Materials for PEM Fuel Cells

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H2FC MATERIALS WORKSHOP

TECNALIA, Donostia • San Sebastian (Spain)

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TECNALIA

Proton Exchange Membrane Fuel cells
Polymeric Fuel Cells

PEMFC

Hydrogen Oxidation Reaction (HOR):

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

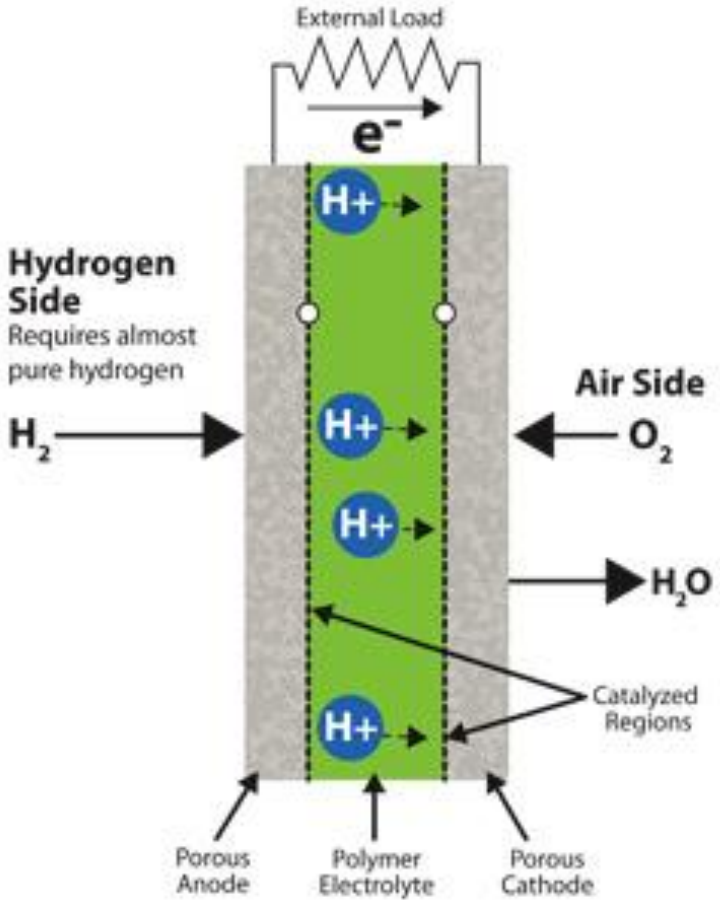
Oxygen reduction reaction (ORR):

$$1/2O_2 + 2H^+ + 2e^- \rightarrow H_2O$$

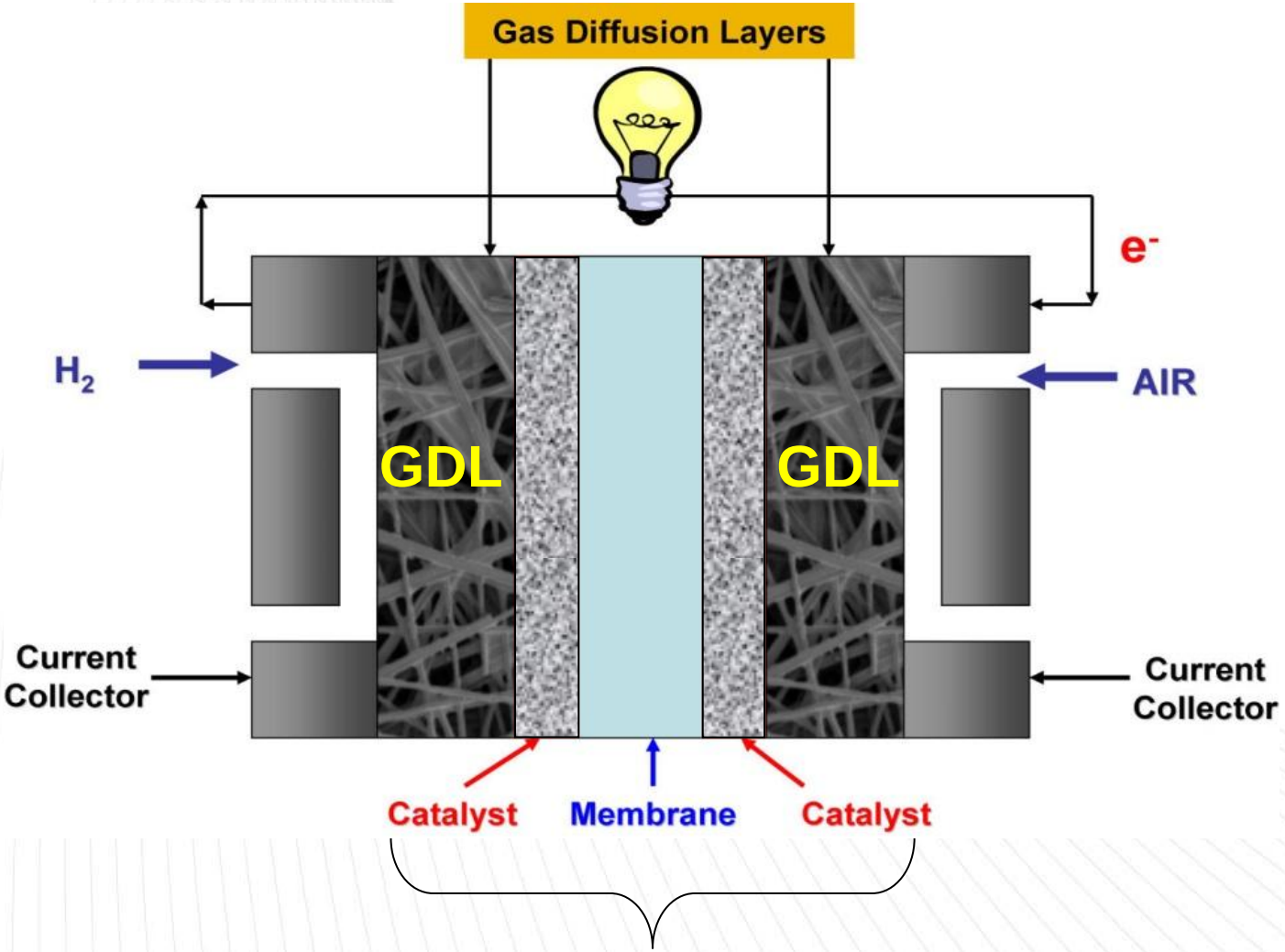
Overall reaction:

$$H_2 + 1/2O_2 \rightarrow H_2O$$

1,23 V

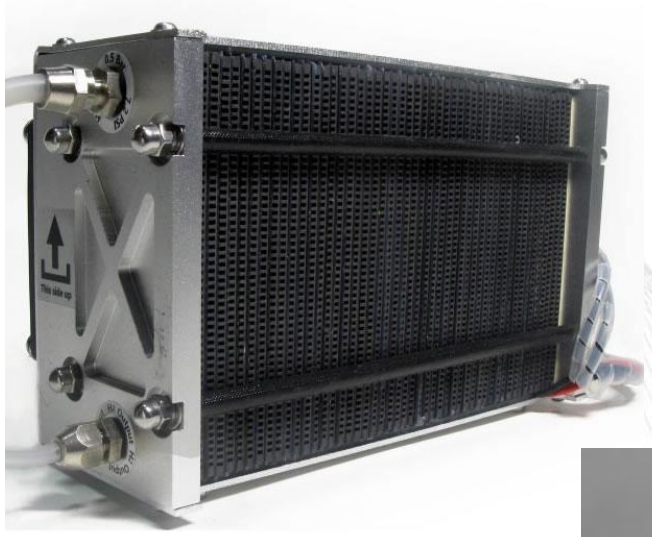


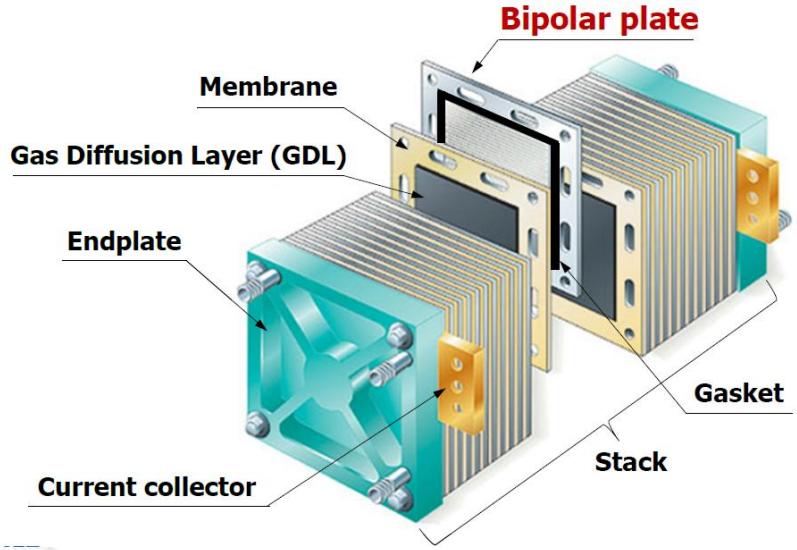
COMPONENTS OF A PEM SINGLE CELL



MEA
(Membrane electrode Assembly)

