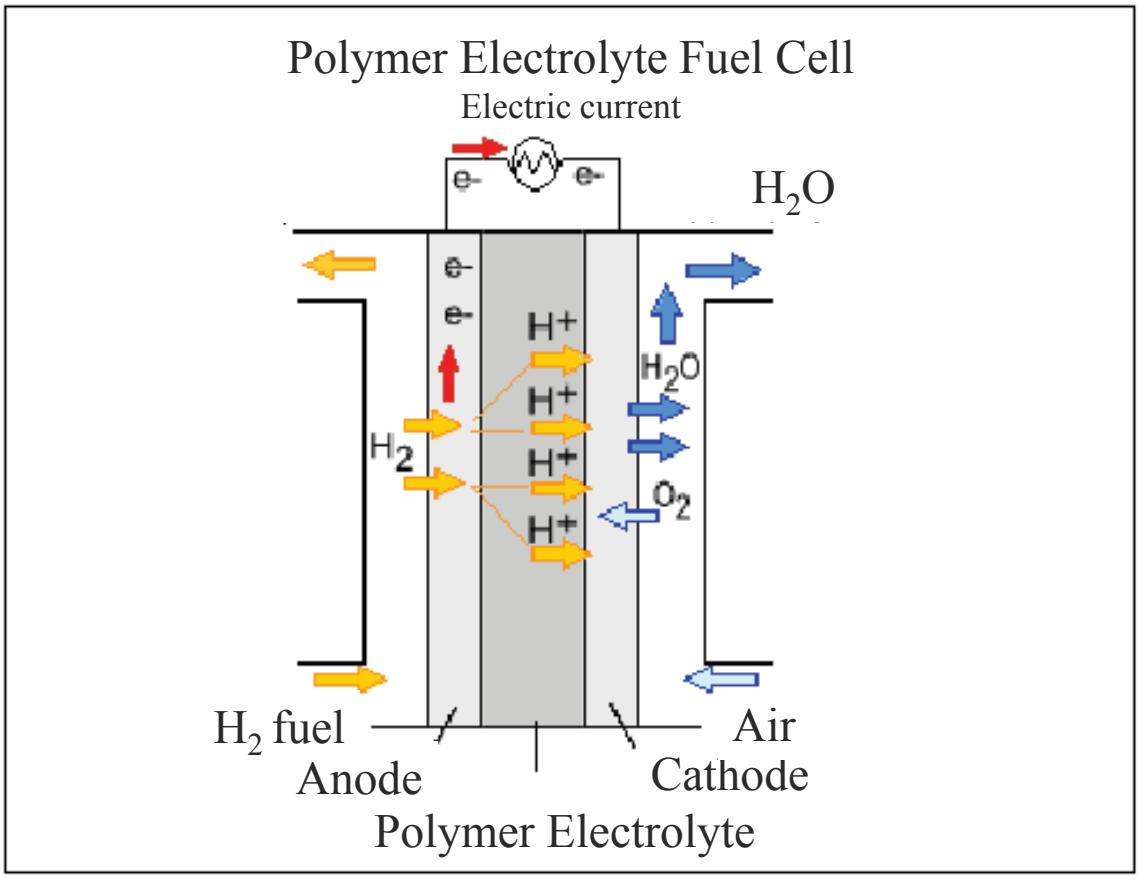
ΔG_f= The maximum work that can be produced by the fuel cell

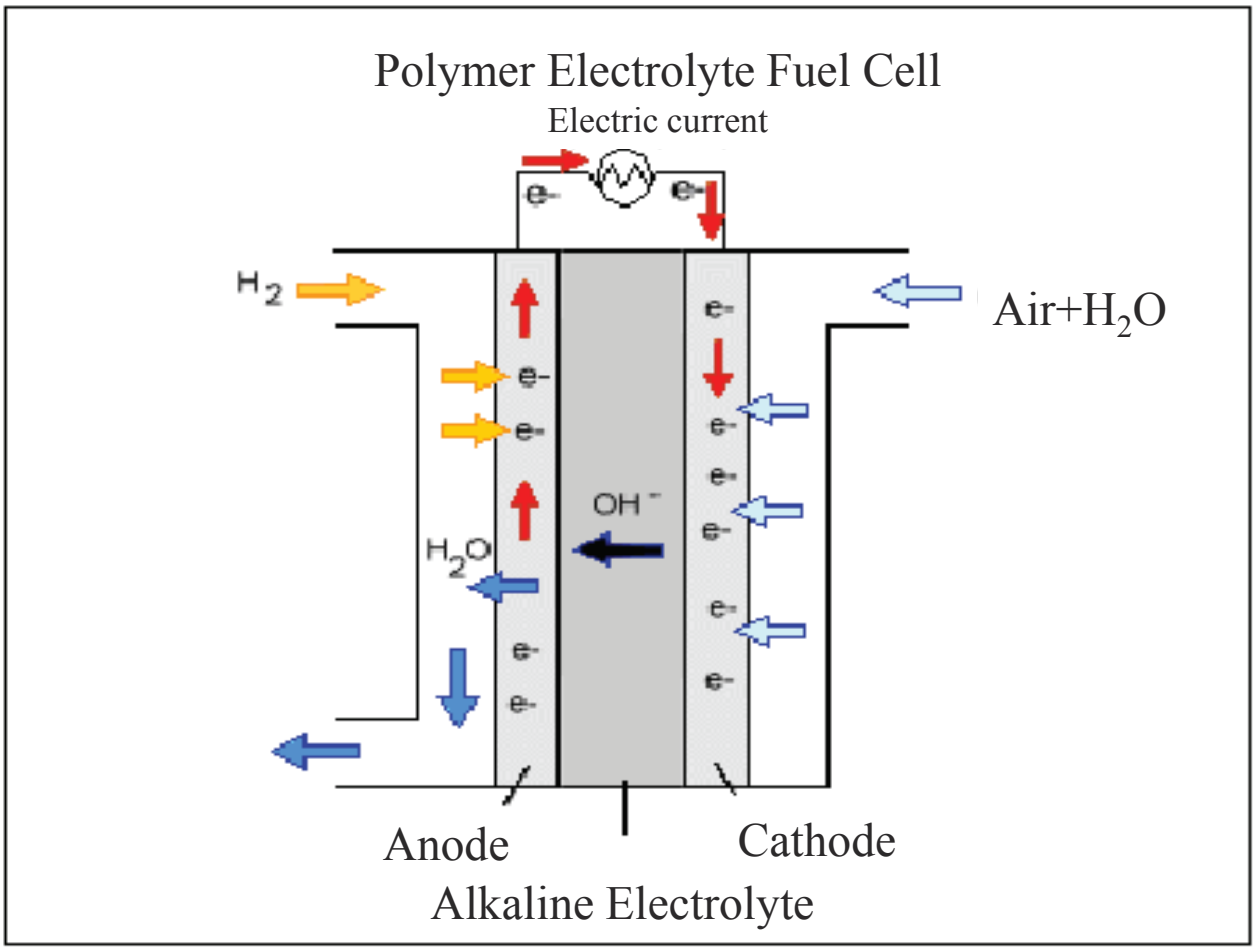
Maximum Thermodynamic efficiency

$$\eta_{\max} = \frac{\Delta G_f}{\Delta H_f} = 0.83$$

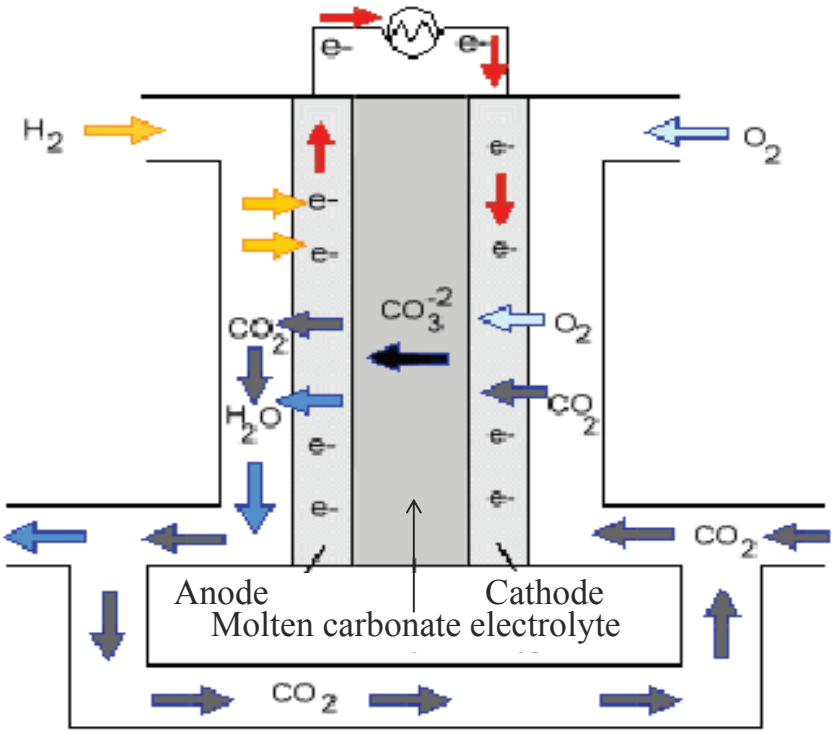
Comparison of Five Fuel Cell Technologies

Fuel Cell	Electrolyte	Operating Temperature (°C)	Electrochemical Reactions
Polymer Electrolyte/ Membrane (PEM)	Solid organic polymer poly-perfluorosulfonic acid	60 - 100	Anode: $H_2 \rightarrow 2H^+ + 2e^-$ Cathode: $1/2\ O_2 + 2H^+ + 2e^- \rightarrow H_2O$ Cell: $H_2 + 1/2\ O_2 \rightarrow H_2O$
Alkaline (AFC)	Aqueous solution of potassium hydroxide soaked in a matrix	90 - 100	Anode: $H_2 + 2(OH)^- \rightarrow 2H_2O + 2e^-$ Cathode: $1/2\ O_2 + H_2O + 2e^- \rightarrow 2(OH)^-$ Cell: $H_2 + 1/2\ O_2 \rightarrow H_2O$
Phosphoric Acid (PAFC)	Liquid phosphoric acid soaked in a matrix	175 - 200	Anode: $H_2 \rightarrow 2H^+ + 2e^-$ Cathode: $1/2\ O_2 + 2H^+ + 2e^- \rightarrow H_2O$ Cell: $H_2 + 1/2\ O_2 \rightarrow H_2O$
Molten Carbonate (MCFC)	Liquid solution of lithium, sodium and/ or potassium carbonates, soaked in a matrix	600 - 1000	Anode: $H_2 + CO_3^{2-} \rightarrow H_2O + CO_2 + 2e^-$ Cathode: $1/2\ O_2 + CO_2 + 2e^- \rightarrow CO_3^{2-}$ Cell: $H_2 + 1/2\ O_2 + CO_2 \rightarrow H_2O + CO_2$ (CO_2 is consumed at cathode and produced at anode)
Solid Oxide (SOFC)	Solid zirconium oxide to which a small amount of ytria is added	600 - 1000	Anode: $H_2 + O^{2-} \rightarrow H_2O + 2e^-$ Cathode: $1/2\ O_2 + 2e^- \rightarrow O^{2-}$ Cell: $H_2 + 1/2\ O_2 \rightarrow H_2O$

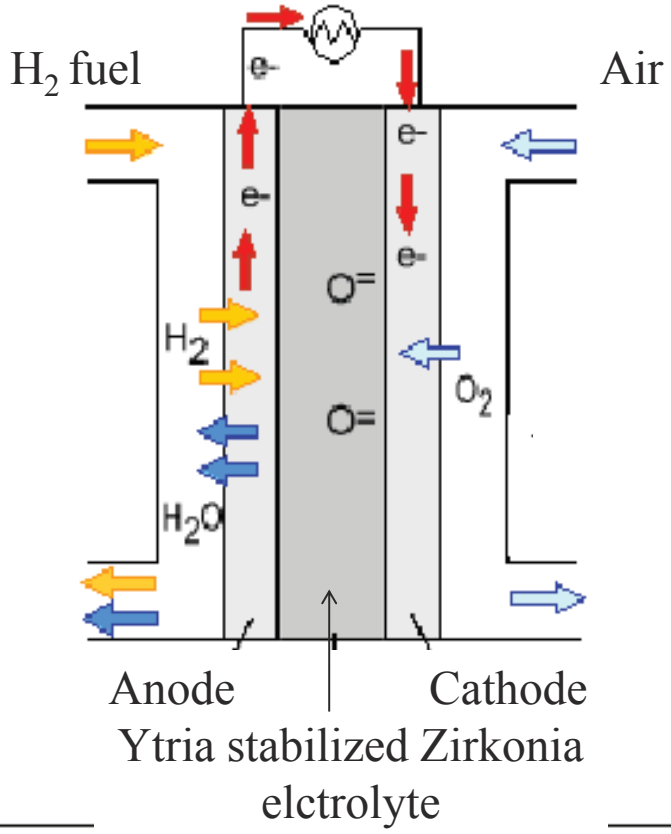

Polymer Electrolyte Fuel Cell
Electric current
e-
e-
H2O
e-
e-
H+
H+
H+
H+
H2O
O2
H2
H2 fuel
Anode
Air
Cathode
Polymer Electrolyte


