GDR n°3339
Piles A Combustible, Systèmes

Basics on Components of the Polymer Electrolyte Fuel Cell

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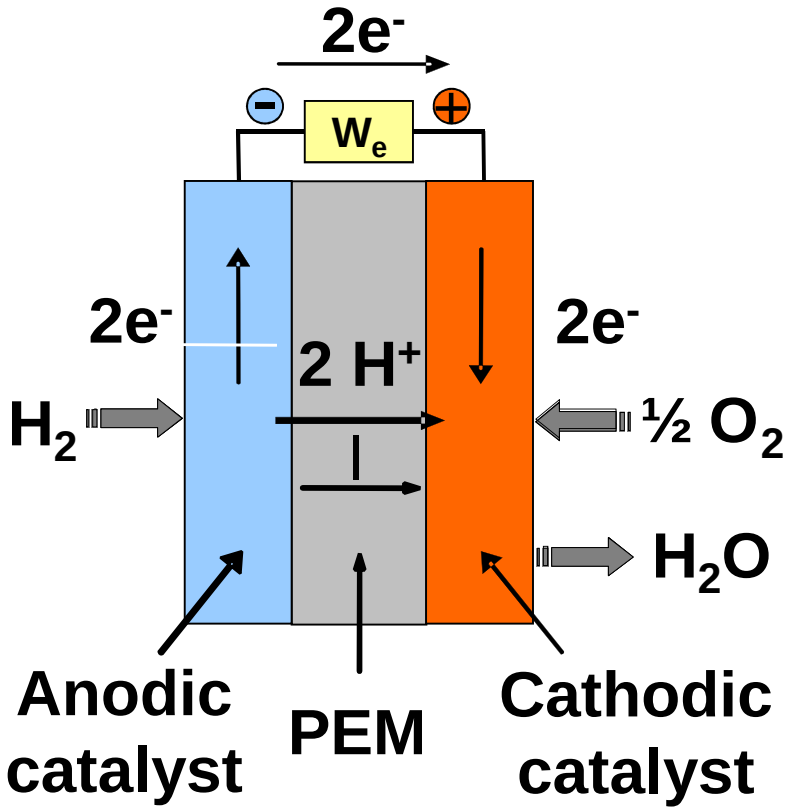
The Polymer Electrolyte Fuel Cell (PEFC)

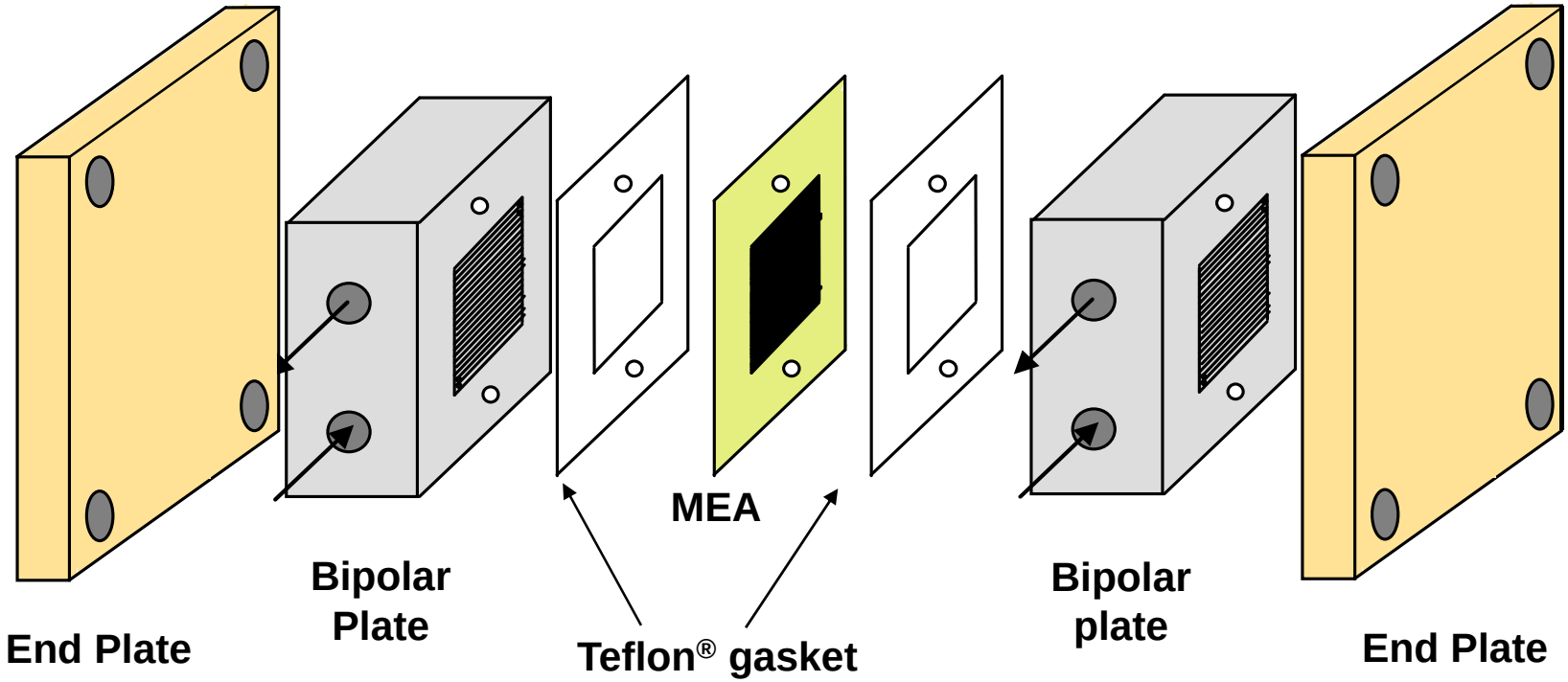
- Principle of a Polymer Electrolyte Fuel Cell
- Cell components (membrane, catalysts, etc.)

Schematic representation of a PEFC elementary cell



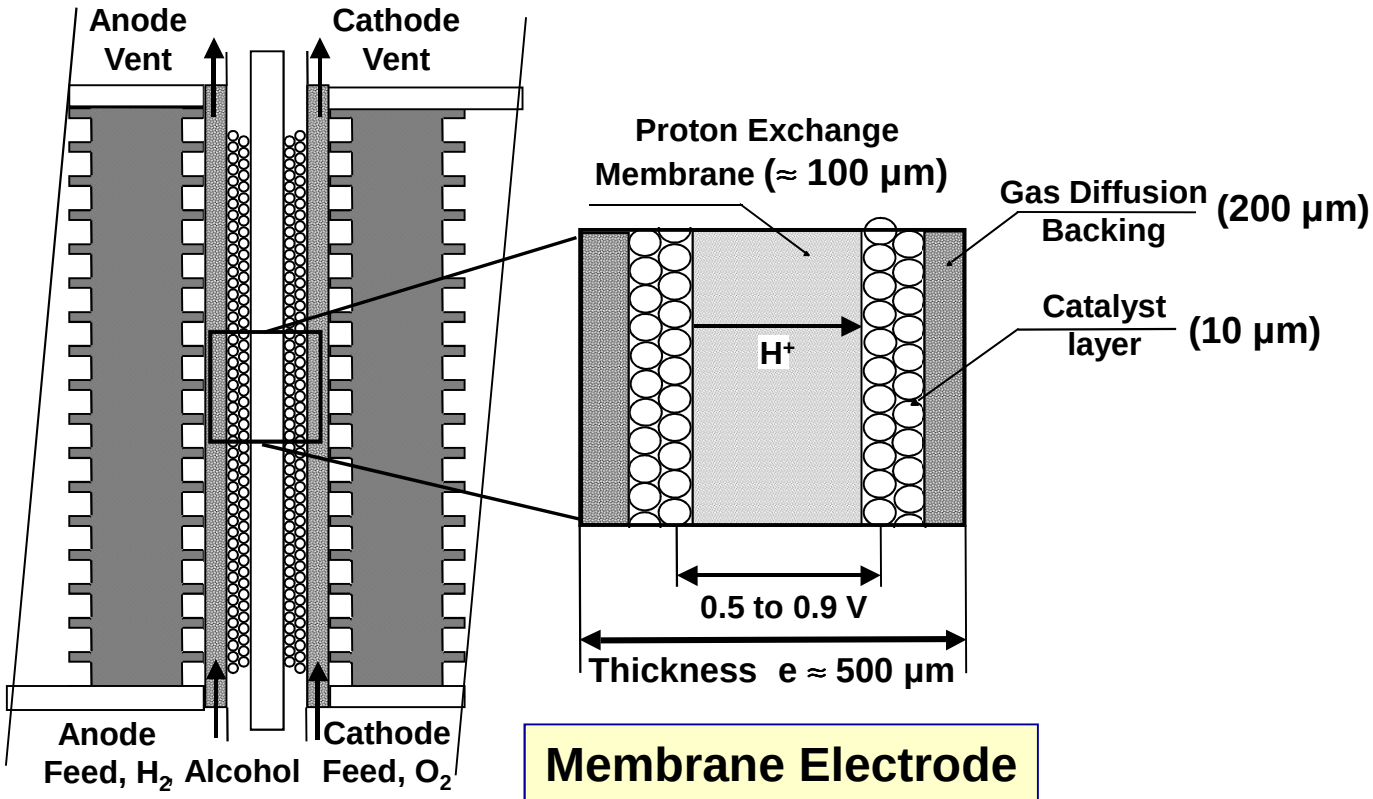
Overall reaction: $H_2 + ½\ O_2 \rightarrow H_2O$ with $\Delta G < 0$

Polymer Electrolyte Fuel Cell (PEFC)



Schematic representation of a PEFC elementary cell

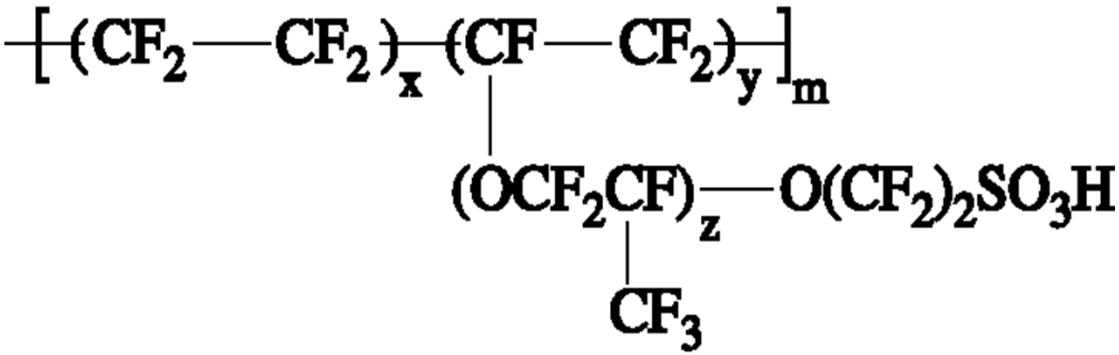
Schematic representation of the Membrane Electrode Assembly (MEA)



Membrane Electrode Assembly (MEA)

Development of new proton exchange membranes with improved conductivity and thermal stability

Nafion is the Reference Membrane: Sulfonic Acid Functionalized Perfluorinated Polymer

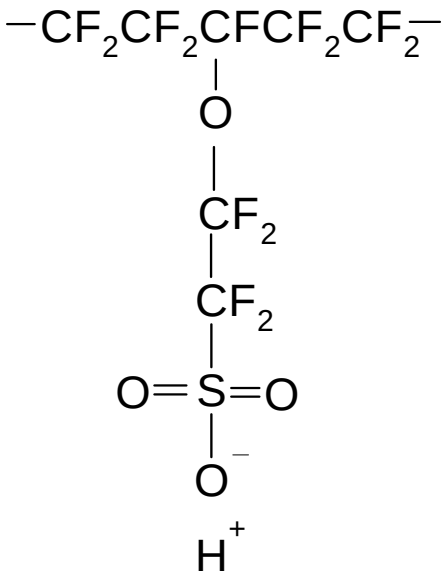


Nafion (Dupont de Nemours - 1966)

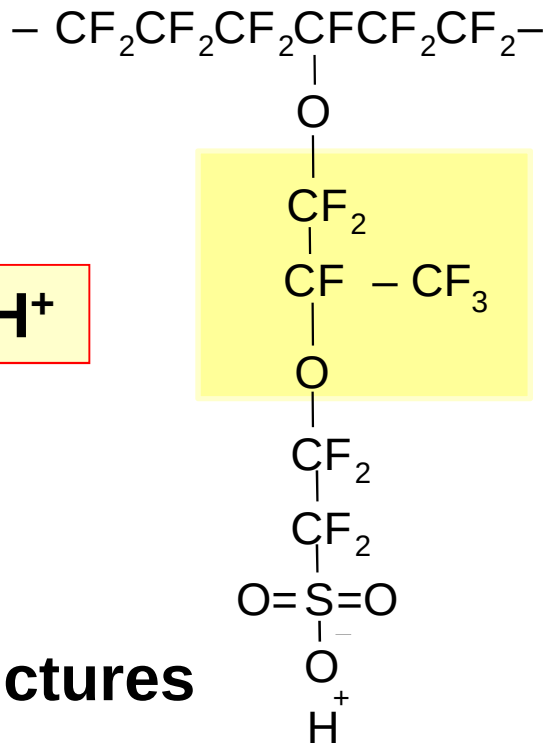
- ✓ Chemical stability : 60 000h - 80℃
- ✓ Good ionic conductivity : 4.10^{-2} to 10^{-1} $S.cm^{-1}$
- ✓ Easy to solubilize ~ colloidal dispersion
- ✓ Complex synthesis : high cost (400 $/m^2), recycling difficulty
- ✓ Good mechanical properties, but low Tg (110℃)
- ✓ Permeation to methanol / swelling

Structures of perfluoronated sulfonic acid ionomers

DOW



DUPONT NAFION®

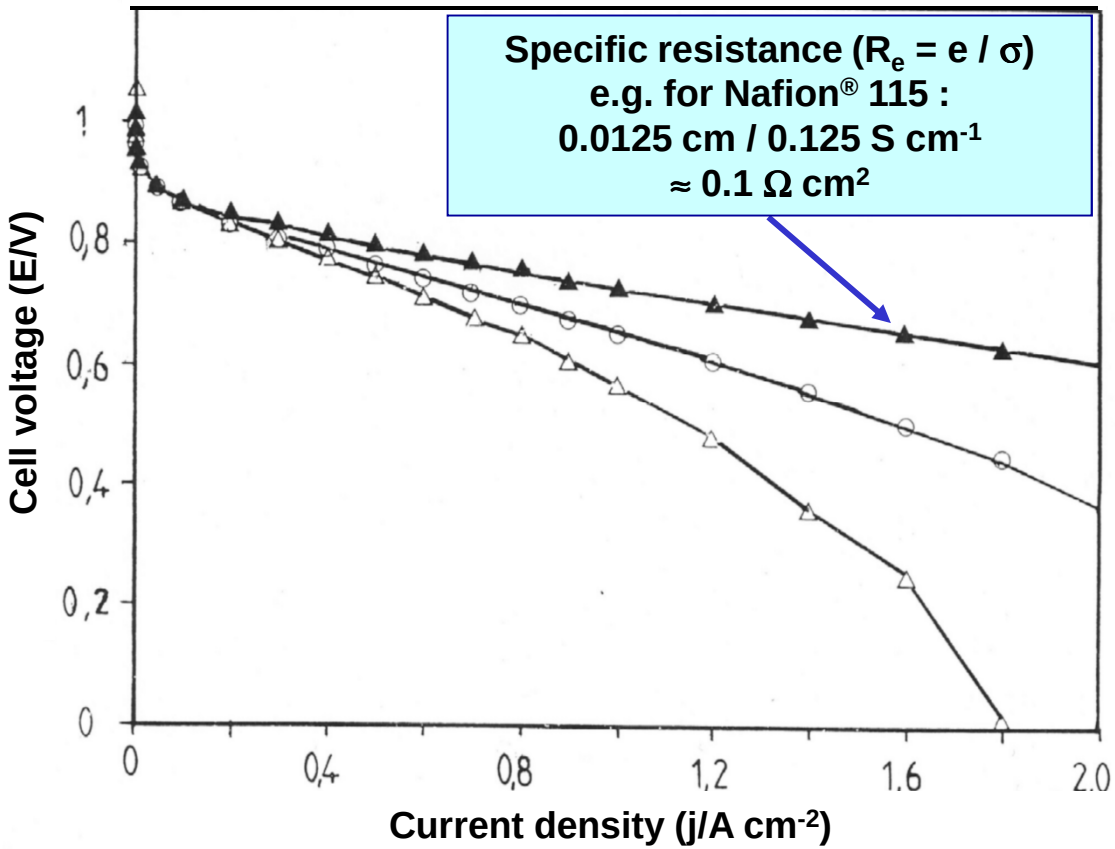


$R_f\text{-}SO_3^-\ H^+$

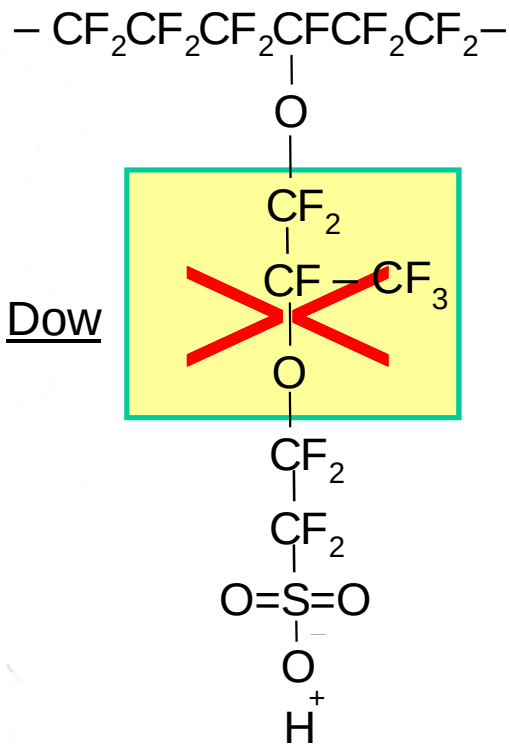
Polymer structures

E(j) characteristics of a PEMFC elementary cell with different membranes :

▲ Dow (e = 125 µm) ; o Nafion® 115 (e = 125 µm) ; Δ Nafion® 117 (e = 175 µm)

