Air Liquide
Paris, 13 October 2017

1. Introduction
2. Water electrolysis technos: SWOT analysis
3. The FlexiPEM project : results and conclusions

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

# 1- Introduction

# Eriée laboratory overview of research topics

**Focus on reactions of societal interest**

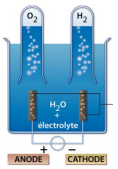
- Water dissociation into $H_2$ and $O_2$
- $CO_2$ electro-reduction
- Lithium insertion

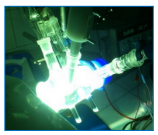

Since 2014

Dr. P. Millet (Prof)
Dr. S. Franger (Prof)
Dr. M. Guymont (Prof)
Dr. A. Ranjbari (A. Prof)
Dr. J.M. Duffault (A. Prof)
Dr. L. Assaud (A. Prof)
Dr. A. Villagra (RI)

**Experimental techniques**

- Electrochemical
- Photo-electrochemical
- Hybrid systems



*Dr. A. Pradon (Post-doc)*
*Dr. W. El Rouby (Post-doc)*
*Mr. B. Verdin (PhD student)*
*Mrs. J. Al Cheikh (PhD student)*
*Mr. M. Antuch (PhD student)*
*Mr. Yi Peng (PhD student)*
*Mr. P. Allazov (PhD student)*
*Mr. Peng Yi (PhD student)*

**Applications**

- Technology development
- Prototype optimization
- Technology transfers

http://www.icmmo.u-psud.fr/Labos/ERIEE/index_eng.php

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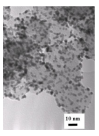
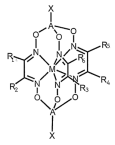
# Eriée: basic research topics

Design, elaboration and multi-physics characterization of electrochemical interfaces

**Electrocatalyst synthesis**

- nanoparticles
- 2D/3D nano-structures
- molecular electrochemistry



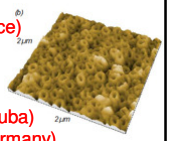


**Surface functionalization techniques**

- catalytic sites at interfaces
- surface particle growth
- molecules at interfaces
- Chemi-sorption, physi-sorption

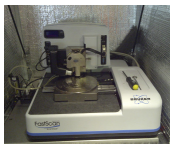
Main Collaborations

Prof. Y. Voloshin (Russian Academy of Science)
Prof. A. Kudo (Tokyo University of Science)
Prof. K. Domen (University of Tokyo)
Prof. S. Chen (Santa Cruz University)
Dr. M. Antuch-Cubillas (Havana University, Cuba)
Prof. J. Bachman (University of Erlangen, Germany)
Dr. A. Zitolo (Soleil synchrotron, Saint-Aubin, France)



**Performance assessment**

- Electrochemical characterization
- Ex-situ characterisation
- In-situ AFM-SECM



http://www.icmmo.u-psud.fr/Labos/ERIEE/index_eng.php

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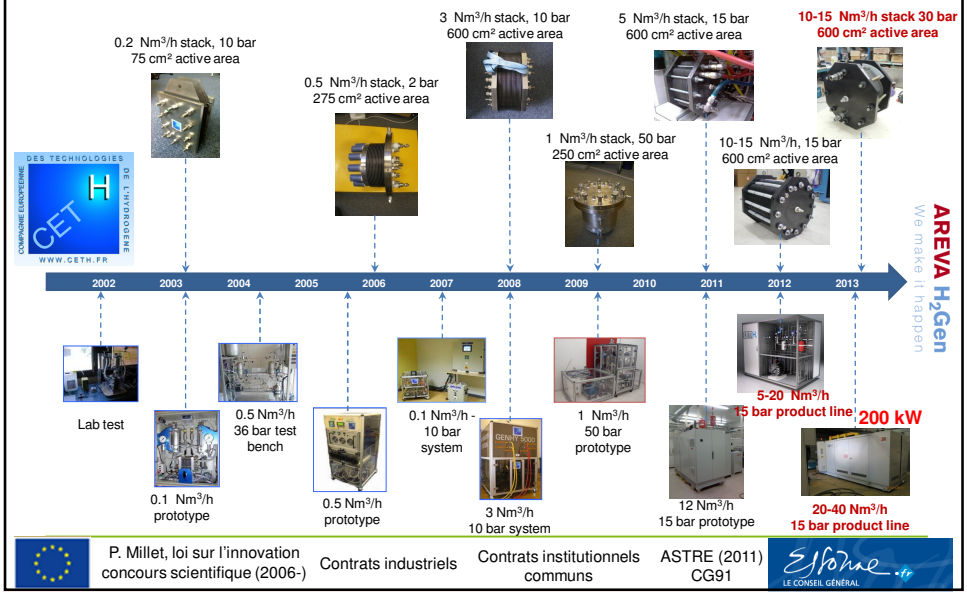
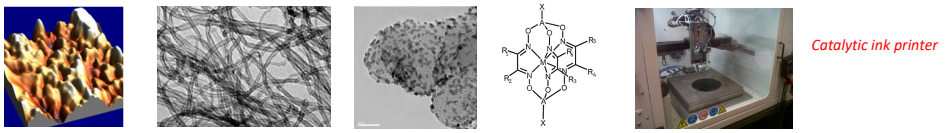
# Eriée: applied research topics