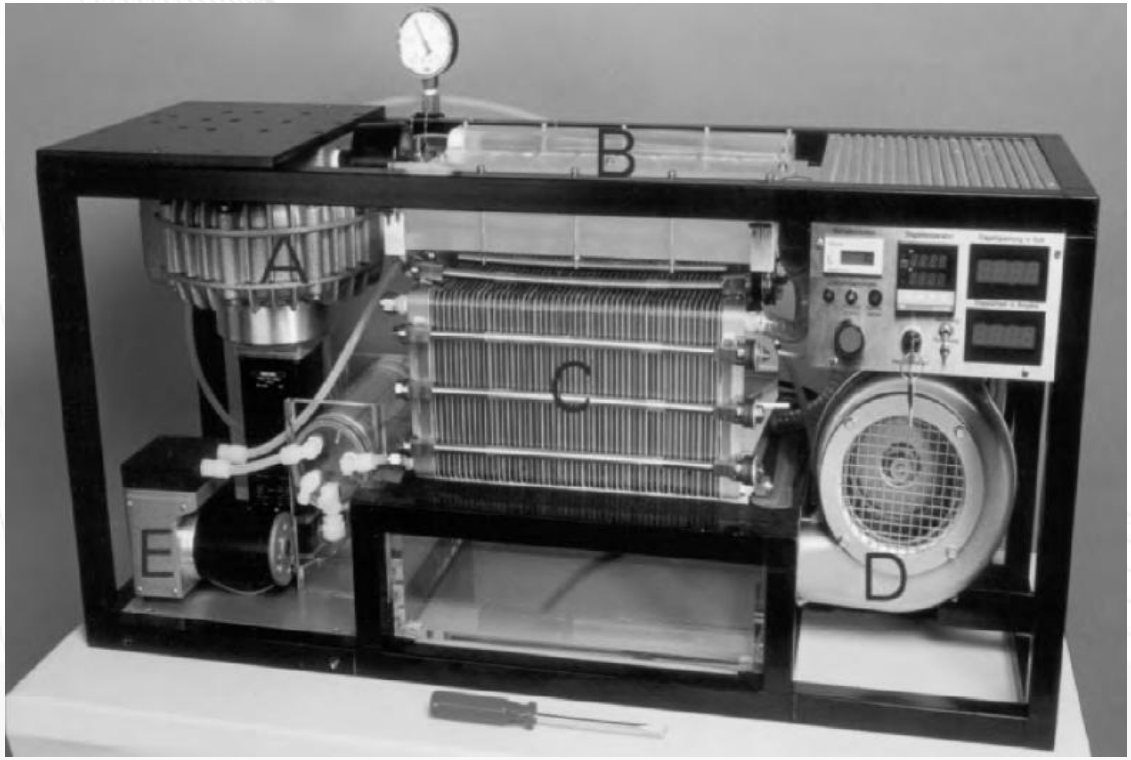
PEMFC STACK





PEMFC SYSTEM (with BoP)

A: Air pump
B: Humidifier
C: Stack
D: blower for cooling
E: Pump for gas supply

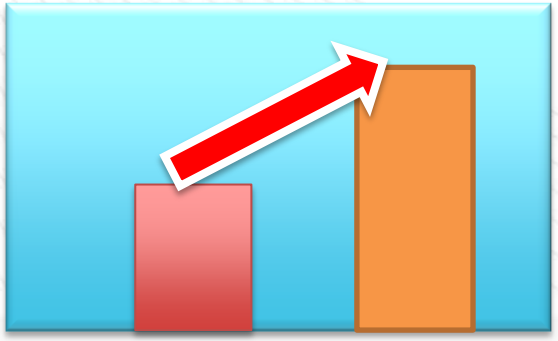


THE GOAL OF MATERIALS OPTIMIZATION IN PEMFC

1. REDUCTION OF COSTS

2. INCREASED PERFORMANCE

3. LONGER DURABILITY



1. REDUCTION OF COSTS

The example of the automotive industry…

The cost of fuel cell power systems must be reduced before they can be competitive with gasoline internal combustion engines (ICEs).

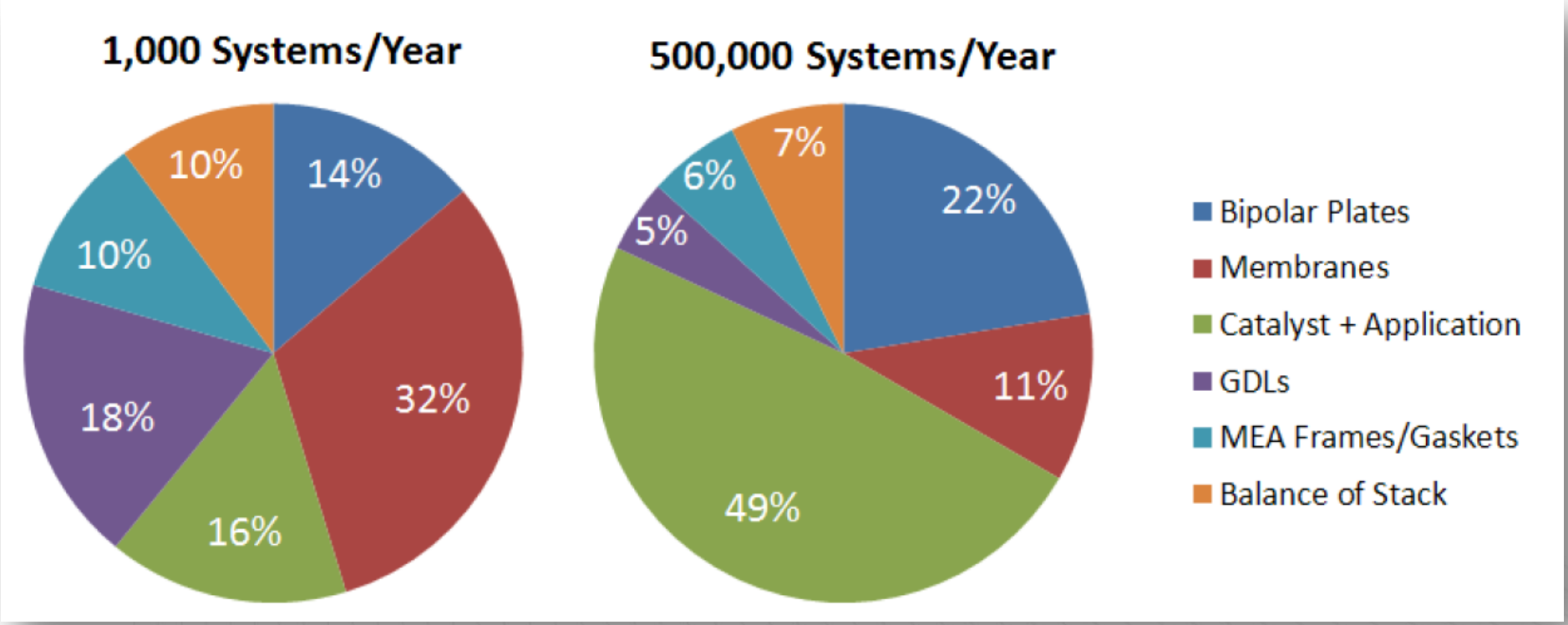
- Conventional automotive ICE engines cost about **$25-$35 / kW.**
- Fuel cell system needs to cost **less than $30/kW** to be competitive.

*"The cost of an 80-kW^{net} automotive polymer electrolyte membrane (PEM) fuel cell system based on 2013 technology and operating on direct hydrogen is projected to be **$67/kW** when manufactured at a volume of 100,000 units/year, and **$55/kW** at 500,000 units/year"*

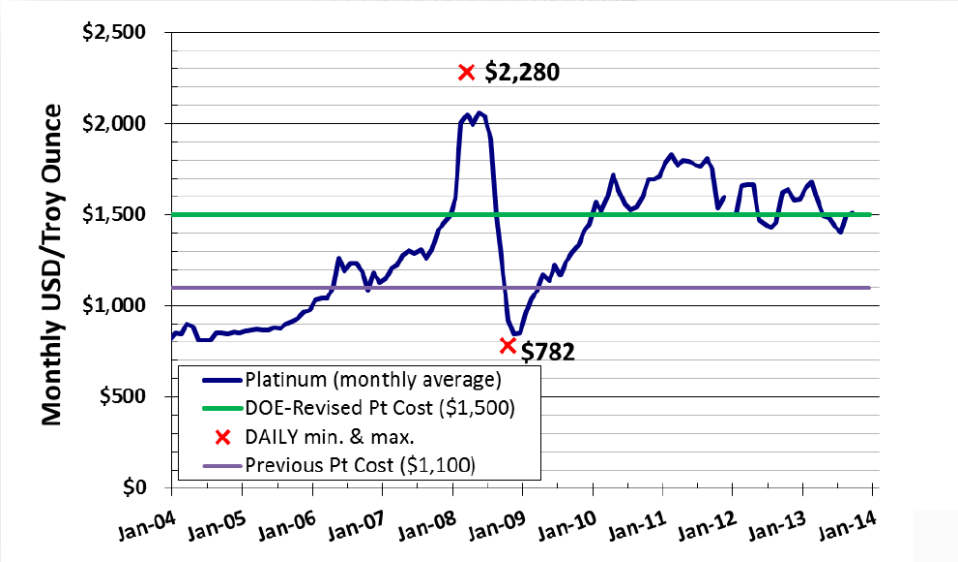
J. Spendelow and J. Marcinkoski, *Fuel Cell System Cost*, DOE Fuel Cell Technologies Office Record, Oct 2013

The **fuel cell stack** accounts for **64%** and **49%** of the total system cost at **1,000** and **500,000** systems per year, respectively.