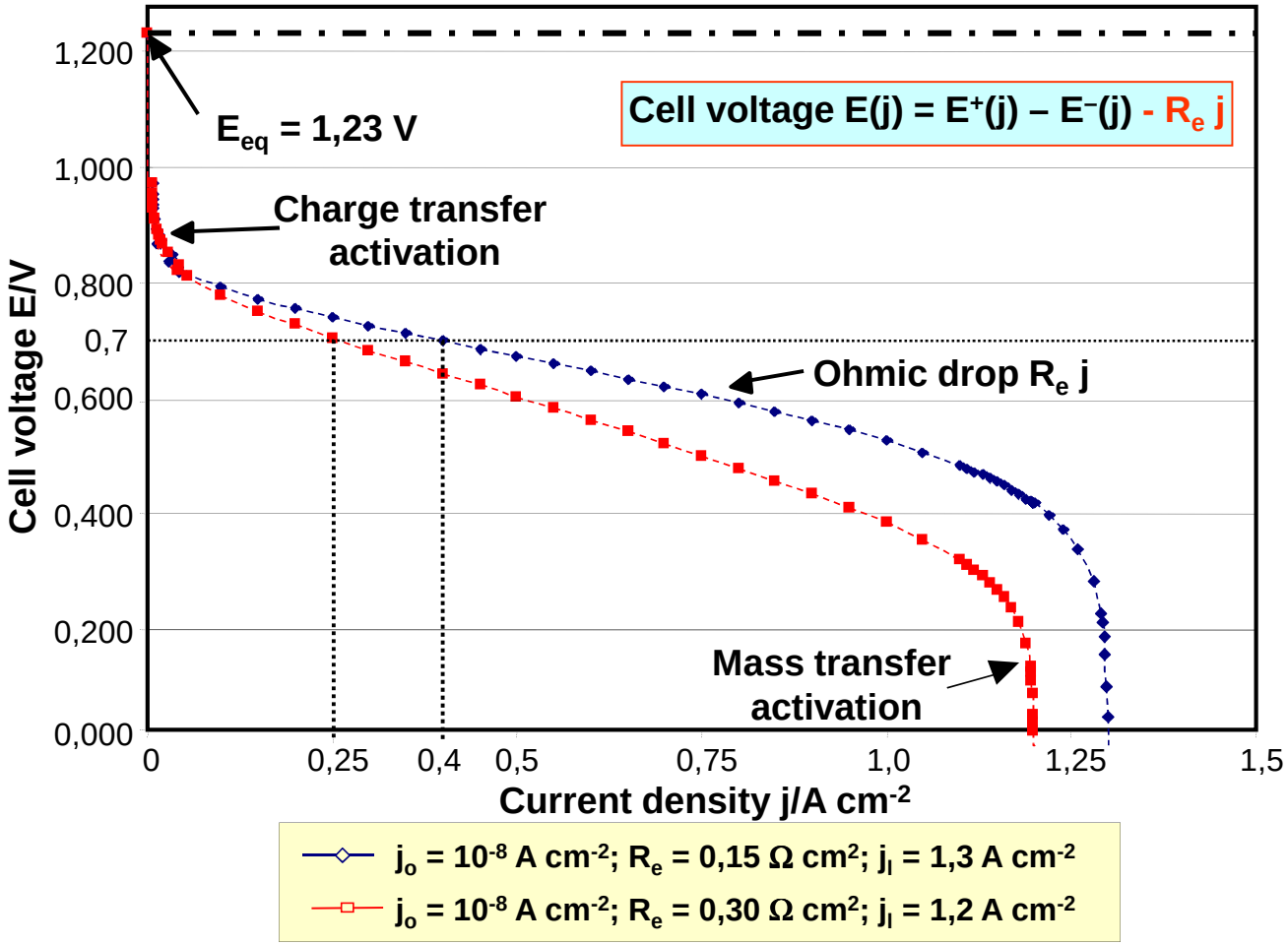


DUPONT NAFION®



After K. Prater (Ballard), J. Power Sources, 29 (1990) 239

Influence of the membrane specific resistance ($R_e = e/\sigma$) on the cell voltage-current density characteristics E(j)



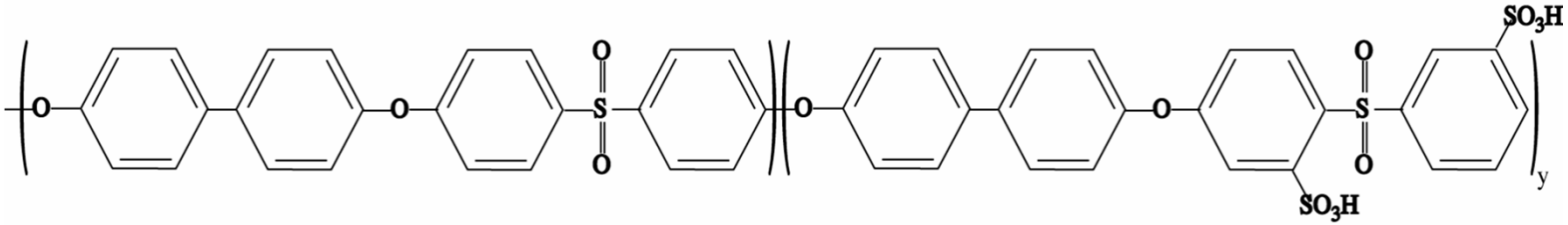
The polyetheretherketones (PEEK) family: ether and ketone units

$$\left[\left[Ar-O\right]_p Ar\left[\left[CO-Ar'\right]_x O-Ar\right]_m\left[O-Ar'\right]_y \cdots\cdots \left[O-Ar\right]_n CO\right]$$

Good stability, conductivity, low cost;
Can be used for hybrid membranes

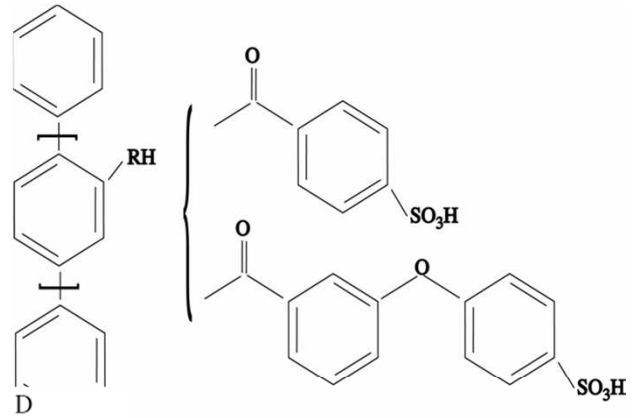
x,y,m = 0 or 1
y=0,1,2 or 3
p=1,2,3,4

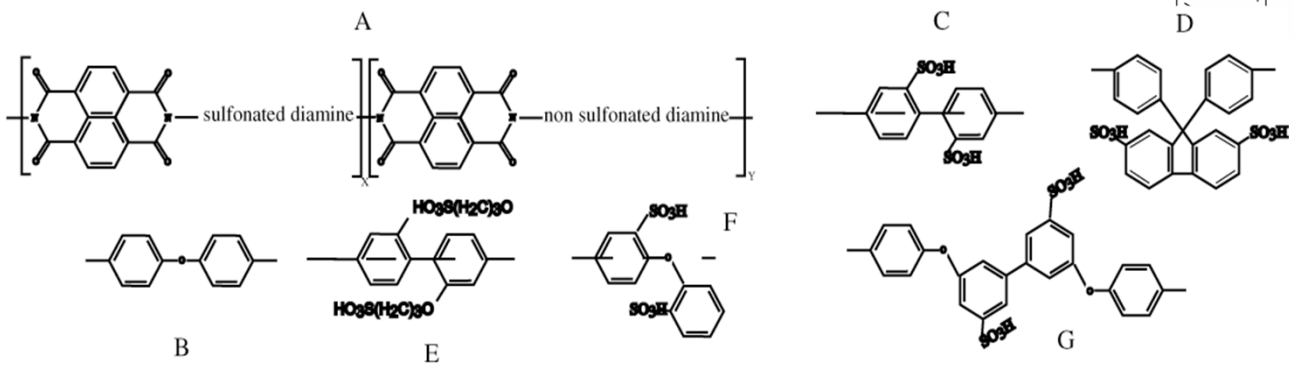
Polyethersulfone: ether and sulfone units



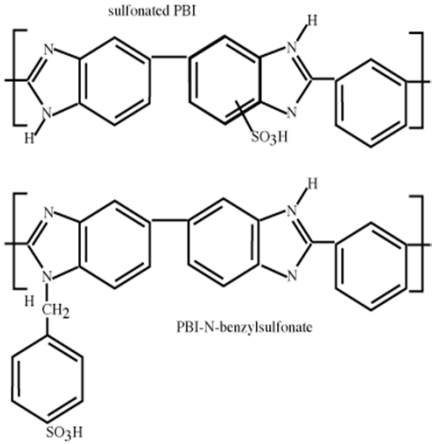
Good stability, conductivity, low permeability to methanol, water retention at high T

Para-Phenylene family



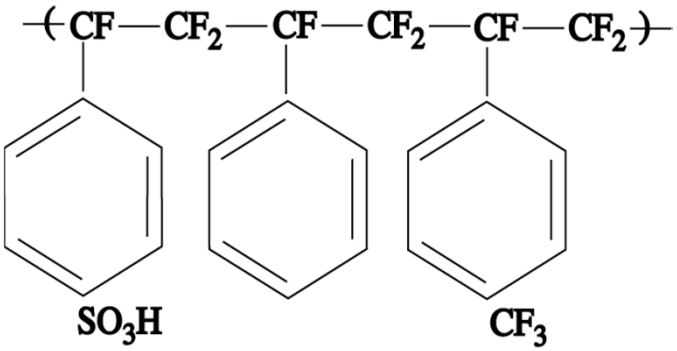


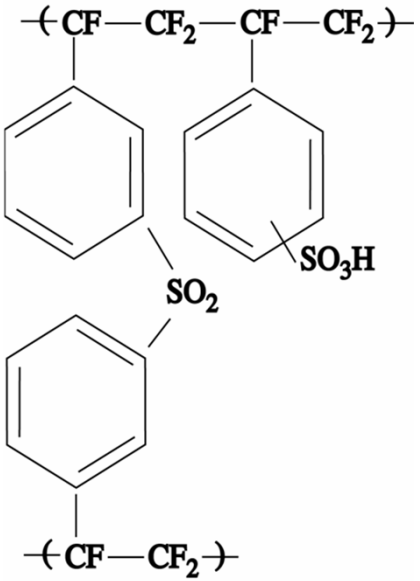
Sulfonated Polyimides (sPI)



Polybenzimidazole (PBI)

Copolymers: e.g. sulfonated polytrifluorostyrene (Ballard)





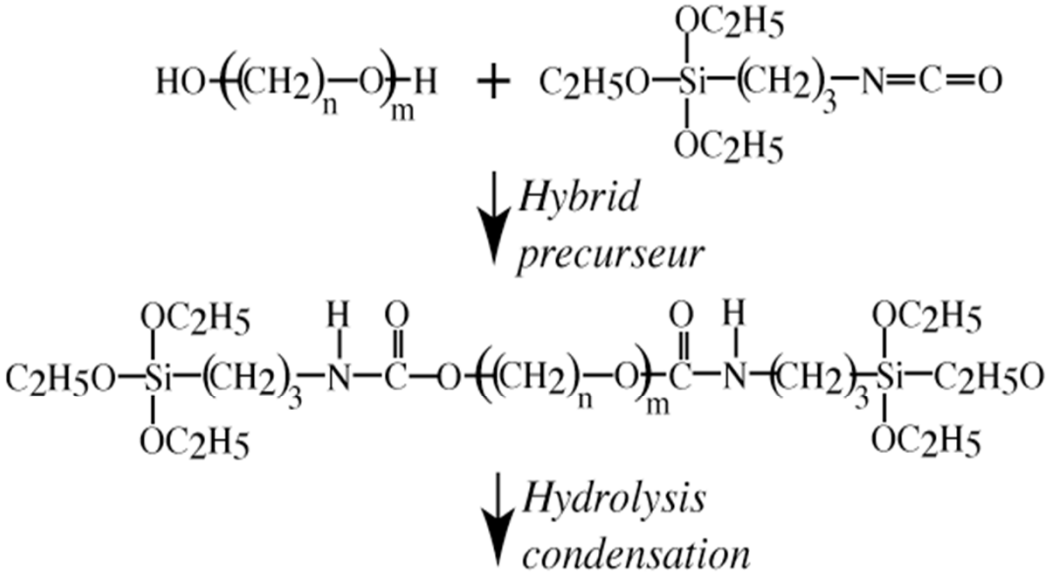
Good performances, 14 000 h at 70℃

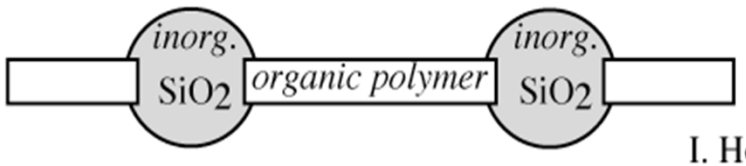
Other means of fabrication :

Irradiation grafting: sulfonated polystyrene on ETFE structure

Co / terpolymerisation of fluoro-aromatic monomers
with VF2, HFP or CTFE

Organic-inorganic copolymers

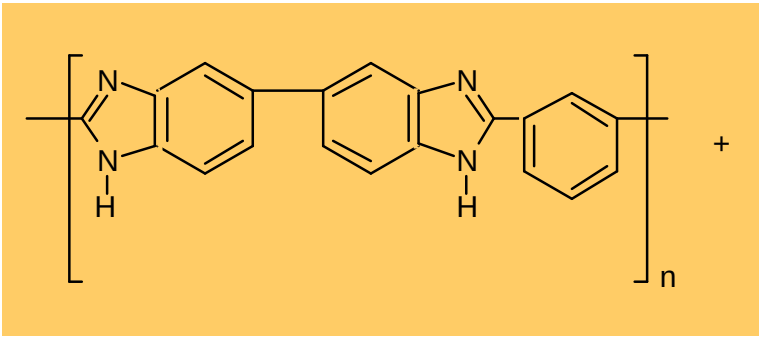




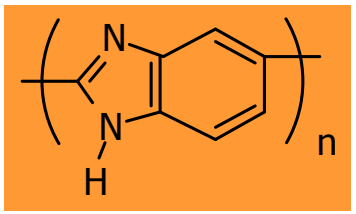
I. Honma et al, JMS 2001

- Inorganic network (SiO_2-PWO acid)
- Splitting of the alkyl-glycol chain by solvated protons
- Low conductivity (10^{-4} S cm^{-1} at 160℃)
- Strong interaction between the polymeric acid and Si

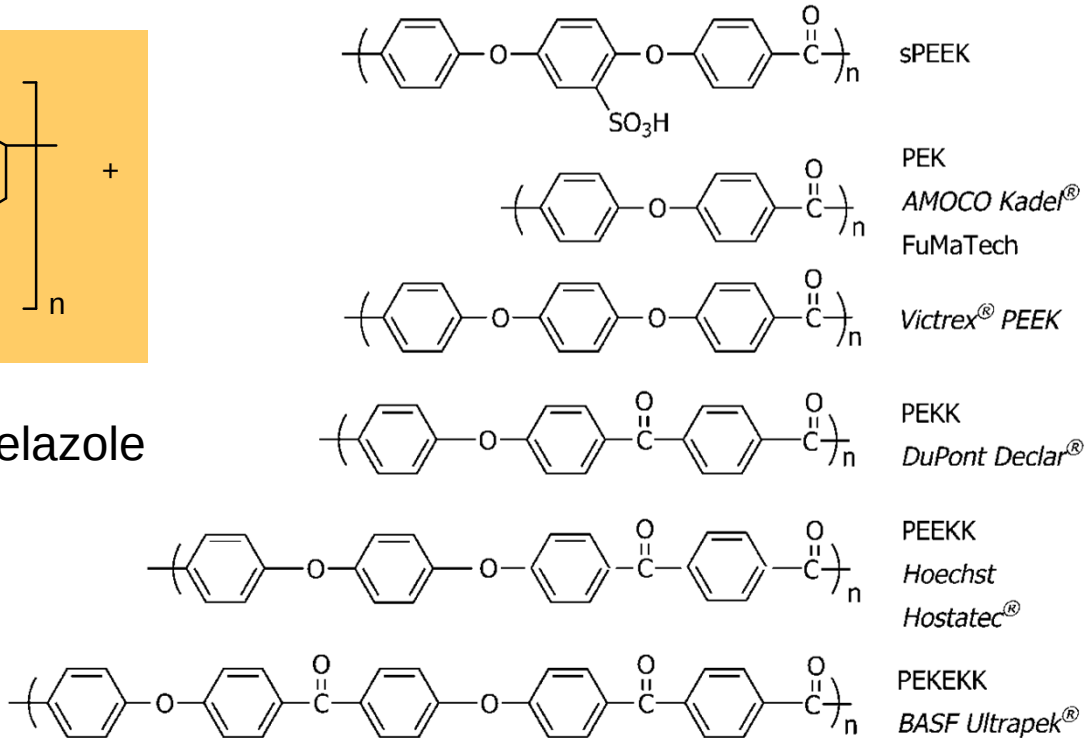
Alternative membranes : Sulfonation of thermostable polymers



Polybenzimidazole (PBI) - Celazole



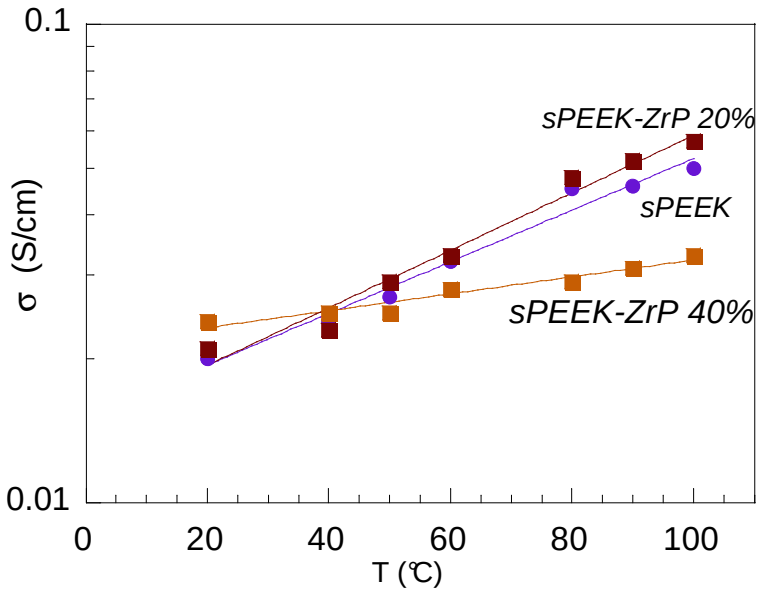
AB-PBI



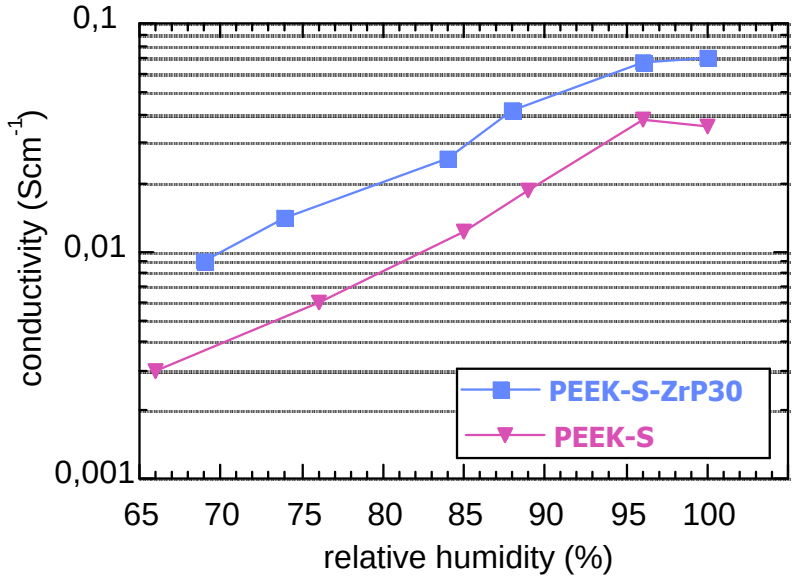
Polyetheretherketones PEEK

ICG-AIME CNRS-Montpellier

Ionic Conductivity



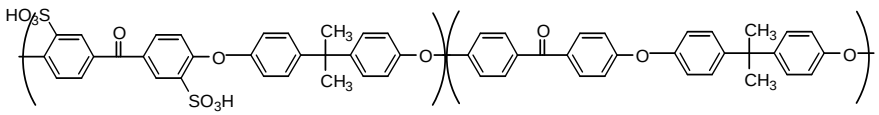
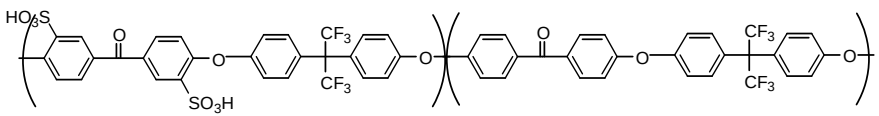
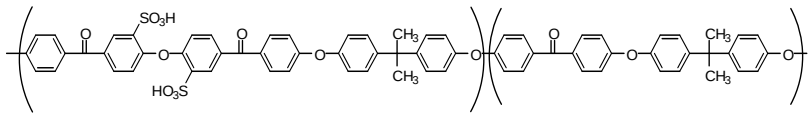
Conductiviy at 100 % relative humidity