# Tools available @ Orsay

*Material science* : synthesis, caracterization, MEA manufacturing

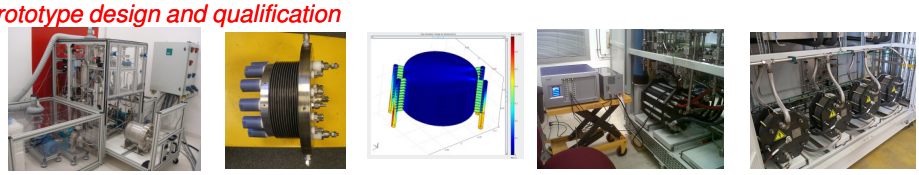


*Catalytic ink printer*

*Laboratory electrochemical tests*

*H2 storage permeation*

*Prototype design and qualification*

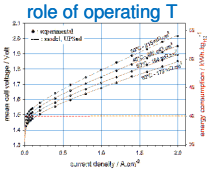


Campus Paris Saclay
Fondation de Cooperation Scientifique

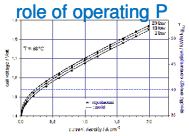
## Eriée services
## process monitoring/quality check
## on-site diagnostic/maintenance

modeling/data fitting

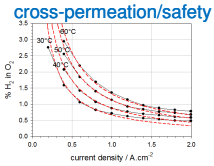
role of operating T



role of operating P

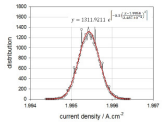


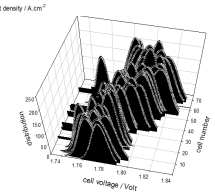
cross-permeation/safety



energy/exergy audits
performance analysis

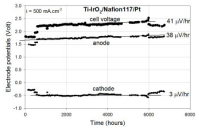
statistical tools

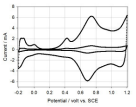




$H_2$ safety

degradation mechanisms





Training
(students and professionals)

P. Millet, loi sur l'innovation
concours scientifique (2006-)

Contrats industriels

Contrats institutionnels
communs

ASTRE (2011)
CG91

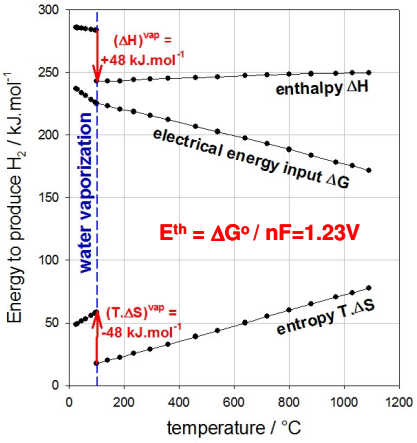
# 2- Comparison of main water electrolysis technologies

# Main thermodynamic features

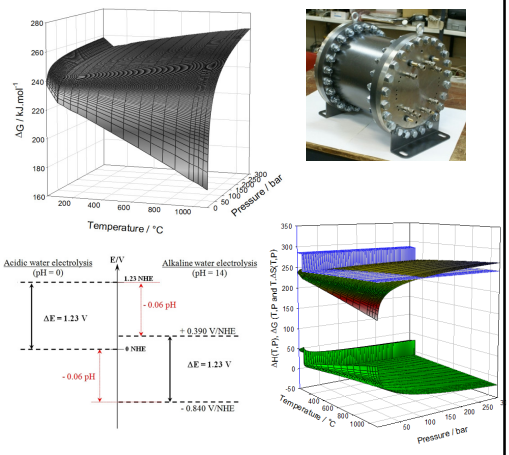
## $H_2O$ (l) → $H_2$ (g) + ½ $O_2$ (g)

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

**Gibbs-Helmholtz: role of T @ 1 bar**




**role of P @ any T**




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

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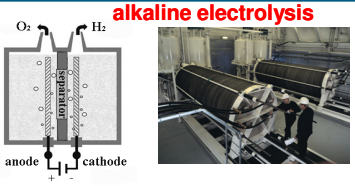
# Main water electrolysis technologies

