2nd International Workshop on Durability and Degradation Issues in PEM Electrolysis Cells and its Components
Freiburg, Germany, February 16-17 2016

ANALYSIS OF DEGRADATION PROCESSES IN PEM WATER ELECTROLYSIS CELLS

P. Millet
University Paris-Sud / University Paris-Saclay
Team of Research and Innovation in Electrochemistry for Energy

Outline

1- Fundamentals of water splitting

- thermodynamics versus kinetics
- water splitting technologies

2- Operating constraints imposed by energy markets

- power grid requirements

3- The ideal PEM cell

- design & main characteristics
- model equations

4- The real PEM cell

- origin of cell irreversibility
- cell operation modes

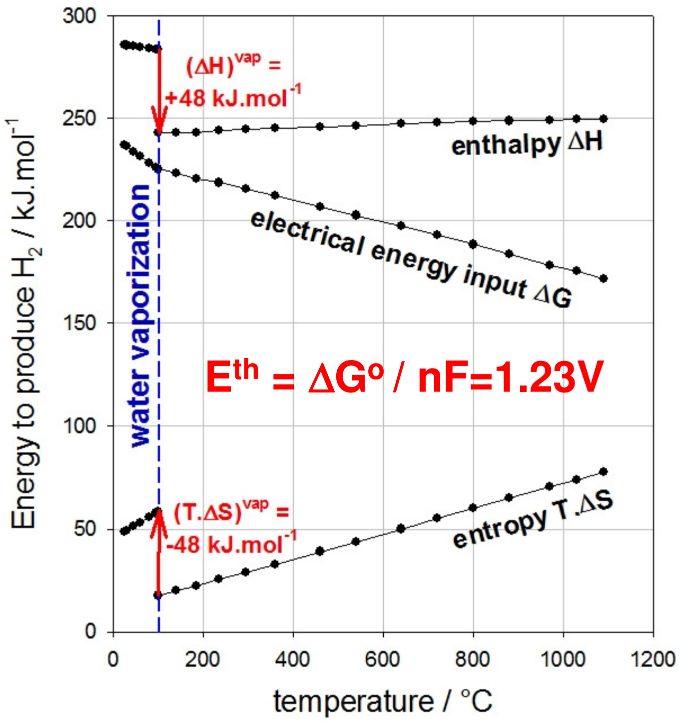
5- Conclusions : working group on test harmonization

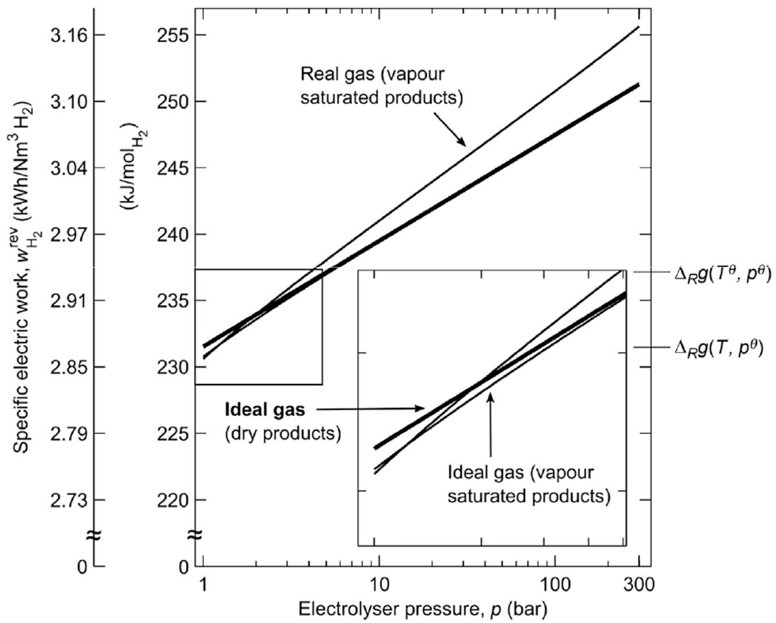
1- Fundamentals of water splitting

Main thermodynamic features

$H_2O\ (l) \rightarrow H_2\ (g) + ½\ O_2\ (g)$

$\Delta H^o = +285$ kJ/mol $\Delta G^o = +237$ kJ/mol
$\Delta S^o = +163$ J/mol/K; $T^o.\ \Delta S^o = 48$ kJ/mol





- **Water splitting is endergonic**
- **Thermo-dissociation occurs at T > 2500°C**
- **Energy requirement is constant ∀ (T,P)**

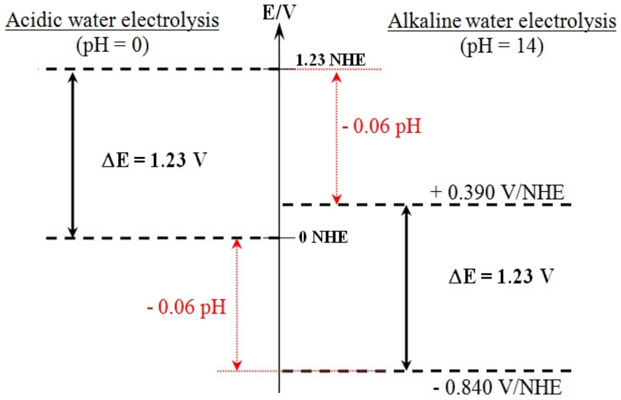
=> thermoneutral voltage constant ∀ (T,P)

- **higher T means more heat and less W^{el}**
- **higher P means less heat and more W^{el}**
- **extra W^{el} at 100 bars ≈ 6%**

P. Millet in : 'Water Electrolysis', chapter 2, *Fundamentals of water electrolysis*, A. Godula-Jopek Editor, Wiley-VCH, ISBN 9783527333424 (**2014**)

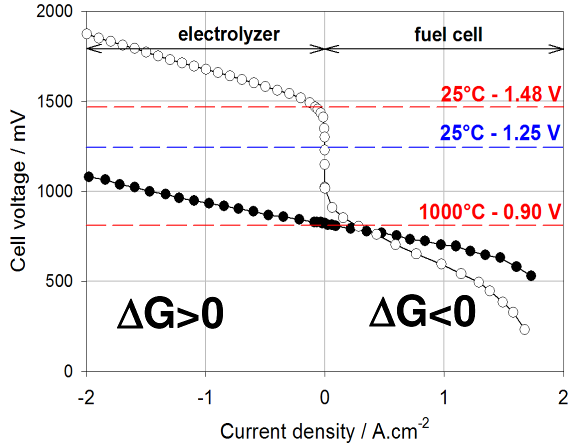
Role of (T, pH): different technologies

role of electrolyte pH

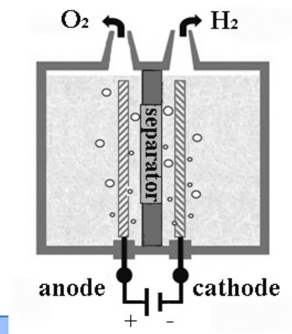


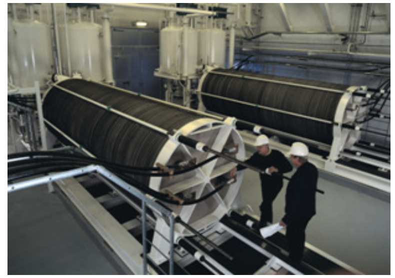
$E^{+} \approx 1.23 - 0.06\,pH$ $\quad E^{-} \approx -0.06\,pH$