Conductivity at 100 ℃

ICG-AIME CNRS-Montpellier

Ionic conductivity of sulfonated PEEKs

STRUCTURE	IEC (meq_{H+}/g)	σ (S/cm)
	1,3 1,6	$0,5\ 10^{-2}$ $0,7\ 10^{-2}$
 BLOCK CO-POLYMER	1,3 1,6 1,6	$0,6\ 10^{-2}$ $1,1\ 10^{-2}$ $1,6\ 10^{-2}$
	1,3	$0,2\ 10^{-2}$
NAFION		$2,4\ 10^{-2}$

LMOPS
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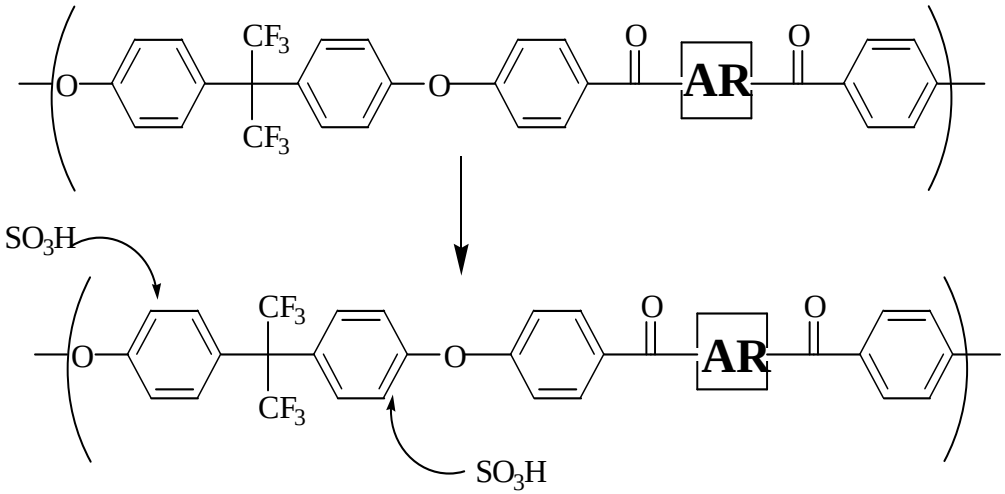
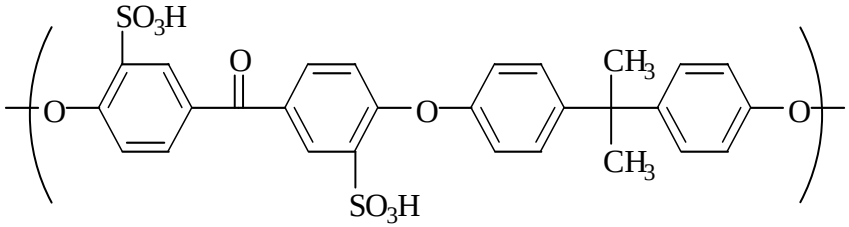
CNRS-Lyon Solaize

Alternative Membranes : POST MODIFICATION of POLYMERS



POLYMERIZATION of SULFONATED MONOMERS



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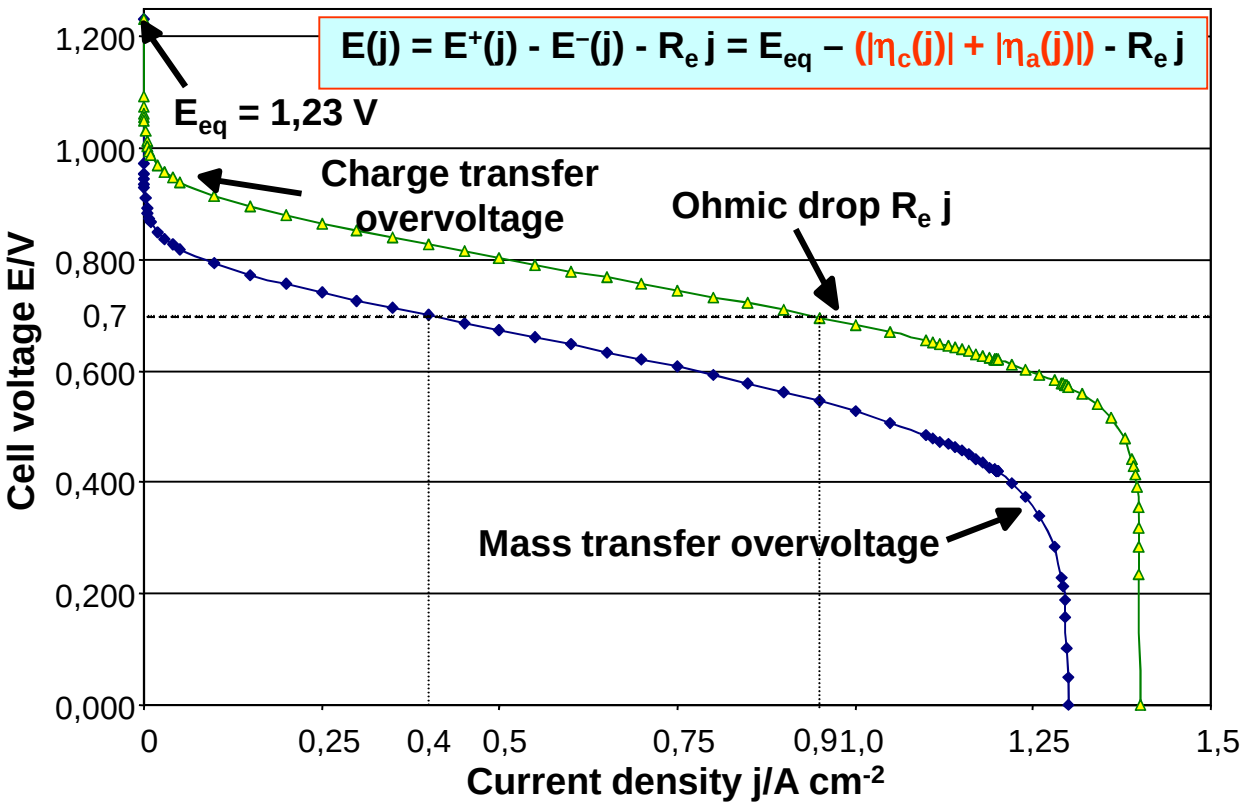
Development of new electrode materials with improved electrocatalytic properties

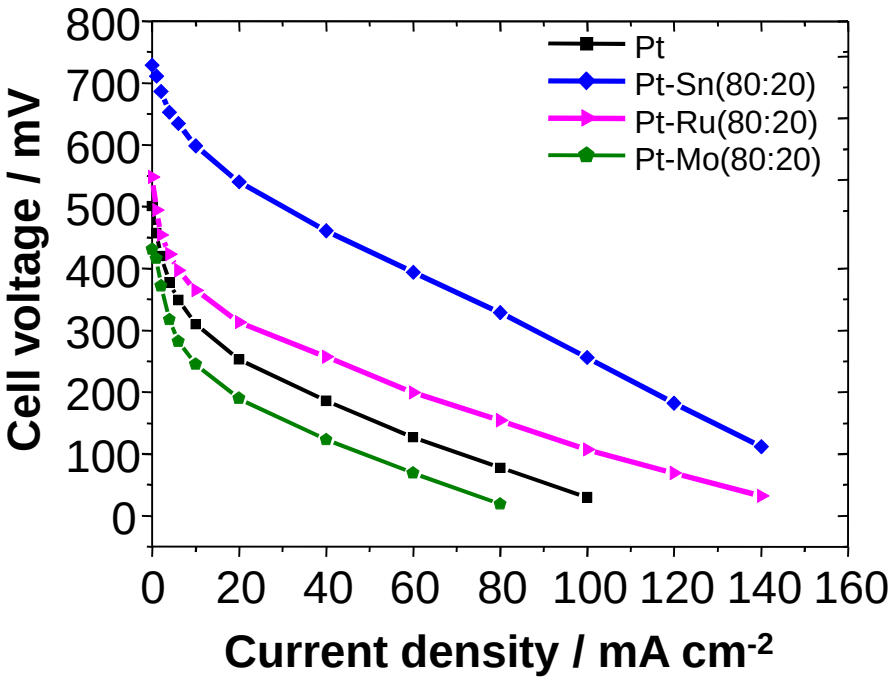
Influence of the catalytic properties of electrodes (exchange current density j_o) on the cell voltage E(j)



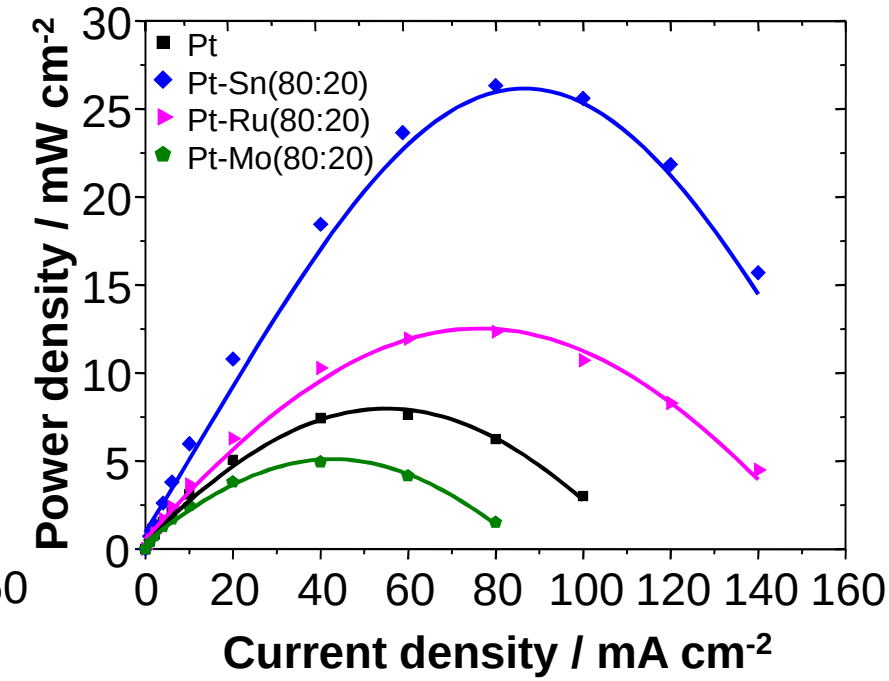
$j_o = 10^{-6}$ A cm^{-2}; $R_e = 0,15\ \Omega$ cm^2; $j_l = 1,4$ A cm^{-2}

$j_o = 10^{-8}$ A cm^{-2}; $R_e = 0,15\ \Omega$ cm^2; $j_l = 1,3$ A cm^{-2}

Fuel cell characteristics of a DEFC recorded at 110°C.
Influence of the nature of the bimetallic catalyst (30% loading).



Polarization curves



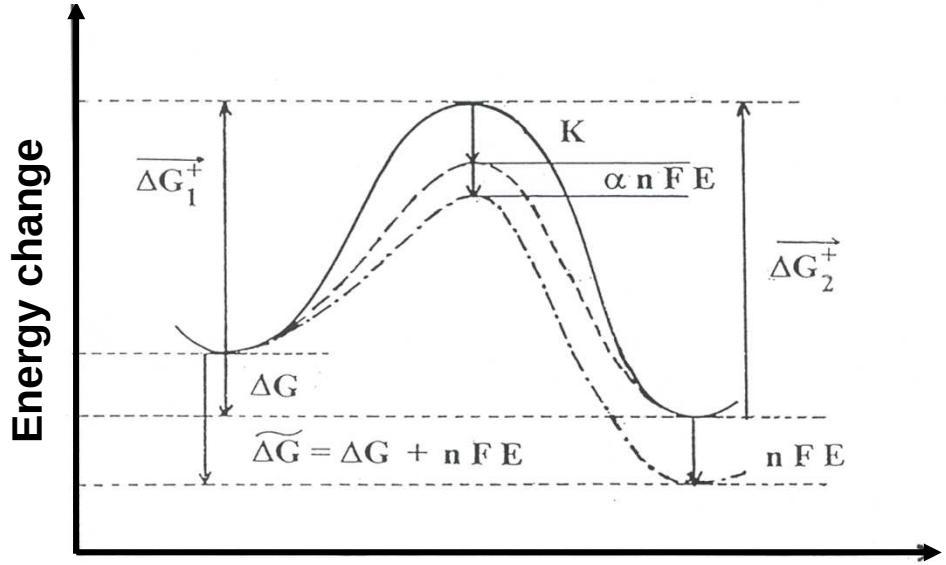
Power density curves

Anode catalyst : 1.5 mg.cm^{-2} ; Cathode catalyst : 2 mg.cm^{-2} (40% Pt/XC72 E-TEK)
Membrane : Nafion® 117; Ethanol concentration : 1 M

After C. Lamy et al., in "Catalysis for Sustainable Energy Production", edited by P. Barbaro and C. Bianchini, Wiley-VCH, Weinheim, 2009, Chap.1, pp. 3-46.

Principle of Electrocatalysis : activation of electrochemical (interfacial) reactions by both the electrode potential and the electrode material

$$j = nF\,v_i = nF\,k(T,E)\,c_i = nF\,k_o\,c_i\,e^{-\frac{\Delta G_o^+}{RT}}\,e^{\frac{\alpha nF\eta}{RT}} = j_o\,e^{\frac{\alpha nF\eta}{RT}} \quad \text{with } j_o = nF\,k_o\,c_i\,e^{-\frac{\Delta G_o^+}{RT}}$$



Abcissa along the reaction path

$$\eta_a^{act} = \frac{RT}{\alpha_a n_a F} \ln \frac{j}{j_{0_a}}$$

$$\left|\eta_c^{act}\right| = \frac{RT}{\alpha_c n_c F} \ln \frac{|j|}{j_{0_c}}$$

Activation barrier for an electrochemical reaction :
K is the decrease in activation energy due to the electrode catalyst, so that the effect of the electrocatalyst is contained in, ΔG^+_o, i.e. in j_o

How to Design Pluri-Metallic Pt-Based Electrocatalysts for Multi-Step Multi-Electron Transfer Reactions, such as Methanol Oxidation:

$$CH_3OH + H_2O \rightarrow CO_2 + 6\ H^+ + 6\ e^-$$

Platinum allows the **breaking of the C-H bonds**.

The role of the **other metals** may be as follows:

* to **provide OH (or O)** species necessary for complete oxidation (towards CO_2) at low electrode potentials,
* to **avoid the formation** of poisoning species,
* to **allow the oxidation** of the poisoning intermediates at lower potentials,
* to **break the C-C bond** at low temperature and low electrode potentials (e.g. for ethanol oxidation).

Preparation and characterization of Pt-based pluri-metallic electrocatalysts

- Preparation by electrochemical pulse methods
- Classical impregnation-reduction methods
- Preparation of the catalysts by the “Bönnemann colloidal” method
- Preparation of the catalysts by the “carbonyl complex” method
- Preparation of the catalysts by the “water-in-oil” micro-emulsion method
- Physical characterizations of catalysts by TEM, EDX, XRD, CV, IRS, HPLC, etc.

Preparation and characterization of Pt-based pluri-metallic electrocatalysts

Electrochemical Methods

- **Potentiostatic or galvanostatic methods**
- **Galvanic pulses**

This allows to prepare mono and pluri-metallic catalysts.

This a clean process, allowing the control of particle size, atomic composition and metal loading.

Chemical methods (non-noble metal based catalysts)

- **Macrocycle catalysts such as MeN_4 : MPc (phthalocyanine)**
- **Chalcogenides : catalysts such as Ru_xSe_y**

=> These catalysts display a good activity for the oxygen reduction reaction (ORR) and are completely tolerant to the presence of alcohols.

Chemical methods (platinum-based catalysts)

- **Colloïdal route** (Bönnemann):

$$MeCl_n + nNalk_4[BEt_3H] \rightarrow Me[Nalk_4Cl]_n + nBEt_3 + n/2H_2$$

This allows to control the particle size, atomic composition and structure of the catalyst (alloying, decoration, etc.)

- **Carbonyl route**:

$$Na_2PtCl_6 + SnCl_4 + NaCH_3CO_2\ [+\ CO\ (24h)] + [C\ (12h)] \rightarrow Pt_xSn_y/C$$

This allows to control the particle size and atomic composition of the catalysts

- **Water-in-oil method**:

$$H_2PtCl_6aq(Brij^{®}30) + NaBH_4aq(Brij\ ^{®}30) + [C\ (0{,}5 – 2h)] \rightarrow Pt/C$$

Easy process, allowing to control the particle size, atomic composition and structure of the catalysts.

⇒ Pluri-metallic anodic catalysts for the oxidation of alcohols and carbon monoxide (reformate gas) and alcohol tolerant cathodic catalysts.