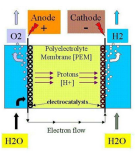
| | Mature technology | | R&D | |
|---|---|---|---|---|
| **indicator** | **Alkaline** | **PEM** | **Medium T** | **Solid Oxide** |
| T range (°C) | room / 120 | room / 90 | 250/600 | 800/1,000 |
| Electrolyte / pH | 25-30 wt.% $(KOH)_{aq}$ | Perfluoro-sulfonic Polymer | $Sr[Ce_xZr_{1-x}]_{0.95}Yb_{0.05}O_3$, $La_{0.6}Ba_{0.4}ScO_{2.8}$ | $Y_2O_3$-$ZrO_2$, $Sc_2O_3$-$ZrO_2$, MgO -$ZrO_2$, CaO-$ZrO_2$ |
| Mobile species | $OH^-$ | $H_3O^+$ | $H_3O^+$ | $O^{2-}$ |
| Cathode catalyst | Nickel foam/ Ni-SS | Platinum | Ni – YSZ or Ni-GDC Cermet with proton conducting electrolyte | Ni – YSZ or Ni-GDC Cermet |
| Cathode carrier | Nickel foam/ Ni-SS Ni-Mo/$ZrO_2$-$TiO_2$ | carbon | | |
| Anode catalyst | $Ni_2CoO_4$, La-Sr-$CoO_3$, $Co_3O_4$ | Ir/Ru oxide | $(La,Sr)MnO_3$, $(La,Sr)(Co,Fe)O_3$, | $(La,Sr)MnO_3$, $(La,Sr)(Co,Fe)O_3$, |
| Anode carrier | - | - | - | Gd-doped Ceria |
| Separator | asbestos, PAM, $ZrO_2$-PPS, NiO, $Sb_2O_5$-PS | polymer electrolyte membrane | ceramic electrolyte membrane | ceramic electrolyte membrane |
| sealant | metallic | synthetic rubber or fluoroeleastomer | glass and vitro-ceramics | glass and vitro-ceramics |
| current distributor | Ni | titanium | | Ferritic SS (Crofer APU) |
| containment material | nickel plated steel | stainless steel | stainless steel | stainless steel |
| P range (bar) | 1 – 200 | 1 – 700 | 1 | 1 - 5 |
| Conventional current density ($A.cm^{-2}$) | 0.2 – 0.5 | 0 - 3 | 0 – 0.1 | 0 – 2 |
| Efficiency (%) (at i $A.cm^{-2}$/ $U_{cell}$ V/ T°C) | 60-80 0.2-0.5 / 2.0 / 80 | 80 1.0 / 1.8 / 90 | lab-scale tests | 100 3.6 / 1.48 / 950 |
| Capacity ($Nm^3$/hour) | 1 – 500 | 1 - 230 | 1 | 1 |
| Durability (hours) | 100,000 | 10,000 | 500 | 500 – 2,000 |
| $H_2O$ specification | liquid | ρ > 10 MΩ.cm | steam | steam |
| load cycling | medium | good | no data av. | no data av. |
| stop/go cycling | weak | good | no data av. | weak |

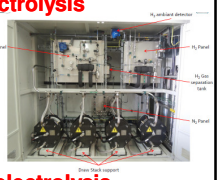
**alkaline electrolysis**



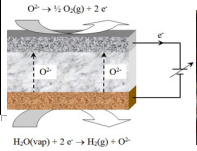


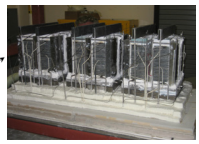

**PEM electrolysis**



**solid oxide electrolysis**



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**).

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# KPI for performance comparison

KPI versus time = roadmap : cf. MAWP FCH-JU

reference case
PEM
Alkaline
SOWE

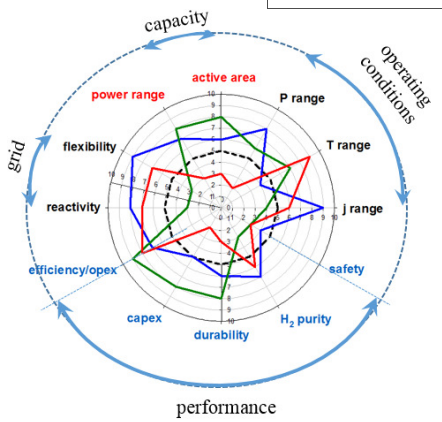
**2017 reference case**

- **j range**: 0 – 2.0 A.cm$^{-2}$
- **T range** : 25-80ºC
- **P range** : 0 – 35 bars

- **cell active area**: 1,000 cm$^2$
- **power range** : 0 – 1 MW

- **flexibility**: stationary @ different j
- **reactivity**: zero -> nominal power < 30 sec

- **efficiency**: < 60 kWh.kg$_{H2}^{-1}$ @ 2 A.cm$^{-2}$
- **capex**: 1,500 €/kW @ 1 MW-scale
- **durability**: 5% efficiency loss/year
- **H$_2$ purity** at delivery : 4 N
- **safety**: %H$_2$ in O$_2$ < 25% ILE




P. Millet, *Characterization of MW-scale PEM water electrolyzers*, 1st International Conference on Water Electrolysis, Copenhague, Denmark, June 13-16, **2017**.

