In-situ electrochemical characterization of PEM Water Electrolysis electrodes

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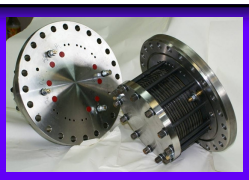
University of Paris - France

01st International Workshop on Durability and Degradation Issues in PEM Electrolysis Cells and its Components
Freiburg, Germany, March 11-12 2013

Outline



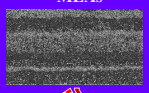
I- From materials to processes : challenges facing PEM WE

- Performance
- Durability
- Reliability
- Cost
- Scale-up

Some PEM WE specifications

Material science

MEAs



Mono cell

Stack

	State-of-art	Targets
Electrocatalysis		
Cathodic PGM (Pt) content (mg/cm²)	1.0-0.5	< 0.05
Anodic PGM (Ir, Ru) contents (mg/cm²)	1.0-2.0	< 0.1
Non PGM catalysts		
Solid Polymer Electrolyte		
SPE ionic conductivity (S/cm at 80°C)	0.17	0.20 – 0.30
SPE gas permeability to H_2 (cm²/s.Pa) (80°C, full humidity)	10^{-11}	10^{-9}
Operating conditions		
Operating current density	0 – 1 A.cm⁻²	0 – 4 A.cm⁻²
Operating temperature	80-90°C	100-120°C
Operating pressure	1-150 bars	1-700 bars
Efficiency		
Energy (kWh/kg H_2 at 80°C, 1 A.cm⁻²)	56	< 48
Enthalpic efficiency with PGM catalysts	80% at 1 A/cm²	80% at 2-4 A/cm²
Enthalpic efficiency with non-PGM cata	30-40% at 1 A/cm²	60% at 1 A/cm²
SPE Voltage drop (mV at 1 A/cm²)	118	70-100
System		
Production capacity of electrolysis units	10 kg/hour (≈ 100 Nm³/hour)	> 1000 kg/hour (≈ 10000 Nm³/hour)
Durability (hours)	10^4	> 10^5
Non-energy cost (€/kg H_2)	5	1

Process

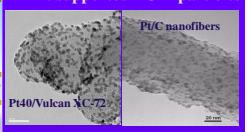
System

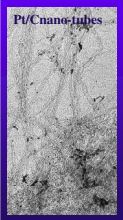
Scale-up ?

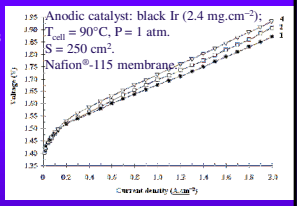
II- Catalysts, SPEs, MEAs, PEM cells and stacks, systems

Conventional PGM electrocatalysts

HER : supported PGM particles





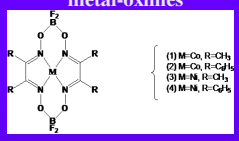


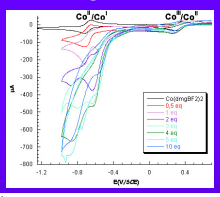
Unsupported PGM particles

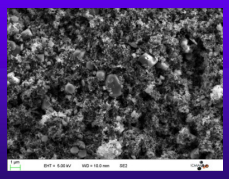
Magnetron sputtering

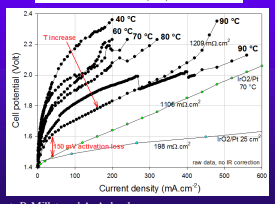
Non-PGM electrocatalysts

metal-oximes



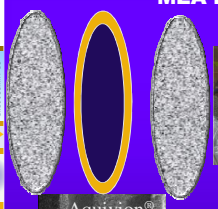


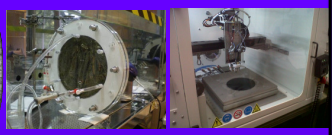




M-T. Dinh Nguyen, A. Ranjbari, L. Catala, F. Brisset, P. Millet and A. Aukauloo *Implementing Molecular Catalysts for Hydrogen Production in Proton Exchange Membrane Water Electrolysers*, Coord. Chem. Review, 256 (2012) 2435 – 2444