Physical methods (platinum-based catalysts) : PVD

- **Plasma sputtering**: this allows to reduce the platinum loading (< 100 µg/cm^2)

EXPERIMENTAL CHARACTERIZATION OF Pt-BASED ELECTROCATALYSTS

♦ **Transmission Electron Microscopy (TEM) :**

- Observation of the morphology and determination of the particle size
- Determination of the particle composition by Energy Dispersive Analysis of X-rays (EDX)

♦ **X-Ray Diffraction (XRD) :**

- Determination of the catalyst structure and lattice parameters
- Evaluation of the particle size of the catalyst

♦ **Cyclic Voltammetry (CV) :**

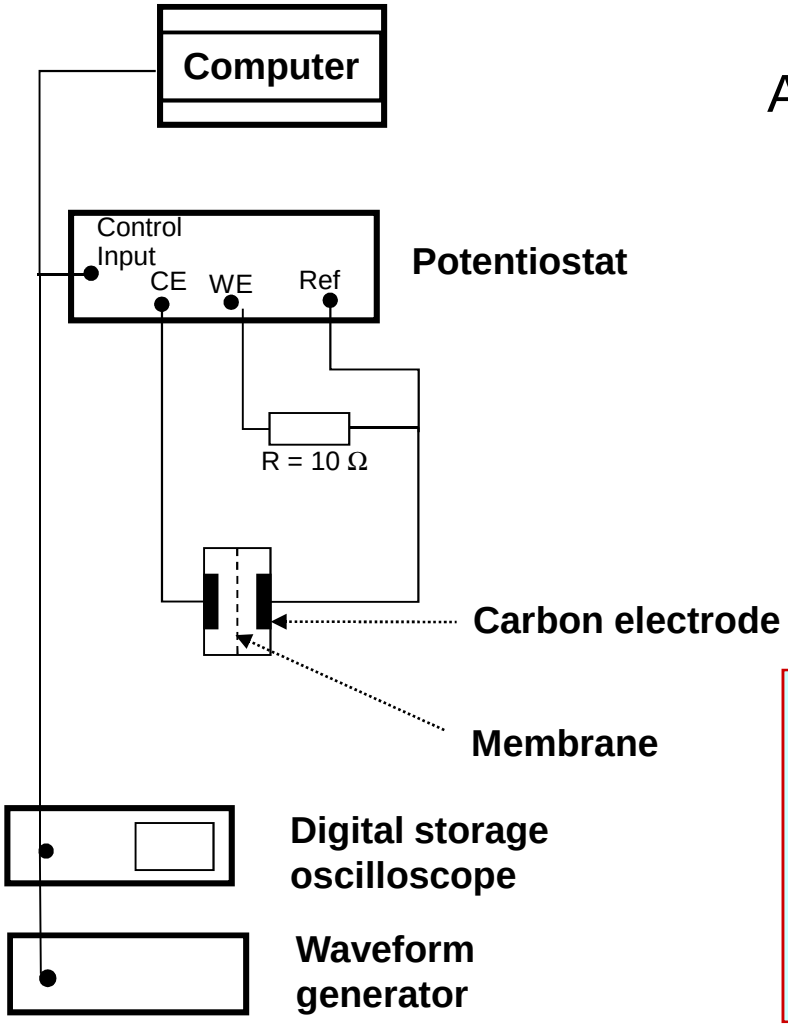
- Determination of the true surface area
- Evaluation of the electrocatalytic activity

♦ **Infrared Reflectance Spectroscopy (IRS) :**

- Identification of the adsorbed species and reaction products by "in situ" Infrared Reflectance Spectroscopy (SNIFTIRS and SPAIRS)

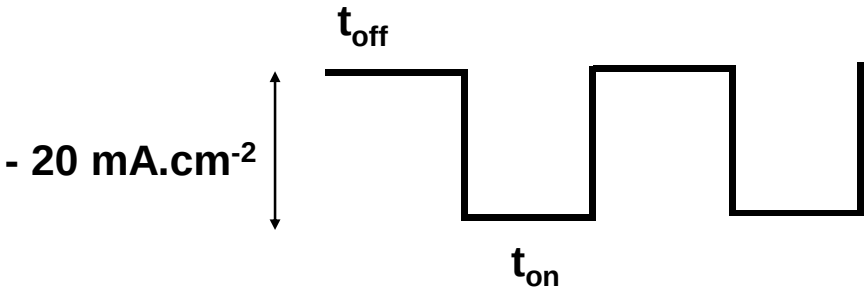
♦ **Chromatographic Analysis (HPLC) of the reaction products**

♦ Catalyst preparation by electrochemical pulse methods



Aqueous solution (1.0 M H_2SO_4) :

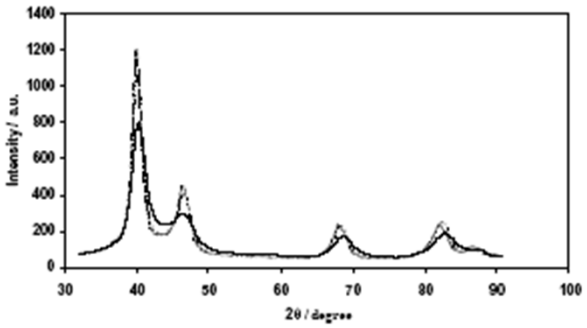
- K_2PtCl_6
- K_2RuCl_5



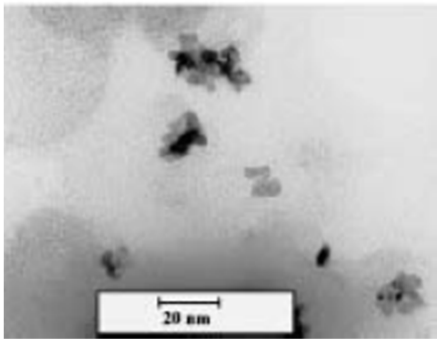
Analysis of the solutions after metal deposition:

=> metal loading between 1.9 and 2.1 mg cm^{-2}

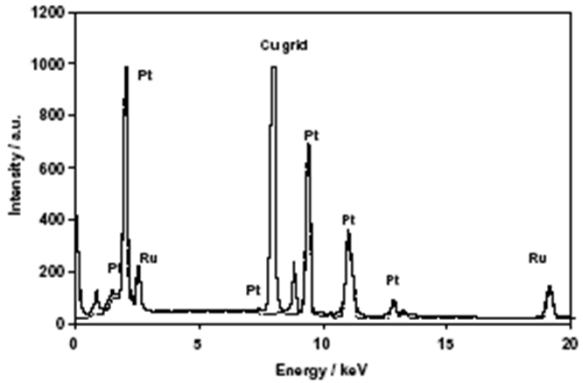
Physical characterization of $Pt_{1-x}Ru_x$ catalysts prepared by the electrochemical deposition method



XRD



TEM



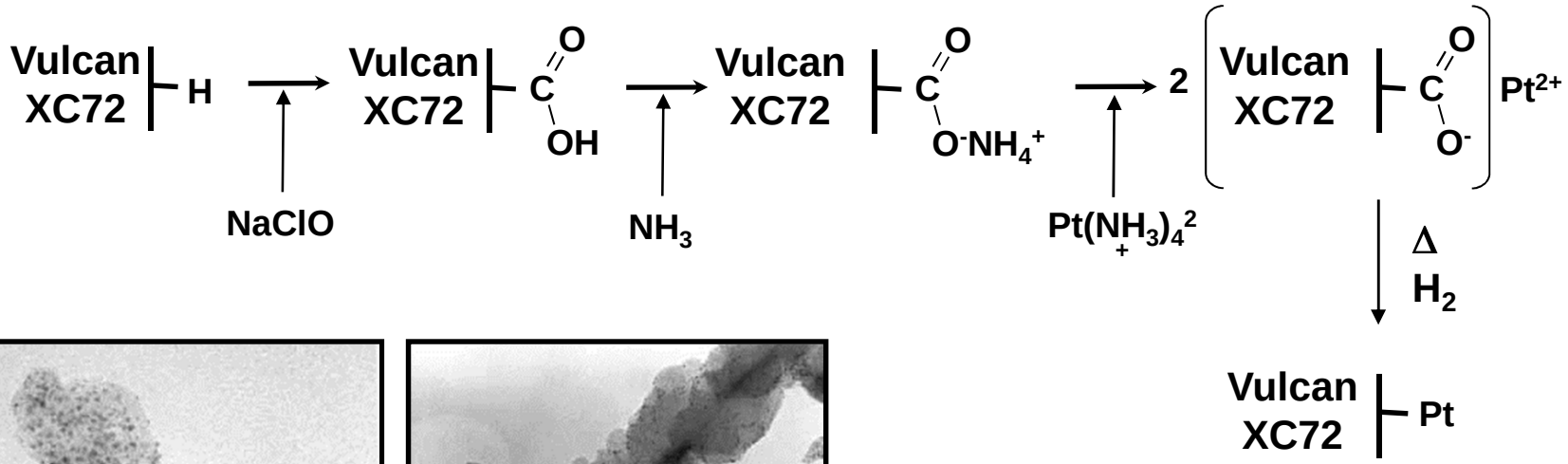
EDX

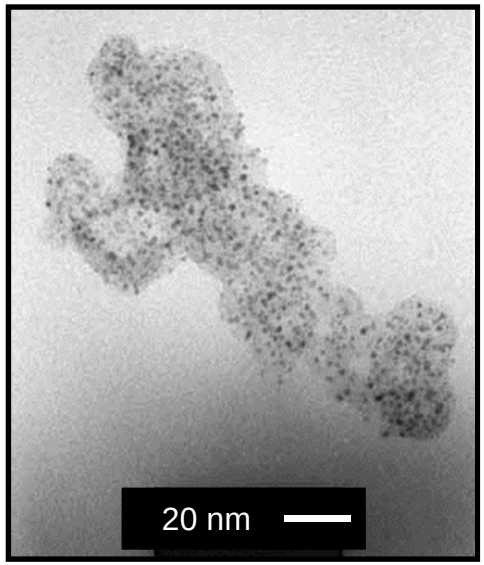
Electrode	Pt/Ru atomic ratio in solution	t_{off} /s	Atomic ratio XRD	EDX	AAS	Particle size /nm
PtRu 50–50	50/50	2.5	55/45	60/40	–	~7–8
PtRu 50–50	50/50	0.3	57/43	53/47	48/52	~5
PtRu 65–35	65/35	2.5	69/31	69/31	–	~7–8
PtRu 65–35	65/35	0.3	66/34	–	69/31	~5
PtRu 80–20	80/20	2.5	75/25	82/18	–	~7–8
PtRu 80–20	80/20	0.3	77/23	78/22	78/22	~5

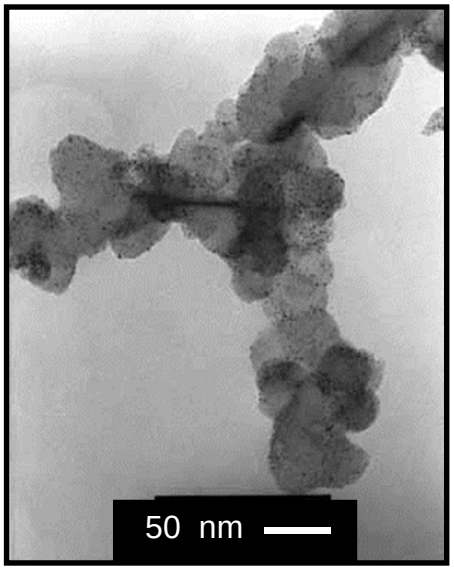
Advantages and disadvantages of catalysts prepared by electrochemical deposition

- **Advantages** :
  - Clean process
  - Easy and reproducible process
  - Controlled atomic composition
  - Controlled particle size
  - Possibility of manufacturing FC electrodes
- **Disadvantages** :
  - Low faradic yield (close to 10%) due to H_2 evolution
  - Long duration of experiments
  - Only formation of alloy compounds

♦ Classical impregnation-reduction method : Cationic exchange

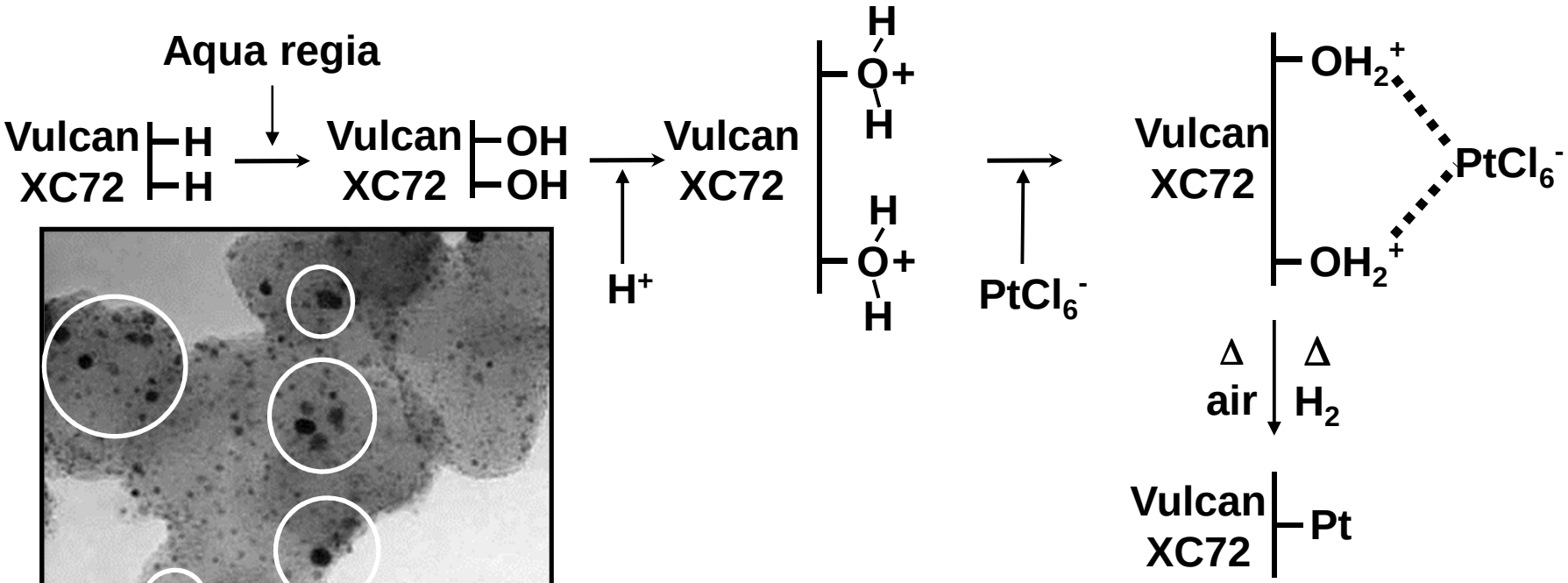


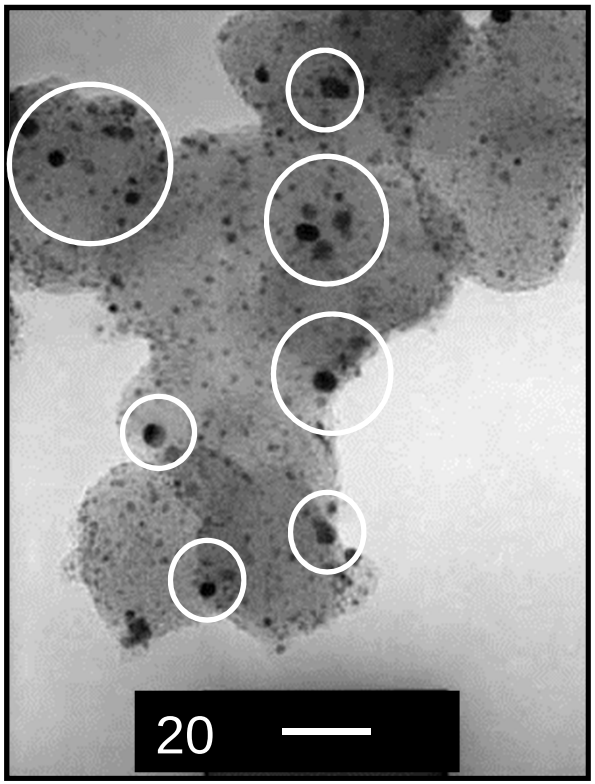




Loading limited to 10 wt. %

♦ Classical impregnation-reduction method : Anionic exchange





TEM pictures of a Pt/C catalyst

=> Preparation of Pt/C and PtSn/C catalysts

⇒ Variation of the Pt/Sn atomic ratio

⇒ Loading up to 30 wt. %

♦ Preparation of Pt-based plurimetallic electrocatalysts by the "Bönnemann colloidal" method

Preparation of the reducing agent
(tetraalkylammonium triethylborohydride):

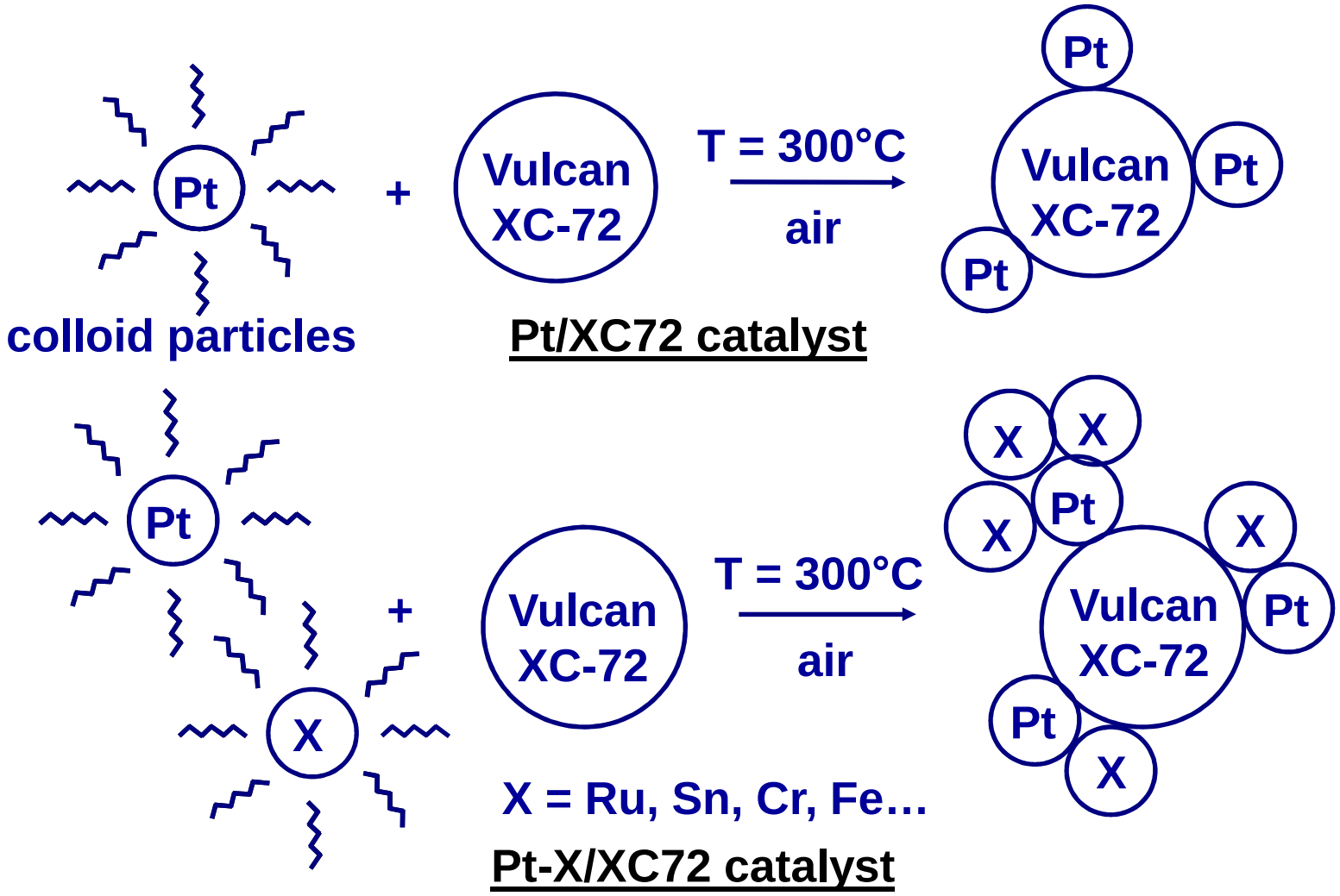
$$N(C_nH_{2n+1})_4Br + KB(C_2H_5)_3H \rightarrow N(C_nH_{2n+1})_4[B(C_2H_5)_3H] + KBr\downarrow$$

Preparation of the mono and bimetallic colloid precursors :