Polymer Electrolyte Fuel Cell
Electric current
e-
e-
H2
Air+H2O
e-
e-
e-
e-
e-
e-
e-
e-
e-
e-
OH-
H2O
Anode
Cathode
Alkaline Electrolyte

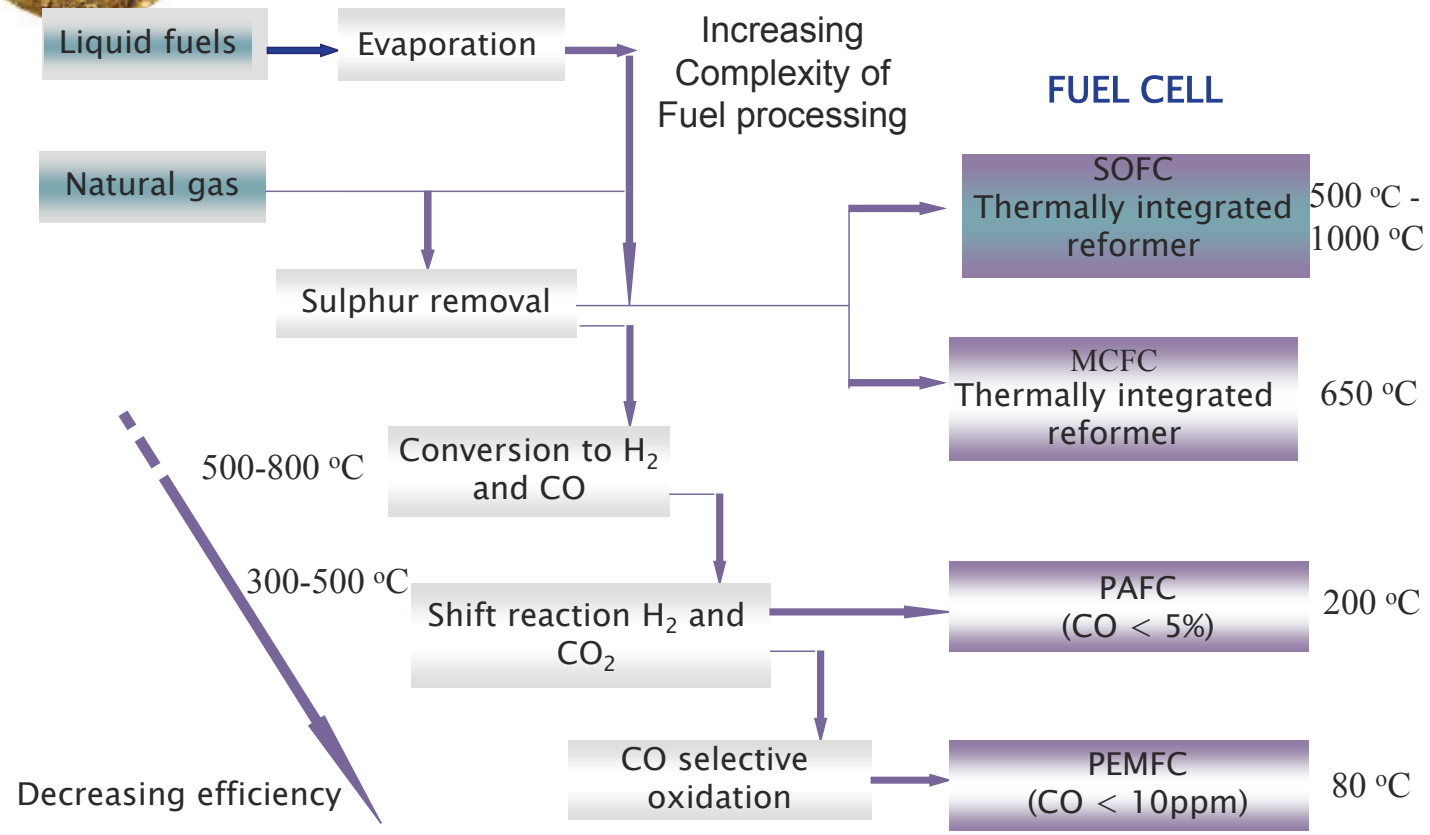
Molten Carbonate Fuel Cell



Solid Oxide Fuel Cell



Fuel Cell types and Hydrogen Processing



Applications	Advantages	Disadvantages
electric utility portable power transportation	• Solid electrolyte reduces corrosion & management problems • Low temperature • Quick start-up	• Low temperature requires expensive catalysts • High sensitivity to fuel impurities
military space	• Cathode reaction faster in alkaline electrolyte — so high performance	• Expensive removal of CO_2 from fuel and air streams required
electric utility transportation	• Up to 85 % efficiency in co-generation of electricity and heat • Impure H_2 as fuel	• Pt catalyst • Low current and power • Large size/weight
electric utility	• High temperature advantages*	• High temperature enhances corrosion and breakdown of cell components
	*High temperature advantages include higher efficiency, and the flexibility to use more types of fuels and inexpensive catalysts as the reactions involving breaking of carbon to carbon bonds in larger hydrocarbon fuels occur much faster as the temperature is increased.	
electric utility	• High temperature advantages* • Solid electrolyte advantages (see PEM)	• High temperature enhances breakdown of cell components

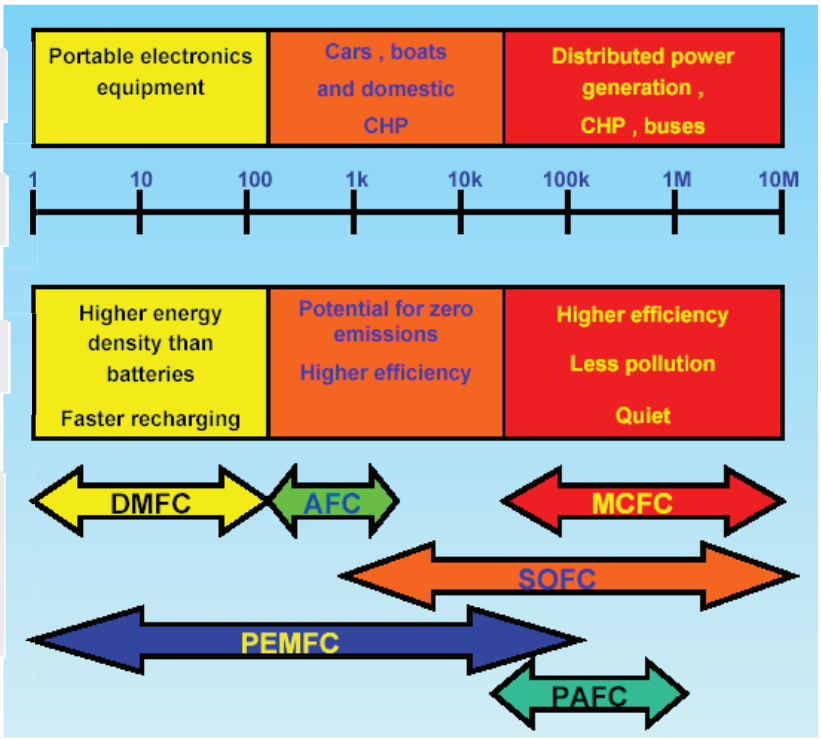
Chart to summarize the applications and main advantages of fuel cells of different types, and in different applications

Typical applications

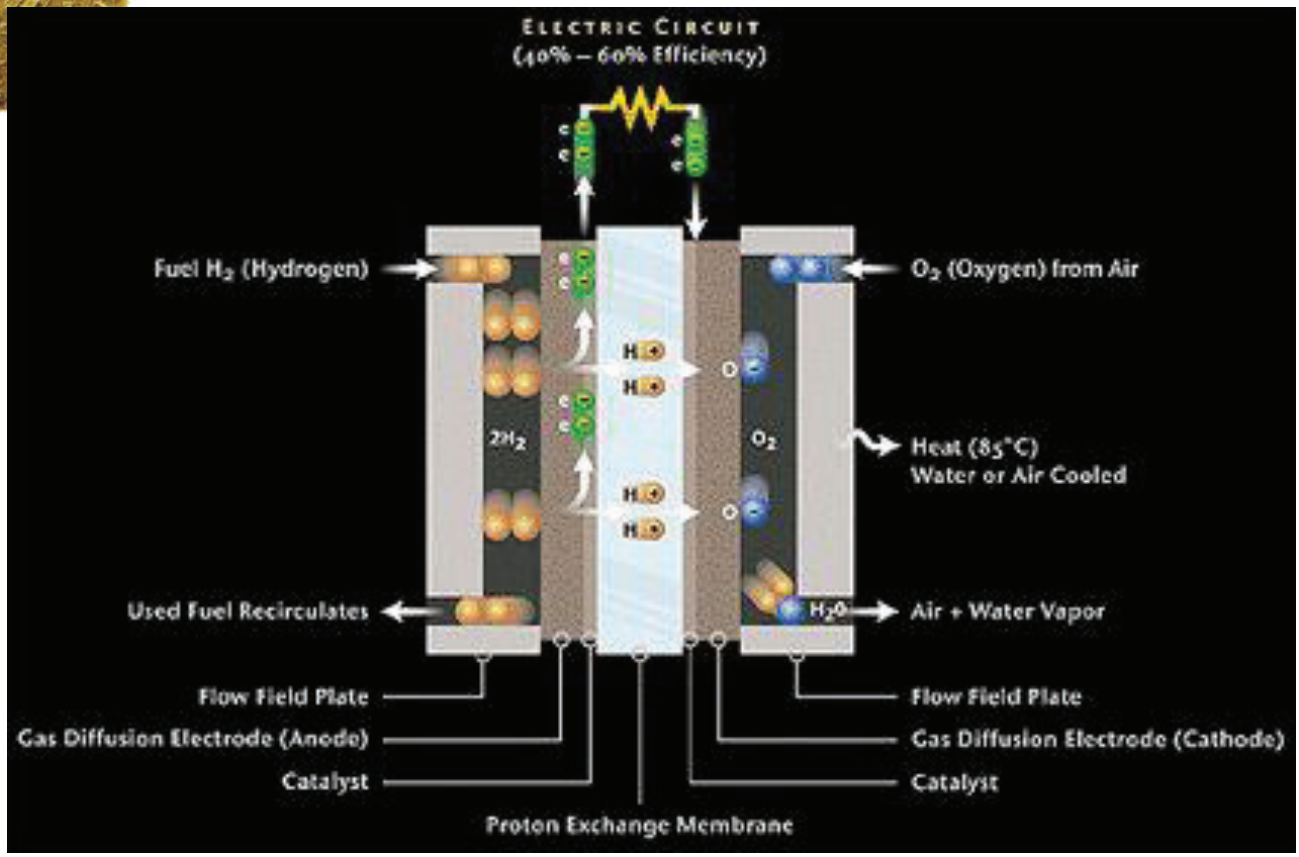
POWER in Watts

Main advantages

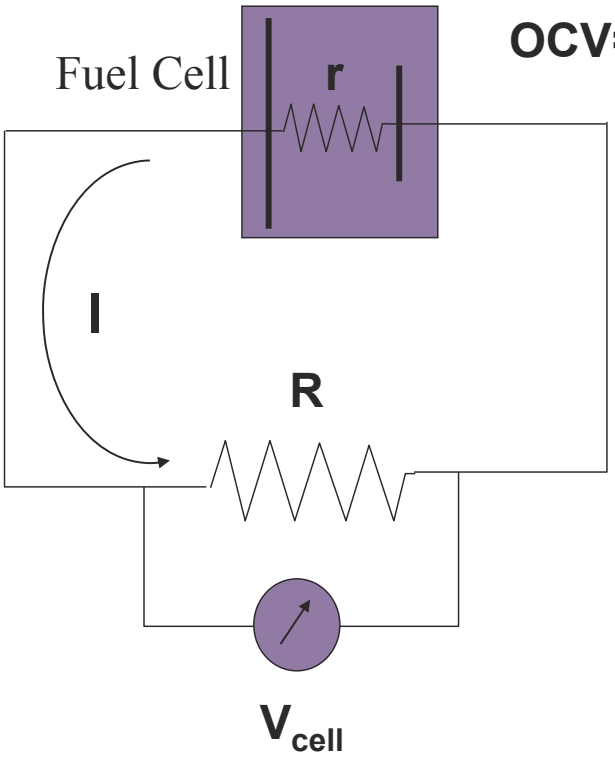
Range of application of the different types of fuel cells