role of operating temperature

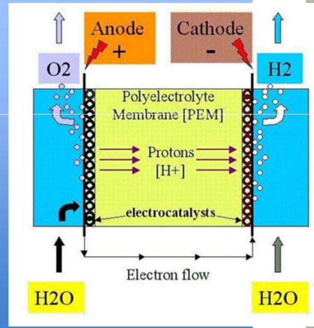


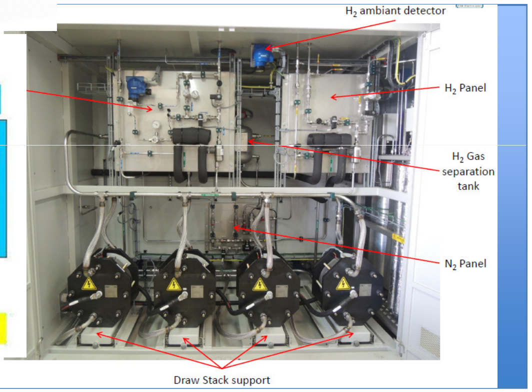
alkaline process



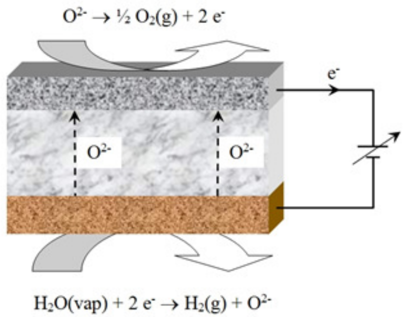


acidic process (PEM)





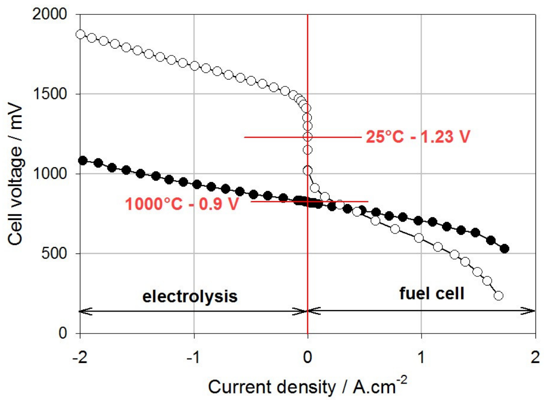
high temperature process



P. Millet, 'Electrochemical Technologies for Energy Storage and Conversion', chapter 9, *Water electrolysis for hydrogen generation*
R-S. Liu, X. Sun, H. Liu, L. Zhang and J. Zhang Editors, J. Wiley & Sons (**2011**).

Kinetics of the water splitting reaction

role of operating temperature on cell reversibility



Cathode: HER

$(-)\ H^{+} + 1e^{-} \rightarrow ½\ H_2$

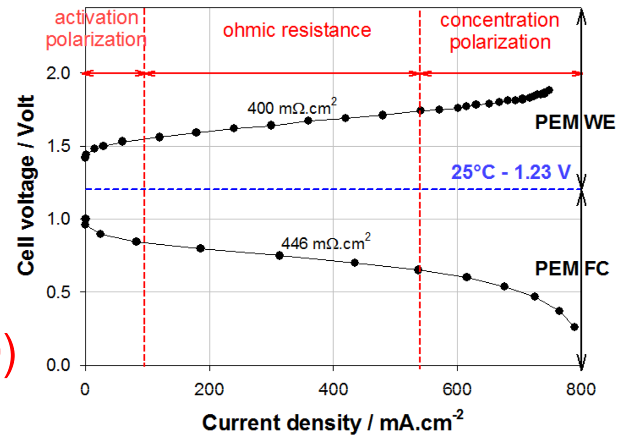
$i_0 = 1\ mA.cm^{-2}$ (Pt, pH=0)

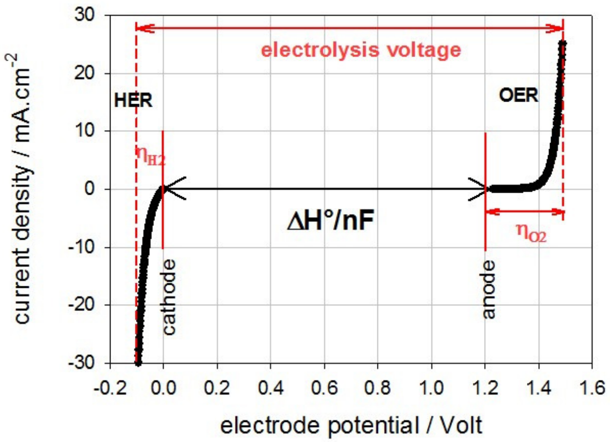
Anode: OER

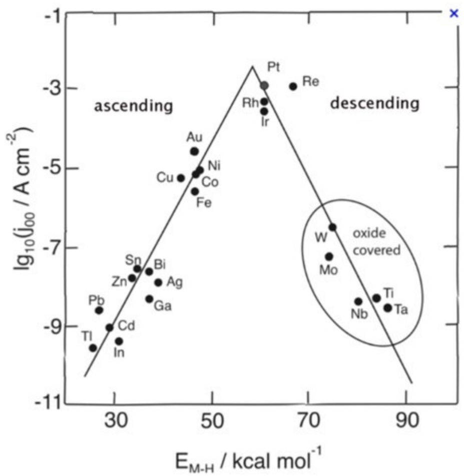
$(+)\ H_2O \rightarrow 2H^{+} + 2e^{-} + O_2$

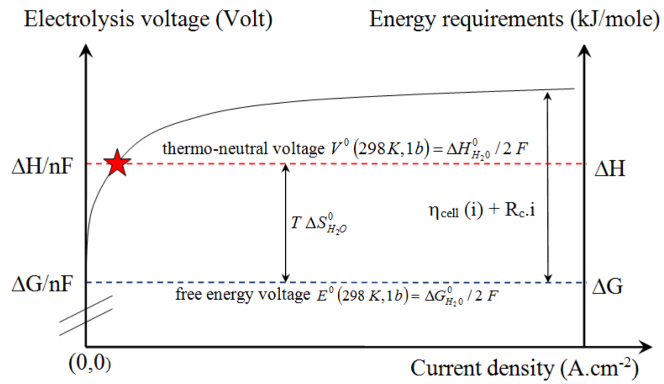
$i_0 = 10^{-3}\ mA.cm^{-2}$ (IrO_2, pH=0)

Reversibility of PEM cells





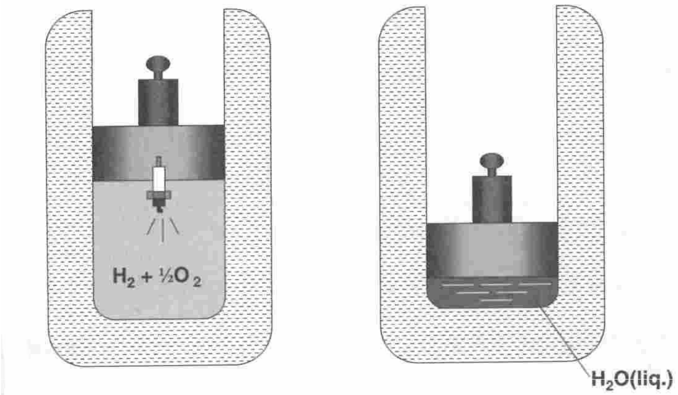


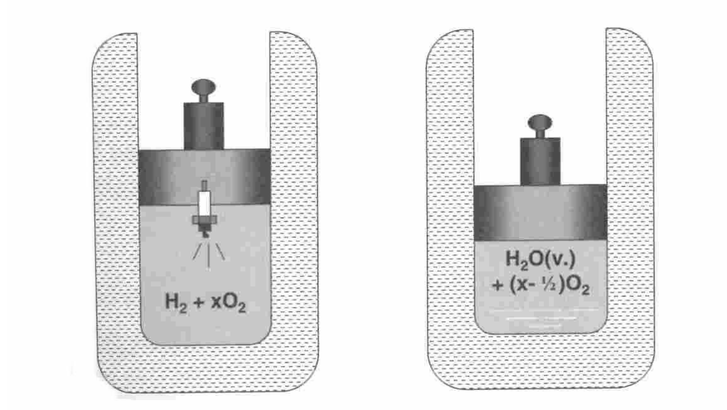


P. Millet In : 'PEM water Electrolysis for hydrogen production: Principles and Applications', chapter 10, *PEM electrolyzer characterization tools*, D. Bessarabov, H. Wand, H. Li, N. Zhao, CRC Press (**2015**)

Efficiency of the water splitting reaction

First issue : HHV or LHV ?