Breakdown of the 2013 projected fuel cell stack cost

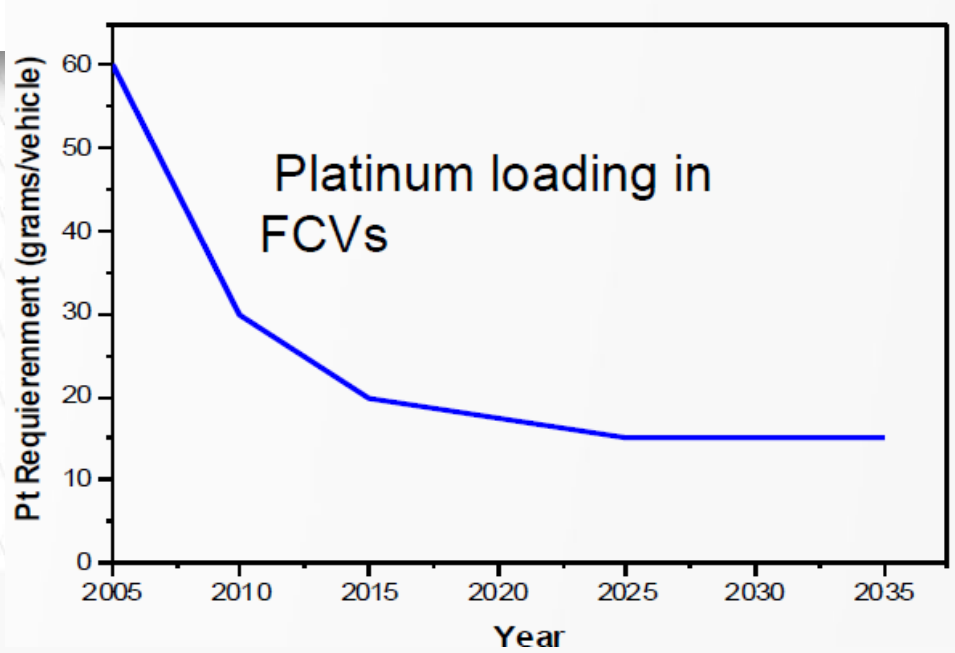


The price of platinum is not stable…



The current General Motors fuel cell uses **30 g** of platinum, which is more than $40,000 for the platinum alone.

The expectations for 2025 are to reduce the total Pt content in the fuel cell system to **15 g**



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2. PERFORMANCE

Increase in PEMFC **power density** in last years:

- **2007** → **583** mW/cm^2
- **2012** → **984** mW/cm^2

An impressive **69%** increase in performance alongside of a huge cost reduction

Innovation in materials and systems was critical to reach these remarkable changes

J. Spendelow and J. Marcinkoski, *Fuel Cell System Cost*, DOE Fuel Cell Technologies Office Record, Oct 2013

3. DURABILITY

To be competitive in the automotive market, fuel cell systems must have durability similar to current ICE systems:

→ **Durability target* : 5,000 hours → 240.000 km of driving**
with less than 10% loss of performance

- with operating temperatures from -20 °C to above the boiling point of water
- with operating humidity levels ranging from dry to wet.
- under dynamic load following start/stop operation, road vibration/shock, and ambient conditions.

** Defined by the U.S. DRIVE Fuel Cell Tech Team*

3. DURABILITY (2)

Fundamental degradation modes:

- Surface area and activity loss due to catalyst dissolution
- Catalyst particle growth and agglomeration
- Activity loss due to catalyst support corrosion
- Degradation due to corrosion of the bipolar plates
- Voltage loss due to increasing contact resistance between individual components
- Membrane degradation due to chemical attack and mechanical stress
- Catalyst and membrane performance loss due to contamination

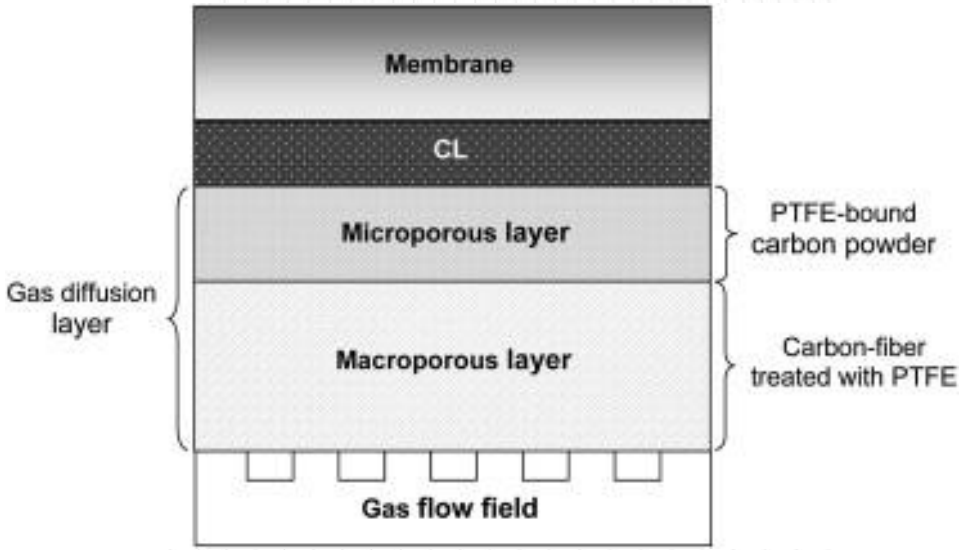
*Durability and cost are both related to **catalyst loading** (optimization of amount of Pt and particle size):*

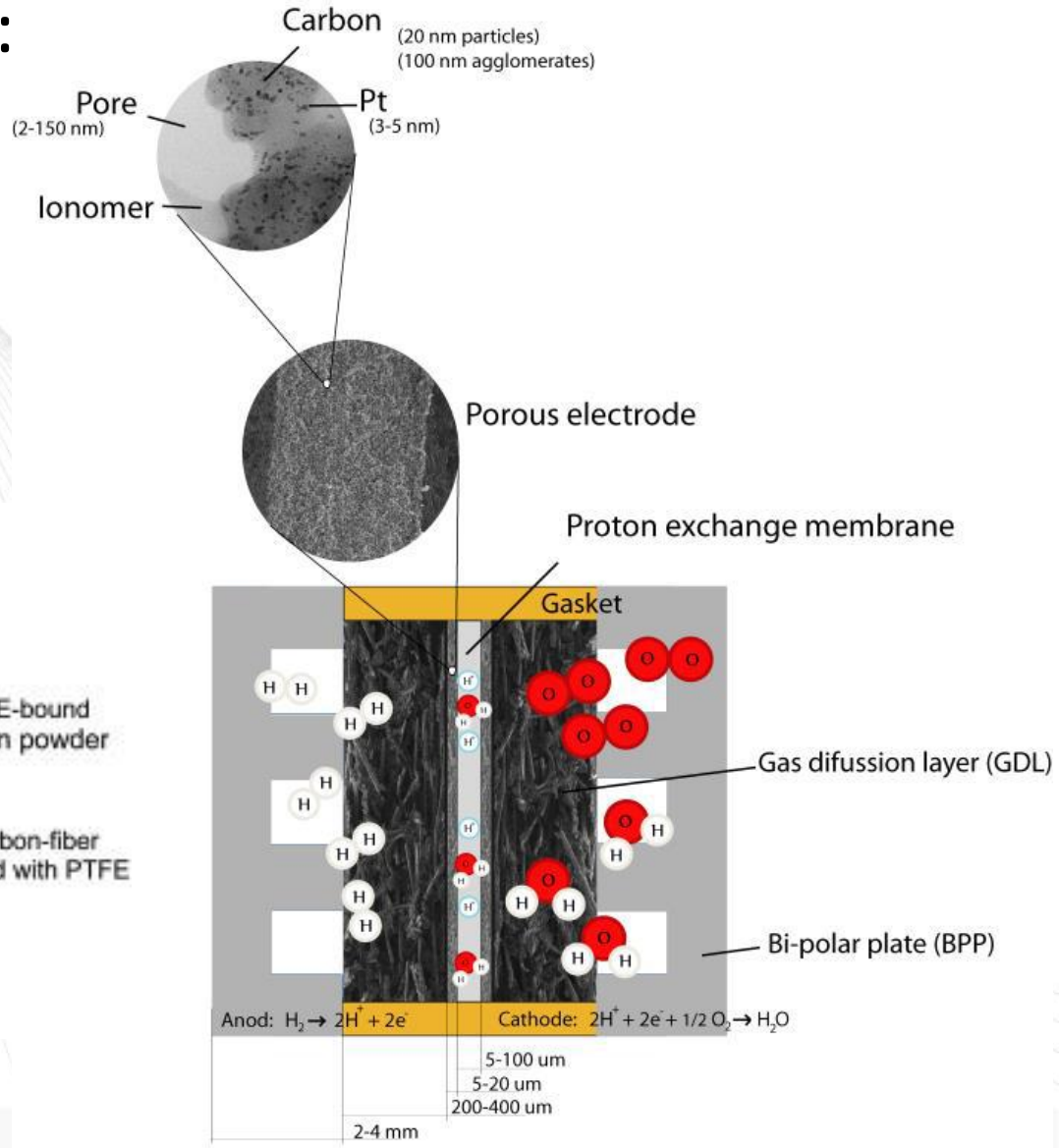
Attempting to decrease cost by increasing the dispersion and decreasing particle size to meet the cost target would decrease durability.