MEA manufacturing

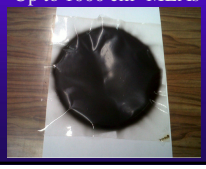




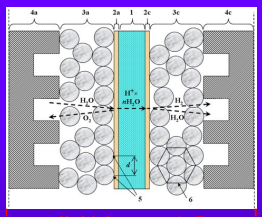
Wet process Dry process

Aquivion®

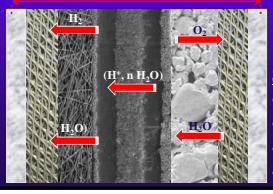
Up to 1000 cm² MEAs

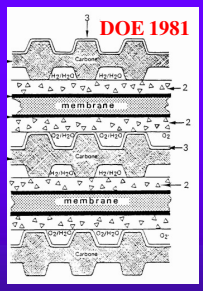


Some cell designs



cell thickness = 4- 7 mm





Some criteria for cell design
- compacity
- reduced ohmic losses
- ease of assembly
- brittleness of cell components

III- Main Electrochemical Investigation Tools & Techniques

- measurement of polarisation curves
- cyclic voltametry
- electrochemical impedance spectroscopy (EIS)
- durability tests

Typical electrochemical equipment

Lab potentiostat

Potentiostat + scanner

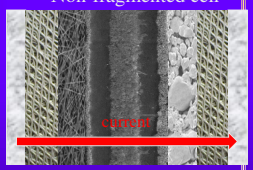
ATEX test plateform

Power potentiostat

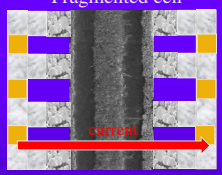
Multi potentiostat

Global versus local measurements

Non-fragmented cell



Fragmented cell

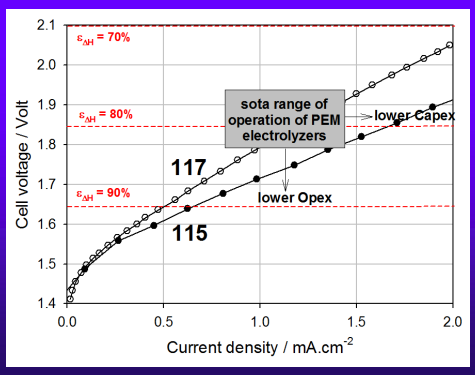


Needs of non-intrusive techniques for :
- MEA and cell characterization & optimization
- production monitoring & quality control
- on-site diagnostic
- maintenance operations

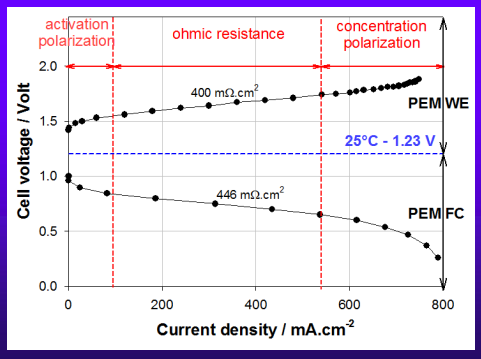
IV- Polarization curves

- a measure of cell efficiency
- information on MEA environment

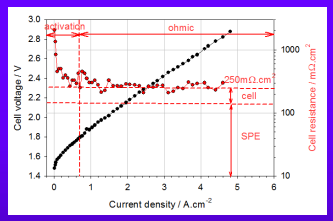
Performances



Distinct regions of polarization curves

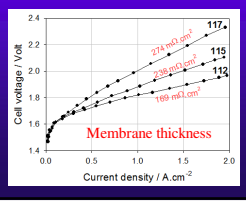


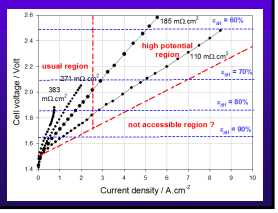
Cell resistance



Polarisation curve

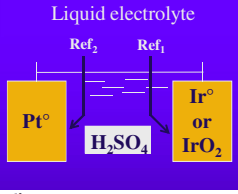
First order derivative ≡ LF cell resistance