PEM Fuel Cell



Fuel Cell electric circuit

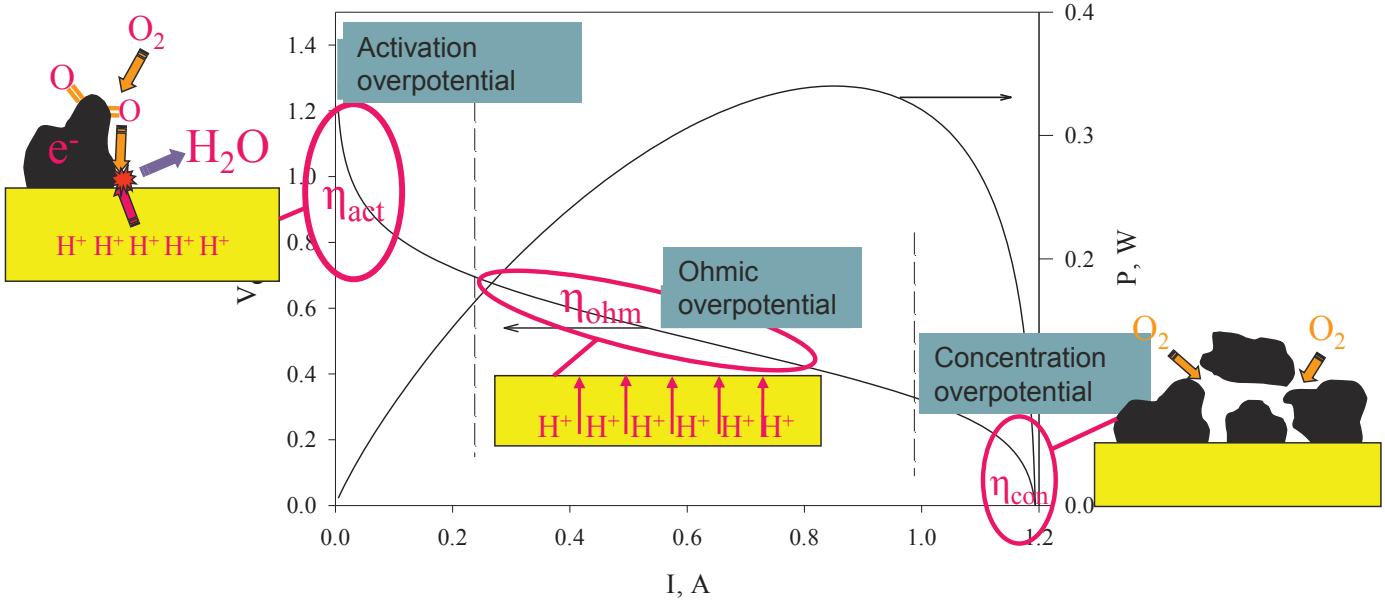


OCV=open circuit potential of the cell

OCV = Ir + IR

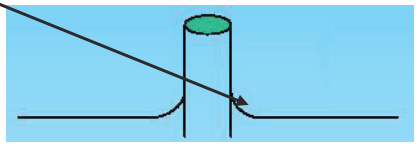
V_{cell}=IR

Typical current-voltage Plot of a fuel cell



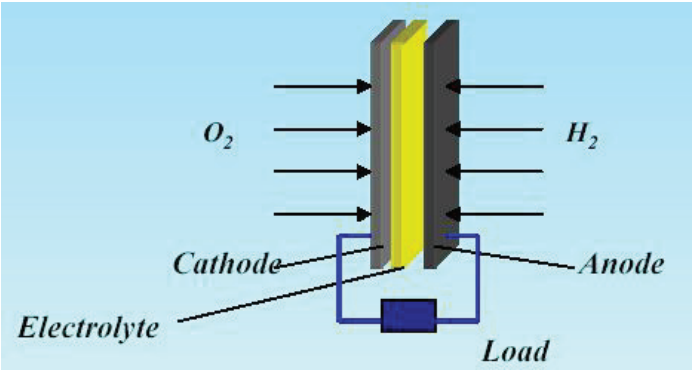
The **amount of current produced** in the experiment is **very small**, due to the following reasons:

① Low contact area at the **triple point** gas/electrode/electrolyte interface (practically just a small ring where the electrodes emerges from the electrolyte)



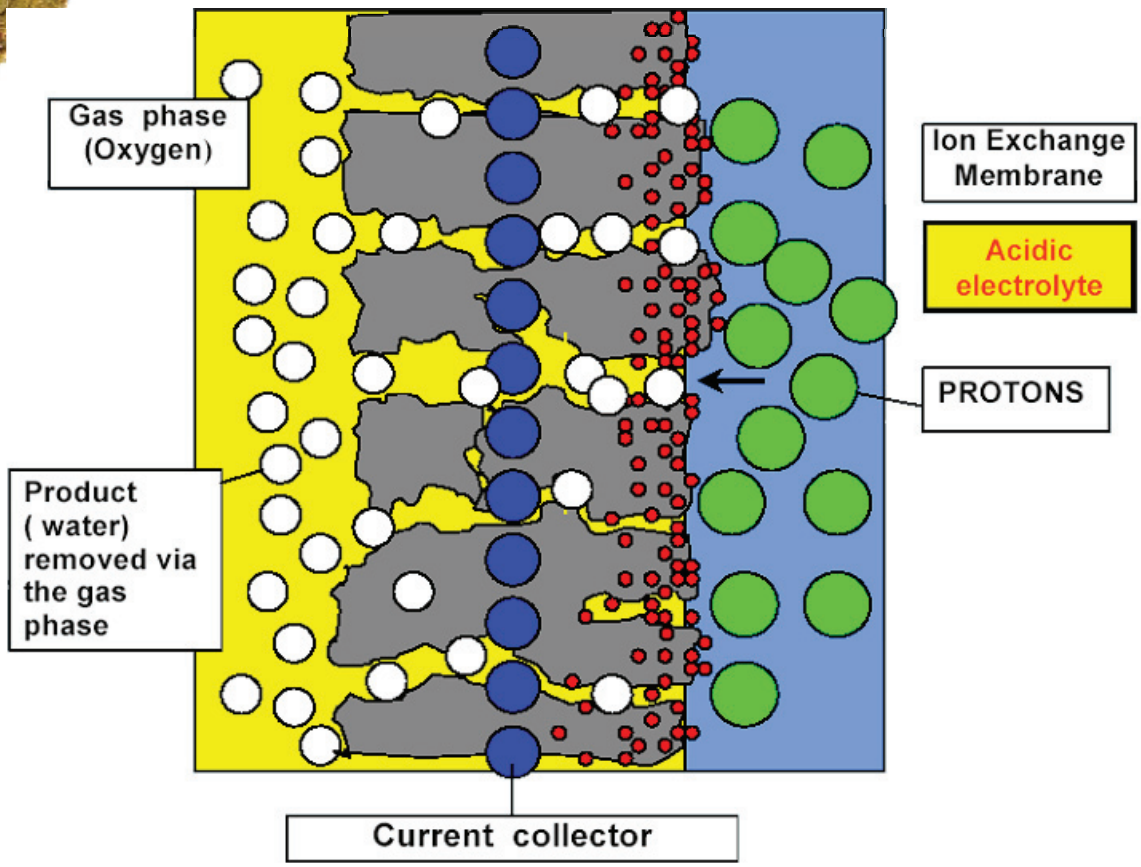
② Large distance between electrodes (high Ohmic losses)

To overcome these problems, the electrodes are usually made flat, with a thin layer of electrolyte in between, as in the following figure:



The structure of the electrode is **porous**, so that the electrolyte from one side , and the gas from the other side, can penetrate it, to obtain the **maximum possible contact between gas, electrode and electrolyte**.

The electrochemical Interface



Four steps to complete the reaction

① Gas penetrates into the porous structure

② Gas dissolves into the electrolyte and diffuses to the electrode's walls

③ Gas is adsorbed and reacts on the catalyst

④ Reaction products are removed

General structure of a GDE "separate electrode type"

- **Conductive support**

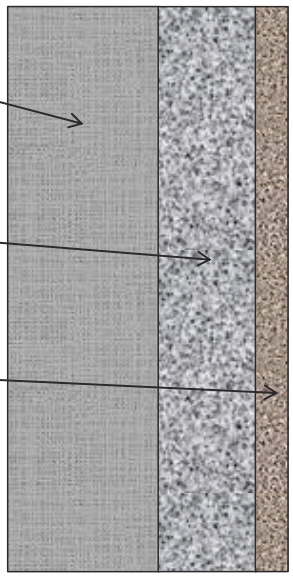
(Zoltek-Textron-Carbon Paper)

- **Hydrophobic layer(s)**

(SAB + PTFE)

- **Catalytic layer**

(Pt/Vulcan XC-72

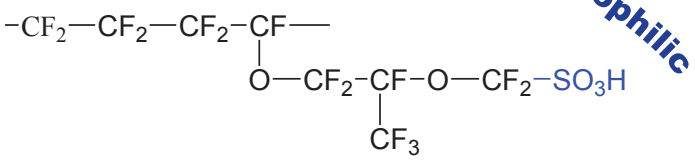


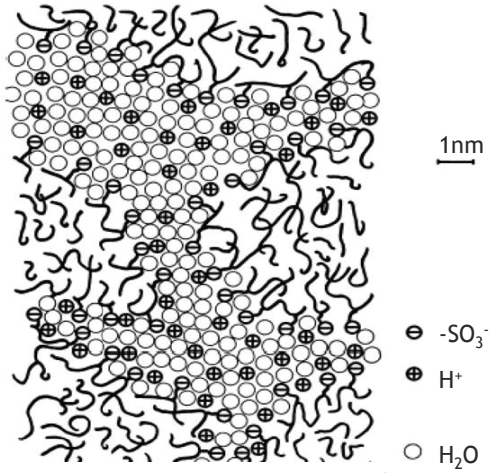
Hydrated Nafion is used as proton conducting Polymer Electrolyte for low Temperature PEM fuel cells

Hydrated Nafion Structure

Hydrophobic

Hydrophilic





K.D.Kreuer, *J.Memb.Sci.*, 185, 29, **2001**.

Nafion Membrane Summary

Advantages

- High ionic conductivity (10^{-1} S/cm, R_H=100%)
- Chemical stability in oxidative and reductive environment (bond strength C-F:485 KJ/mol)
- Strong acid
- Good mechanical properties
- Low rates of gas crossover even with membrane thickness <100 μm (on the order of 10 mA/cm² equivalent hydrogen or oxygen fluxes)
- Excellent long-term stability > 60000h operating at 80°C in fuel cell maintaining the high initial protonic conductivity

Disadvantages

- Reduction of ionic conductivity > 80°C (membrane dehydration)
- Methanol crossover (10^{-6} mol /cm²s)