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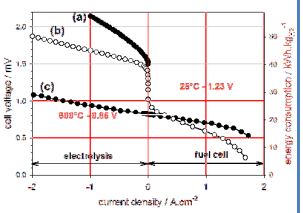
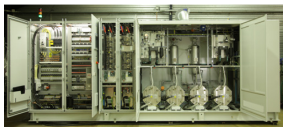
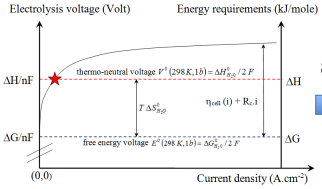
# Kinetics/efficiency thermo-neutral point

## comparison of IV curves

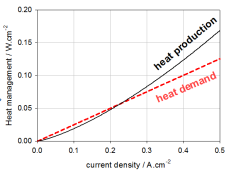



## low temperature PEM & alkaline

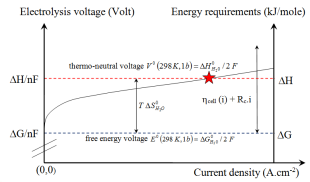




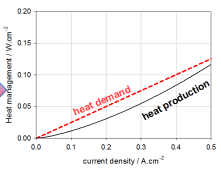

PEM alcaline




## high temperature solid oxide




HT SE




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**).

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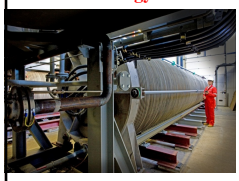
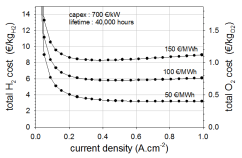
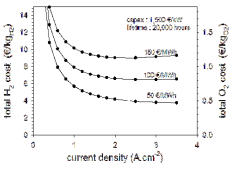
# Capex/opex analysis

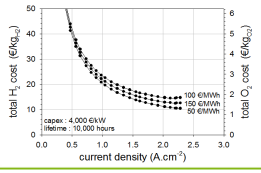
technology



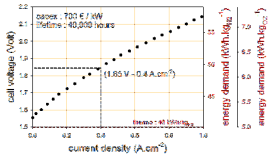
capex/opex

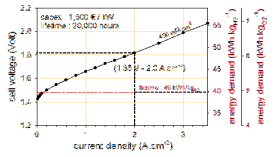


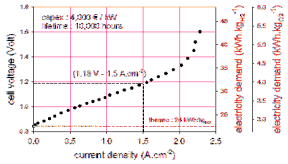




setpoint IV curve




D. Bessarabov, P. Millet, in : 'PEM water Electrolysis', Elsevier (**2017**)

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# 3-a-PEM : from stationary to flexible operation

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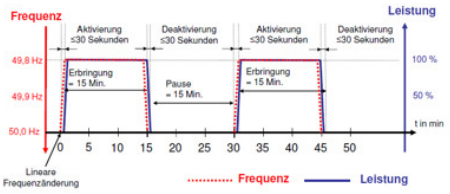
# Power grid requirements

business model

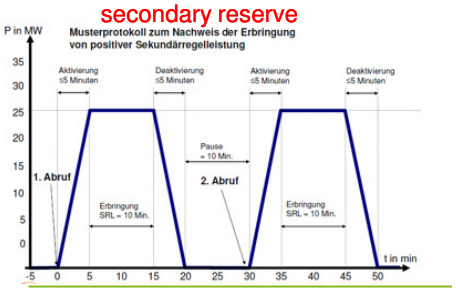
grid → Electrolyzer → mobility

*grid service*
*reduced kWh cost ?*

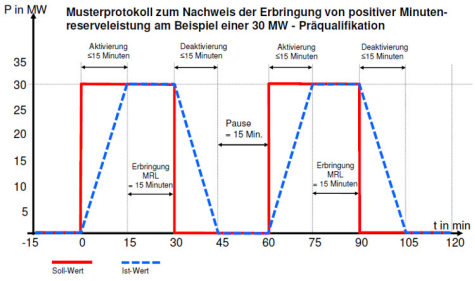
primary reserve




secondary reserve




tertiary reserve




(source: www.regelleistung.net)