- $PtCl_2 + 2\ N(C_nH_{2n+1})_4[B(C_2H_5)_3H] \rightarrow$
  $Pt[N(C_nH_{2n+1})_4Cl]_2 + 2\ B(C_2H_5)_3\downarrow + H_2\uparrow$

- $m\ PtCl_2 + n\ XCl_y + (2m + yn)\ N(C_nH_{2n+1})_4[B(C_2H_5)_3H] \rightarrow$
  $Pt_mX_n[N(C_nH_{2n+1})_4Cl]_{(2m + yn)} + (2m + yn)\ B(C_2H_5)_3\downarrow + (2m+ yn)/2\ H_2\uparrow$

Deposition of the colloid particles on a carbon powder



Deposition of the colloid particles on a carbon powder (Vulcan XC72)

Coreduction

$xPtCl_2 + yRuCl_3 + (2x+3y)N(alk)_4BEt_3H$

↓

$Pt_xRu_y[N(alk)_4Cl]_{(2x+3y)}$

300°C air | XC72

↓

Pt_x-Ru_y/C

Codeposition

Colloid Pt | Colloid Ru

↓

$x\ Pt[N(alk)_4Cl]_2 + y\ Ru[N(alk)_4Cl]_3$

300°C air | XC72

↓

Pt_x+ Ru_y/C

Mixture of catalysts

Colloid Pt | Colloid Ru

300°C air | XC72 | 300°C air | XC72

↓ ↓

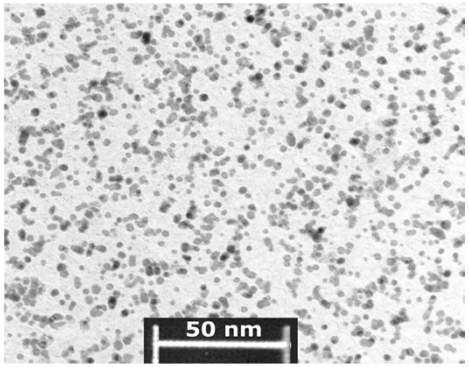
Pt/C | Ru/C

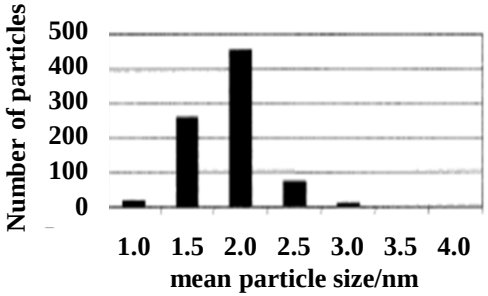
↓

xPt/C+ yRu/C

Characterization of $Pt_{0.8}Ru_{0.2}$ catalysts prepared by the colloidal method

Coreduction Pt-Ru/C

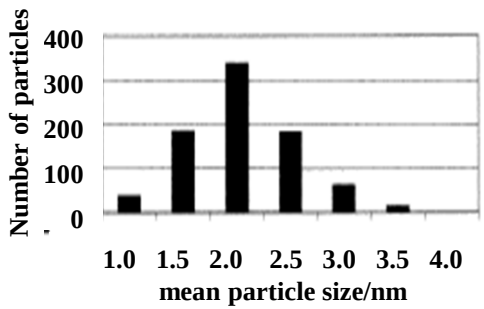


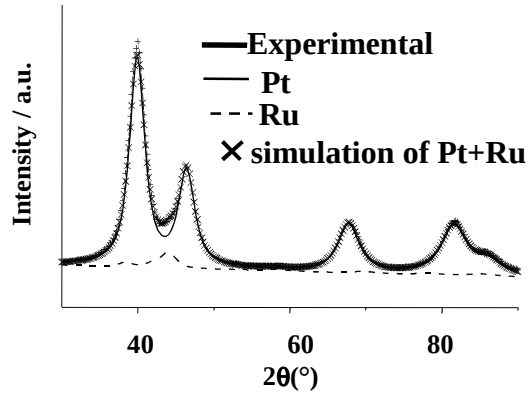


From XRD measurement: alloy character

$$\bar{d}_{TEM} = \frac{\sum_i n_i d_i}{n}$$

Codeposition Pt+Ru/C

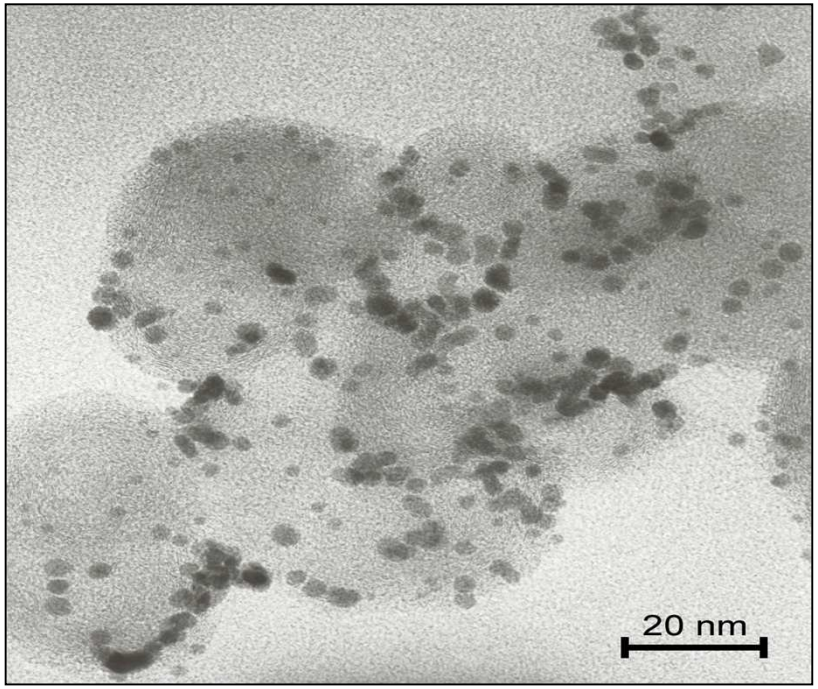


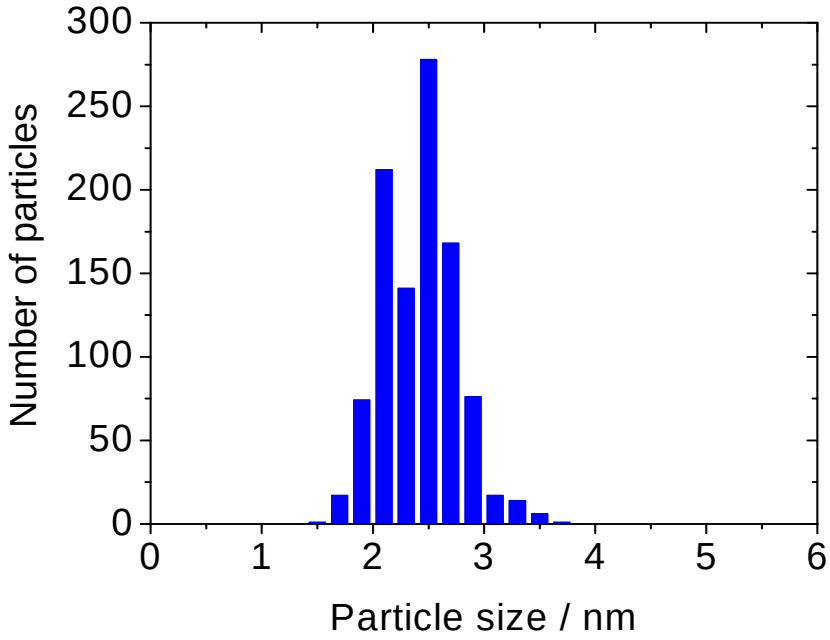


Characterization of $Pt_{0.8}Ru_{0.2}$ catalysts prepared by the colloidal method

Catalysts	d_{TEM}	Crystallographic structure
Pt/XC72	2.2	fcc
Pt+Ru/XC72 (80:20)	2.1	Pt fcc + Ru hc in interaction
Pt-Ru/XC72 (80:20)	1.9	fcc alloy
Pt/XC72+Ru/XC72 (80:20)	Pt(2.1)+Ru(1.5)	Pt fcc + Ru hc
Ru/XC72	1.5	Hexagonal compact (hc)

Characterization of a $Pt_{0.9}Sn_{0.1}$ catalyst prepared by the colloidal method



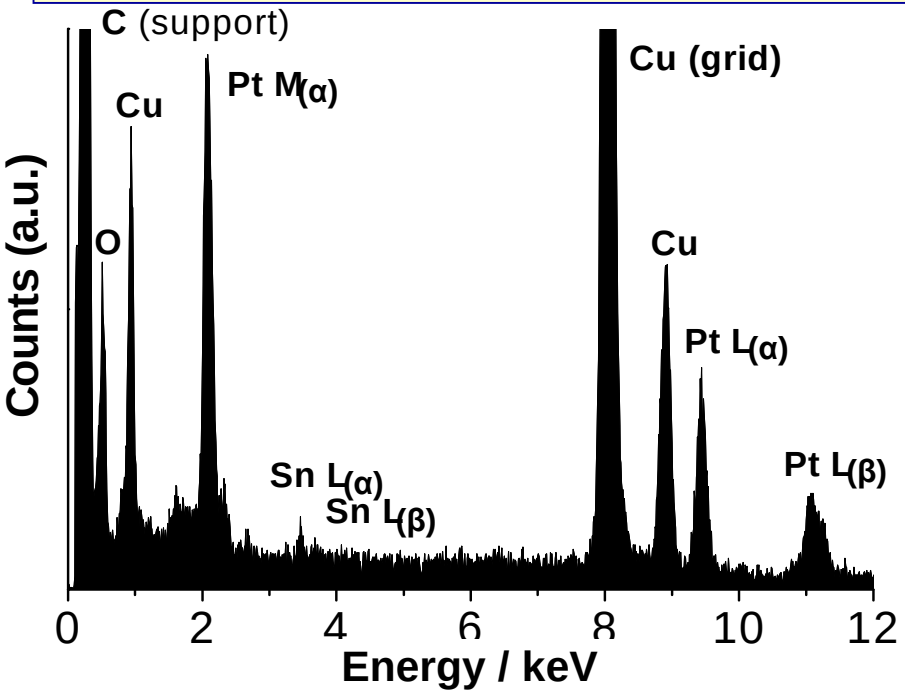


TEM image of a Vulcan supported Pt-Sn(90:10)/XC72 catalyst (with a metal loading of 30%) prepared by the colloidal method

Particle size distribution of a Pt-Sn(90:10)/XC72 catalyst
(based on the observation of 1005 particles)

Mean diameter : 2.4 ± 0.3 nm

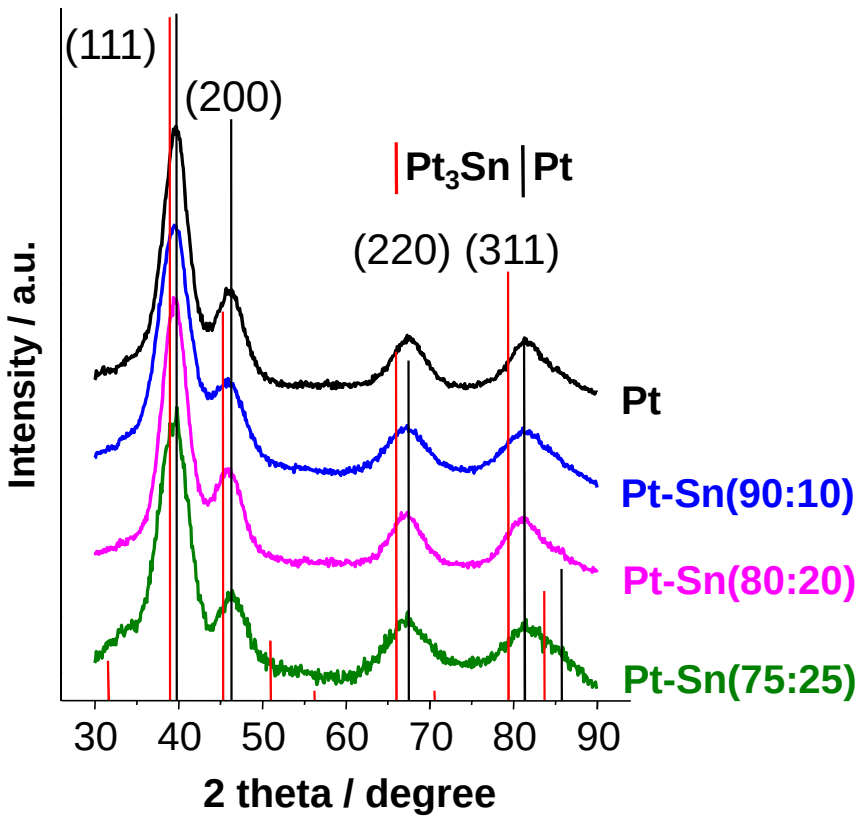
Physical characterizations of 30% $Pt_{1-x}Sn_x$/XC72 catalysts prepared by the Bönnemann method (colloidal method)



Element	Pt	Sn
Zone n°1	89.7	10.3
Zone n°2	91.1	8.9
Zone n°3	89.7	10.3

EDX analysis of a 30% Pt-Sn(90:10/XC72 catalyst

XRD patterns of Pt-Sn/XC72 catalysts with different atomic composition



Values of the physical and electrochemical parameters of different Pt-Sn electrocatalysts prepared by the colloidal method

Electrocatalyst	d_{TEM} / nm	Dispersion / %	d_{XRD} / nm	Atomic composition (EDX)	S / $m^2.g^{-1}$
30% Pt/XC72	2.4	44	2.1	/	39
30% Pt-Sn(90:10)/XC72	2.4	45	1.9	89.7 / 10.3	24
60% Pt-Sn(90:10)/XC72	2.8	40	3.4	89.8 / 10.2	11
30% Pt-Sn(80:20)/XC72	2.7	41	2.1	80.4 / 19.6	15
30% Pt-Sn(75:25)/XC72	2.9	38	2.0	74.1 / 25.9	8

♦ Preparation of Pt-based plurimetallic electrocatalysts by the "carbonyl complex" method

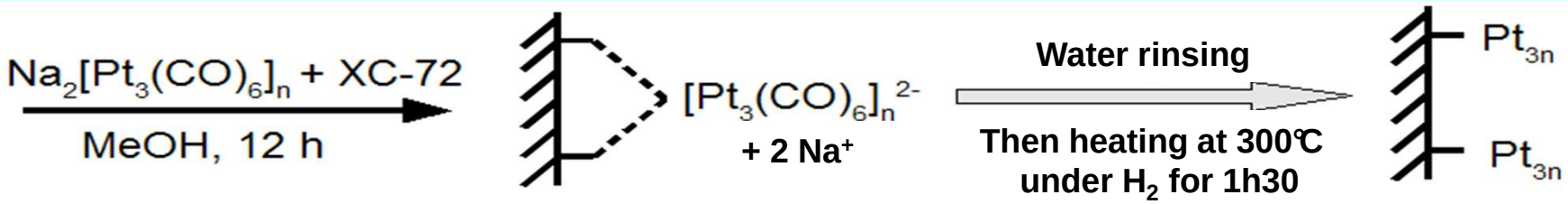
Preparation of a Pt carbonyl complex :

$$3n\,[PtCl_z]^{2-} + (3nz/2 + 3n + 1)\,CO + (3nz - 6n + 2)\,OH^- \rightarrow$$
$$[Pt_3(CO)_6]_n^{2-} + 3nz\,Cl^- + (3nz/2 - 3n + 1)\,CO_2 + (3nz/2 - 3n + 1)\,H_2O$$

Preparation of bimetallic $Pt_{1-x}M_x$ carbonyl complex :

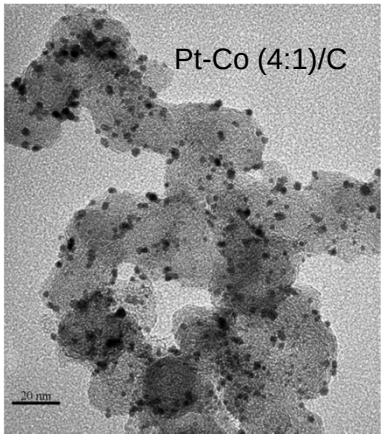
$$3n(1-x)\,[PtCl_6]^{2-} + 3nx\,[MCl_z]^{2-} + [3n\,(4 - 6x + zx)/2 + 6n + 1)]\,CO$$
$$+ [3n\,(4 - 6x + zx) + 2)]\,OH^- \rightarrow [(Pt_{1-x}M_x)_3(CO)_6]_n^{2-} + 3n\,[6(1 - x) + zx)]\,Cl^-$$
$$+ [3n\,(4 - 6x + zx)/2 + 1)]\,CO_2 + [3n\,(4 - 6x + zx)/2 + 1)]\,H_2O$$

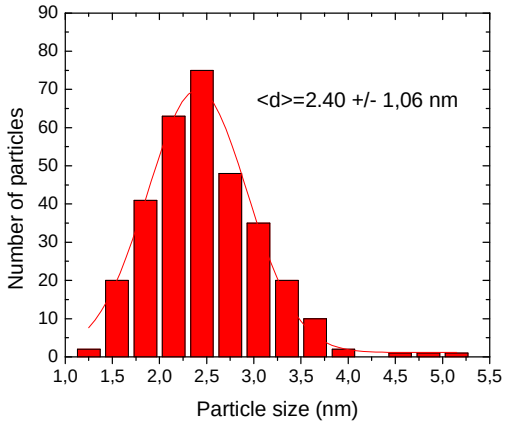
Deposition of the metallic particles on Vulcan XC72 :

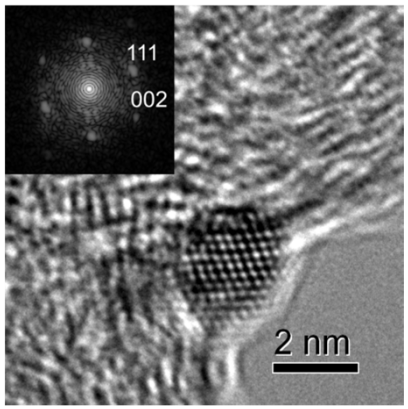


Physical characterization of a (4:1)Pt-Co/C catalyst prepared by the carbonyl complex method