Catalyst poisoning in low temperature PEM fuel cells

[illegible] al [illegible] an [illegible] [illegible] art [illegible] [illegible] atnu [illegible] etal [illegible] e [illegible]

$$H_2 + 2\ Pt \rightarrow 2\ Pt\text{-}H_{ads} \quad (a)$$

$$2\ Pt\text{-}H_{ads} \rightarrow 2\ Pt + 2\ H^+ + 2\ e^-$$

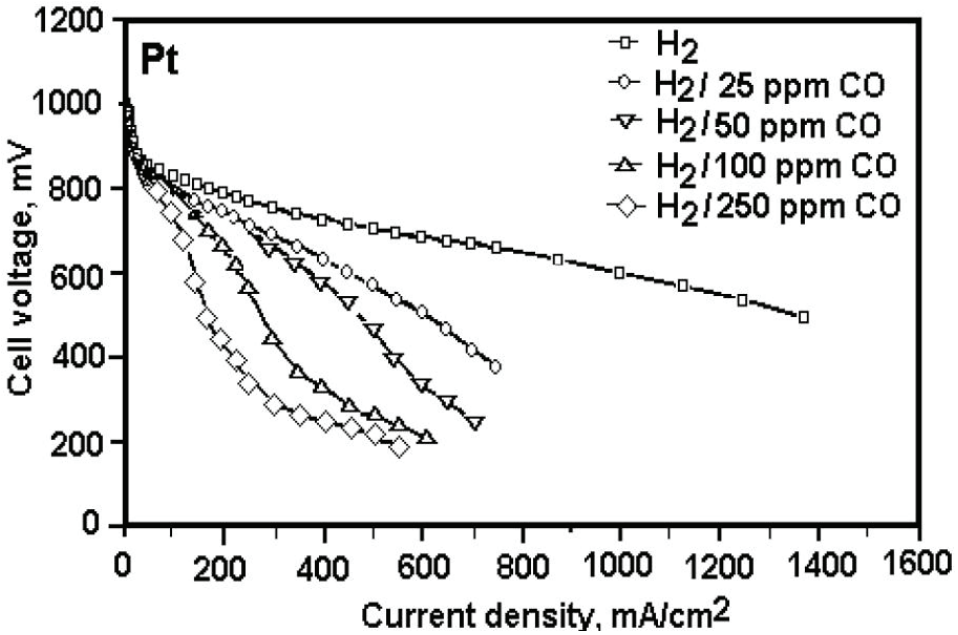
At normal PE[illegible] FC operatin[illegible] temperature ([illegible][illegible]C)[illegible]C[illegible] contained in the re[illegible]ormate [illegible]as is stron[illegible]ly bonded to the Pt catalytic sites (Pt–C[illegible])[illegible] even at lo[illegible] concentration[illegible]preventin[illegible] reaction (a)[illegible]The result is a lo[illegible]erin[illegible] o[illegible]cell potential[illegible]

The most common C[illegible]–tolerant catalyst (PtRu/C) is supposed to act throu[illegible]h a bi[illegible]unctional mechanism (*[illegible]atanabe and [illegible]otoo[illegible][illegible] Electroanal[illegible] Chem[illegible][illegible][illegible]7[illegible][illegible][illegible][illegible]27[illegible]*)[illegible]involvin[illegible] [illegible]ater activation by Ru[illegible]and subse[illegible]uent C[illegible] electrooxidation on a nei[illegible]hbourin[illegible] Pt atom[illegible]

$$Ru + H_2O \rightarrow Ru\text{-}OH + H^+ + e^-$$

$$Pt\text{-}CO + Ru\text{-}OH \rightarrow CO_2 + H^+ + e^- + Pt + Ru$$

CO Poisoning of Low Temperature PEMFC



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What the Technology is expecting

- C□ tolerant catalysts□□ith hi□h de□ree o□tolerance also durin□ transients (start up)□able to □uickly recover the per□ormance

- □evelopment o□materials technolo□ies speci□ically polymer electrolytes to substitute □AF□□ that can operate at temperatures as hi□h as □7□-2□□ºC so that C□ covera□e is less□

- This □ill consistute the □EA □or the **hi□h temperature PE□ □uel cell**

Why high temperature PEM fuel cells?

➢Potentially higher reaction kinetics

Lower quantity of the expensive Pt catalyst on the electrodes

➢Increase of the catalysts' CO tolerance
(10-20 ppm 80°C, 40000 ppm 180°C)

Possibility to use not so pure H_2 or other fuel

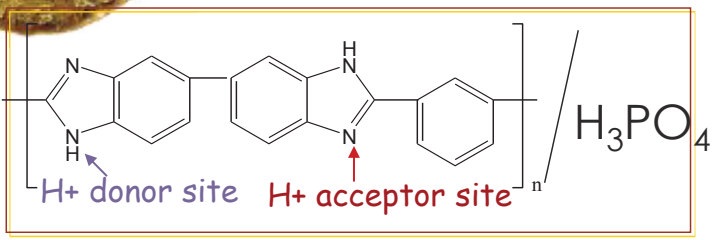
➢Simplifications
(fuel processor/reformer, no humidification
small cooling system)
Threefold increase of system's volume Power Density

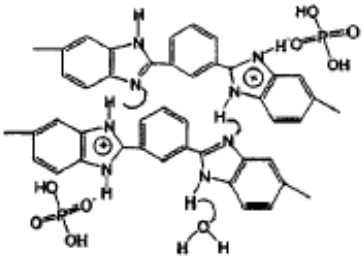
- Less complexity
- Reduced cost

Properties of the Ideal Electrolyte

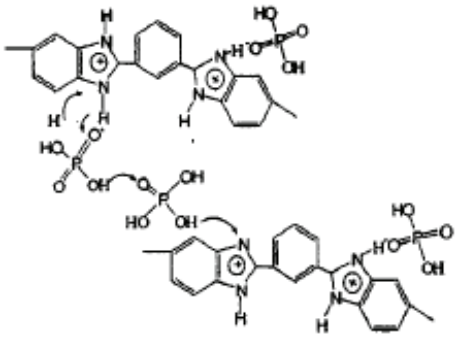
- High ionic conductivity
- Electron insulator
- Good mechanical properties
- Chemical stability
- Thermal stability
- Oxidative stability
- Low gas permeability
- Low cost

PBI/H_3PO_4





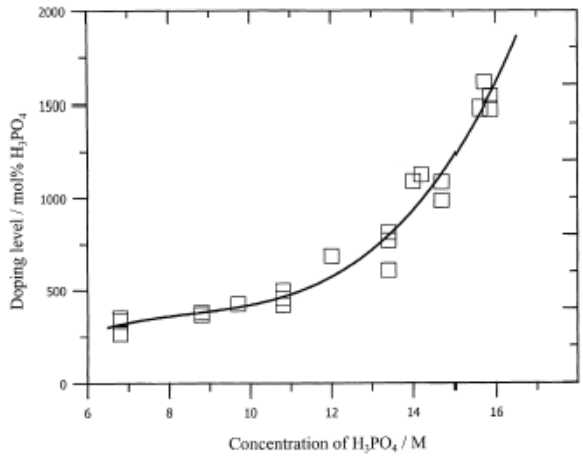
- High thermal stability (Td=500 °C)
  - High Tg(~440 °C)
    - High ionic conductivity



Drawbacks

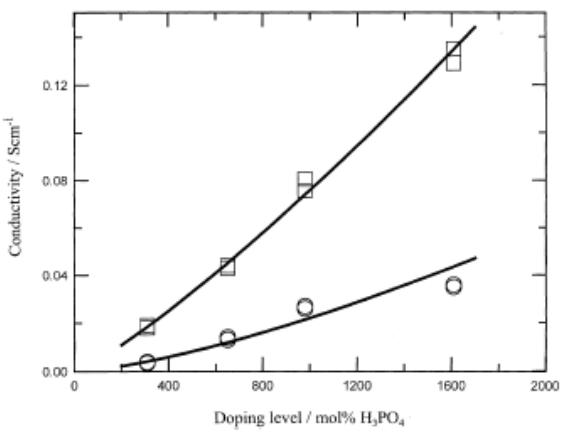
- **Brittle**
  - **Low TG when imbibed with H_3PO_4**
    - **Low oxidative stability (in H_2O_2)**

Doping Ability and Conductivity

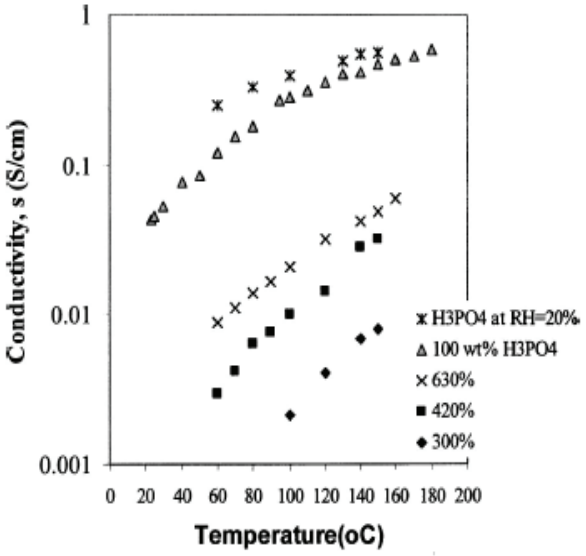


Conductivity versus doping level at 25 °C(o) and 150 °C(□), R_H=80-85%

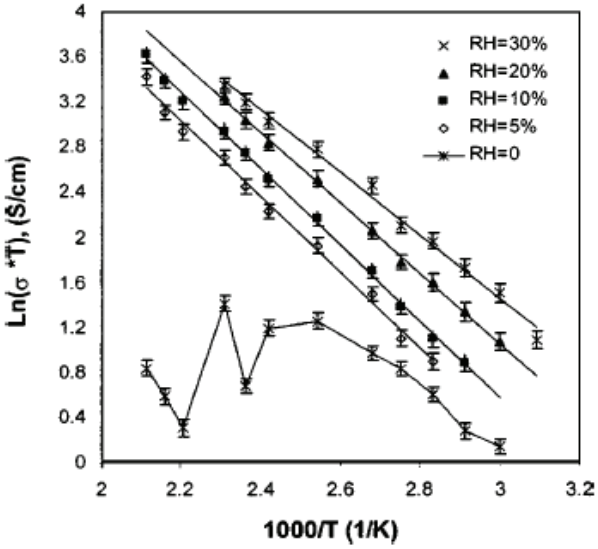
Doping level of H_3PO_4 as a function of the H_3PO_4 concentration



Conductivity of Acid Doped PBI



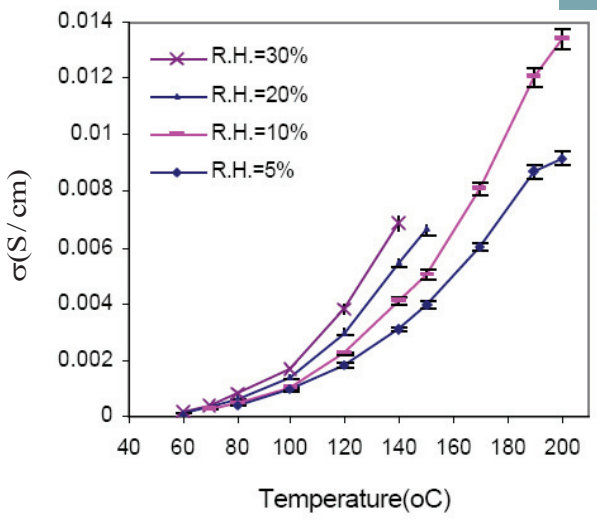
arison of conductivity of H3PO4 doped PBI and H3PO4 aqueous solution at 150°C and ambient pressure

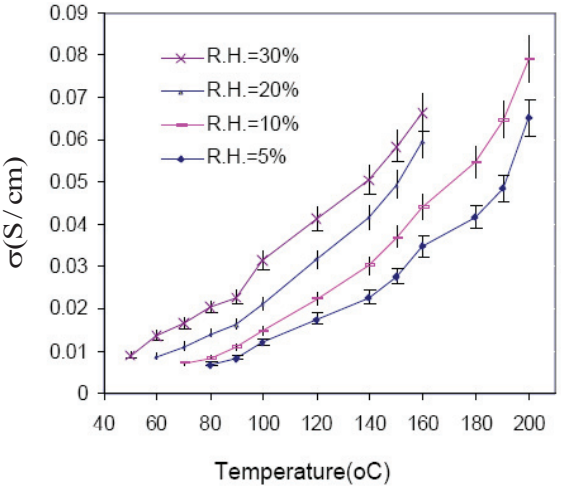


erature dependence of the conductivity of acid doped PBI

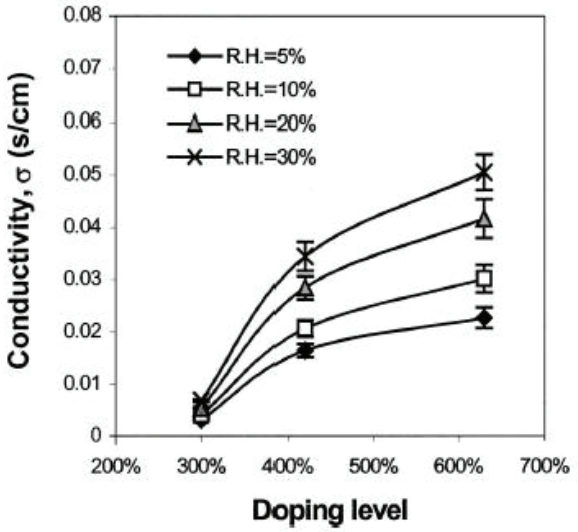
a et al, *Electrochem. Solid-State Lett.*, **151**