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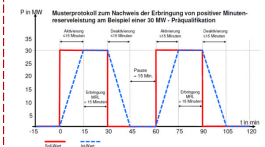
# Power-to-$H_2$: FlexiPEM

**Load profile specification**

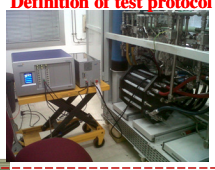


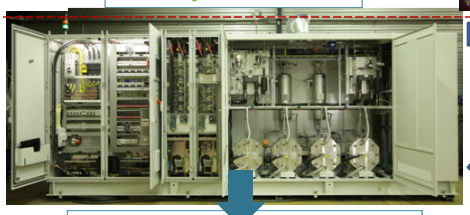
(source: www.regelleistung.net)

PS2E Paris-Saclay Efficacité Energétique

**PEM electrolyzer @ system level**

**Definition of test protocol**





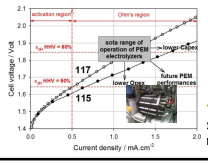
(source: ArévaH2Gen)

AIR LIQUIDE

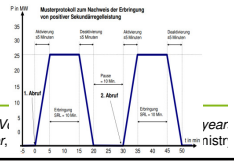
EDF

**Data analysis - modeling**

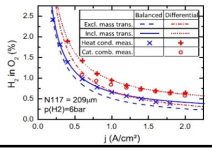
**KPI1: efficiency**



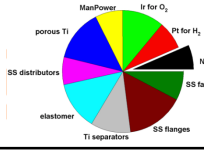

**KPI2-3: flexibiliy/reactivity**




**KPI5: safety aspects**




**KPI6-7: Capex/Opex**

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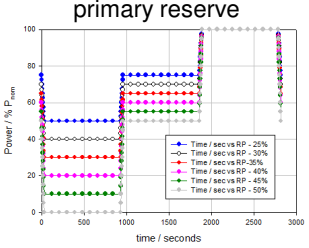
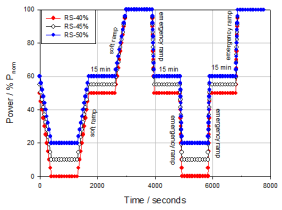
# Flexible test overview

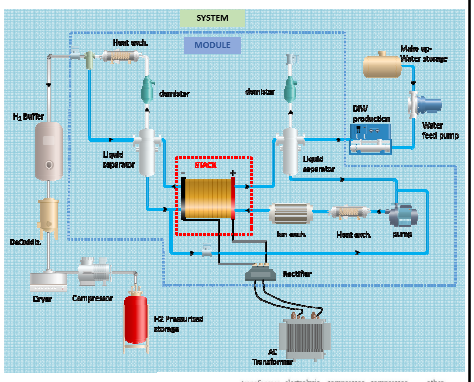
primary reserve

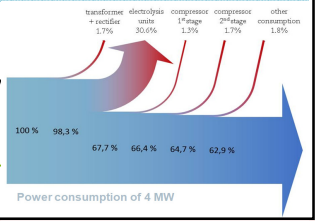



secondary reserve




process flowsheet (*)



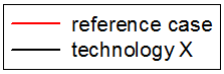




*Sankey diagram of a 4 MW PEM water electrolysis plant during $H_2$ filling of a pressurized truck trailer (Siemens Co.)*

(*) G. Tsotridis, A. Pilonga, *Low Temperature Water Electrolysis Terminology*, JRC (**2017**)

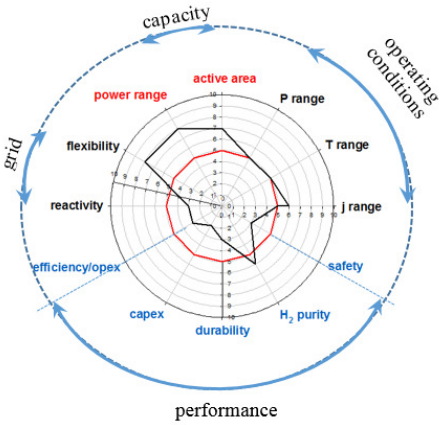
# KPI for performance comparison

KPI versus time = roadmap : cf. MAWP FCH-JU




**2017 reference case**

- j range: 0 – 2.0 A.cm$^{-2}$.
- T range : 0-60ºC.
- P range : 0 – 35 bars.
- cell active area: 600 cm$^2$.
- power range : 0 – 1 MW.
- flexibility; full flexibility between zero and peak power.
- reactivity; zero -> nominal power < 30 sec.
- efficiency: < 50 kWh.kg$_{H2}^{-1}$ @ 2 A.cm$^{-2}$.
- capex: 1,500 €/kW @ 1 MW-scale.
- durability: 2% efficiency loss/year.
- $H_2$ purity at delivery : 4 N.
- safety: %H2 in $O_2$ < 25% ILE.