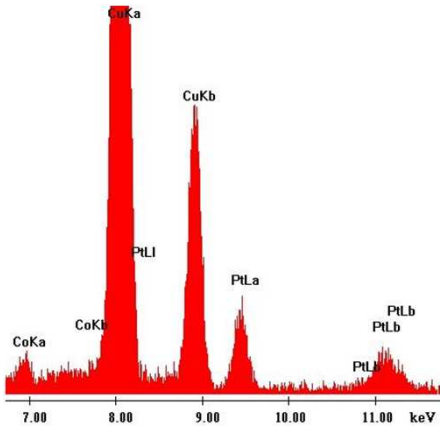
TEM image



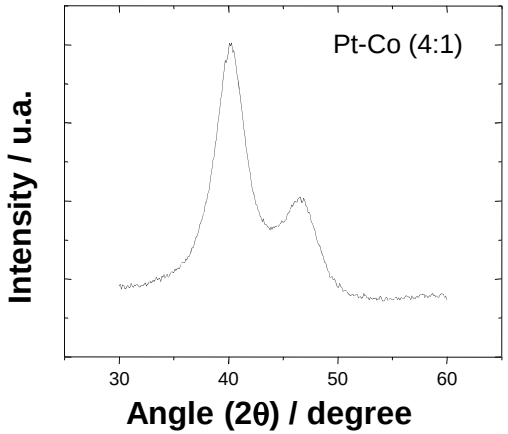




High resolution TEM

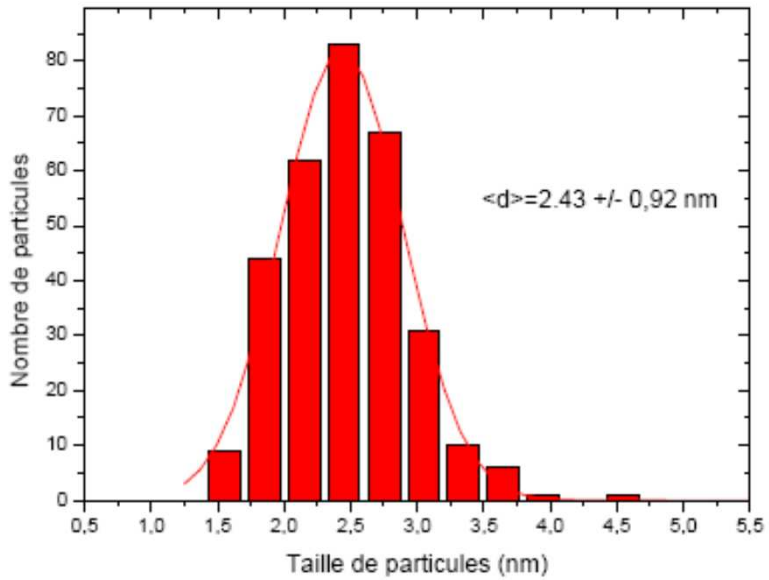


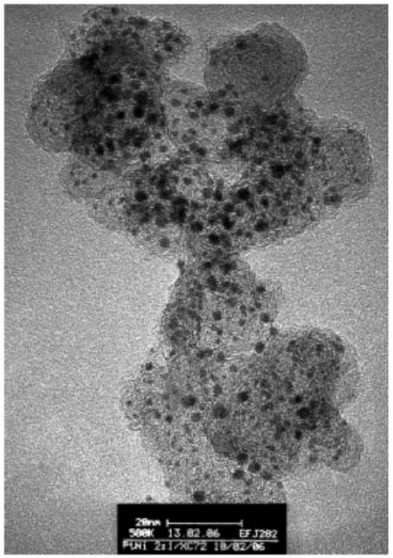
EDX

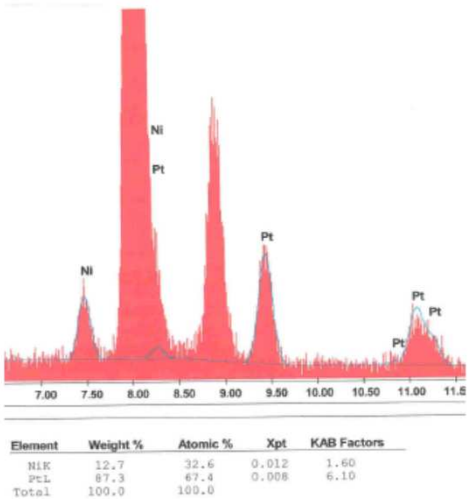


XRD

Physical characterization of (2:1)Pt-Ni/C prepared by the carbonyl complex method







Particle size distribution (from TEM) **TEM micrograph** **EDX analysis**

Catalyst	Nominal atomic composition (%)	Experimental composition (%)	Particle size (nm)	Dispersion (%)
Pt/C	100	100	1,75 ± 1,06	60
Pt-Ni (4:1)/C	80:20	82,5:17,5	2,60 ± 1,13	43
Pt-Ni (2:1)/C	66:33	67,4:32,6	2,43 ± 0,92	46
Pt-Ni (1:1)/C	50:50	45,7:54,3	2,64 ± 1,82	43

♦ Preparation of Pt-based plurimetallic electrocatalysts by the "water-in-oil" method

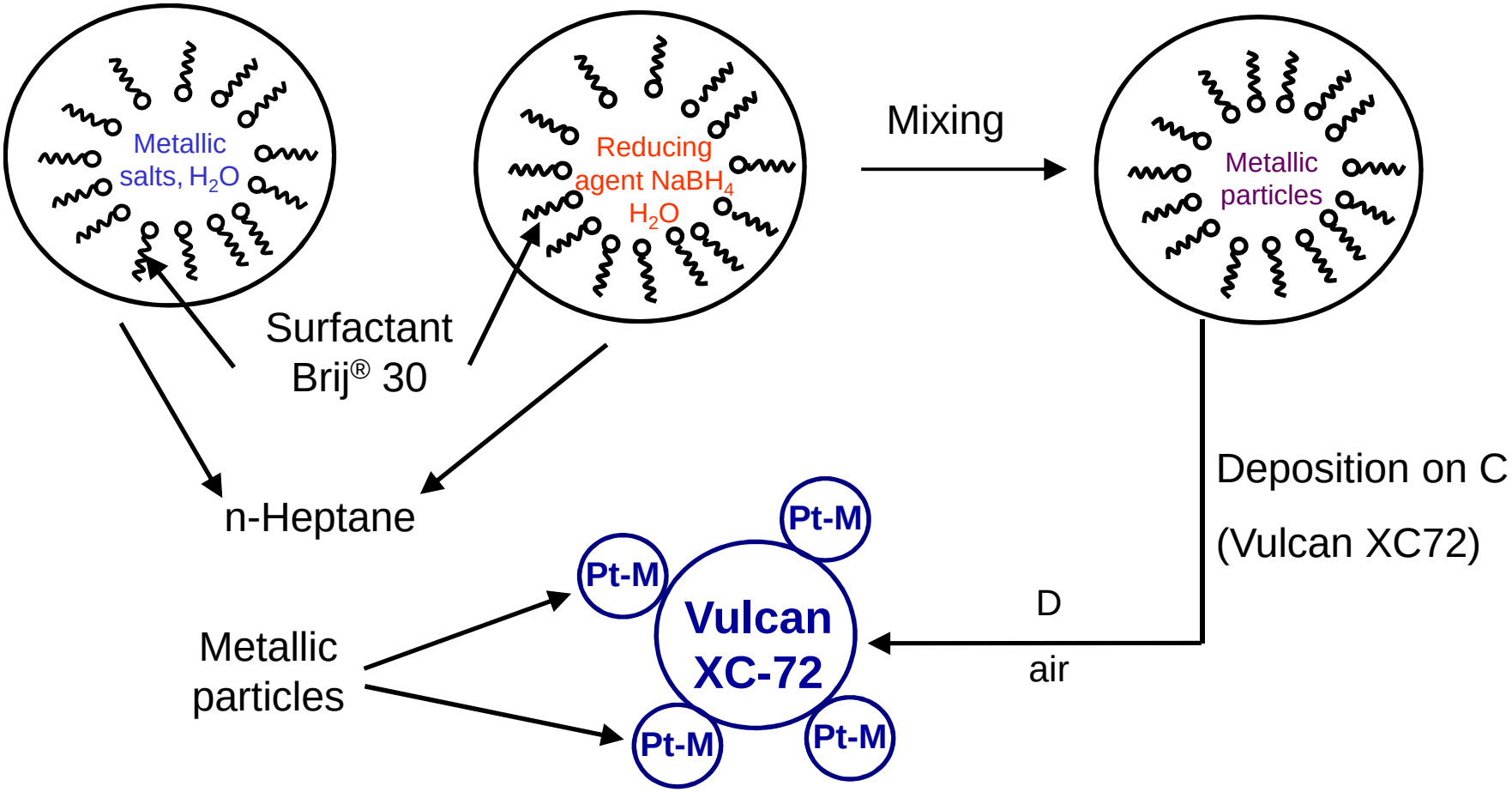
$$PtCl_6^{2-} + 4\,e^- \rightarrow Pt(s) + 6\,Cl^-$$

$$BH_4^- + 3\,H_2O \rightarrow BO_3^{3-} + 2\,H_2 + 6\,H^+ + 4\,e^-$$

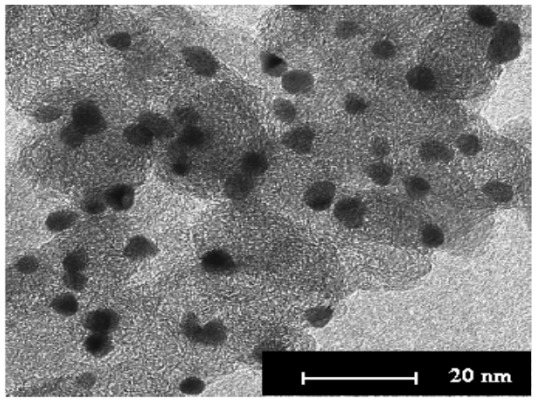
$$(PtCl_6^{2-})_{aq} + 3H_2O + (BH_4^-)_{aq}$$

$$\rightarrow Pt(s) + BO_3^{3-} + 2\,H_2 + 6\,H^+ + 6\,Cl^-$$

Description of the "water-in-oil" microemulsion method

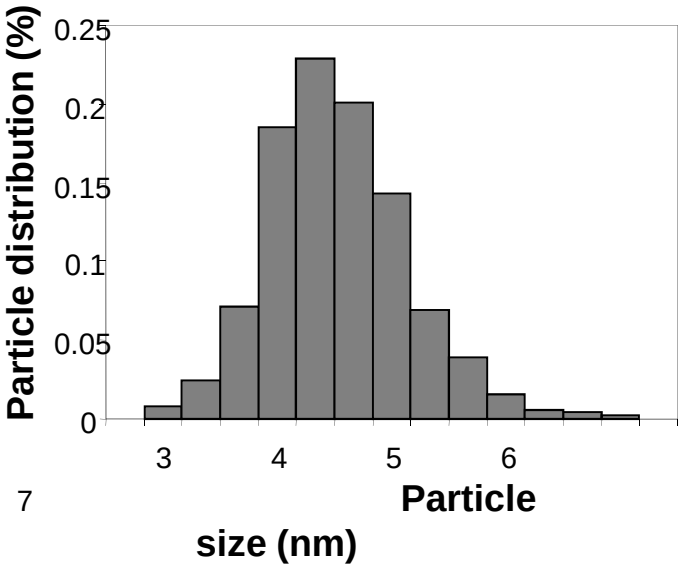


Physical characterization of a $Pt_{0.9}Bi_{0.1}$/C catalyst prepared by the "water-in-oil" method

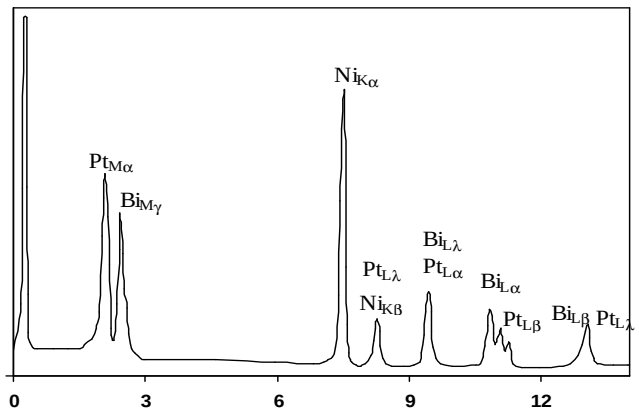


$Pt_{0.9}Bi_{0.1}$ 50%/C

TEM image



Mean particle size :
5 ± 1.2 nm

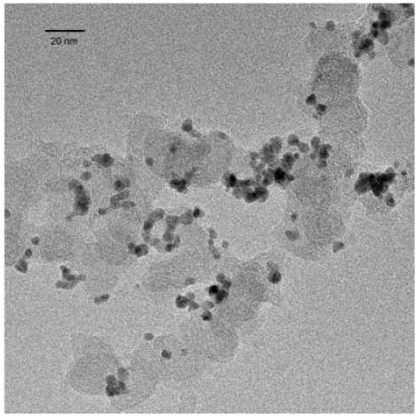


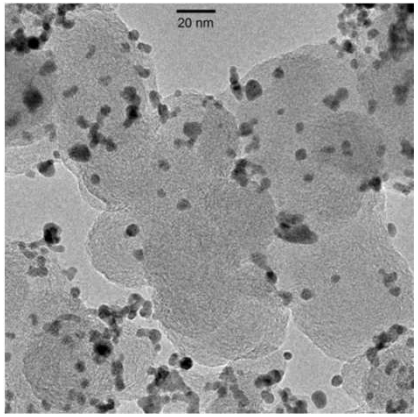
EDX analysis of a $Pt_{0.9}Bi_{0.1}$ 50%/C catalyst

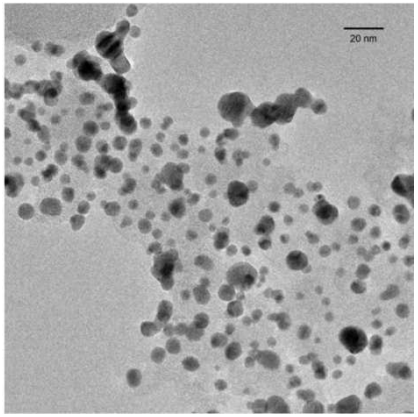
Result : Pt 88%, Bi 12%

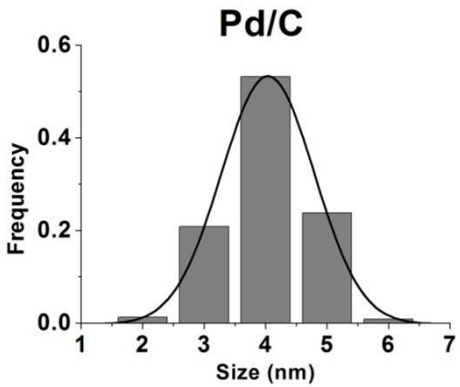
TEM characterization of 40%Pd_xAu_{1-x}/C electrocatalysts prepared by the "water-in-oil" method

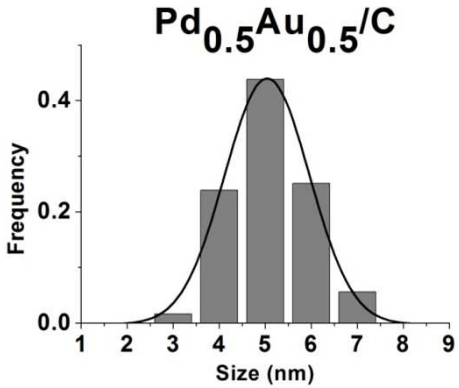
(a) (b) (c)

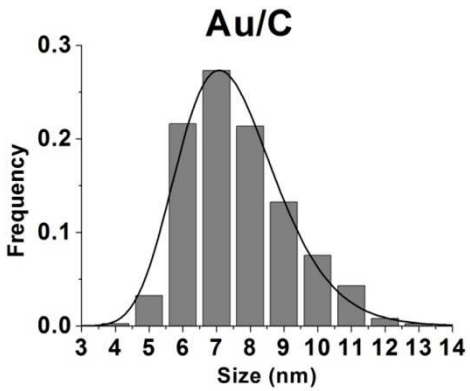












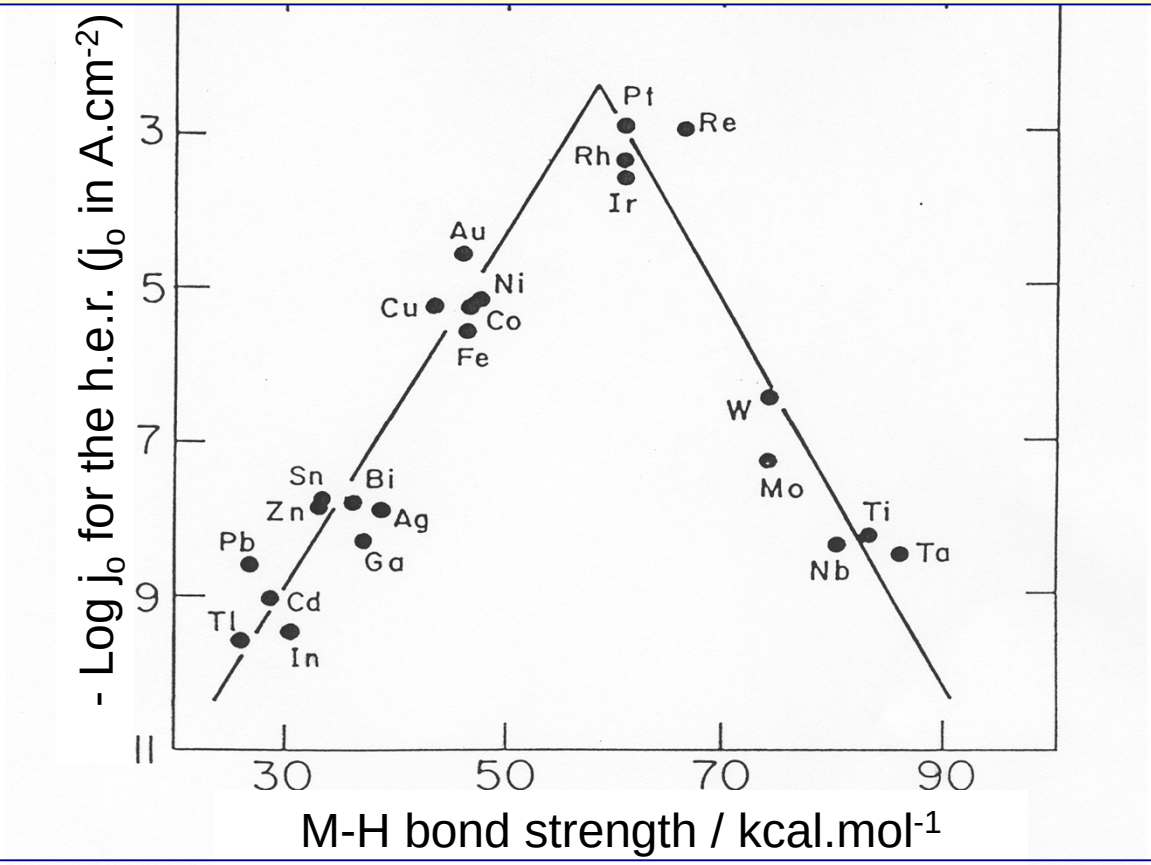
Mean particle size :