Conductivity of PBI vs Temp for Various Relative Humidities



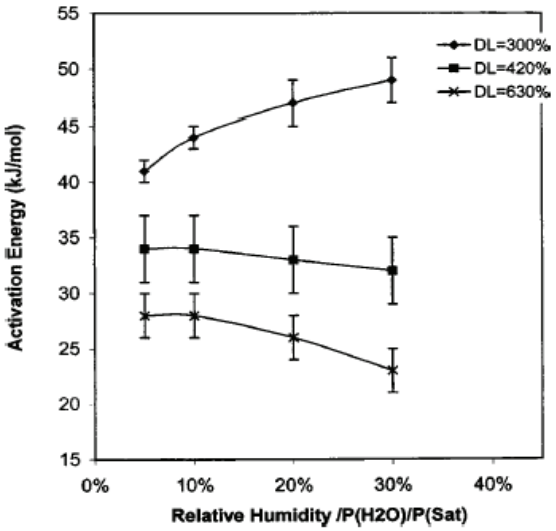


Conductivity of Acid Doped PBI



[illegible]

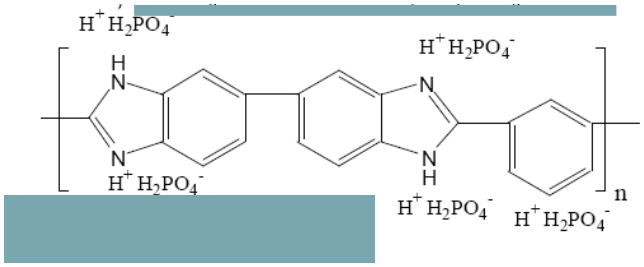
[illegible]



PBI/Acid Interaction

H_3PO_4 Protonates PBI

- IR measurements indicate max protonation at n=2
- FTIR experiments support also the formation of [2]-H-bonding instead of salt formation
- $H_2PO_4^-$ predominates over concentration range
- Solid state ^{13}C NMR shows interaction between acid and polymer
- ^{31}P NMR indicates additional phosphoric-acid species are weakly tied to PBI structure



H_2SO_4 Protonates PBI

- IR measurements indicate max protonation at n=1
- FTIR measurements indicate protonation
- Anion SO_4^- at n < .6; HSO_4^- at .6<n<1.5; H_2SO_4 at n=3.2

Evidence of Grotthus Mechanism Involving N-H - Acid

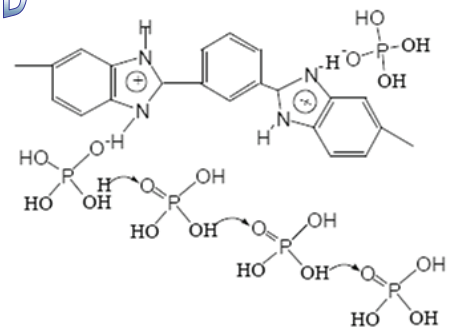
- Low activation volume
- Activation energy consistent with Grotthus mechanism
- Dependent on anion type
- Very low conductivity with n<2 indicating little N-H to N-H proton hopping
- H_2SO_4 conductivity > H_3PO_4 due to easier reorientation and higher acidity of HSO_4^-

Pintenella, Electrochimica Acta 43
Pu et al, Solid State Ionics 145

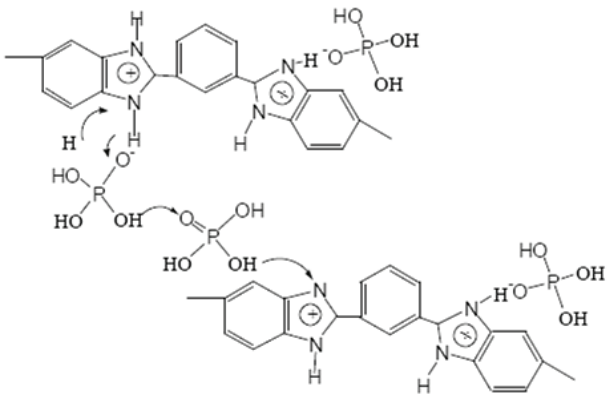
Conductivity Mechanism of PBI Membranes

- Acid protonates PBI
- Proton hops from acid-acid and acid-N-H
- No proton hopping between N-H and N-H
- Hydrogen-bonded structures facilitating proton switching

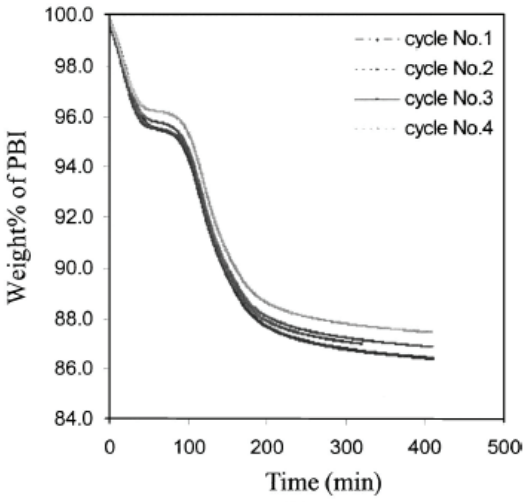
ACID-ACID



ACID-BI-ACID



Stability of the Doped PBI



TGA of PBI doped with H_3PO_4 (630%)

30-100 °C(100-96%):

- Removal of free water H_3PO_4

100-180 °C(96-89%):

- Removal of water from two molecules H_3PO_4

$$2H_3PO_4 \longrightarrow H_4P_2O_7 + H_2O\uparrow \quad (a)$$

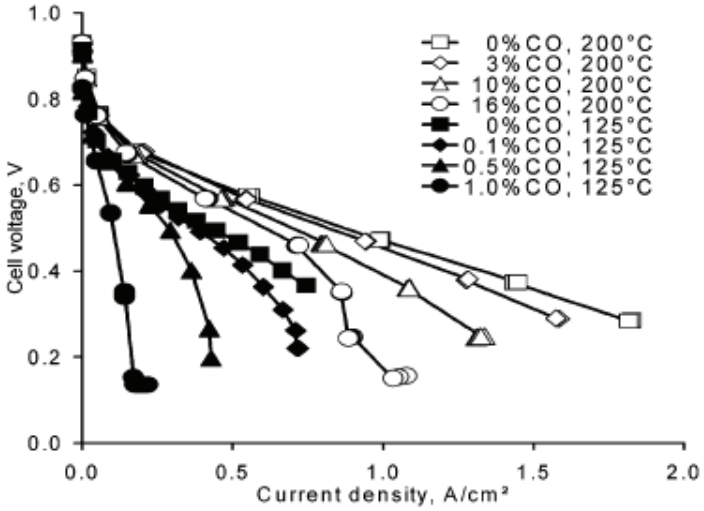
200 °C, 4h(89-87%):

- (a)
- Removal of water from three molecules H_3PO_4

$$H_4P_2O_7 + H_3PO_4 \longrightarrow H_5P_3O_{10} + H_2O\uparrow \quad (\beta)$$

- Polyphosphoric acid

Cell Performance of High Temperature PEMFC



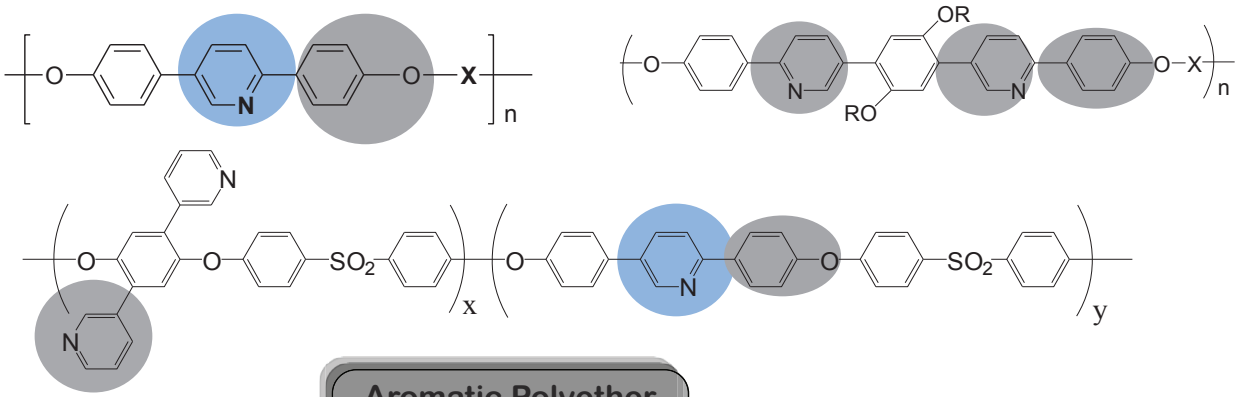
Polarization curves of a PBI-based PEMFC with oxygen and hydrogen or hydrogen containing CO at 125 and 200 °C under ambient pressure

Li, Q. et al. *J. Electrochem. Soc.* **150**, A1599, (2003)

□ri□i□e □a□e□aromatic □ol□ether□

Route to Design and Synthesis of Novel Polymers

(Aromatic Polyethers bearing Polar Groups)



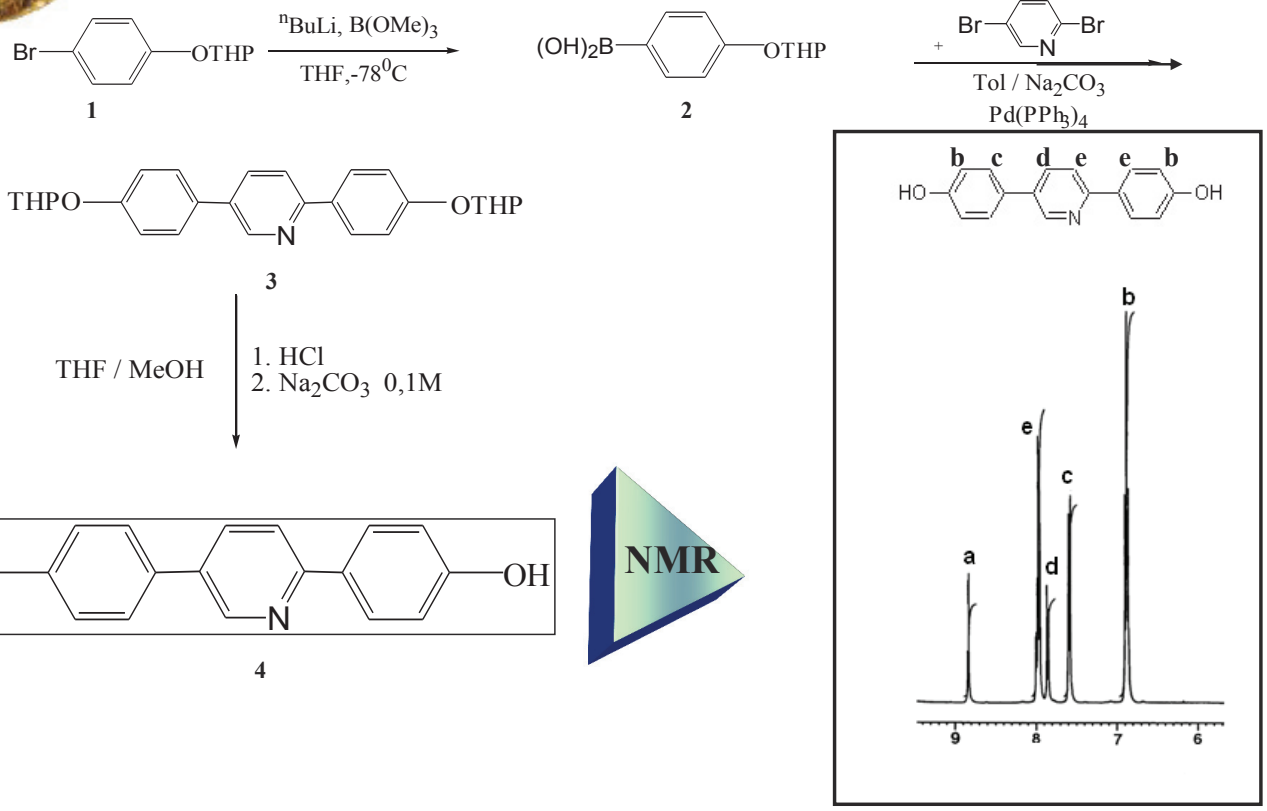
Structural Characteristics

Aromatic Polyether
- High Thermal Stability
- High Chemical Stability

Pyridine Polar Group
- H^+ Acceptor site
- Hydrogen Bond site

- Monomer Preparation
- Polymerization via polycondensation
- Characterization via H-NMR, GPC, DMA, TGA, FT-iR, Tensile testing
- Selection of the best membranes for MEA construction and testing