Experiment 1 : $H_2(g) + ½\ O_2(g) \rightarrow H_2O(liq)$

Heat recovered: $\Delta H = -286{,}02\ kJ.mol^{-1}$
(HHV or higher heating value)

Experiment 2 : $H_2(g) + ½\ O_2(g) \rightarrow H_2O(gaz)$

Heat recovered : $\Delta H = -241{,}02\ kJ.mol^{-1}$
(LHV or lower heating value)

Δ = 45 kJ/mol; heat of water vaporization (**25C**)

Second issue : ΔG(T,P,i) or ΔH(T,P,i) ?

Energy efficiency @ i

$$\varepsilon_{\Delta G}(T,P,j) = \frac{E(T,P)}{U_{cell}(T,P,j)} \qquad \varepsilon_{\Delta H}(T,P,j) = \frac{V(T,P)}{U_{cell}(T,P,j)}$$

Third issue : cross-permeation

Faraday efficiency

$$(\varepsilon_F)^{anodic} = F\ (dn_{O2}/dt)\ /\ i * 100$$
$$(\varepsilon_F)^{cathodic} = F\ (dn_{H2}/dt)\ /\ i * 100$$

2- Operating constraints imposed by energy markets

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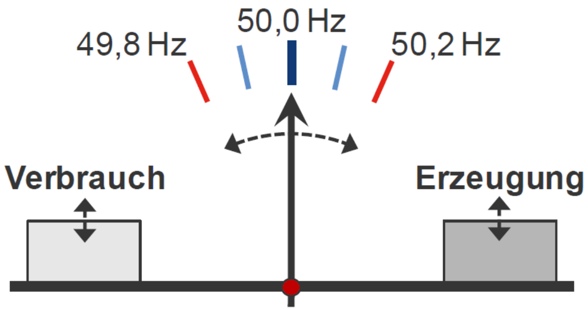
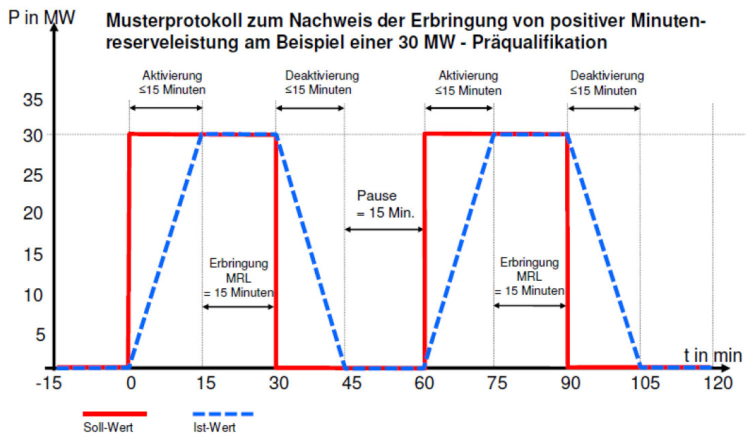
Power grid requirements

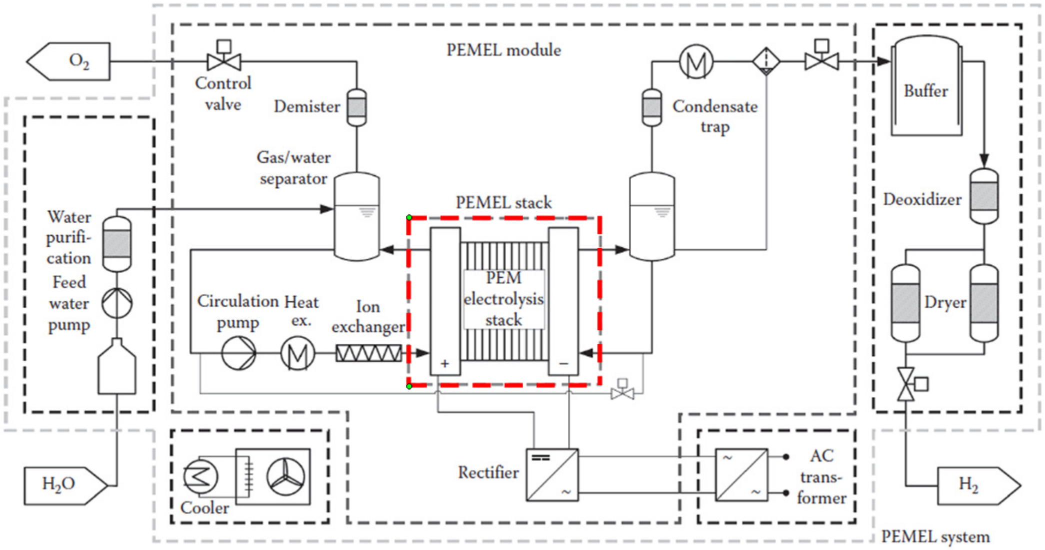
preserve the frequency set point of 50.0 Hz



power grid requirements



(source: www.regelleistung.net)



need to customize PEM @ system level to catch cheap kWh for automotive H_2

flexible/reactive design

Source: *PEM water Electrolysis for hydrogen production: Principles and Applications*, D. Bessarabov, H. Wand, H. Li, N. Zhao, CRC Press (**2015**).

PEM KPI

Target values of key performance indicators
for future PEM water electrolysis systems

		State-of-the-art	2017	2020	2023	
KPI 1	H2 production electrolysis, energy consumption (kWh/kg) @ rated power	57-60 @100kg/d	55@500kg/d	52 @1000+kg/d	50 @1000+kg/d	Efficiency
KPI 2	H2 production electrolysis, flexibility with a degradation < 2% year (refer to KPI 3)	5% - 100% of nominal power	5% - 150% of nominal power	0% - 200% of nominal power	0% - 300% of nominal power	Flexibility
KPI 3	H2 production electrolysis, hot start from min to max power (refer to KPI 4)	1 minute	10 sec	2 sec	< 1 sec	Reactivity
KPI 4	H2 production electrolysis, efficiency degradation @ rated power and considering 8000 H operations / year	2% - 4% / year	2% / year	1,5% / year	<1% / year	Durability
KPI 5	H2 concentration in oxygen @ rated stationary power load	< 25% ILE	< 25% ILE + flexibility	< 25% ILE + reactivity		Safety
KPI 6	H2 production electrolysis, CAPEX @ rated power including ancillary equipements and comissioning	8.0 M€/(t/d)	3.7 M€/(t/d)	2.0 M€/(t/d)	1.5 M€/(t/d)	Capex/Opex