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# 3-b-PEM: stationary operating conditions

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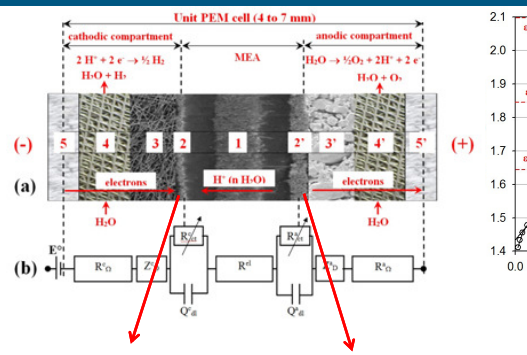
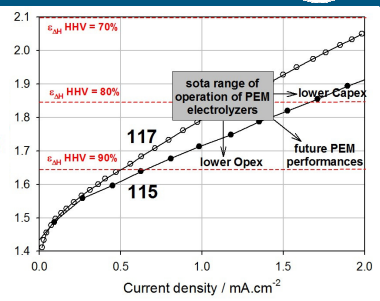
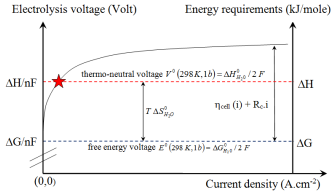
# The PEM cell




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

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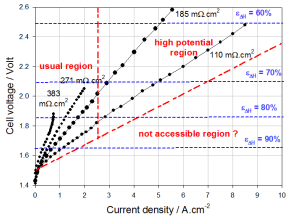
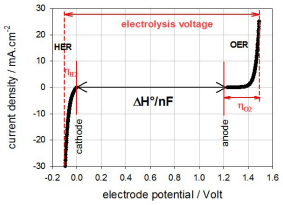
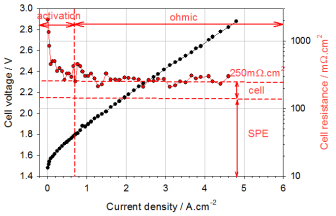
# Best practices 2017

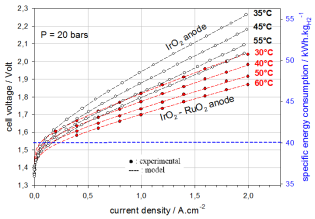
## operating current densities

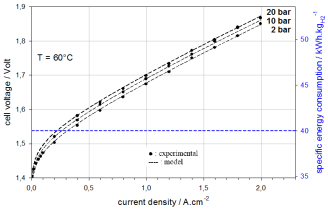


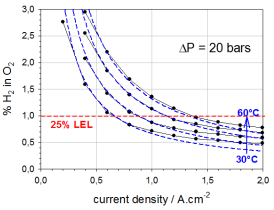




## typical T,P,j performance levels

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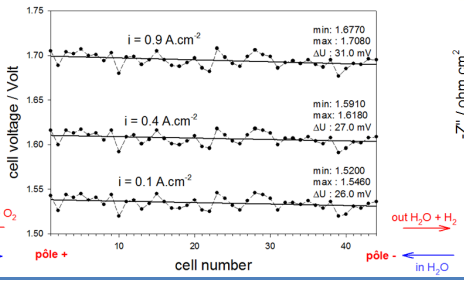
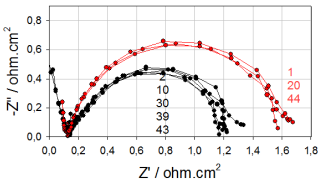
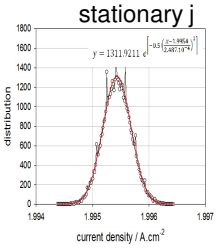
# Stack engineering

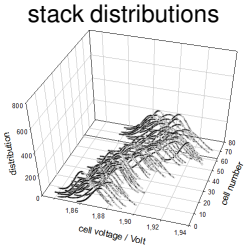


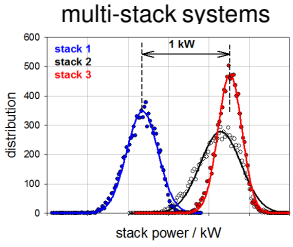

## stationary j




## stack distributions




## multi-stack systems

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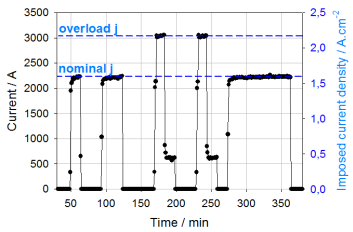
# 3-c-PEM: flexible operating conditions