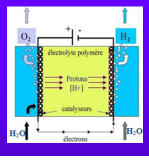


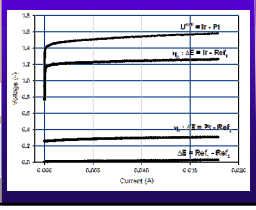
Cell constituents with liquid electrolyte (the problem of the reference electrode)

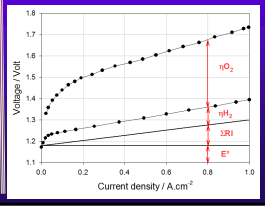
Liquid electrolyte



Polymer electrolyte

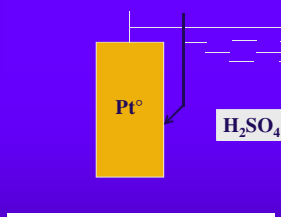


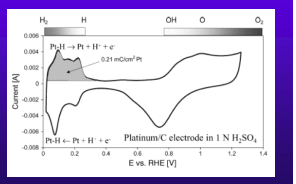


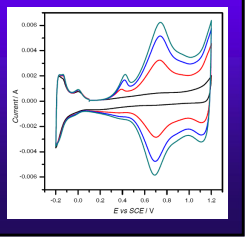


V- Cyclic voltametry

Liquid water electrolysis cell



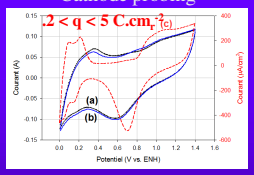




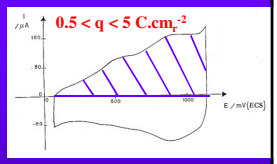
Electrode / polymer electrolyte interfaces

Charge density is function of (i) roughness; (ii) scan rate

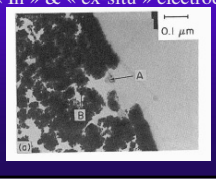
Cathode probing



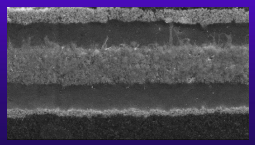
Anode probing



« In » & « ex-situ » electrodes

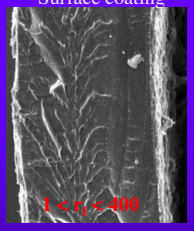


« Ex-situ » electrodes

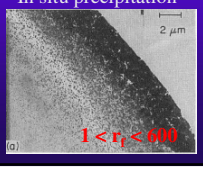


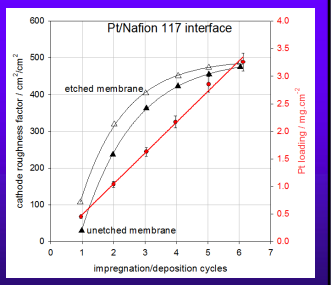
Roughness factors of interfaces

Surface coating

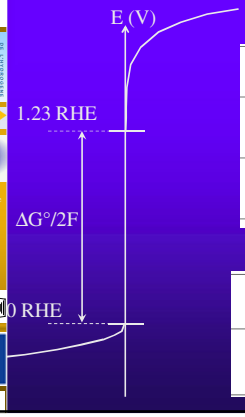


In situ precipitation





Interfacial kinetics: are all sites active ?



OER

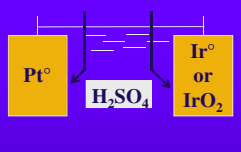
Electrode	$\frac{\partial \eta_{anodic}}{\partial \log j}$ (mV)	Measured j_0^a (A cm^{-2}) (geometrical area)	Roughness Factor (cm^2/cm^2)
Pt			
25 °C	110	1 x 10^{-7}	200
80 °C	130	2 x 10^{-5}	200
Pt-Ir			
25 °C	110	2 x 10^{-4}	200
80°C	130	6 x 10^{-3}	200