4.0 ± 1.0 nm **5.0 ± 1.2 nm** **7.4 ± 1.4 nm**

➢ **Electrocatalysts for fuel cell reactions at low temperatures (< 90℃)**

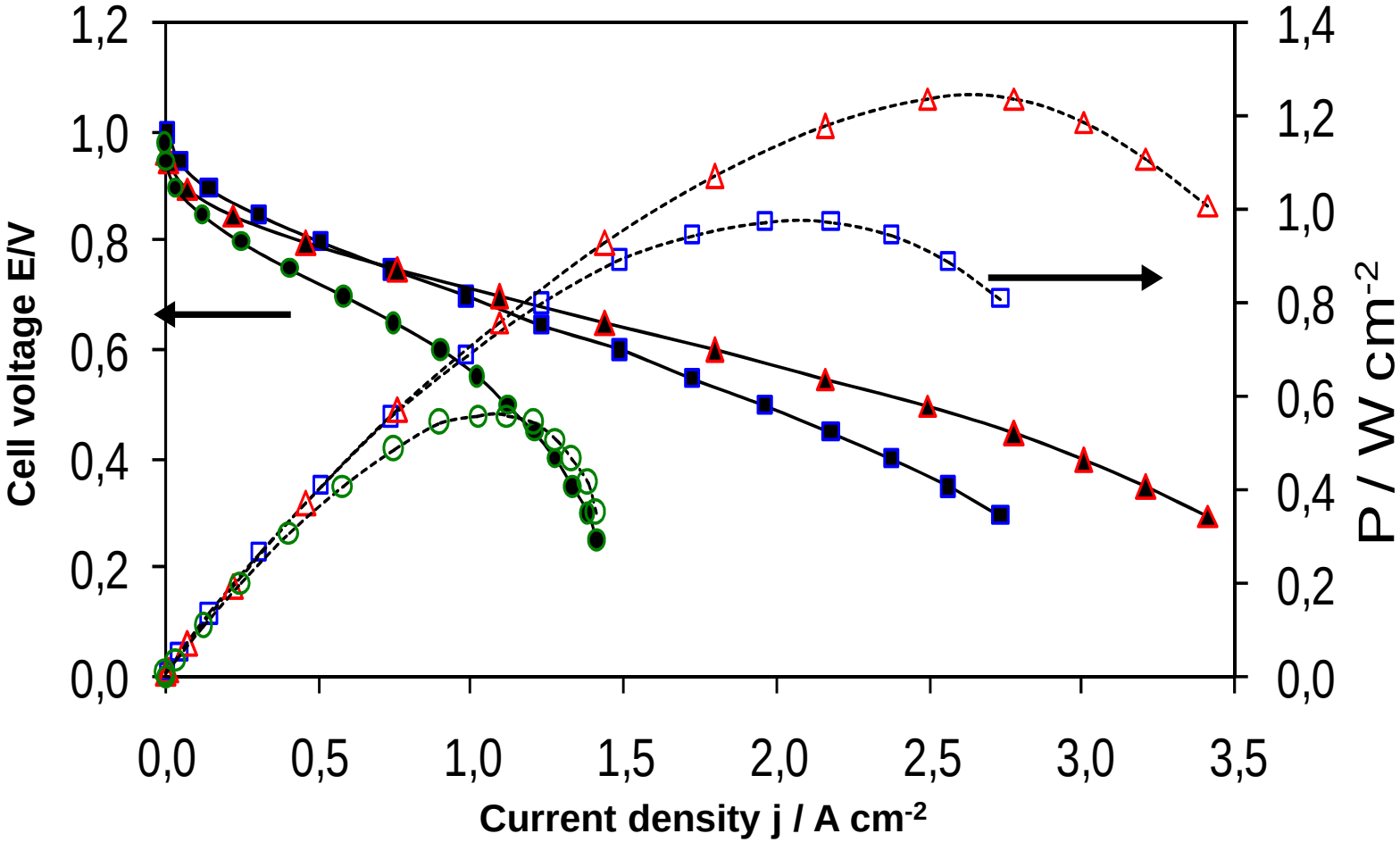
- ♦ Electrocatalytic oxidation of hydrogen
- ♦ Electrocatalysts for CO oxidation
- ♦ Electrocatalytic reduction of dioxygen

Exchange current density j_o of the hydrogen evolution reaction as a function of the metal-hydrogen bond energy



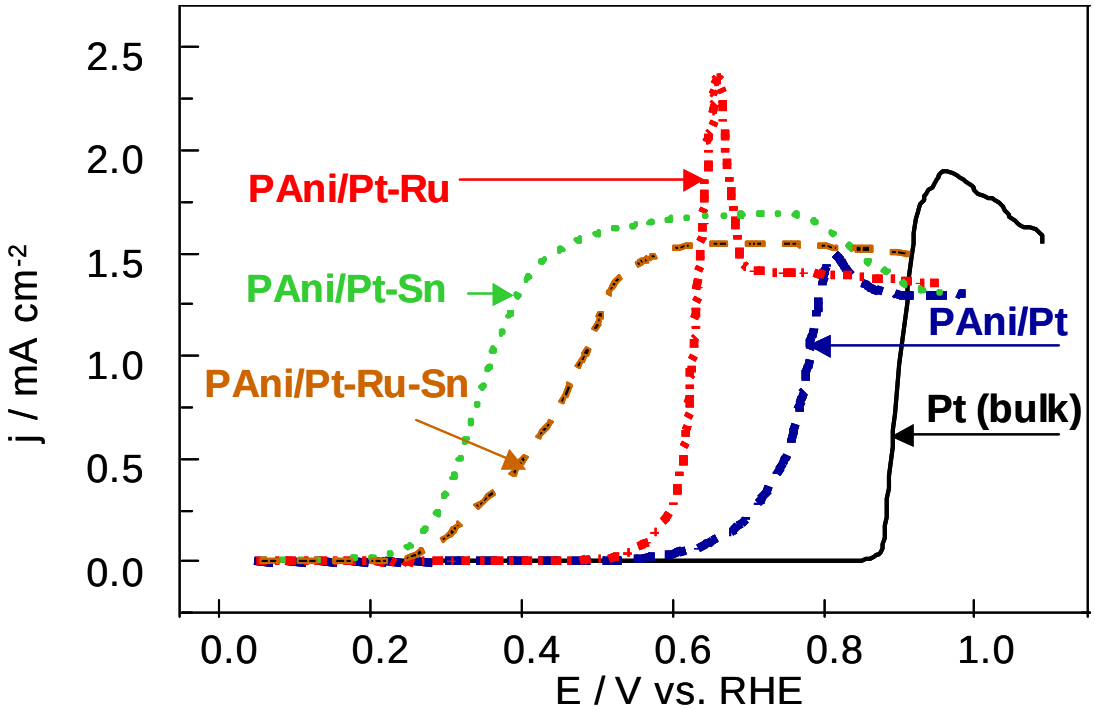
$2\ M + H_2 \rightarrow 2\ M\text{-}H_{ads}$	**Dissociative H_2 adsorption**	$v_1 = k_1\ (1-\theta)\ e^{\beta\lvert\Delta G_{M-H}\rvert/RT}$
$2\ (M\text{-}H_{ads} \rightarrow H^+_{aq} + e^- + M)$	**Electron transfer reaction**	$v_2 = k_2\ \theta\ e^{-(1-\beta)\lvert\Delta G_{M-H}\rvert/RT}\ e^{\alpha nFE/RT}$
	(θ is the degree of coverage of the surface by H_{ads})	
$H_2 \rightarrow 2\ H^+_{aq} + 2\ e^-$	**Overall oxidation reaction**	$v = v_1 = v_2$ (stationary state)

Polarization and power density curves of a PEMFC obtained with a homemade MEA.
T_{cell}=85°C, T_{huma}=80°C, T_{humc}=35°C, f_a=600 ml mn^{-1}, f_c=400 ml mn^{-1}, p_a=p_c=3 bar

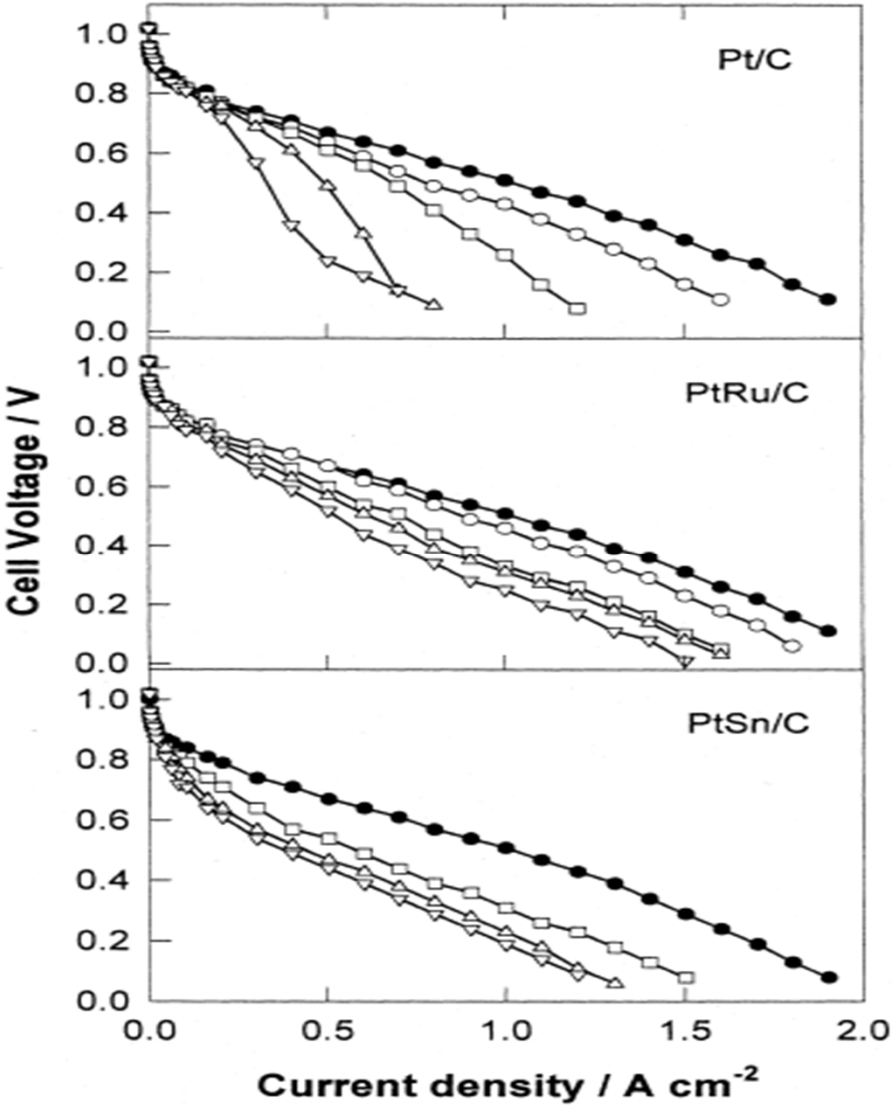


Δ : cathode and anode prepared in LACCO, 0.35 mg_{Pt} cm^{-2} (Bönnemann colloidal method)
: cathode LACCO 0.35 mg_{Pt} cm^{-2} and anode LACCO+GREMI 0.1 mg_{Pt} cm^{-2} (Plasma PVD)
O : anode LACCO 0.35 mg_{Pt} cm^{-2} and cathode LACCO+GREMI 0.1 mg_{Pt} cm^{-2} (Plasma PVD)

Electro-oxidation of CO on different Pt-based electrodes dispersed in polyaniline (PAni) : (——) bulk Pt ; (– – –) PAni/Pt ; (• • • •) PAni/Pt-Ru ; (• — • — • —) PAni/Pt-Sn ; (- - - -) PAni/Pt-Ru-Sn



$Pt + CO \rightarrow Pt\text{-}CO_{ads}$	CO adsorption
$M + H_2O \rightarrow M\text{-}OH_{ads} + H^+_{aq} + e^-$	Dissociative adsorption of water
$Pt\text{-}CO_{ads} + M\text{-}OH_{ads} \rightarrow Pt + M + CO_2 + H^+_{aq} + e^-$	Surface reaction
$CO + H_2O \rightarrow CO_2 + 2\,H^+_{aq} + 2\,e^-$	Overall oxidation reaction



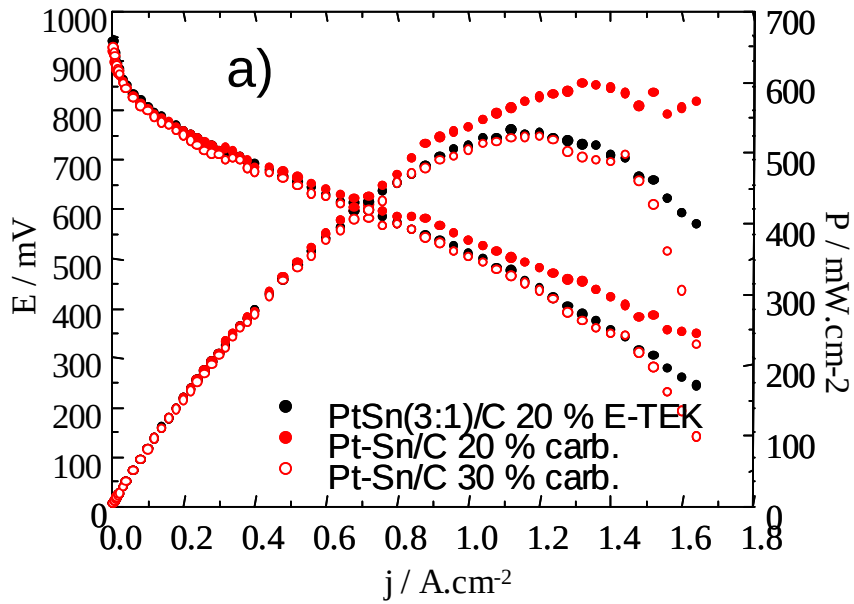
Effect of a few ppm of CO on the E(j) characteristics of a H_2/O_2 PEMFC fed with a reformate gas

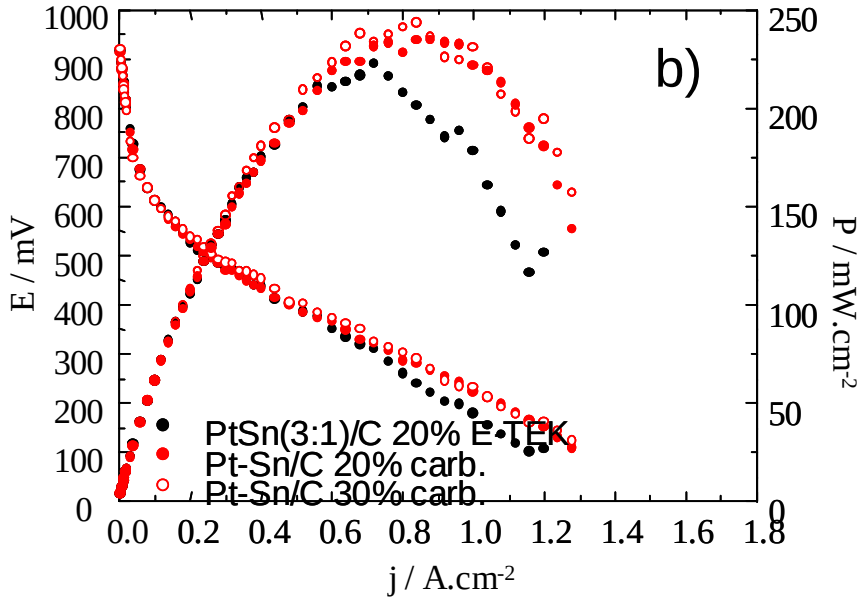
Single Cell performance plots for Pt/C, PtRu/C and PtSn/C at 85℃ at several CO concentrations:
(●) 0 ppm; (O) 5 ppm; (□) 20 ppm; (△) 50 ppm and (▽) 100 ppm.

After Mukerjee et al., Electrochim. Acta, 44 (1999) 3283

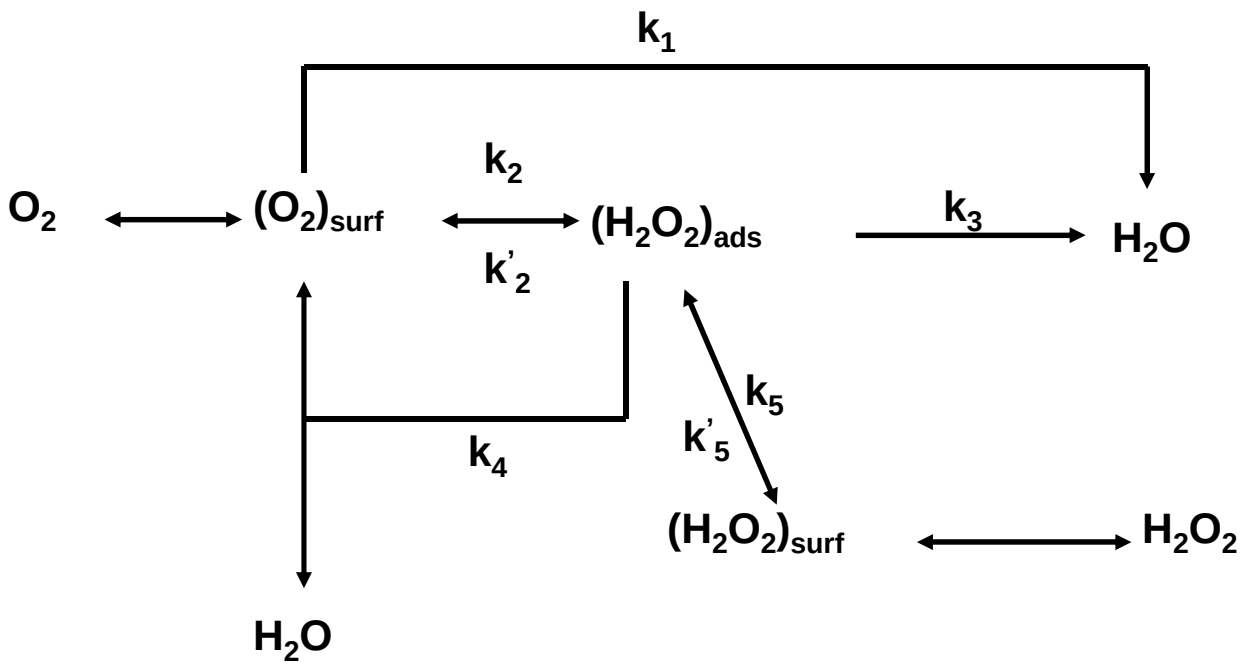
Polarization and power density curves of a PEMFC with a homemade MEA (Nafion® 112) : a) with pure H_2; b) with H_2 + 100 ppm CO.