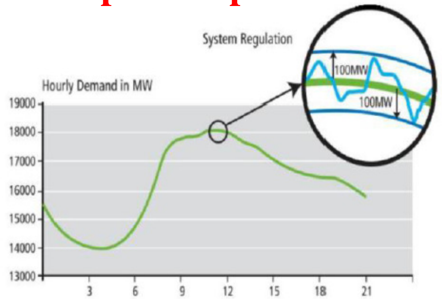
KPI : Key Performance Indicators

FCH-JU Call 2016 : *FCH-02-1-2016: Establish testing protocols for electrolysers performing electricity grid services*

http://www.fch.europa.eu/

Power-to-H_2: FlexiPEM

Load profile specification



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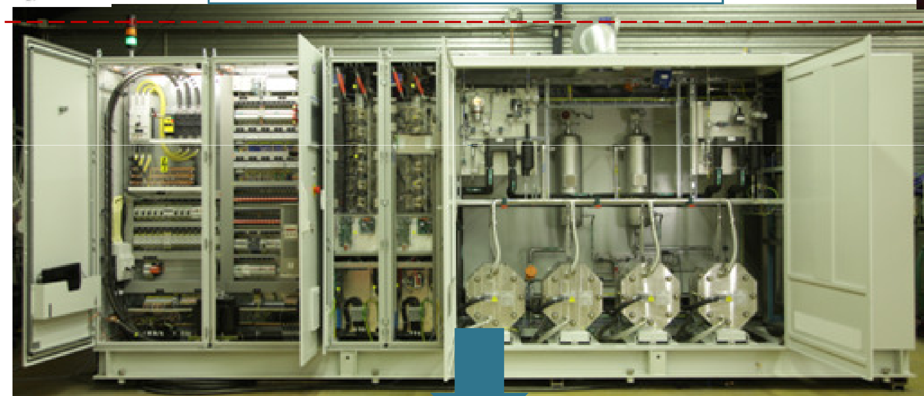
PEM electrolyzer @ system level

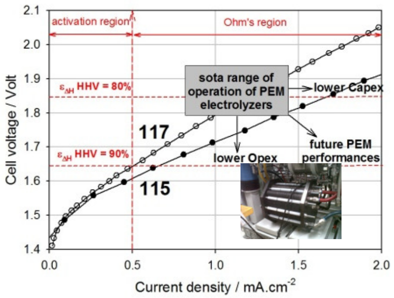
Definition of test protocol



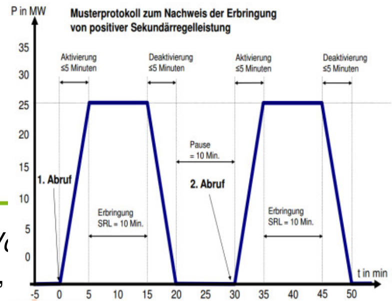
(source: ArévaH2Gen)

Data analysis - modeling

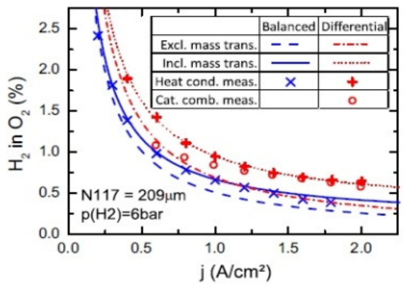
KPI1: efficiency



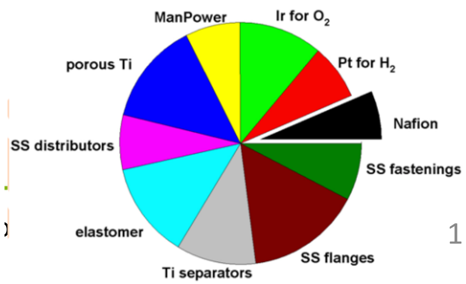
KPI2-3: flexibiliy/reactivity



KPI5: safety aspects



KPI6-7: Capex/Opex

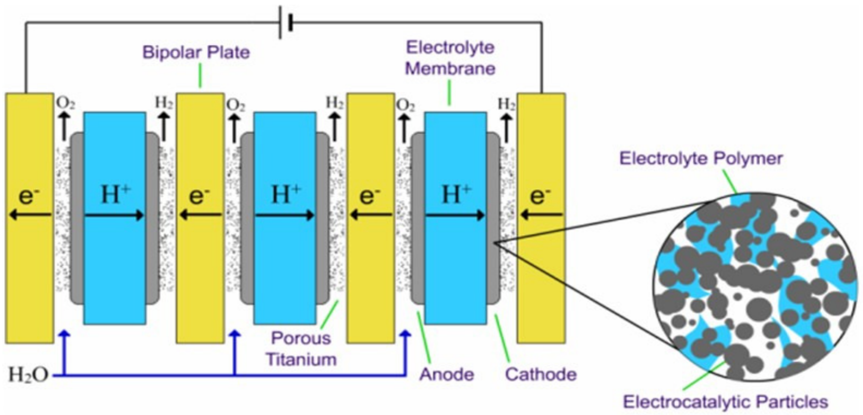


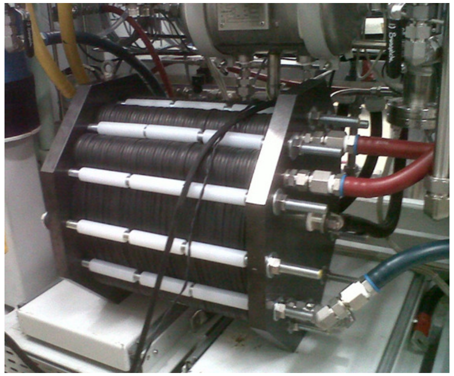
3- The ideal PEM cell

Definition

The ideal PEM cell is a PEM cell that:

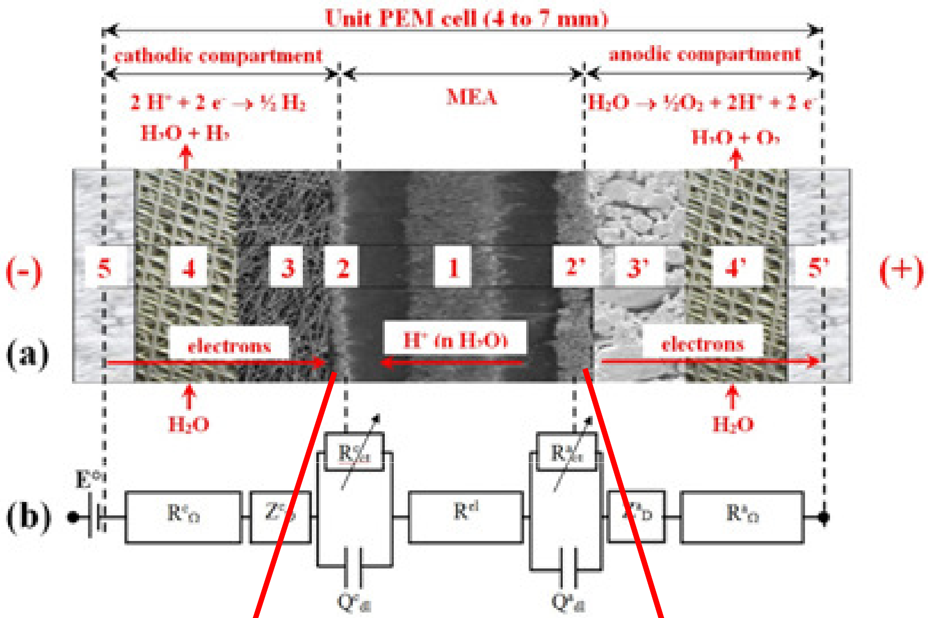
- presents high efficiency (80% @ 1 A.cm^{-2} in soa) and high gas purity @ 50-60 bars
- maintains this high level of efficiency indefinitely
- can operate efficiently under transient power loads, no impact on gas purity
- is scalable in size without significant impact on efficiency and durability
- can be stacked up to several hundred cells without significant impact on efficiency and durability