Synthesis proceedure of the Pyridine diol Monomer

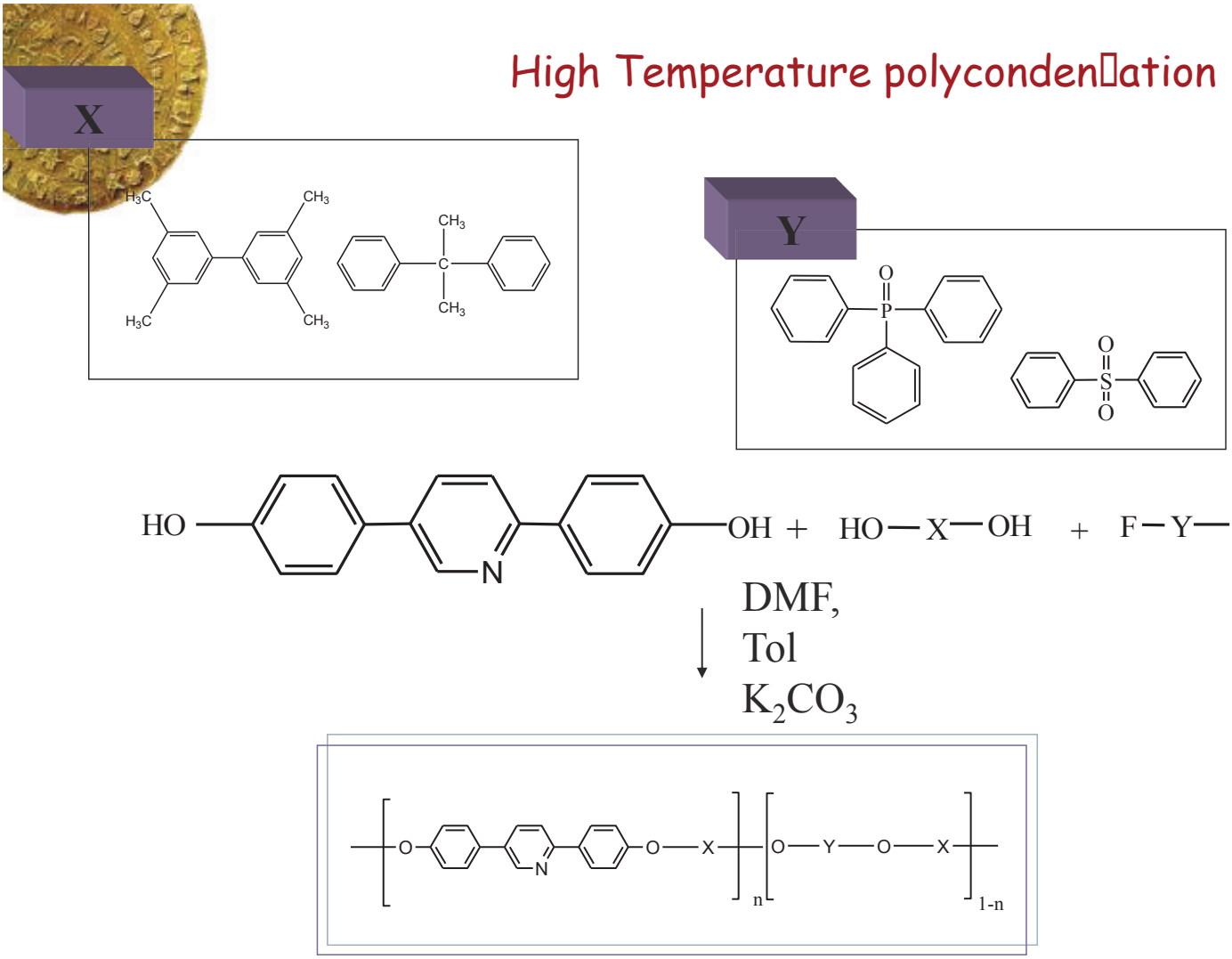


N.Gourdoupi, A.K. Andreopoulou, V. Deimede, J.K. Kallitsis, *Chem.Mater.*, **2003**, *15*, 5044

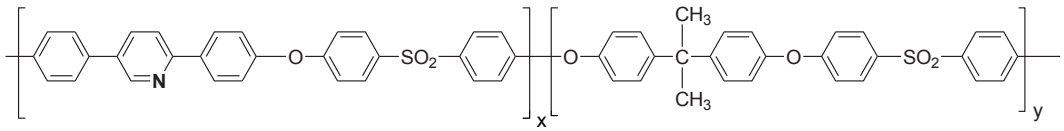
- The synthesized pyridine diol is polymerized with a variety of commercially available monomers following the high temperature Polycondensation reaction.

- It is possible to synthesize a whole family of copolymers with varying physicochemical properties.

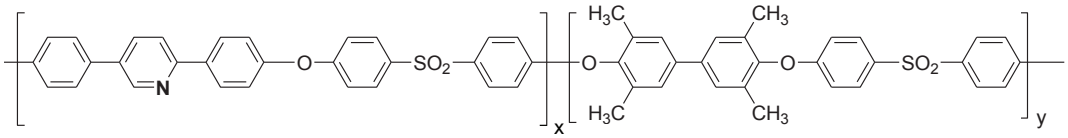
High Temperature polycondenation



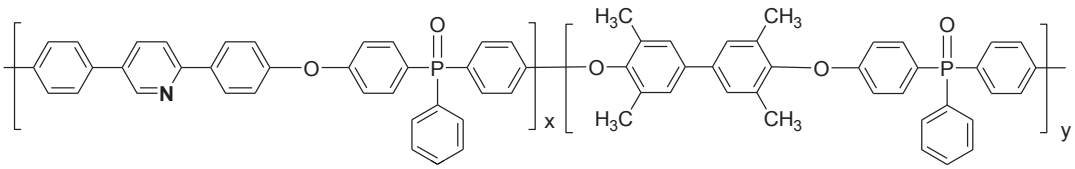
Copolymers of Aromatic Polyethers Bearing Polar Pyridine and Methyl Groups



PPycoPSF



TMPySF

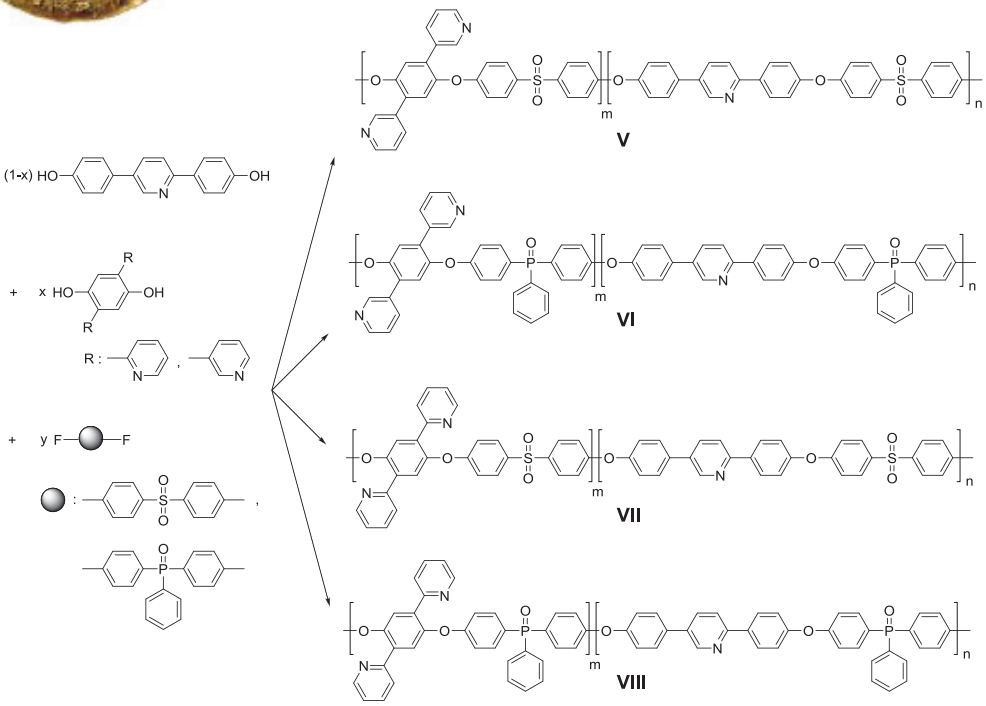


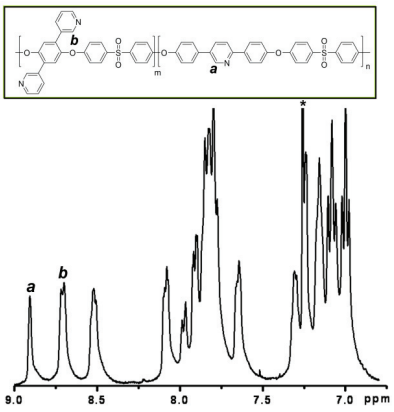
TMPyPOSF

M. K. Daletou, M.Georgezi, E. K. Pefkianakis, C.Morfopoulou, J.K. Kallitsis FUEL CELLS 10, **2010**, . 1, 35–44

E.K. Pefkianakis, V. Deimede, M.K. Daletou, N. Gourdoupi, J.K. Kallitsis *Macromol. Rapid Commun.*, *26*, 1724, **2005**

Synthesis of copolymers with side pyridine groups





dPPy(x)coPES

M. Geormeli, □□ □□o□□os, J.K. Kallitsis, □ Neop□□tides
□d□anc□d □unc□onal Ma□□rial□□□□, □mi□□□d □**20**□□

Oxidative Stability (Fenton□s test)

Inside the Fuel Cell

□□e primar□ reason for Mem□rane De□radation is t□e formation of □□□•, □□□$_2$•

□$_2$ □ 2□• (onto t□e Pt□
□• + □$_2$ □diffused t□rou□□t□e PEM onto t□e anode□ □□□$_2$•
□□□$_2$• + □• □ □$_2$□$_2$ □a□le to □e diffused t□rou□□t□e PEM□
□$_2$□$_2$ □ M$^{2□}$ □ M$^{□□}$ + HO• + HO$^-$
•OH + H$_2$□$_2$ □ □$_2$□ □ □□□$_2$•

Preliminar□ in□esti□ation for mem□rane inte□rit□ □□a □enton test

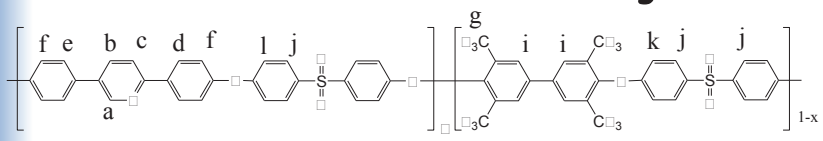
□enton
□$_2$□$_2$ □ □e$^{2□}$ □ □e$^{□□}$ + HO• + HO$^-$
HO• + RH □ □$_2$O + R•
HO• + H$_2$□$_2$ □ □□$_2$• + H$_2$□

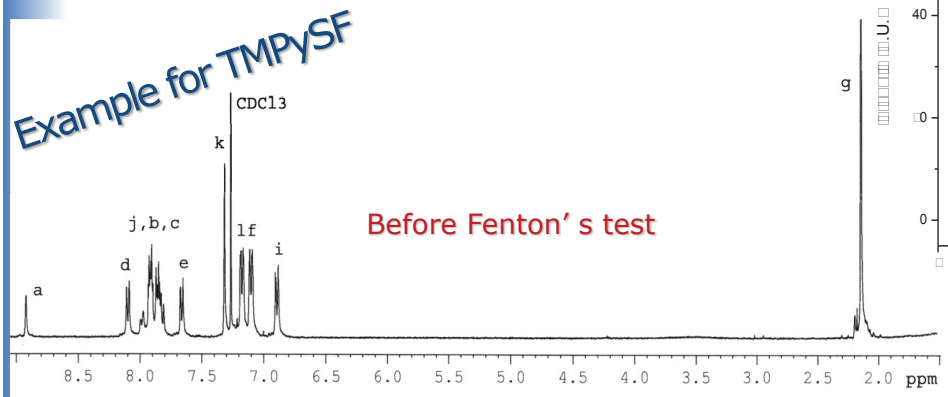
□reatment of t□e mem□ranes □it□ □□drogen perox□de solution in t□e presen□e of □errous ions for 72□at □□□