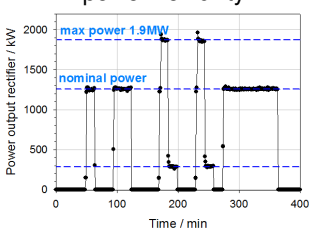


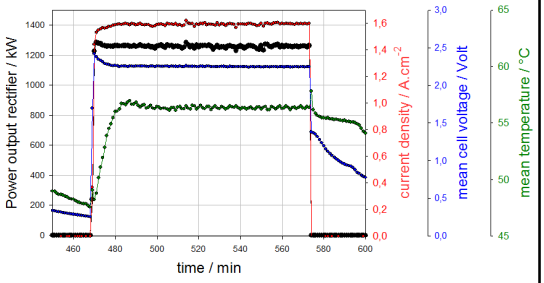
# System flexibility

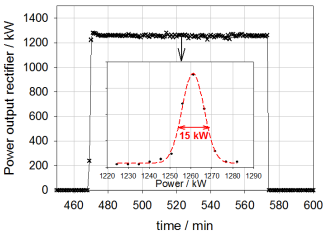
current flexibility




power flexibility

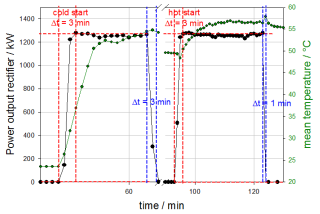


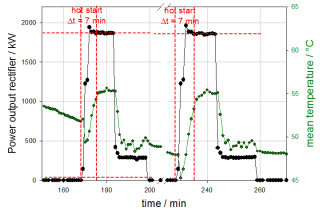



# System reactivity

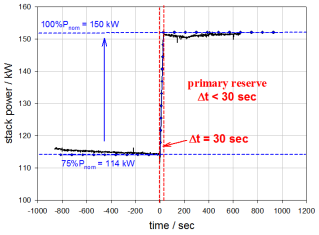
reactivity: 0 up to nominal j



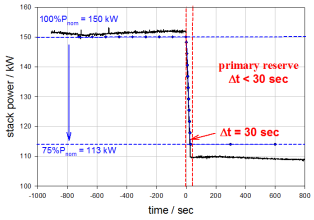

reactivity: 0 up to max j




primary reserve: ramp up (75% → 100%).




primary reserve: ramp down (100% → 75%).

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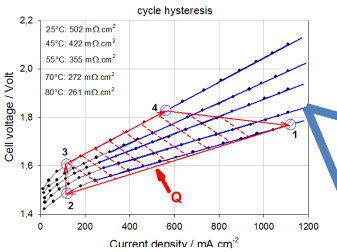
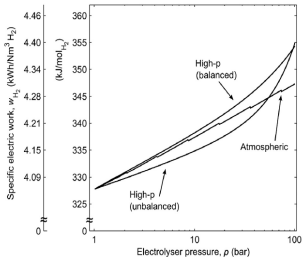
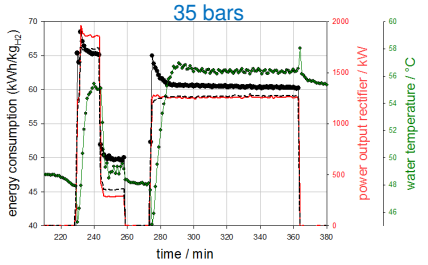
# System efficiency

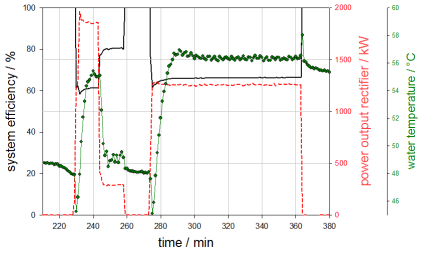



(1) atmospheric electrolysis + compression.
(2) balanced high-pressure electrolysis;
(3) unbalanced high-pressure electrolysis.

35 bars




Référence : $\Delta H^0$ = 285 kJ/mole HHV = 40 kWh/kg.