MATERIALS FOR PEMFC ELECTRODES

ELECTRODE STRUCTURE:

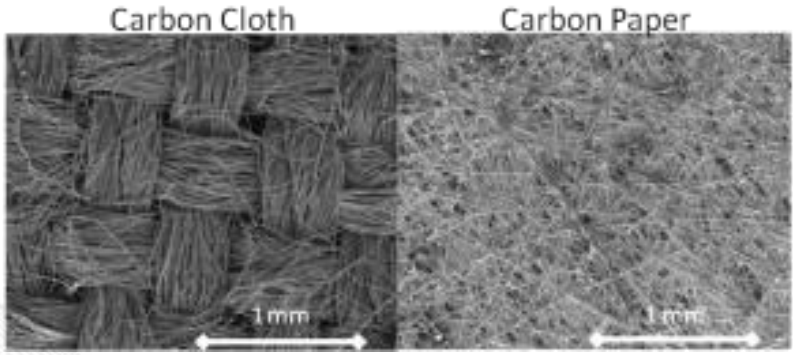
- Gas Diffusion Layer (GDL)
- Microporous Layer (MPL)
- Active layer (with catalyst)





Gas Diffusion Layer (GDL)

→ Comprised of carbon fibers randomly oriented to form a porous layer + PTFE for water management



→ Typically constructed from porous **carbon paper**, or **carbon cloth**, with a thickness in the range of 100–300 µm

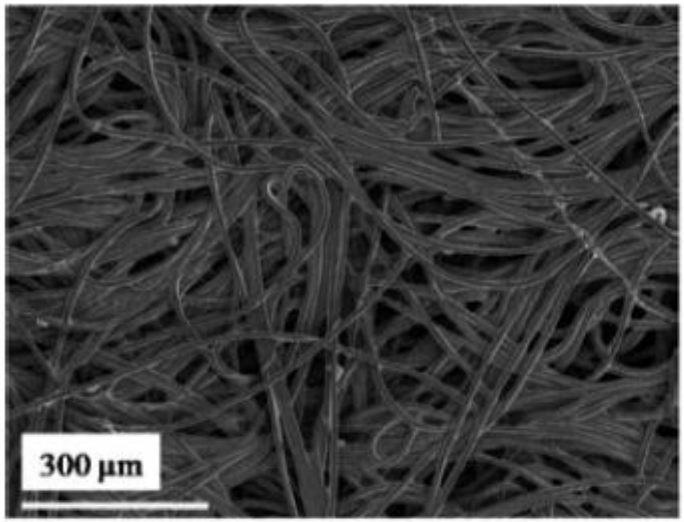
Functions in the electrode:

→ Ensures that reactants effectively **diffuse** to the catalyst layer

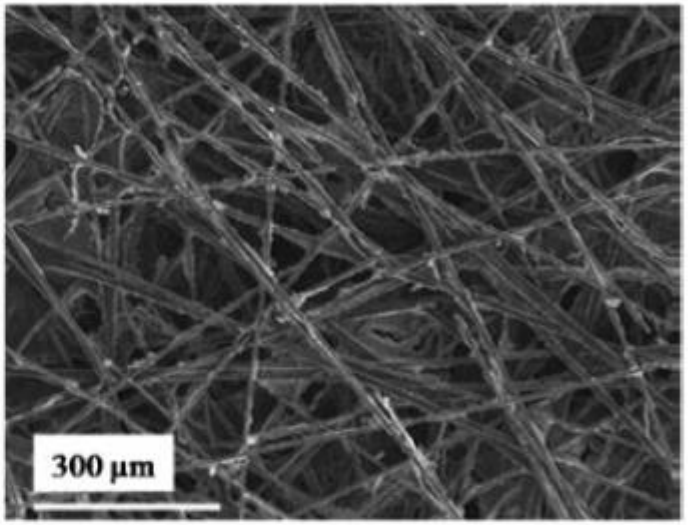
Source: GAPC

→ Is the **electrical conductor** that transports electrons to and from the catalyst layer.

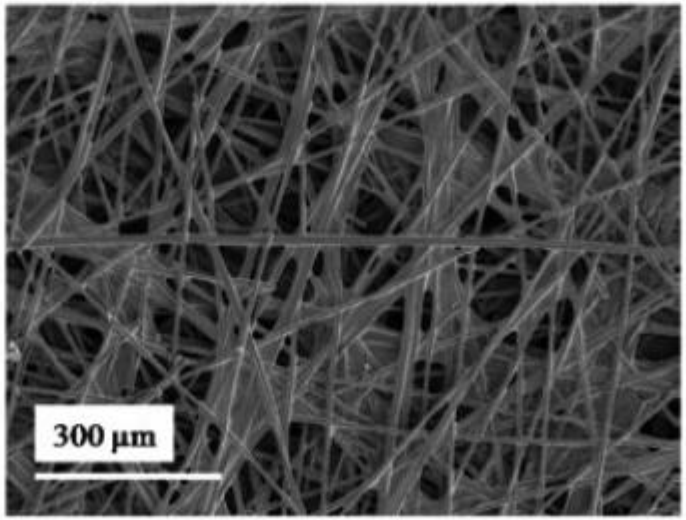
→ Assists in **water management** by allowing an appropriate amount of water to reach, and be held at, the membrane for hydration



(a)



(b)



(c)

SEM images of GDL samples:
(a) Freudenberg,
(b) SGL (Sigracet)
(c) Toray.

Microporous Layer (MPL)

Composition: carbon black (Vulcan XC-72) and PTFE (or PVDF)

The properties of microporous layers can be adjusted by changing the carbon (particle and agglomerate structure), and the hydrophobicity.

Functions in the electrode:

→ Reduces the contact resistance between the catalyst layer and the macroporous GDL

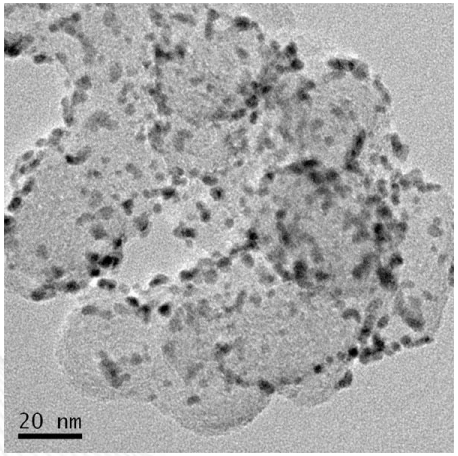
→ Control of porosity for the uniform acces of gases to the catalyst

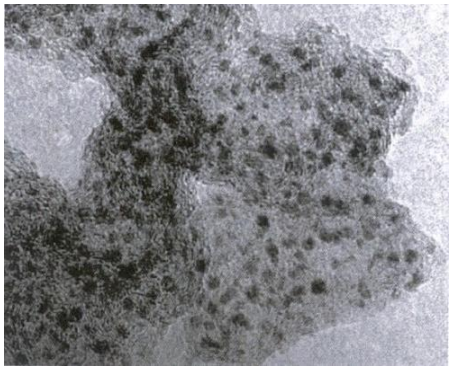
→ Water management between the catalyst layer and the GDL

Active Layer / Catalytic Layer

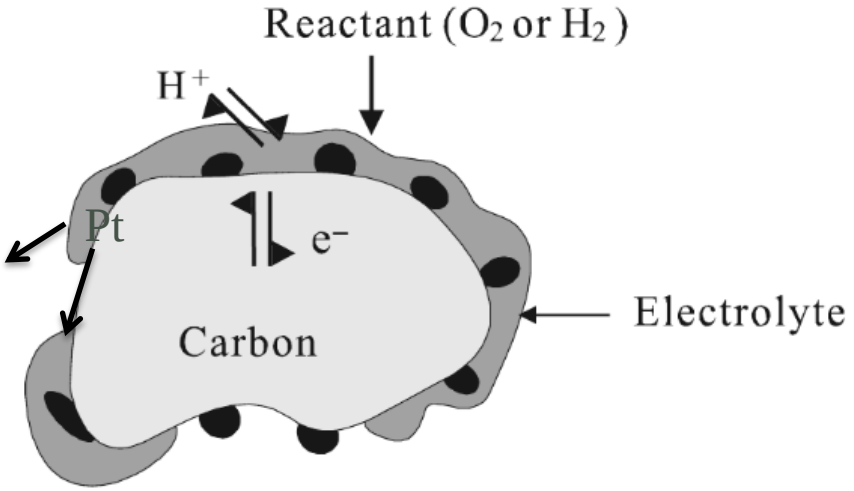
Ink composition:

- Pt supported on carbon (Pt/C)
- Ionomer
- PTFE





Three-phase interface:
contact between ionomer, gas and catalyst



TRENDS IN MATERIALS FOR ELECTRODES

→ Carbon nanomaterials with improve specific surface and electrical conductivity → **graphene , CNTs** and **CNFs**

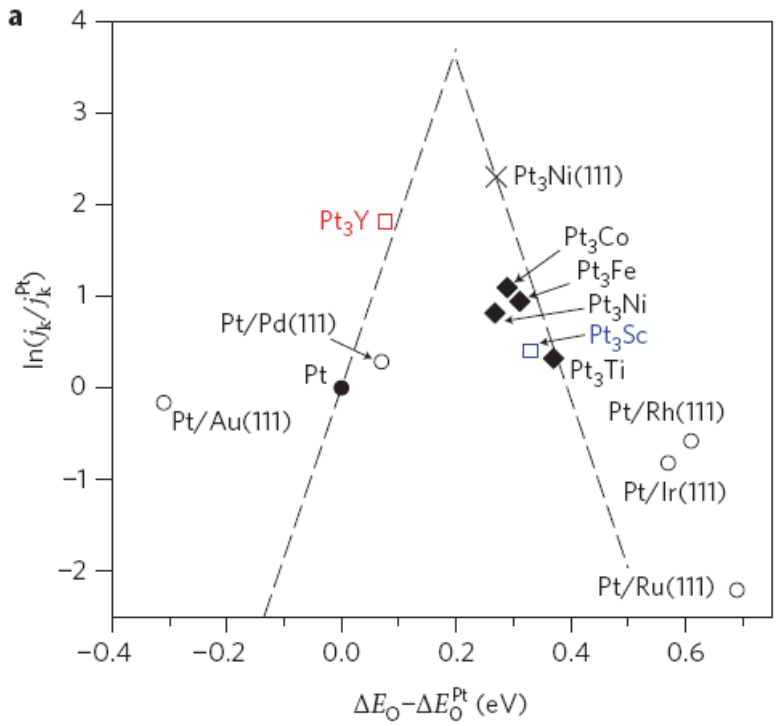
→ Non-carbonaceous supports for the catalyst, to avoid the corrosion problem of carbon supports → **electrically conducting ceramics** (titanium suboxides, tin oxide, metal nitrides,…)

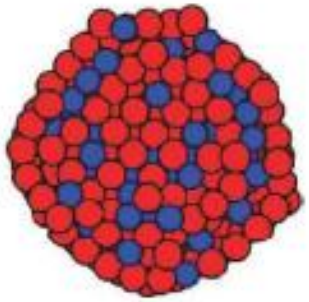
→ Cheeper catalysts:

- → **Using less platinum in the composition**
- → **Novel platinum-free catalysts**

Low-platinum catalyts

→ Alloying Pt with other metal (e.g. Ni, Co,…)

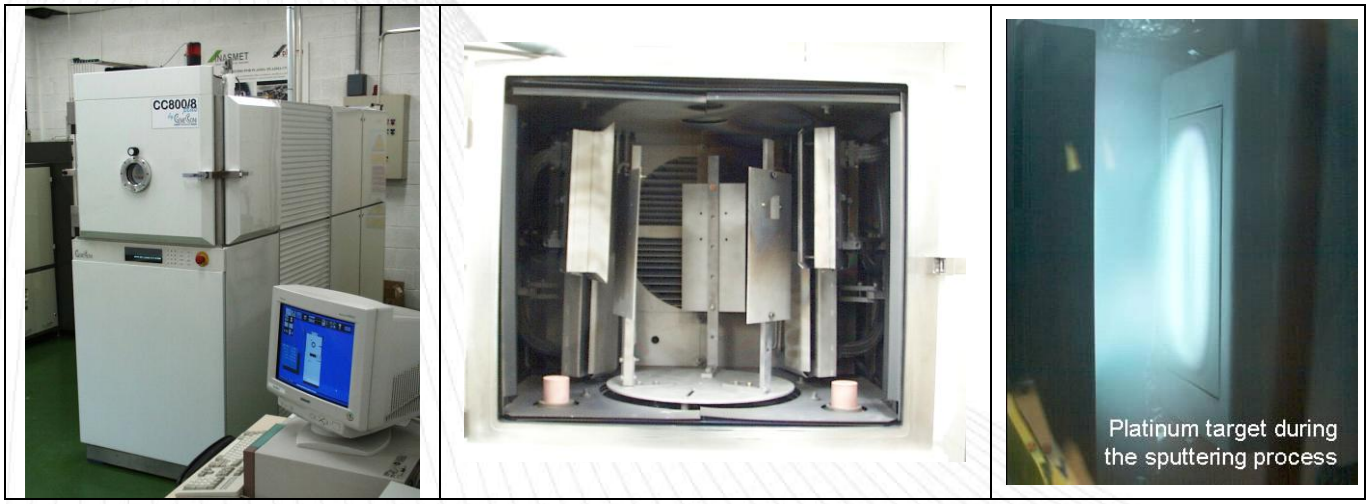


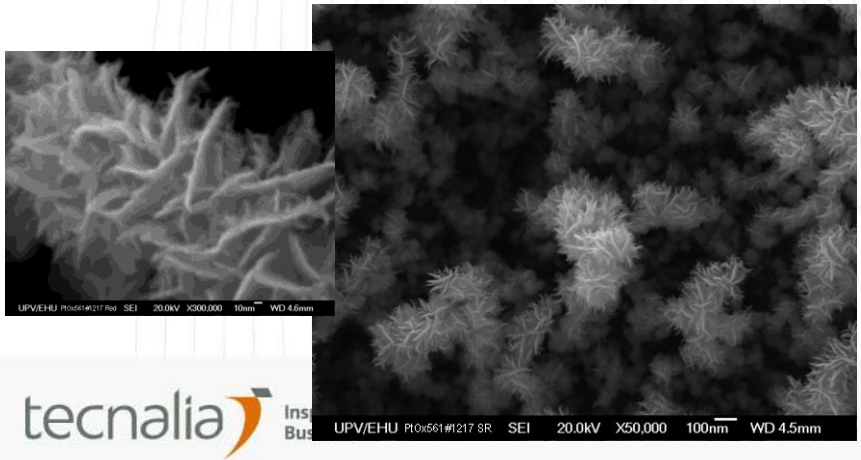


Many Pt alloys were also found to have better activity than Pt. Traditionally, researchers have focused on relatively low M-content alloys, e.g. Pt_3Ni and Pt_3Co, which are quite stable in the fuel cell environment.

Low-platinum catalyts

→ Reducing Pt content by PVD-sputtering application





- Very low Pt loads: < 0,05 mg Pt/cm^2
- Uniform deposition onto the MPL
- More Pt concentration close to the membrane
- Reproducible and scalable method.

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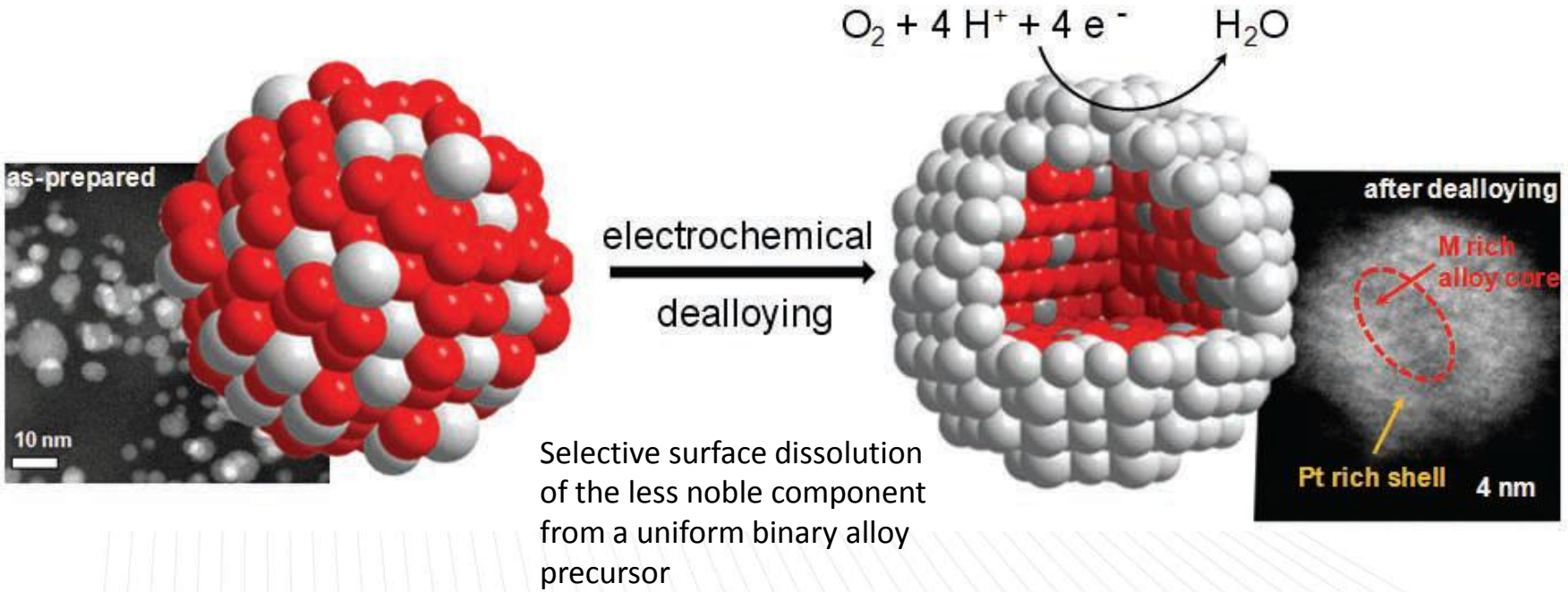
Low-platinum catalyts