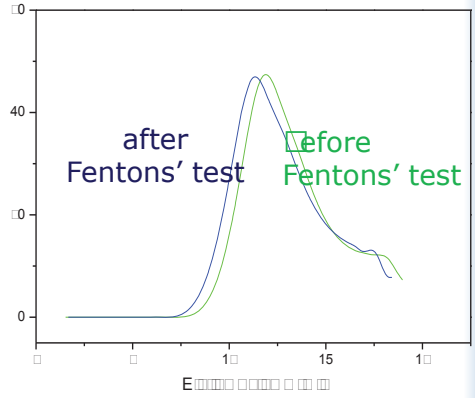
□e, J., □ood, D.□, □a□ne, D.M., □a□od□inski, □□, □tanasso□, P., □orup, □□ □□/□t□doc□□m. □oc. □1□2□1□, □14, **2005**□
□osnako□i□, □, □□□i□k, □, □.□□□□C□□m. □□1□□□14□, 4□□2–4□□7, **200**□□

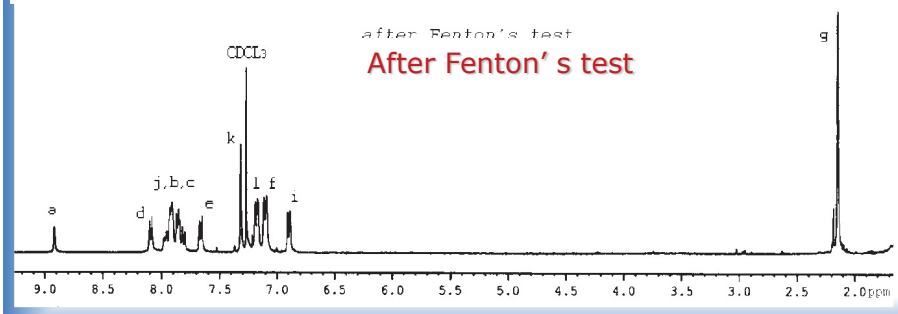
□od□don, □, □o□a□k, J.□, □a□onti, □□, □d□an□e De□elopment and □a□orator□□e□□hni□al □eport, No. □□DE□, General Ele□tri□□o.,
□est □□hn, M□, □.□□ □□□□□

Examination of Chemical integrity and Oxidative stability after Fentons' test





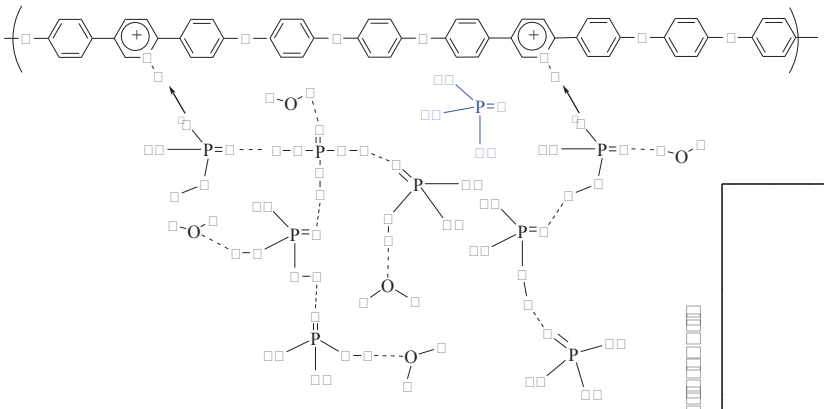




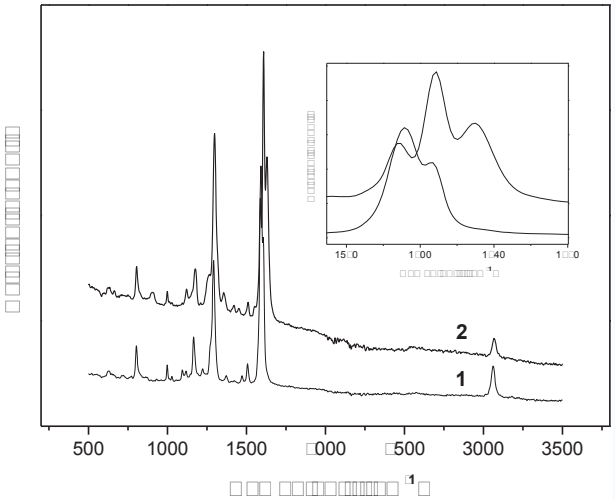
Polymer	Mn	Mw	Disp
MP	4 7	7	2.2
MP after enton	4147		2.1

J.K. Kallitsis, M. Georme , Neop tides
Polym Int 00 1 –1 33

Protonation of Pyridine units

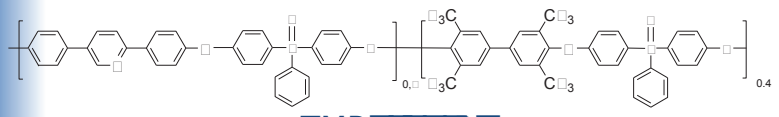


Proof of protonation of t e p ridine units aman and a possi le s ematic representation of t e intera tion it p osp ori a id

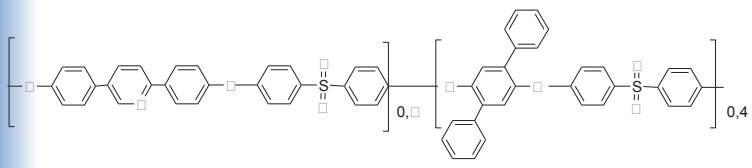


N.Gourdoupi, K. ndreopoulou, V. Deimede, J.K. Kallitsis,
C m.Ma r., , 44, **200**

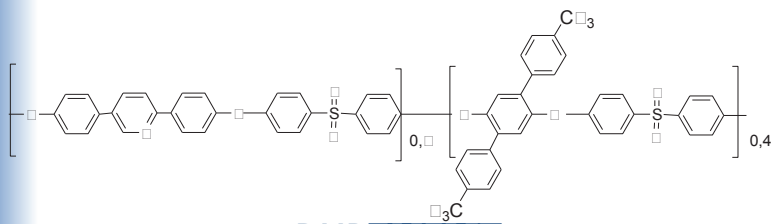
Comparison of the Phosphoric acid doping ability



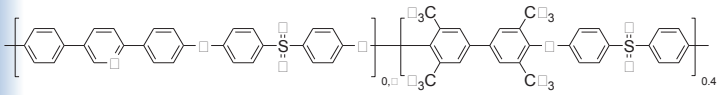
TMP□□□□P□



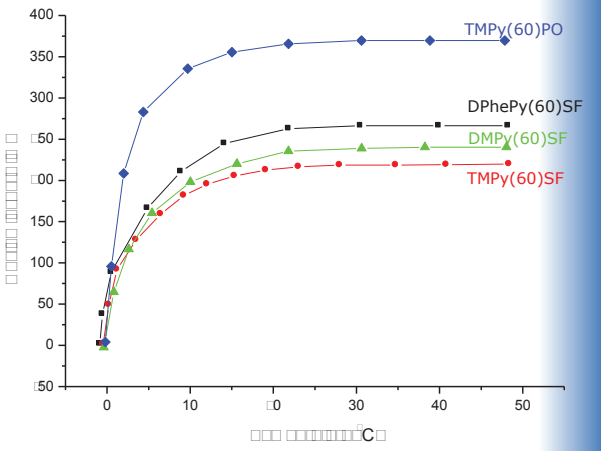
DP□eP□□□□□F



DMP□□□□□F

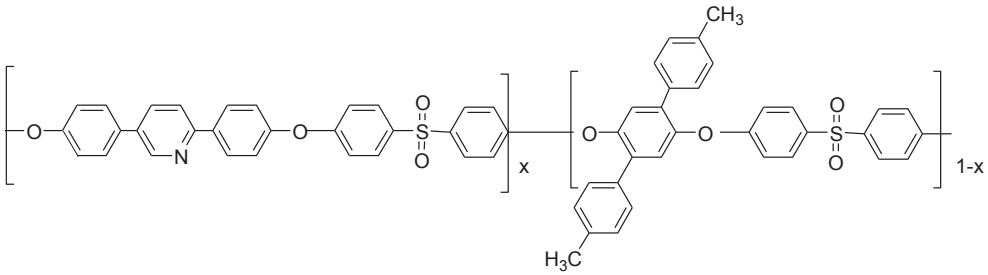


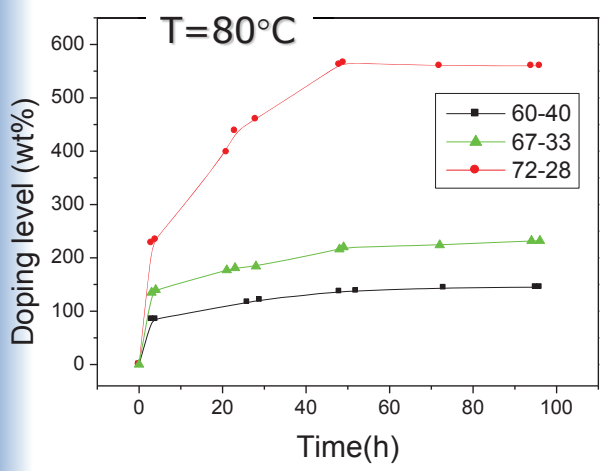
TMP□□□□□F

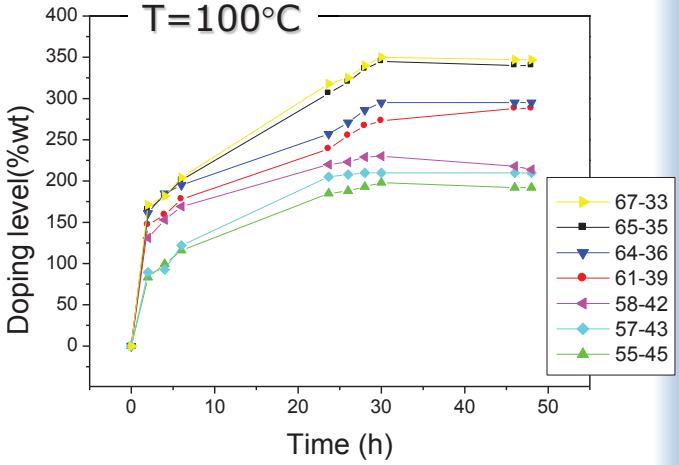


□ime dependen□e of dopin□le□el □□t.□ □of t□e □opol□mers □□□□□□ □□◆□, □□□□□□□□□□□■□, □□□□□□□▲-), **TMPySF (-●-) at 100°C**

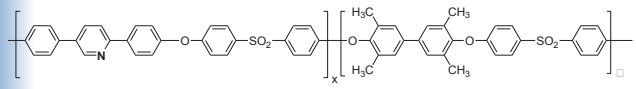
Influence of the copolymer structure on the Phosphoric acid doping ability



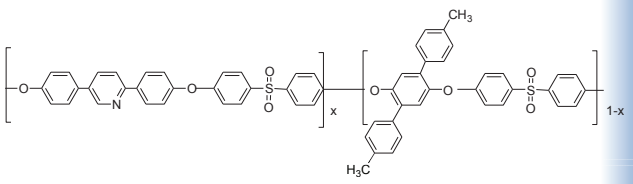




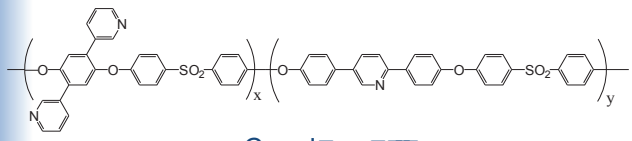
Comparati□e Conducti□ity □easurements



Copol□me□□



Copol□me□□□



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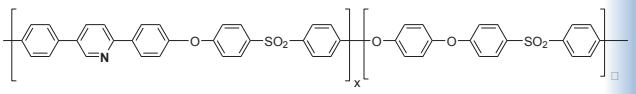
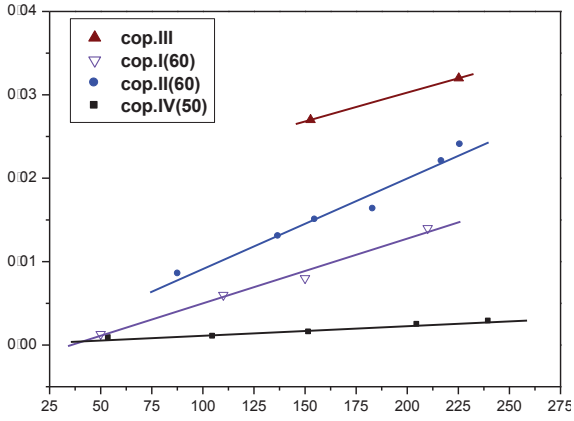