T_{cell} = 85°C, catalyst loading : 0.4 mg cm^{-2} Pt for the cathode; 0.4 mg cm^{-2} PtSn(3:1)/C for the anode





The rather difficult oxygen reduction kinetics



Possible reaction paths for oxygen reduction

Detailed reaction mechanism of the ORR involving the possible formation of H_2O_2

$$Pt + O_2 \rightarrow Pt - O_{2ads}$$

$$Pt - O_{2ads} + H^+ + e^- \rightarrow Pt - O_2H_{ads}$$

either $\mathbf{Pt - O_2H_{ads} + H^+ + e^- \rightarrow Pt + H_2O_2}$

or $Pt + Pt - O_2H_{ads} \rightarrow Pt - O_{ads} + Pt - OH_{ads}$

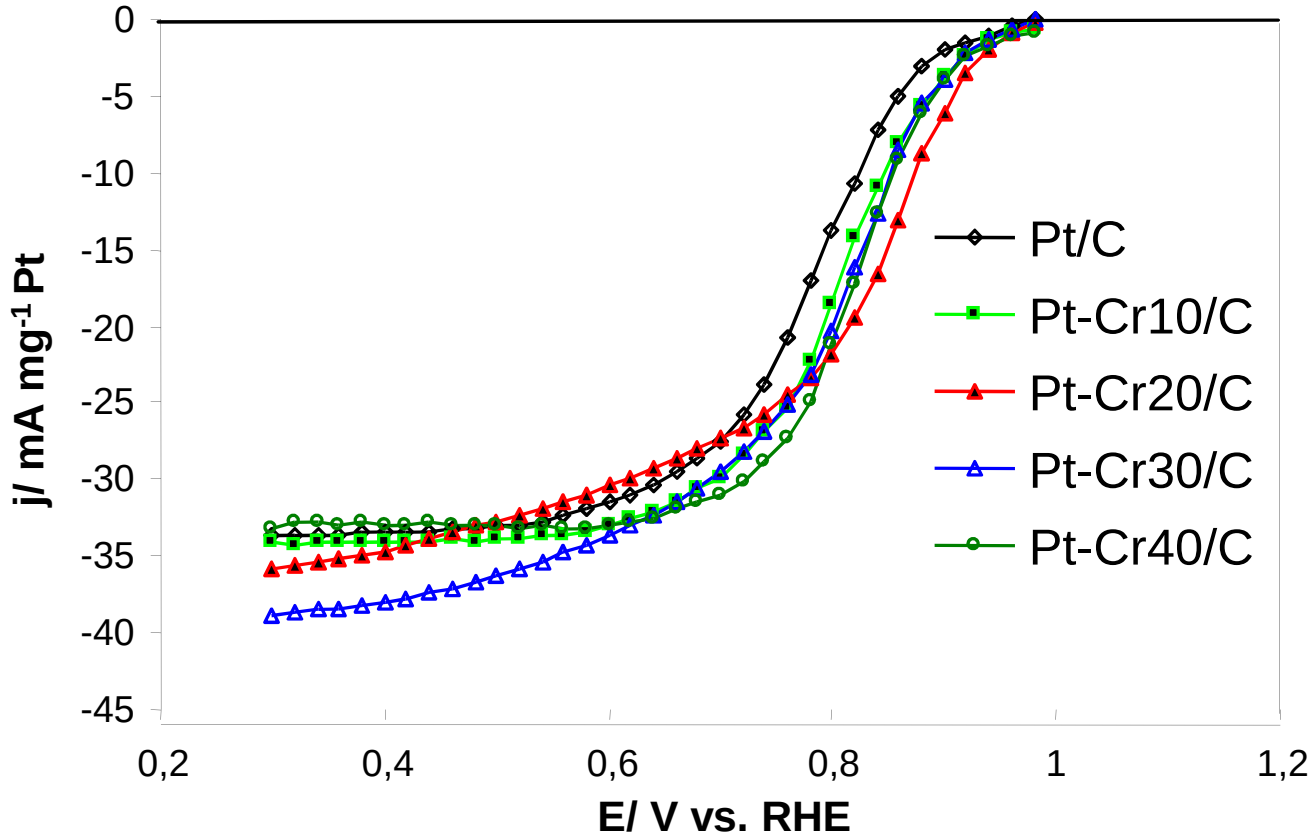
$$Pt - O_{ads} + H^+ + e^- \rightarrow Pt - OH_{ads}$$

$$2\ Pt - OH_{ads} + 2\ H^+ + 2\ e^- \rightarrow 2\ Pt + 2\ H_2O$$

Overall reaction : $O_2 + 4\ H^+ + 4\ e^- \rightarrow 2\ H_2O$

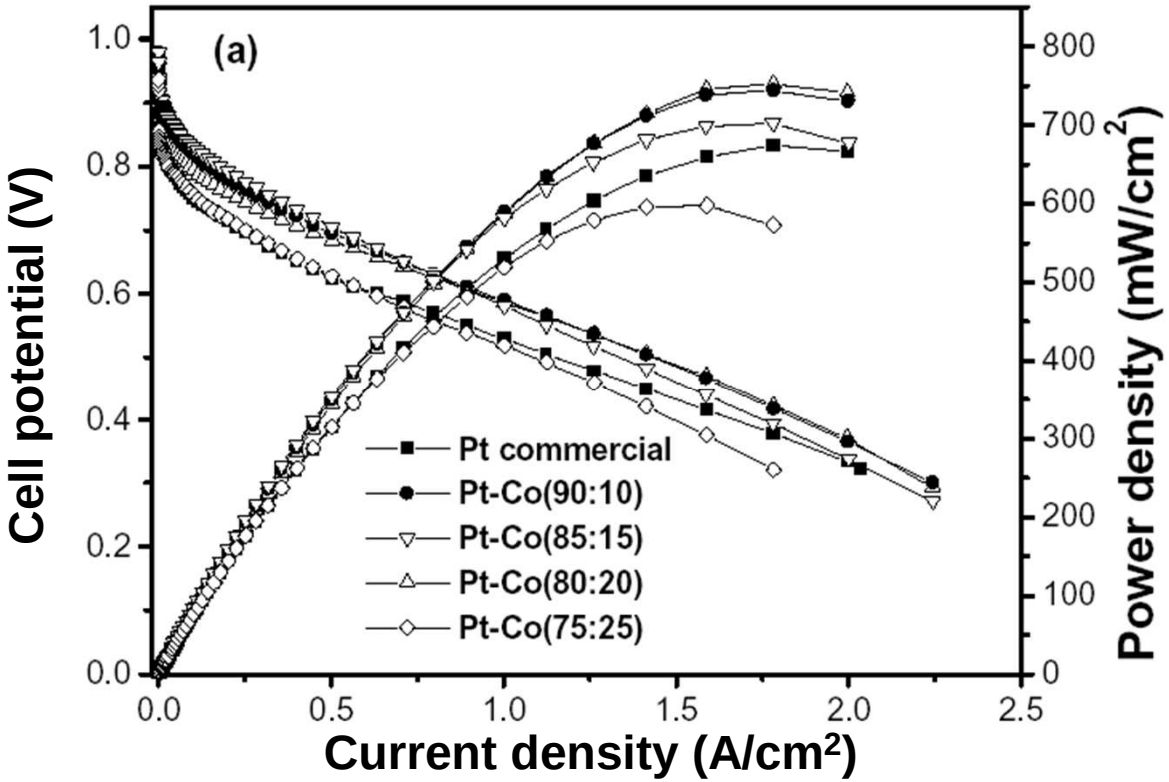
This complex 4-electron transfer reaction leads to high overvoltages ($|\eta| \approx 0.2$ to 0.6 V)

Mass Activity for Oxygen reduction ; effect of Cr composition
0.5 M H_2SO_4 ; T= 25°C ; v = 5 mV s^{-1} ; Ω = 2500 rpm.



After Hui Yang et al. J. Phys. Chem. B, 108(6), 1938, 2004.

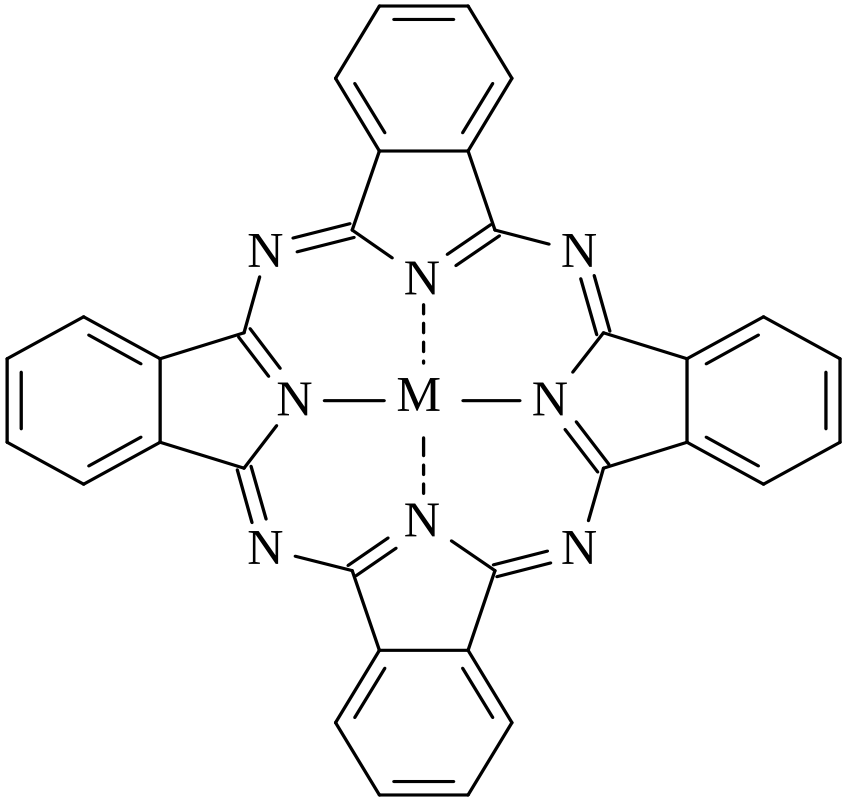
Effect of Pt alloying on the oxygen reduction overvoltage



Comparison of the performances of several Pt-Co alloys in a PEMFC single cell (alloys prepared by hydrogen reduction of cobalt hydroxide)

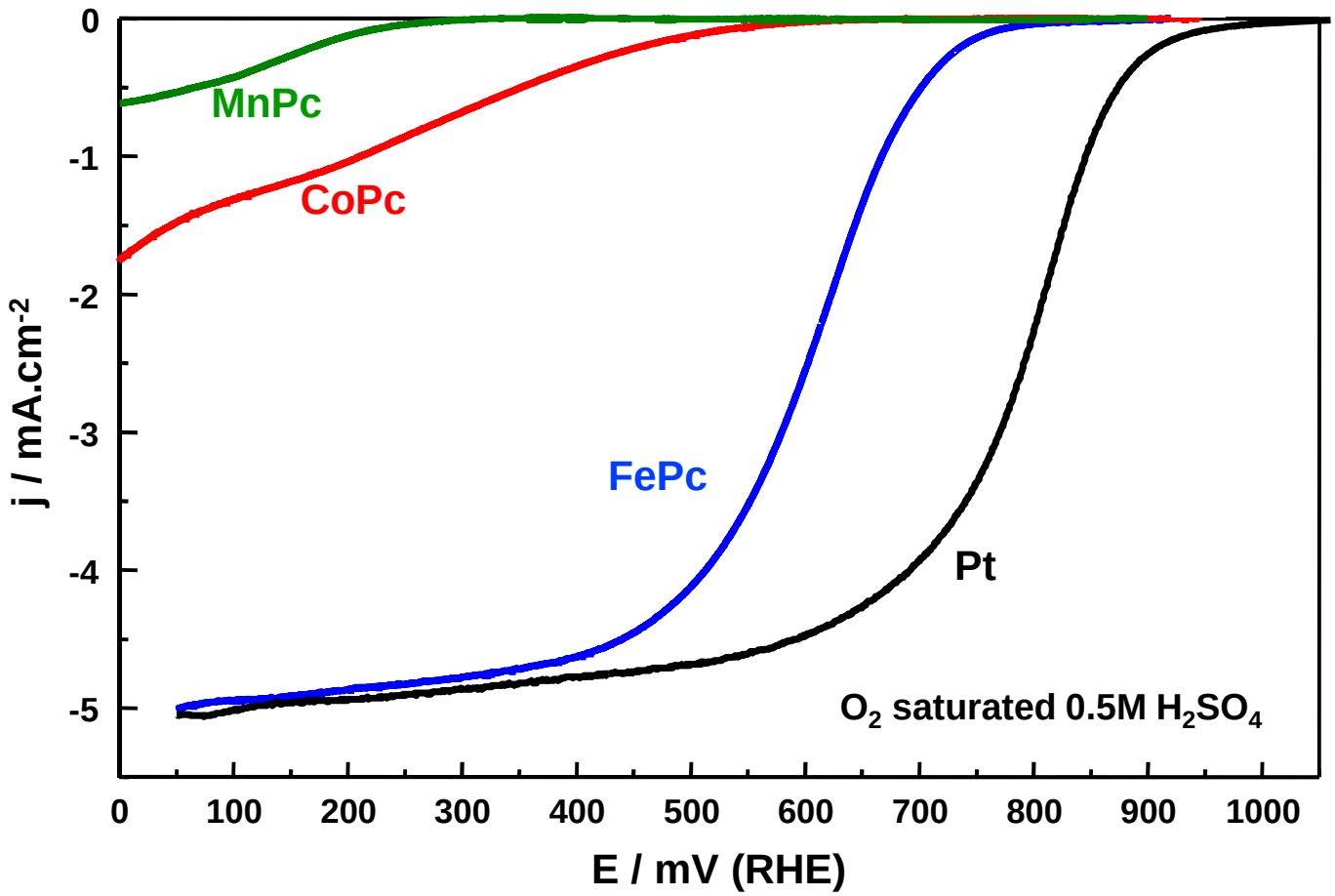
After Xiong et al., 204th ECS Meeting, Orlando, October 2003

Transition metal phthalocyanines (MPc) as Oxygen Reduction Catalysts

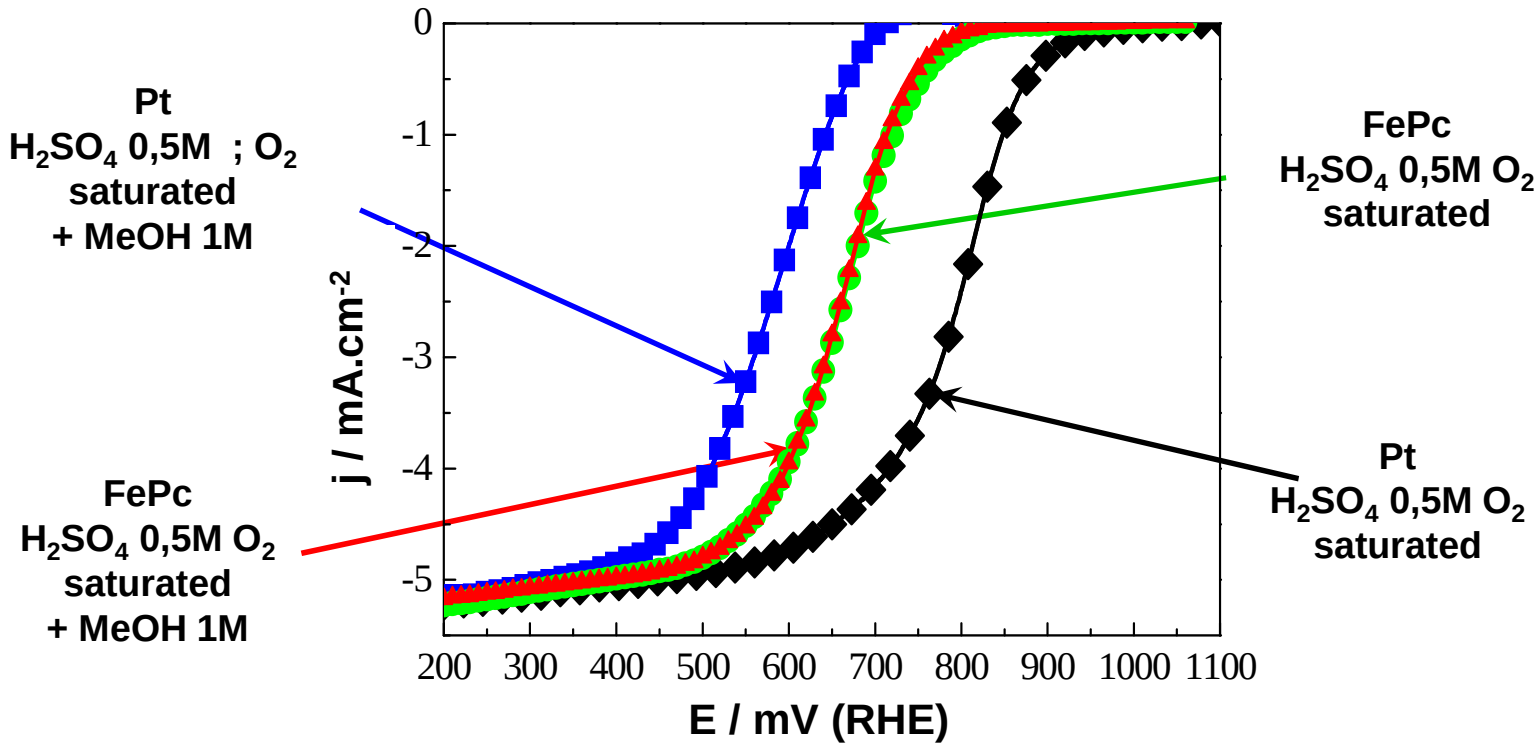


The catalytic active site for oxygen reduction is the central metal atom M (under its 2 oxidation states M^{2+} / M^{3+}) with M = Fe, Co, Ni, Mn, etc.

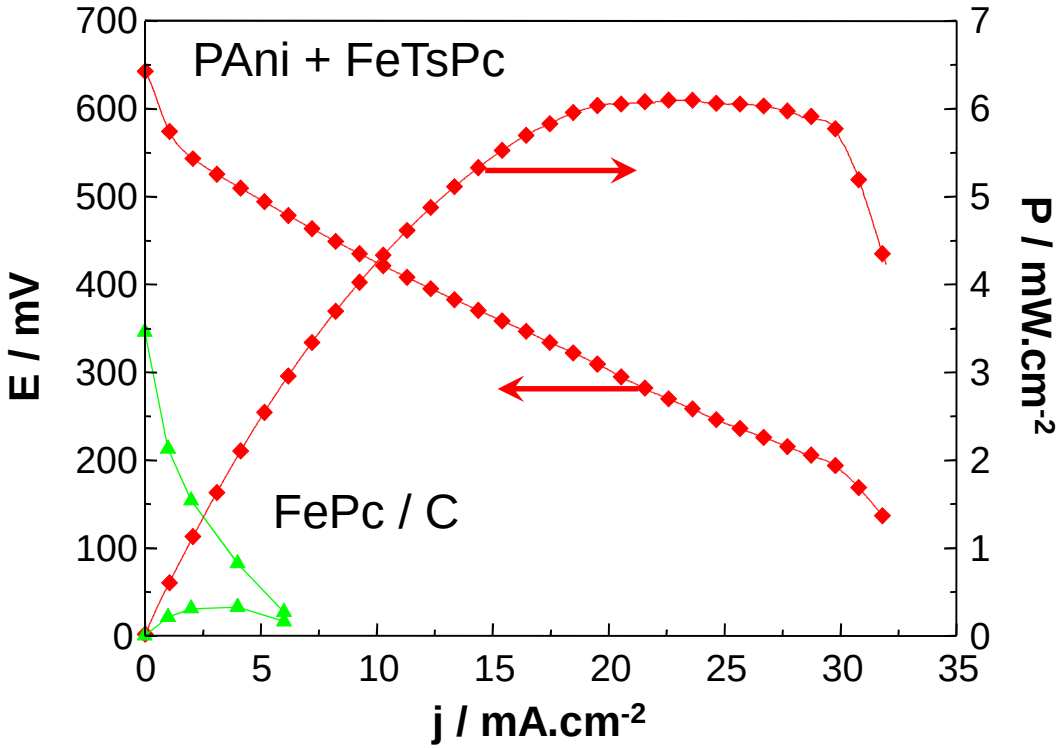
Oxygen reduction at metal phthalocyanine



Effect of methanol on oxygen reduction at metal phthalocyanine



Direct Methanol Fuel Cell with a FePc cathode



Anodes: PtRu/C E-Tek ; 5M MeOH ; room temperature

FePc / C (O_2) ⇨ P < 1 mW cm^{-2}

PAni + FeTsPc (O_2) ⇨ P = 6 mW cm^{-2}

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ACKNOWLEDGEMENTS

We acknowledge the support of different research agencies :

- ✪ CNRS, Institute of Chemical Sciences
- ✪ Agence de l'Environnement et de la Maîtrise de l'Energie ADEME/ AGRICE Programme),
- ✪ Ministry of Research (French Fuel Cell Network),

to which we are greatly indebted.

Thank you for your kind attention