→ Pt core-shell structures



Selective surface dissolution of the less noble component from a uniform binary alloy precursor

→ Dealloyed **$PtCu_3$** is currently the alloy nanoparticle electrocatalyst which meets and exceeds the cathode catalyst activity targets in real MEA experiments for automotive applications

Platinum-free catalyts:

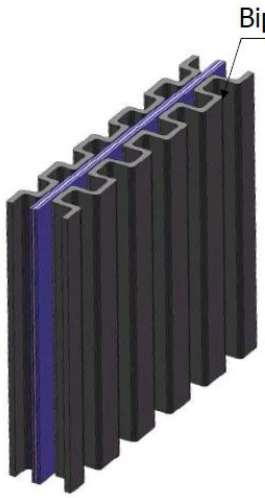
- New-generation chalcogenides (Ru-Mo sulfide, selenides)
- Non-precious metal/heteroatomic polymer nanocomposites
- Bio-inspired catalysts: Fe or Co-N4 macrocyclic compounds (e.g. Fe/Co porphyrins, phthalocyanines)

*Even if the potential of the catalytic activity of this novel family of products has been shown in half cell measurement, the **current densities** obtained still suffer to be around several orders of magnitude lower than the classical Pt catalyst. Also, **durability** must be demonstrated for these new catalyts.*

OPEN FIELD FOR MATERIALS RESEARCH

MATERIALS FOR PEMFC BIPOLAR PLATES

BIPOLAR PLATES



Requirements of bipolar plate

- Low electrical resistance
- High chemical resistance
- Thin thickness
- High mechanical properties
- Productivity

Key Technical Targets

Characteristic	Unit	2011 Status	2017 Targets	2020 Targets
Cost	$ /kW	5-10	**3**	**3**
Corrosion	$\mu A/cm^2$	<1	**<1**	**<1**
Resistivity	$\Omega.cm^2$	<0.03	**<0.02**	**<0.01**

Raw materials

Protective coatings

Manufacturing methods

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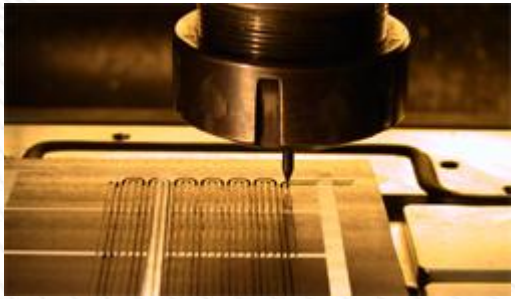
GRAPHITE

- ☺ Excellent corrosion resistance,
- ☺ Low interfacial contact resistance
- ☺ Low surface energy and contact angle

- ☹ Brittleness
- ☹ Lack of mechanical strength
- ☹ High cost of machining



Manufacturing process: MACHINING

CARBON COMPOSITES

- Graphite-polymer composites
- With termoplastic of thermostet matrices
- Standard composition: graphite flakes, expanded graphite, carbon black, and phenolic resin.
- Commercially availables with polypropylene (PP), polyphenylene sulfide (PPS), polyvinylidene fluoride (PVDF)

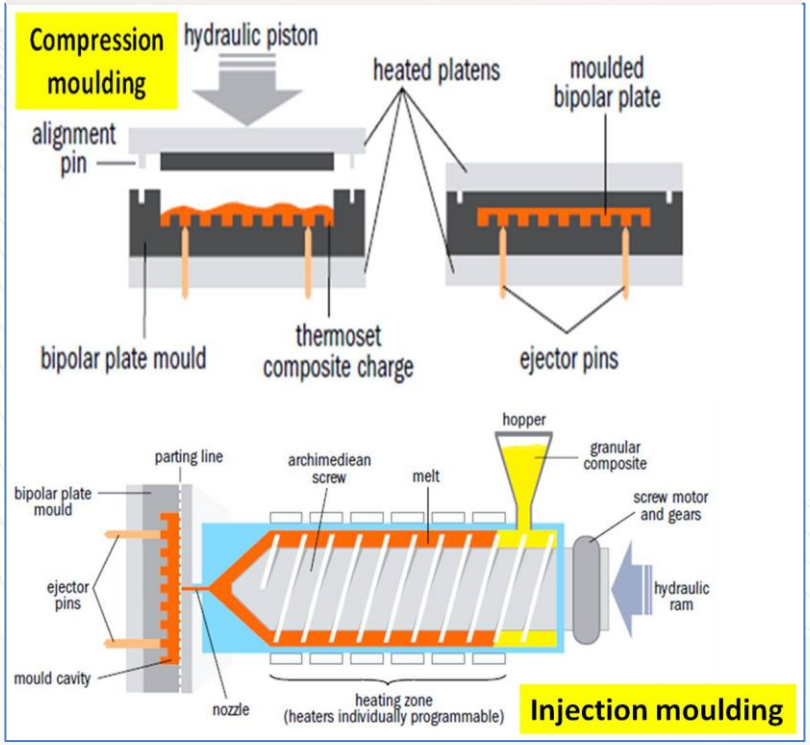
☺ Excellent corrosion resistance,

☺ Low weight

☺ Low manufacturing cost (moulding)

☹ Low bulk electrical conductivity

☹ Relatively low mechanical resistance



METALLIC BPs

☺ High strength

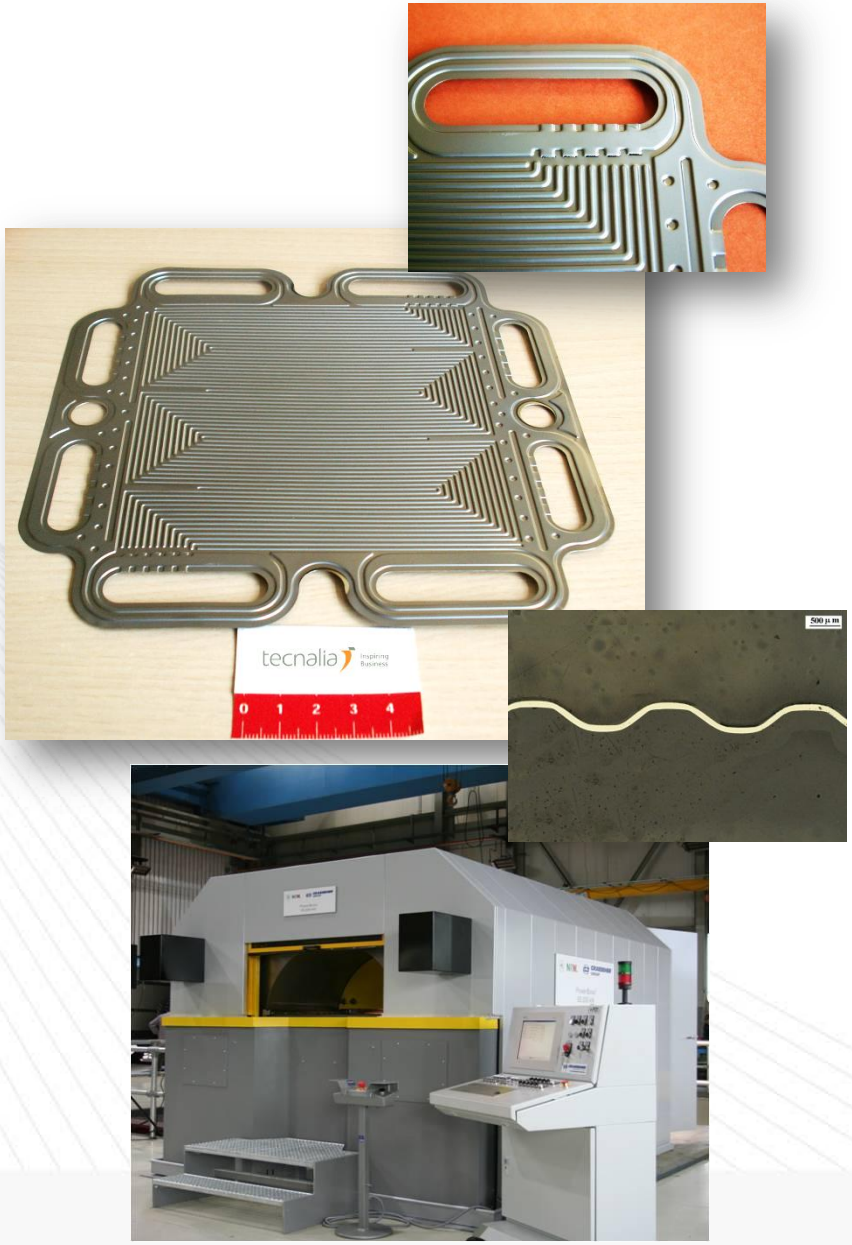
☺ High bulk electrical and thermal conductivity

☺ Low cost and high volume manufacturing methods (e.g. stamping, embossing,…)

☹ High surface contact resistance (oxide formation at the surface)

☹ Corrosion resistance under acidic media in the stack

Need of protective coatings



Protective coatings for metallic bipolar plates

METALLIC COATINGS:

- *Gold coating (plating)*

CERAMIC COATINGS:

- *TiN coating (PVD)*
- *CrN/Cr_2N coating (PVD, ion nitriding)*
- *Carbide-based coatings (PVD, HVOF)*

CARBON COATINGS

- *Carbon based coating (PACVD, PVD)*

Optimization of CrN coatings for metalling bipolar plates

Substrates

AISI 316L stainless steel samples with different roughness (Ra):

- 5,67 µm Ra (laminated plate 5 mm thickness)
- 0,10 µm Ra (laminated sheet 0,2 mm thickness)
- 0,01 µm Ra (mirror polished 5 mm thickness)

Coating deposition

DC-Magnetron Sputtering (*CemeCon CC800/8 equipment*) using 4 Cr targets (200x88 mm) in a mixture of Ar/N_2.