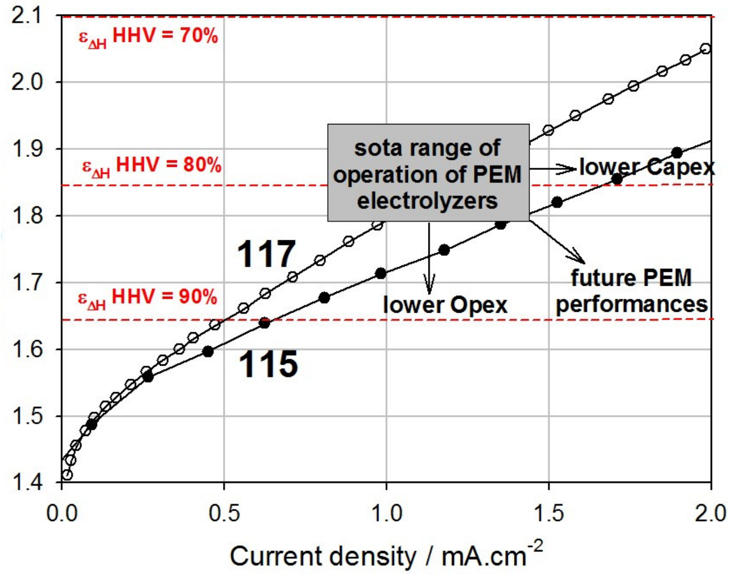




(source: ArévaH2Gen)

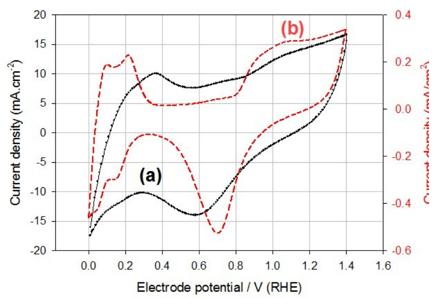
The PEM cell and its electrical equivalent circuit

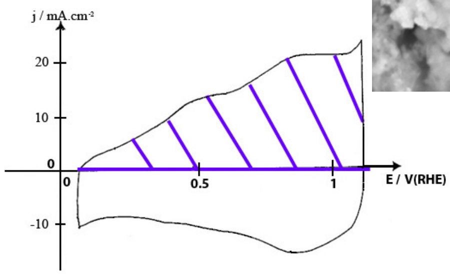


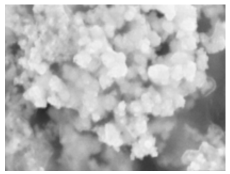


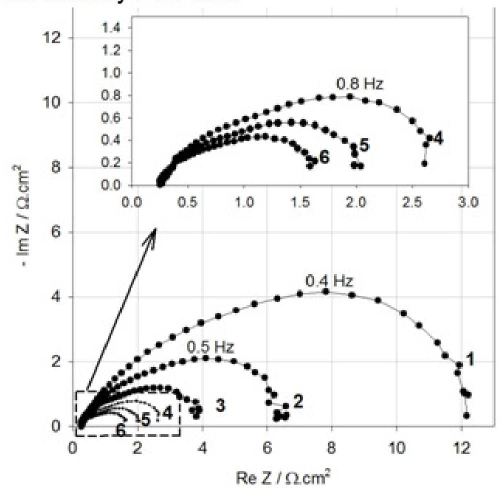
HER: Pt

OER: IrO_2







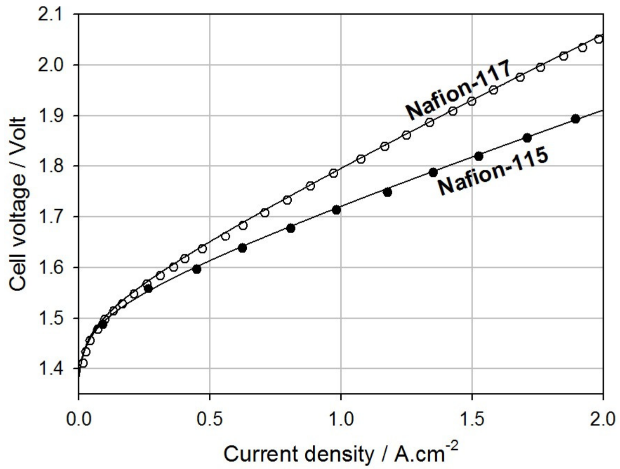


C. Rozain, P. Millet, *Electrochemical characterization of Polymer Electrolyte Membrane Water Electrolysis Cells,* Electrochimica Acta, 131 (**2014**) 160-167.

Model equations and best fits

Current-voltage relationship

$$U_{cell}(T,P) = V_{T,P} + i\sum_{k=1}^{n} R_k + \eta_{H2}\, i + \eta_{O2}\, i$$



OER and HER overvoltages

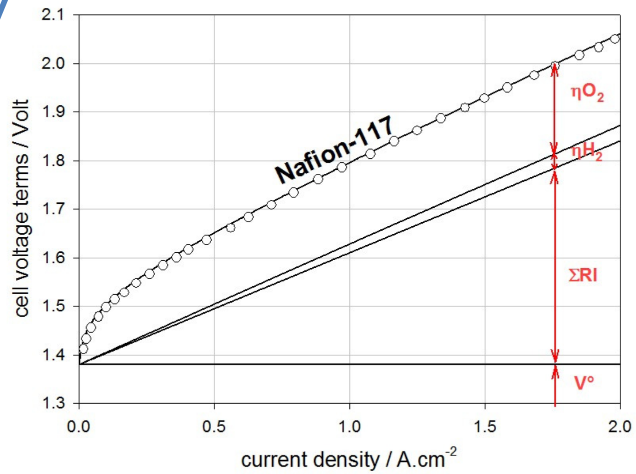
$$\eta_{O2} \approx \frac{R_{PG}\, T}{\overleftarrow{\alpha}_a\, F} Ln\left(\frac{i^a}{i_0^a\, r_f^a}\right) \qquad \eta_{H2} \approx \frac{R_{PG}\, T}{\overrightarrow{\alpha}_c\, F} Ln\left(\frac{-i^c}{i_0^c\, r_f^c}\right)$$

temperature

mechanism

catalyst

roughness



	$R_{cell} = \sum_{k=1}^{n} R_k$ (mΩ.cm²)	i_0^a ($A.cm^{-2}$)	r_f^a (adim)	i_0^c ($A.cm^{-2}$)	r_f^c (adim)
Curve 1	230	5×10^{-6}	800	1×10^{-3}	800
Curve 2	155	5×10^{-6}	800	1×10^{-3}	800

Table 11.1: parameters of Eq. (11.5) used to fit experimental polarization curves of figure 11.6.
T = 80°C; $\beta^a = \beta^c = 0.5$.