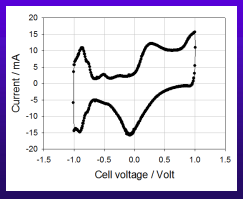
HER

Electrode	$\frac{\partial \eta_{cathodic}}{\partial \log j}$ (mV)	Measured j_0^c (A cm^{-2}) (geometrical area)	Roughness Factor (cm^2/cm^2)
Pt			
25 °C	125	0.17	200
80 °C	105	0.14	200

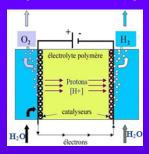
CVs without Reference Electrode

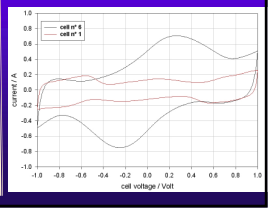
Liquid electrolyte





Polymer electrolyte

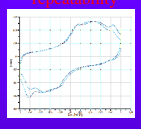


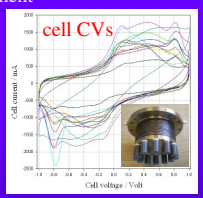


Charge density measurements

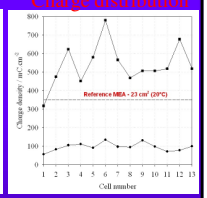
- easy to implement
- non-intrusive

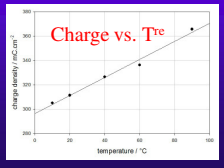
repeatability

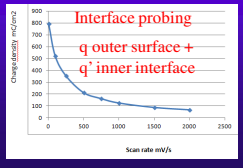




Charge distribution

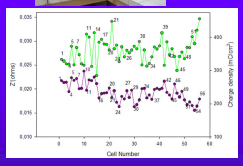


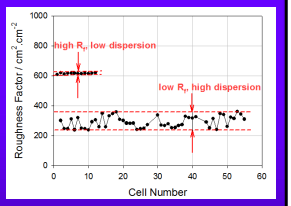


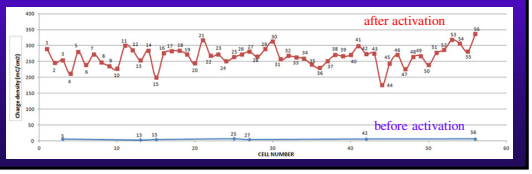


T^{re} + dissolved species change charge densities.

Optimization of charge density distribution

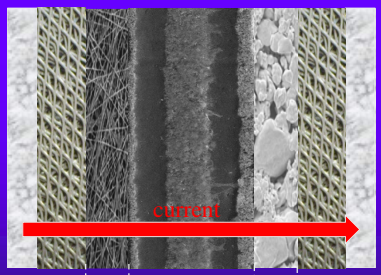


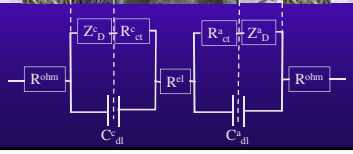




VI- Electrochemical Impedance Spectroscopy (EIS)