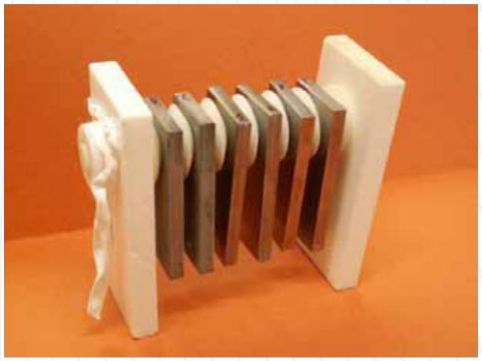
Three type of coatings have been deposited:

- ✓ Single CrN coating (6 µm thickness)
- ✓ CrN with Cr interlayer (5 µm total thickness)
- ✓ Cr/CrN multilayer (5 µm total thickness)

Corrosion test

The corrosion resistance of the coated samples has been tested in accelerated conditions than those encountered into the HT-PEMFC:

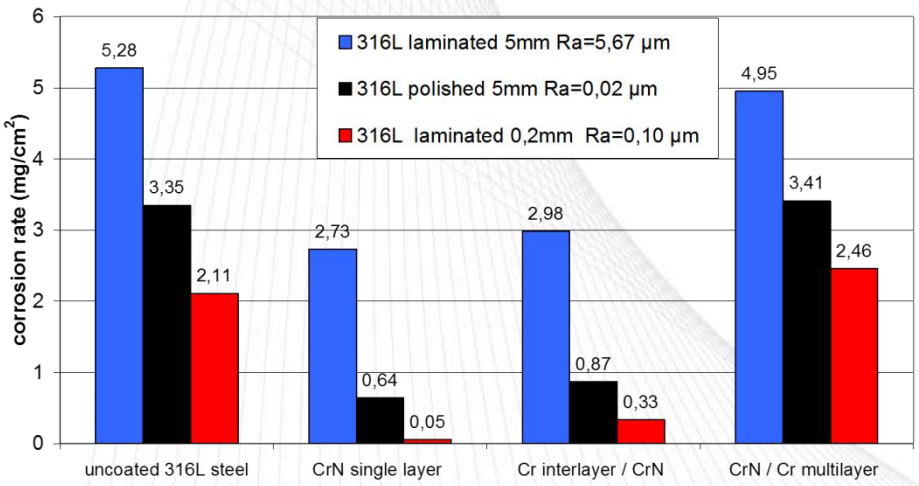
- Immersion in H_3PO_4 85% wt
- Temperature: 150 °C
- Time: 6 hours (under reflux)



The corrosion rate was measured by weighting the samples before and after the test. Metallographic samples in section were prepared to evaluate the change in the coatings after the test.

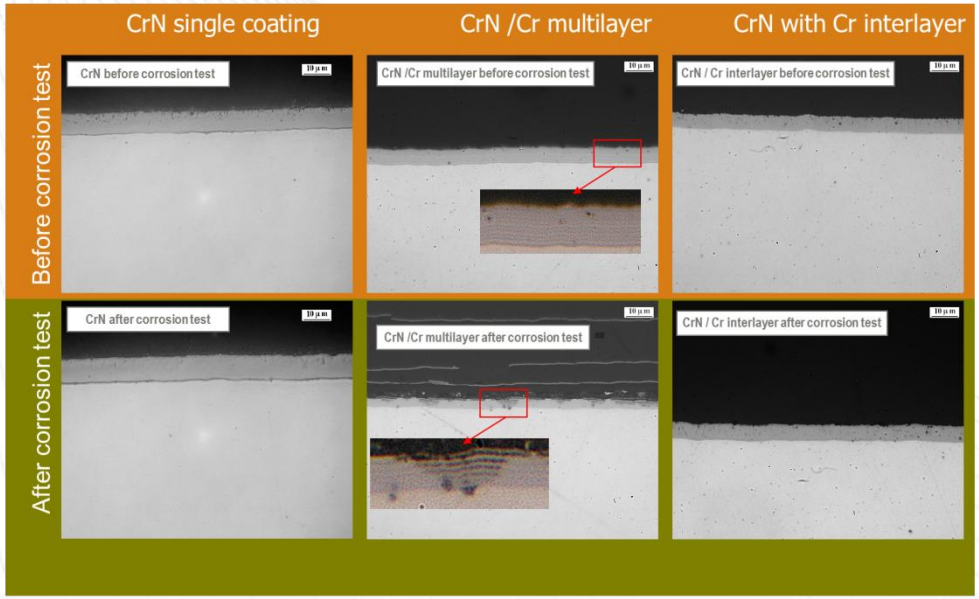
CORROSION TEST RESULTS

Corrosion rate

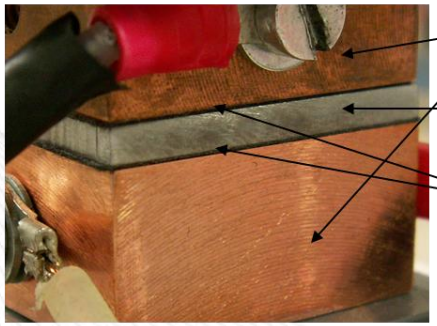


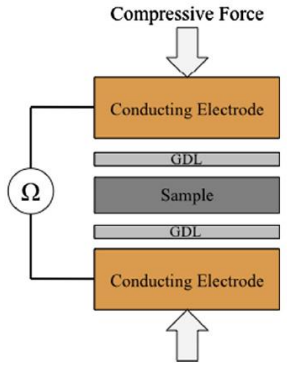
- The corrosion rate of the uncoated stainless steel is very high and not acceptable for this application
- High roughness of the substrate lead to an increase in the corrosion rate (by the increase of the specific area)
- The lower corrosion rate is found in the laminated steel sheet (0.2 mm thick). Therefore the use of this material (stamped) is beneficial in the bipolar plate application

- The CrN coating itself shows a very good corrosion resistance
- The application of a Cr interlayer to the CrN coating does not improve the behaviour of the CrN alone
- The Cr/CrN multilayer shows a poor behaviour because of delamination into the coating system (due to acid dissolution of the Cr interlayers).



Interfacial Contact Resistance (ICR) measurements





The interfacial contact resistance (ICR) has been measured, before and after the corrosion test, by means of a test configuration that simulates the positioning of the bipolar plate in the HT-PEMFC stack. Two pieces of conductive carbon felt were sandwiched between the coated 316L stainless steel sample (a plate 5 mm thick) and the two copper plates.

The pressure range from 52 to 260 N/cm^2 and the voltage drop was measured with a potentiostat at a constant current of 0.2 A/cm2

INTERFACIAL CONTACT RESISTANCE (ICR) RESULTS

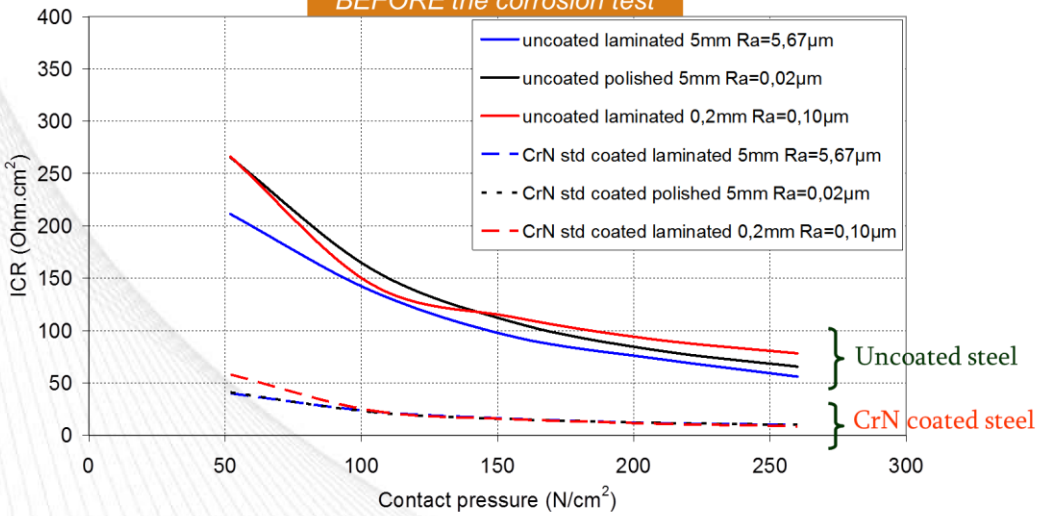
ICR tests were carried out to compare contact resistance of the uncoated stainless steel and the CrN coating that performed better in the corrosion test (without Cr inter-layer).