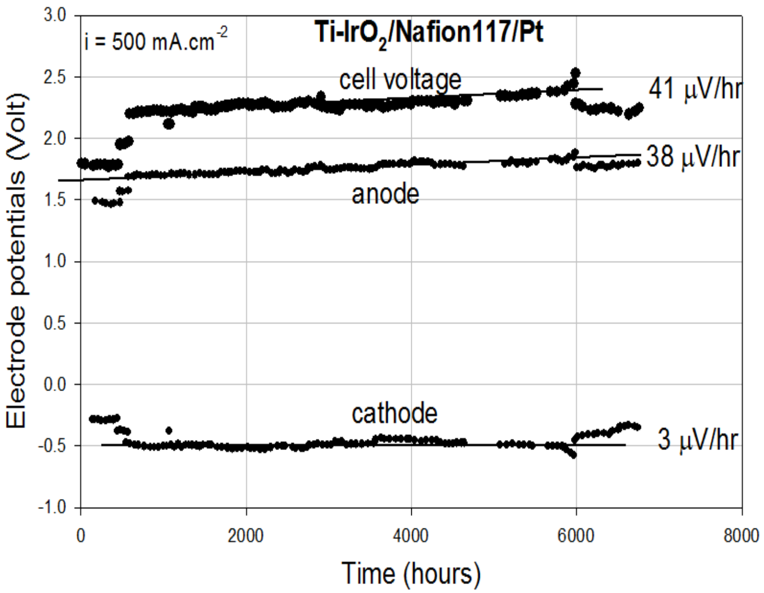
C. Rozain, P. Millet, *Electrochemical characterization of Polymer Electrolyte Membrane Water Electrolysis Cells,* Electrochimica Acta, 131 (**2014**) 160-167.

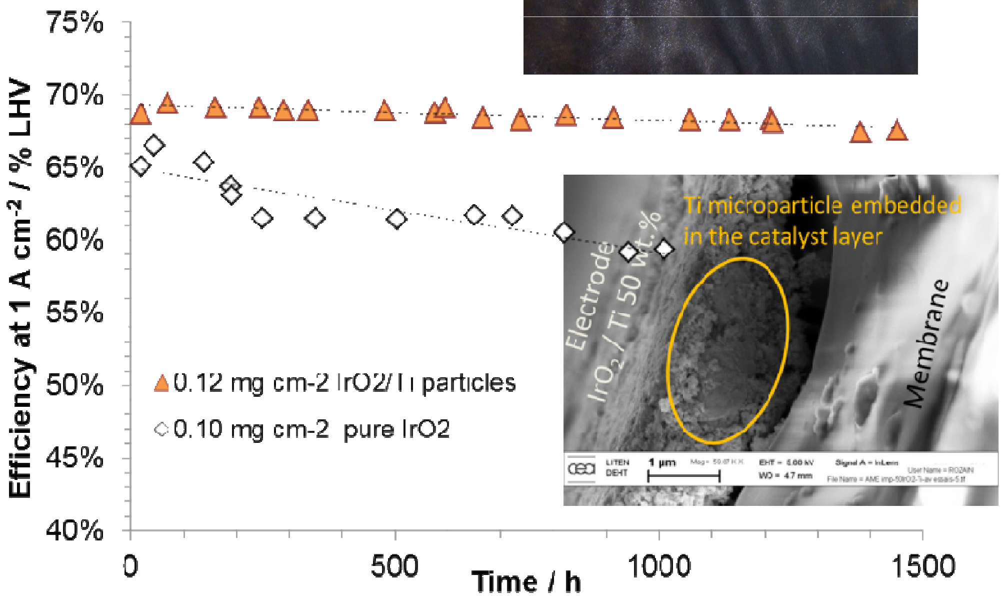
4- The real PEM cell

Global picture

The real PEM cell is a PEM cell that:

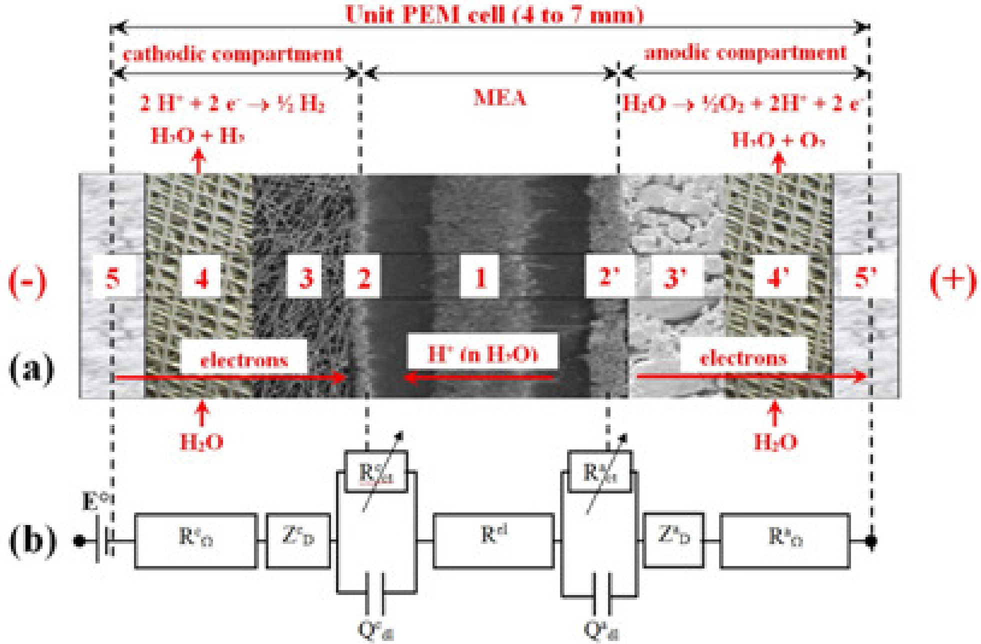
- operates at 1.0-2.5 A.cm^{-2}
- presents initial (BoL) high efficiency
- sees its performances degraded during operation
- state of art in the field is ≈5-10 µV/hr at 1 A.cm^{-2}; this is equivalen
to a cell voltage increase of ≈ 100-200 mV after 20,000 hrs of opera
- S ≈ 1,000 cm^{2}, 100 cells/stack





Transient operating conditions may accelerate cell ageing & raise safety issues

Cell components

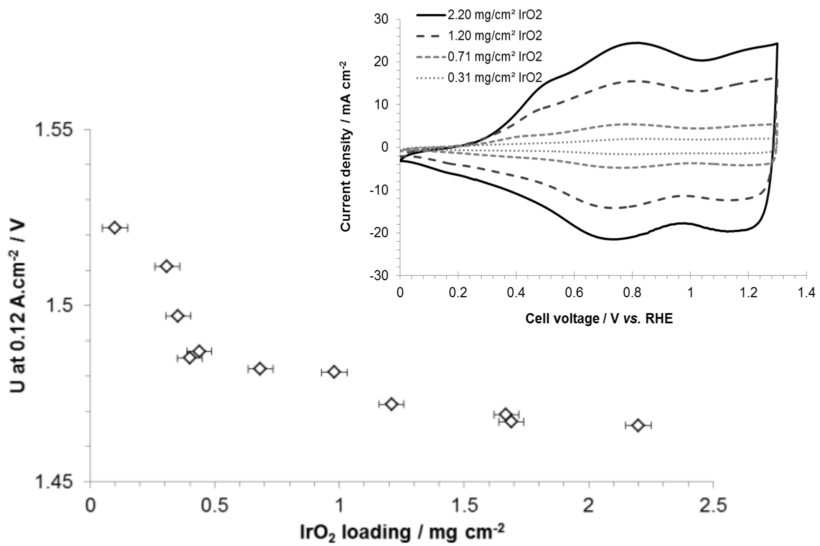


Cell components

- solid polymer
- catalytic layers
- current distributors
- bipolar plates
- gaskets