Copol□me□□□



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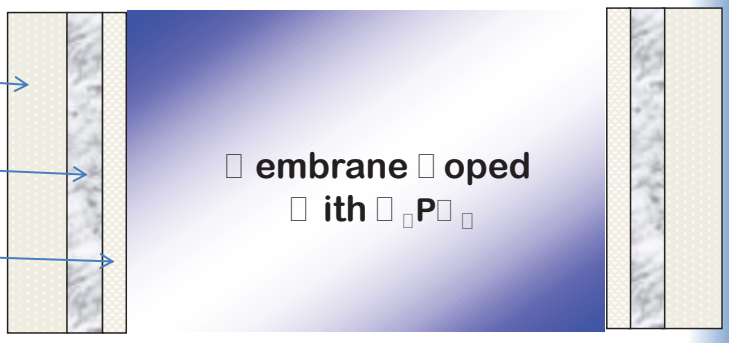
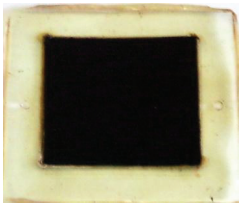
□ embrane □lectrode □ssembly □□ □□□Preparation

- C□□□□□□ □□□e□□□□□□□□□□ □□□□h
- □□□D□□□□□□□□□ □□ye□
- C□□□□y□□□(P□□C)





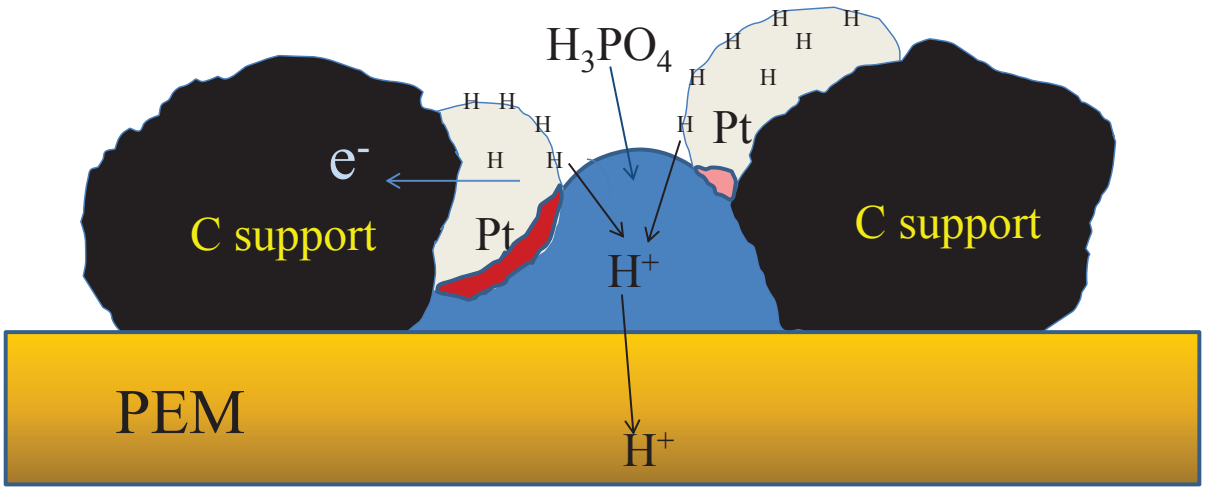
MEA

□□□□□e□□□□□□ □□1□0°C, 10 □□□
P□e□□□□e□0□1 □□□□□□□□□□□□□

Electrode

- The **carbon cloth** functions as the current collectors and the support of the gas diffusion and catalytic layers
- The **gas diffusion layer (GDL)** is usually composed of carbon powder and 30wt% PTFE. It functions as the support for the catalytic layer. It must be porous enough to permit the fast diffusion of reacting gases to the electrochemical interface
- The **catalytic layer** consists in the case of HT PEM MEAs only from Pt/C. The ionic link of the Pt nanoparticles with the membrane is achieved by impregnation of certain quantities of H3PO4.

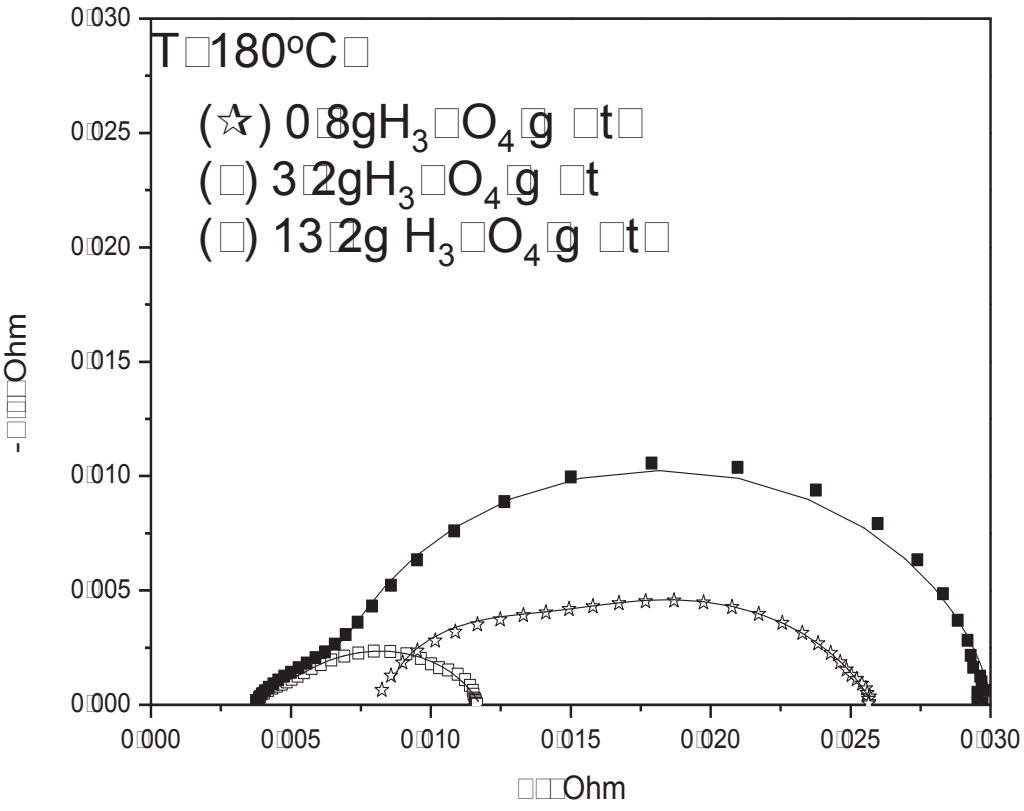
Schematic representation of the Electrochemical Interface in HT PEM MEA



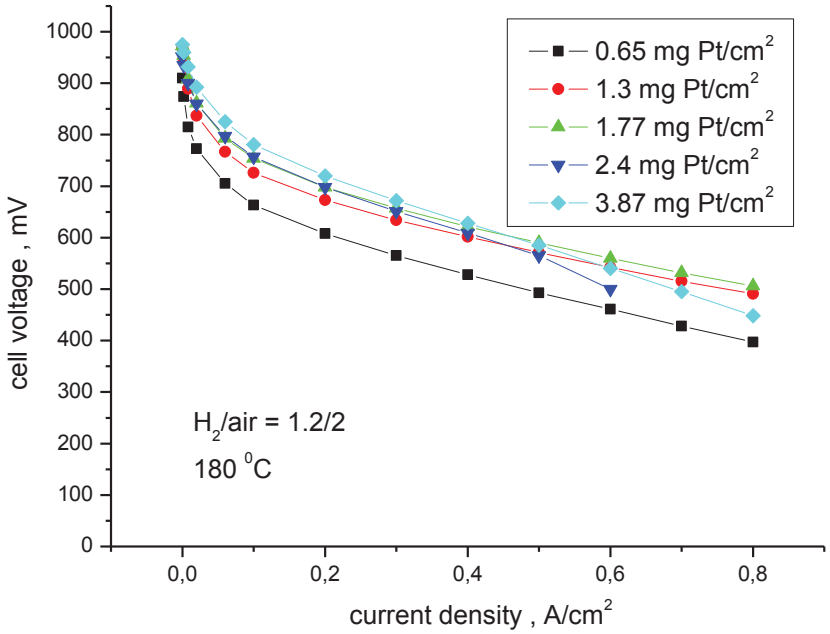
Effect of the amount of H3PO4 on the Electrochemical Impedance of the MEA

- Low amount of H3PO4 will result in limited pathways between the Pt particles and the membrane. This is expected to affect both the ionic and polarization resistance of the MEA.
- Large amount of H3PO4 in the electrode will result in the electrode flooding with main negative effect on the polarization resistance of the MEA.

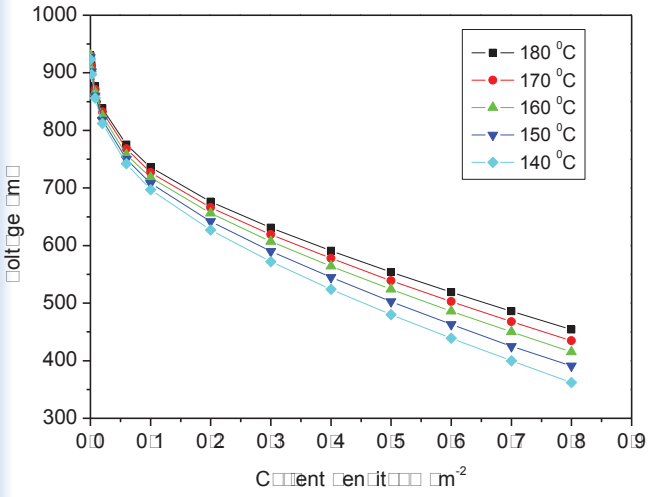
Nyquist plots depicting the effect of H_3PO_4 doping level within the electrochemical interface.



Effect of Pt loading on the MEA performance



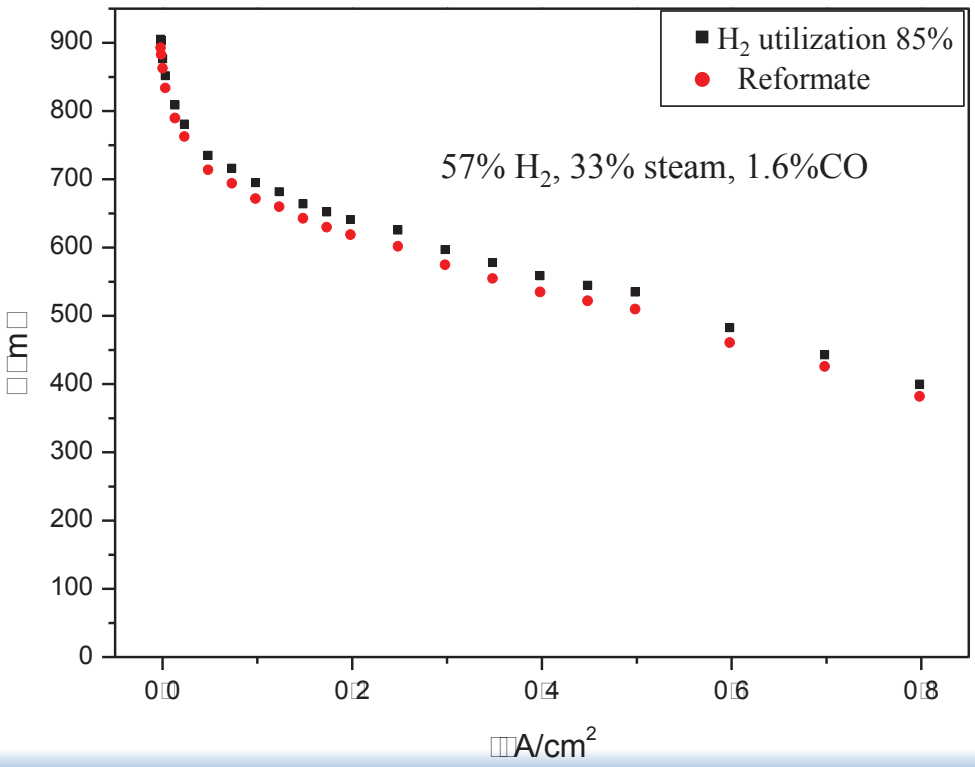
MEAs based on aromatic polyethers with pyridine groups (Advent TPS®)



Temperature: 180-140°C
Ambient pressure
Feed: H_2/Air
Anode: 1.2
Cathode: 2

Temperature	Rel (mOhm□□m²)	Current density (mA/cm²) at 600mV
180°C	140	377
170°C	145	346
160°C	150	317
150°C	160	280
140°C	175	249

Performance under H_2 and reformate gas



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