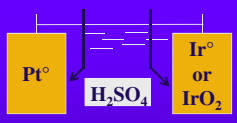
EIS measurements



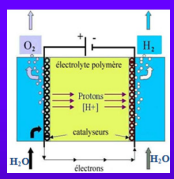


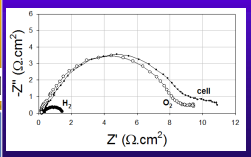
Single cell impedance

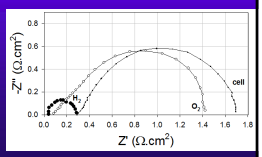
Liquid electrolyte



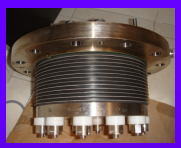
Polymer electrolyte

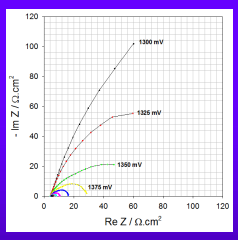




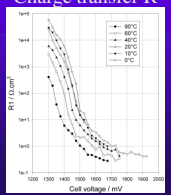


Stack characterization : Z distribution

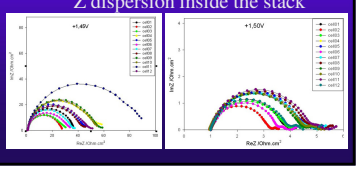




Charge transfer R

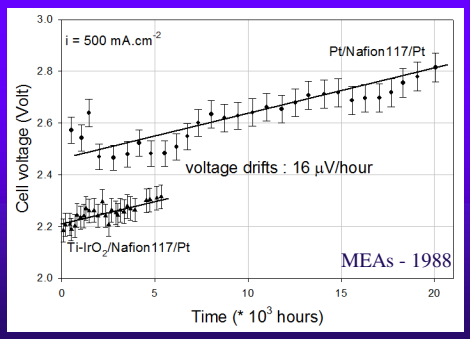


Z dispersion inside the stack



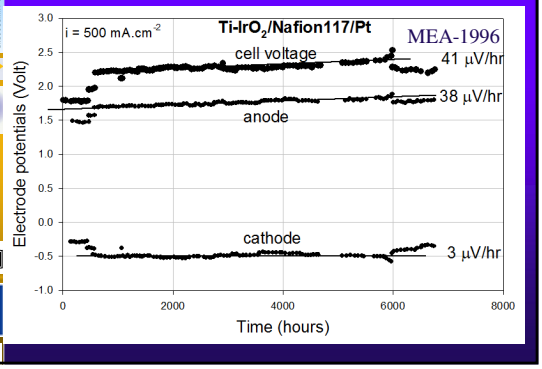
VII- Durability tests

MEA durability measurements

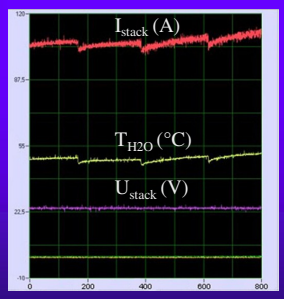


Electrodes durability measurements

(internal reference; half SPE resistance on each electrode)



Stack durability measurements



VIII- Degradation processes

Need for :

- Process monitoring
- On-site diagnostic
- Maintenance

Some cell degradation processes

Reversible processes

observation

- activity losses
- increasing SPE resistivity

causes

- SPE poisoning
- cathode poisoning

solutions

- maintenance
- MEA treatment

Irreversible processes

observation

- performance degradation
- increasing gas cross-permeation
- explosions, combustion

causes

- activity losses (r_f decrease)
- membrane thinning
- rising parasite ohmic losses
- SPE perforation

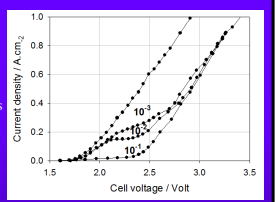
solutions

- component replacement

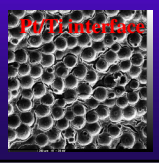
Example 1 : SPE and cathode poisoning

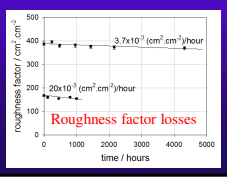
SPE in contact with deionized water circulating in SS pipes

≈ 24% SPE sites occupied by Fe^{3+} species
≈ 3% SPE sites occupied by Ni^{2+} species
≈ 1% SPE sites occupied by Cr^{3+} species



Example 2 : activity losses





Conclusions & perspectives

Main limitations of PEM water electrolysis

- cost (capex)
- durability
- scale-up

Some improvement targets

- reduced PGM contents and non-PGM catalysts
- operation at higher current densities
- better performances at higher current densities (opex)
- stationary and cycling operating conditions
- improved durability ($\rightarrow 10^4 - 10^5$ hr)
- scale-up ($\rightarrow 10^2$ - 10^3 Nm^3 H_2 / hr)

Durability : elements for accelerated stress test protocols

- load profiles combining i, T, τ
- ageing : i, T cycles

Thanks to …

M.-F. Charlot — DFT
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European R&D projects : GenHyPEM, ReversPEM

Thank you for your attention !