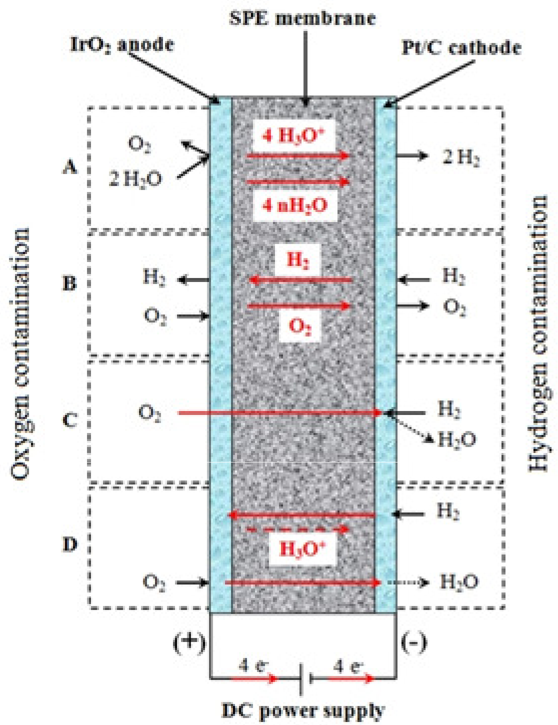
Current-voltage relationship

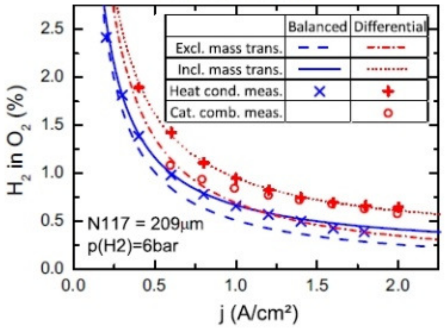
$$U_{cell}(T,P) = V_{T,P} + i\sum_{k=1}^{n} R_k + \eta_{H2}\, i + \eta_{O2}\, i$$

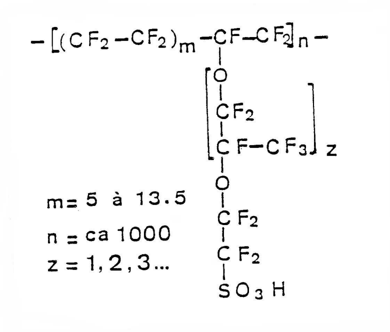


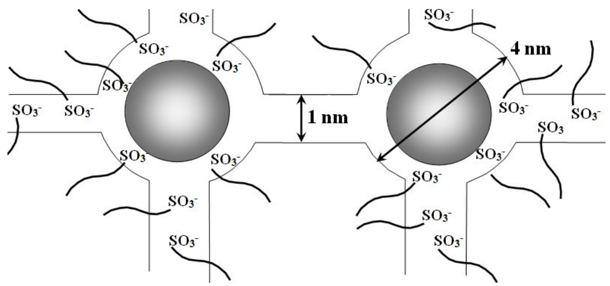
C. Rozain, E. Mayousse, N. Guillet, P. Millet, *Influence of iridium oxide loadings on the performance of PEM water electrolysis cells: Part I – Pure IrO_2-based anodes,* J. Appl. Catalysis B: Environmental, 182 (**2016**) 153 - 160.

Ex. 1: Solid polymer electrolyte









Stress factors
- anode potential
- thermal cycling + swelling
- rest potential
- need for AST ?

Degradation mechanisms
- chemical attack
- fluorine emission
- thinning

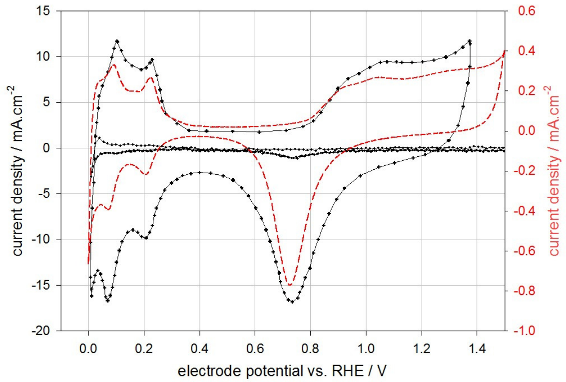
(bulk & catalytic layers)

loss in energy efficiency
loss in faradaic efficiency
loss in gas purity & safety

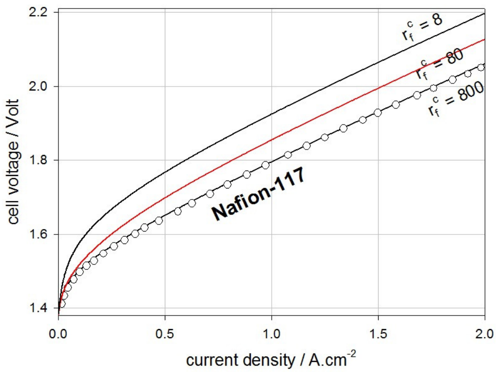
M. Schalenbach, M. Carmo, D.L. Fritz, J. Mergel, D. Stolten, *Pressurized PEM water electrolysis: Efficiency and Gas Crossover,* Int. J. Hydrogen Energy, 8 (**2013**) 14921-14933.

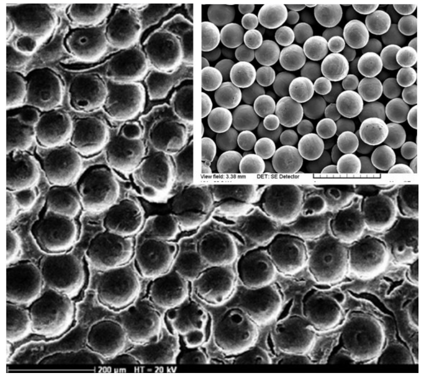
Ex. 2: activity losses (catalytic sites in CCM)