► The bare stainless steel has a higher contact resistance than the CrN coating, due probably to the natural oxide coating present on the surface of the steel.

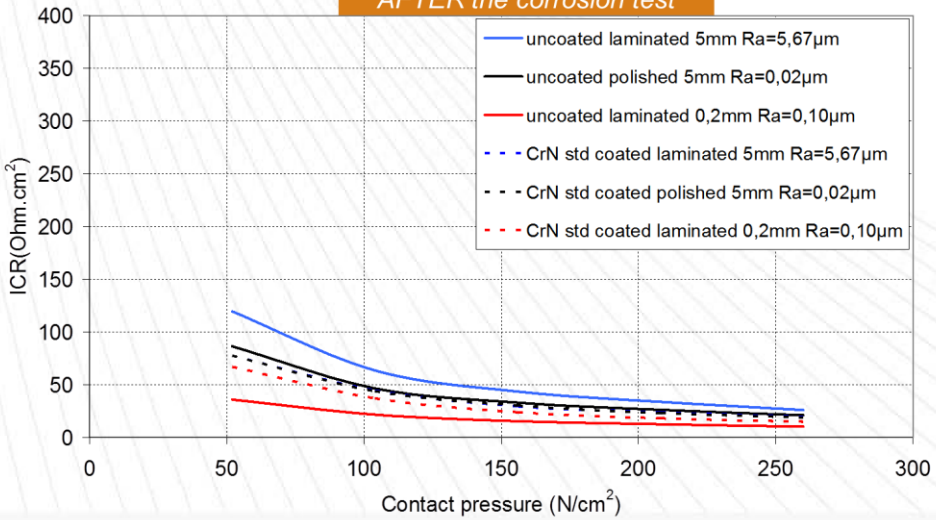
► The ICR results of the stainless steel and the CrN coating after the corrosion test are quite similar.

► The CrN coating maintain a good conductivity in the acidic oxidant conditions, what is evidence of chemical stability and no formation of oxides on the surface

BEFORE the corrosion test



AFTER the corrosion test

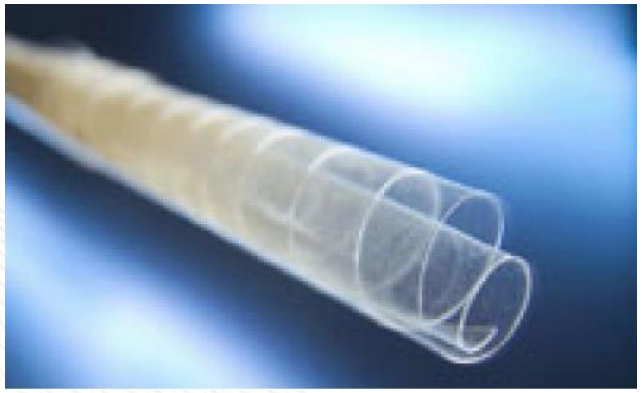


MATERIALS FOR PEMFC MEMBRANES

ION CONDUCTING MEMBRANE

Functions:

- To separate the anode and cathode
- To prevent mixing of the fuel and oxidant
- To provide the proton conduction

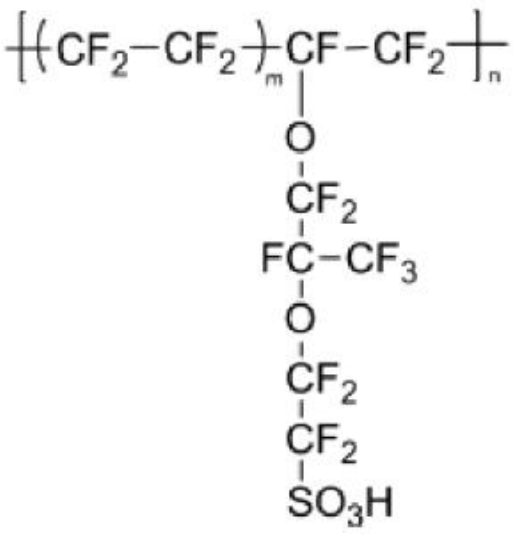


Required properties:

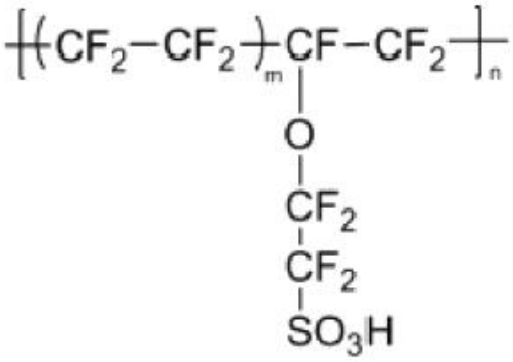
- High ionic conductivity
- Electrically insulating
- Chemical and thermal stability
- Good mechanical strength
- Interfacial compatibility with catalyst layers
- Low cost

Standard commercial PEMFC membranes

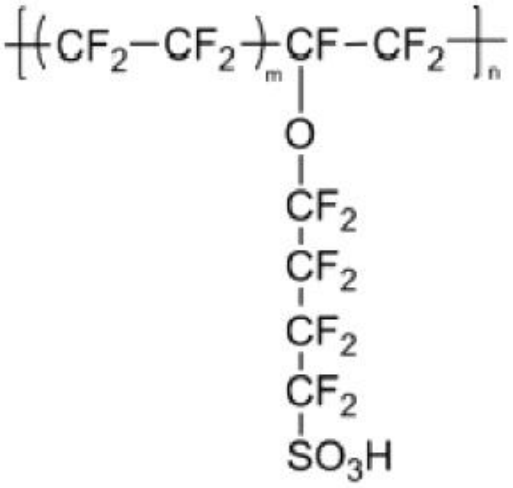
a)



b)



c)



Nafion *Aquivion* *3M-ionomer*

Other: *Fumapem,…*

CHALLENGES FOR ION CONDUCTING MEMBRANES

- Croosover of methanol in DMFC
- Temperature resistance *(Nafion dehydrates at T>80 ℃ and RH < 100 %)*
- COST

Ideal membranes:

- A membrahe with high proton conductivity and low methanol crossover
- A membrane that operates without water at elevated T

DEVELOPMENTS FOR ION CONDUCTING MEMBRANES

Modifications to Nafion to reduce methanol crossover

- **Addition of loads to Nafion**:
  - Nafion / silica
  - Nafion / zirconium phospate
  - Nafion / polyvinyl alcohols
  - Nafion / sepiolites
- **Surface modification of Nafion (crosslinking):**
  - Plasma etching
  - Low dose EB irradiation
- **Multilayer systems:**
  - Nafion / Nafion-PVDF / Nafion

Results have not met expectations

DEVELOPMENTS FOR ION CONDUCTING MEMBRANES

Strategies for HT-PEMFC membranes

- **Modifications to Nafion**:

  Addition of water-retaining (hydrophilic) additives:

  - *Non-conducting inorganic particles (SiO_2, TiO_2)*
  - *Proton conducting inorganic salts (zirconium phosphate)*
  - *Heteropolyacids (phosphotungstic* acid)

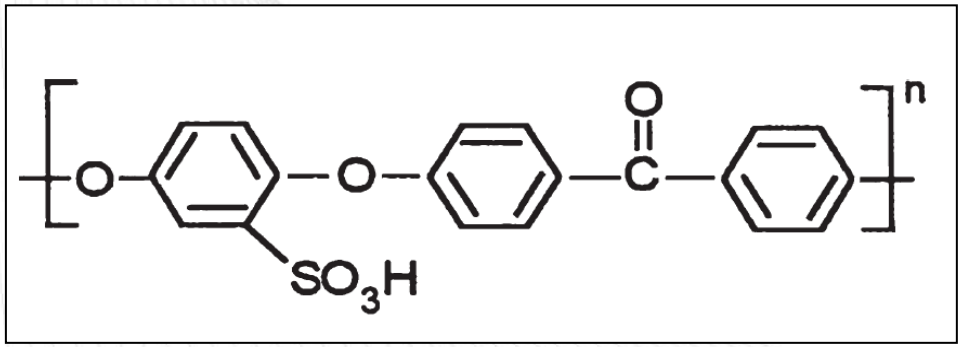
- **Eliminate the need for water in a proton exchange membrane**

  - *PBI doped with concentrated phosphoric acid*
  - *Suphonated polymer with adsorbed imidazoles or benzimidazoles*
  - *Inorganic solid acids in a polymeric matrix*

DEVELOPMENTS FOR ION CONDUCTING MEMBRANES

Reduction of cost:

- Non-fluorinated polymer material → SPEEK



Chemical structure of SPEEK

- Problems with degradation and solubility at high sulphonation degrees *(needed to achieve high ion conductivity)*

→ ***Possible solutions:***

- *Polymer crosslinking without loosing –SO_3H*
- *Incorporation of proton conducting nanoparticles (e.g. zirconium phosphates)*

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THANKS FOR YOUR ATTENTION

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