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# 4- Harmonisation FCH-JU/IEA

## FCH-JU / JRC

EU Harmonised Test Protocols for Electrolysis Applications

**EU HARMONISED TEST PROTOCOLS FOR WATER ELECTROLYSIS APPLICATIONS**

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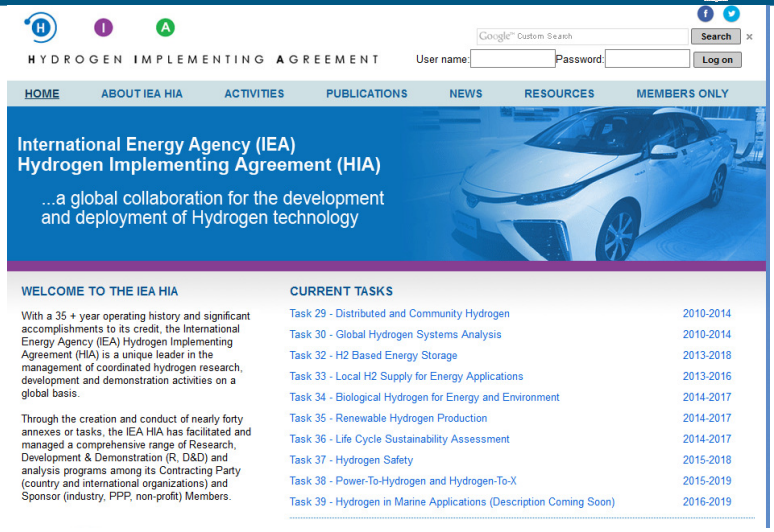
# IEA / HIA




Task 30 : next meeting in Orsay, France, April 2018

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# 6- Conclusions & perspectives

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# Conclusions & perspectives

## Conclusions

- market is calling for larger and more flexible water electrolyzers
- flexibility and reactivity offer some cheap kWh opportunities than could make electrolytic H2 cost-competitive with SMR-H2
- there is a need to customize large PEM water electrolyzers for such operation
- in turn, impact on performance, safety and durability must be analyzed
- **MW-scale PEM water electrolyzers have demonstrated their capability to satisfy most stringent grid requirements.**
- BoP flexibility/reactivity is not an issue; optimization is required.

## Perspectives

- in 2017, 1-10 MW range PEM systems are commercially available.
- 10-100 MW developments are on-going
- surface area are increasing (from 500-1,500 $cm^2$ to > 5,000-10,000 $cm^2$).
- **thermal optimization and heat buffering strategy are still required.**

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# Acknowledgements


Eriée (since 2014)

Permanent staff
Dr. P. Millet (Prof)
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*Mrs. J. Al Cheikh (PhD student)*
*Mr. M. Antuch (PhD student)*
*Mr. Yi Peng (PhD student)*
*Mr. P. Allazov (PhD student)*
*Mr. Peng Yi (PhD student)*


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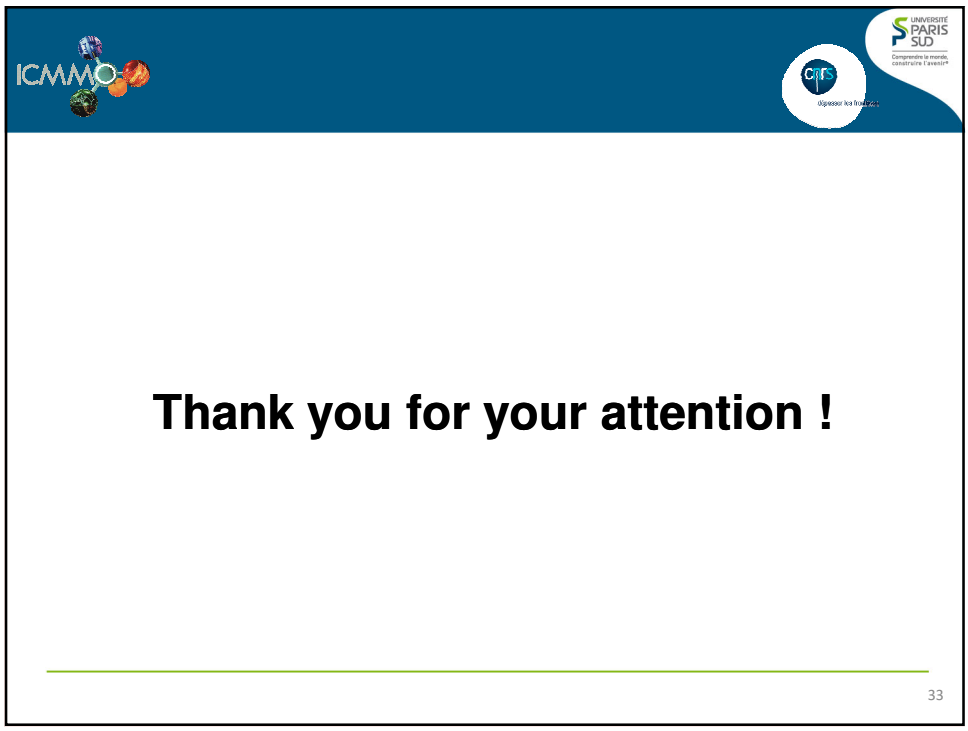


**Thank you for your attention !**