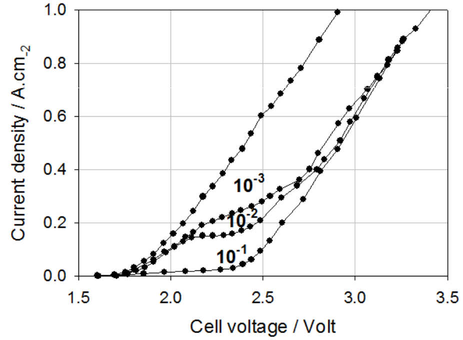
Cathode: HER

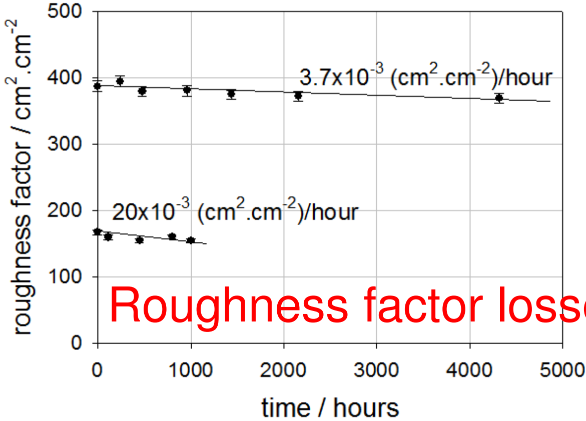


decreasing HER roughness

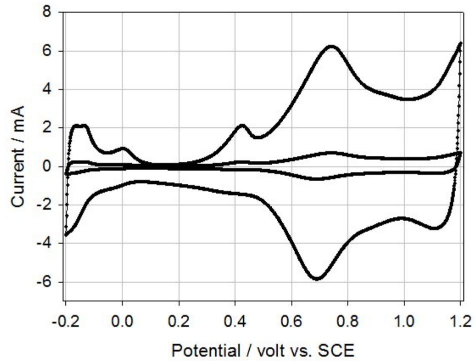




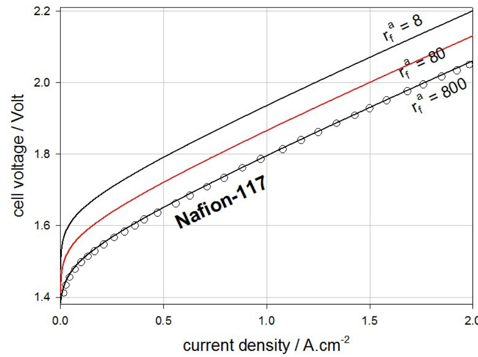




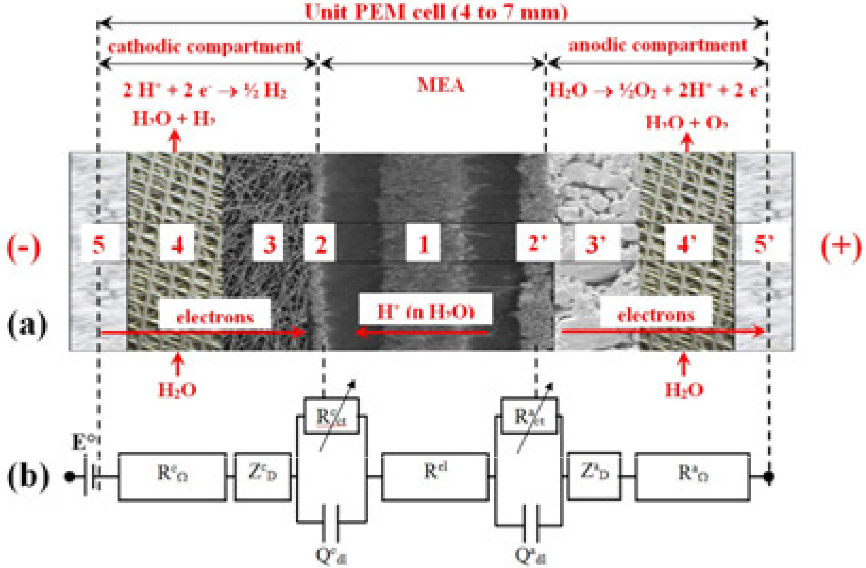
Anode: OER

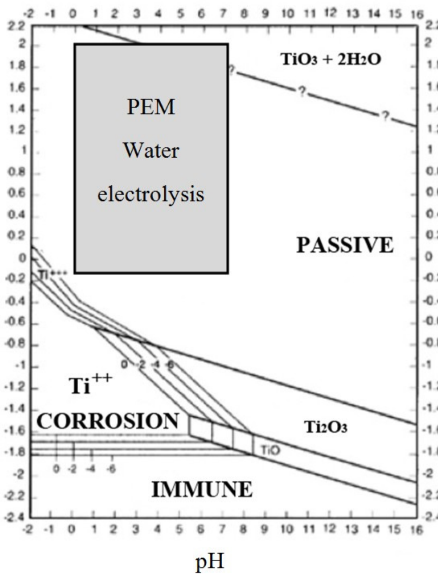


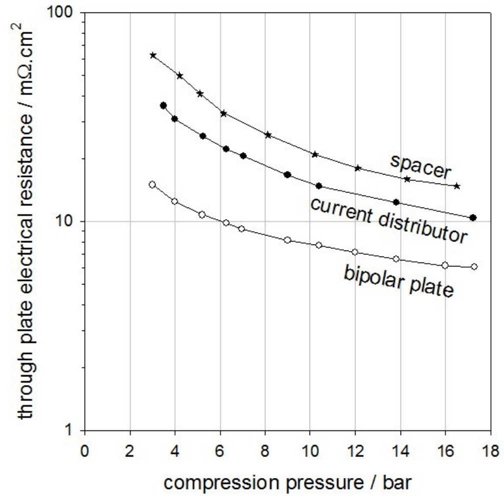
decreasing OER roughness

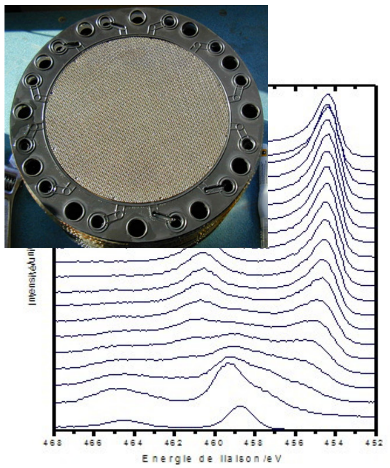


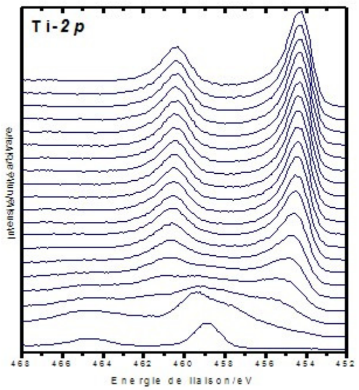
Ex. 3: Other cell components





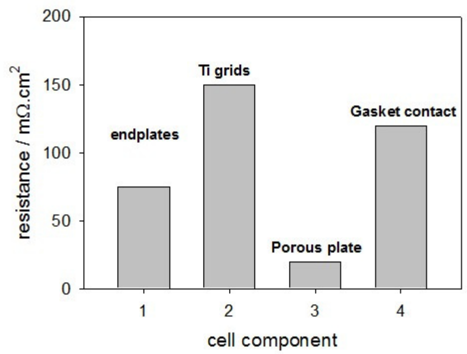






Bulk properties
(H_2 embrittlement)

Surface properties
ICR resistance
- **surface state**
- **coatings**



PEM water Electrolysis for hydrogen production: Principles and Applications, D. Bessarabov, H. Wand, H. Li, N. Zhao, CRC Press (**2015**).

5- Conclusions: European initiative on test harmonization

Harmonization of testing protocols for electrolysis applications

Georgios Tsotridis

European Commission,
Directorate-General Joint Research Centre,
Institute for Energy and Transport,
Petten, the Netherlands

Contact:
georgios.tsotridis@ec.europa.eu

Objectives

To harmonize among electrolyser applications

- Load Cycles
- Testing Protocols and Testing Methodologies for:
  - Single cells
  - Stacks
  - Systems ??
- With the objective of providing **Comparable test results**
- Provide research institutions/industry with harmonized load cycles & testing protocols

Scope of harmonization

Materials

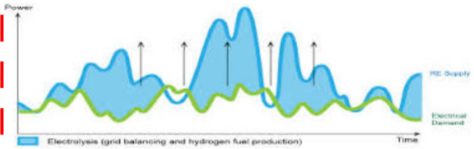
Single cells

Stacks

Harmonisation of testing protocols

Harmonisation of testing methods for materials and load cycles

Load cycles for single cells and stacks



Harmonised operating cycles depending on applications (i.e. solar, wind)

LOAD CYCLES

Grid connection

Electrolysis Harmonisation