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DEGRADATION PHENOMENA AND TEST METHODOLOGY

PEM Water Electrolysis

P. Millet, Sept. 29, 2023

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Outline

1. PEM Water Electrolysis: general features
- *the PEM Water Electrolysis unit cell*
- *the PEM Water Electrolysis stack of cells*
- *PEM Water electrolysis durability data*

2. Review of main cell ageing processes
- *the PEM Water Electrolysis iV curve*
- *cell voltage contributing terms*
- *iV curve degradation phenomena*

3. ASTs : Ageing Stress Tests
- *chronopotentiometric analysis*
- *EIS analysis*

4. Conclusions & Perspectives

Section 1

PEM Water electrolysis **general features**

The PEM Water Electrolysis unit cell

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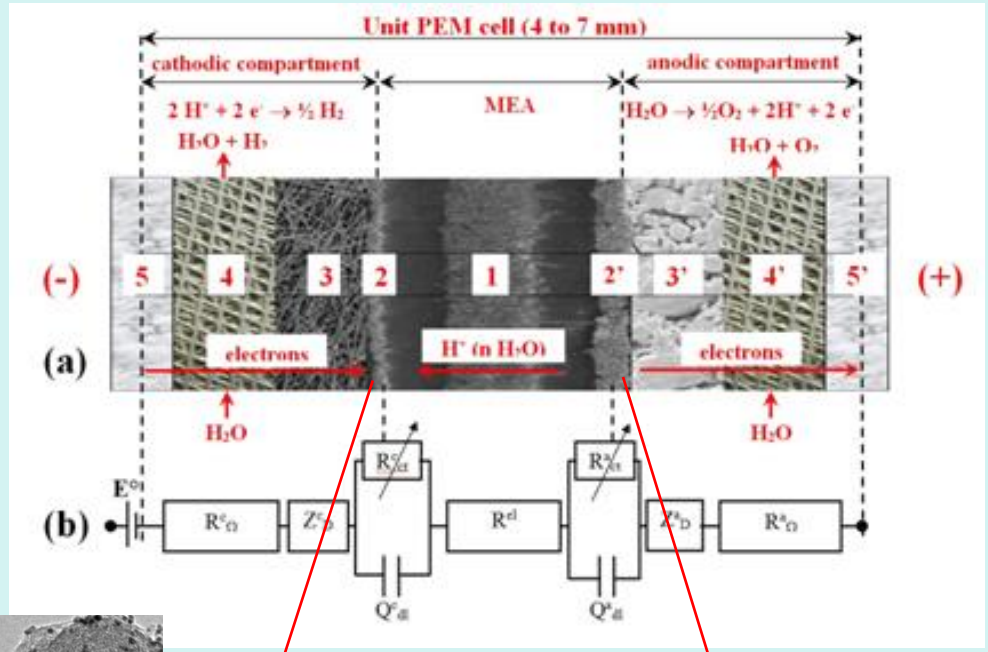
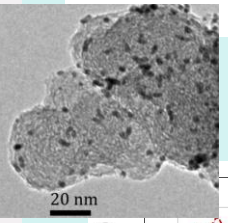
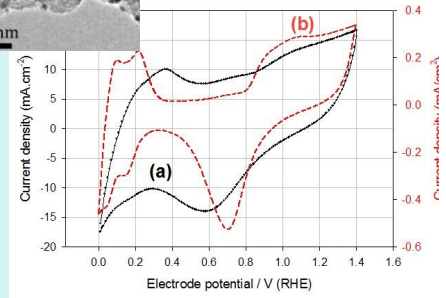
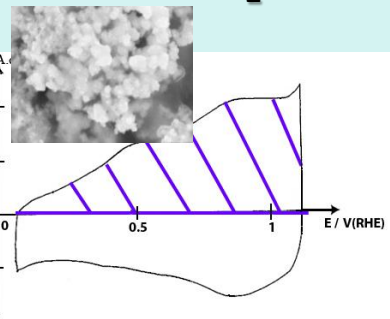




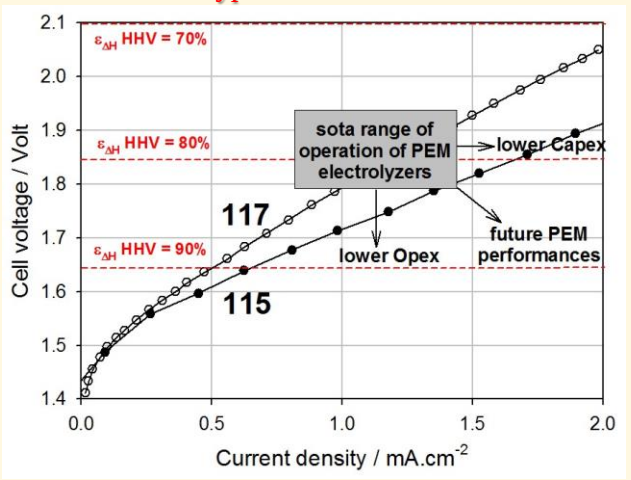
HER: Pt/C



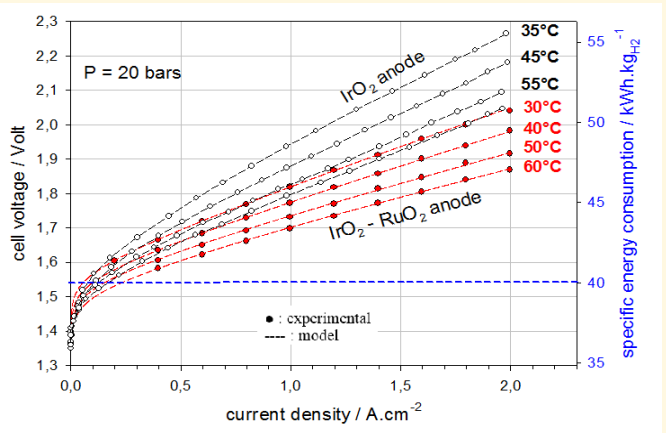
OER: IrO_2

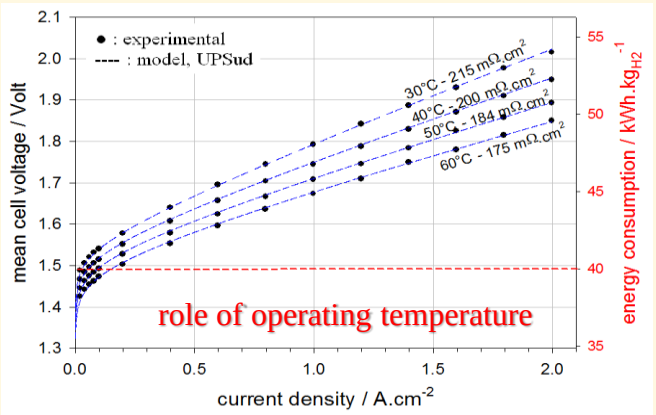


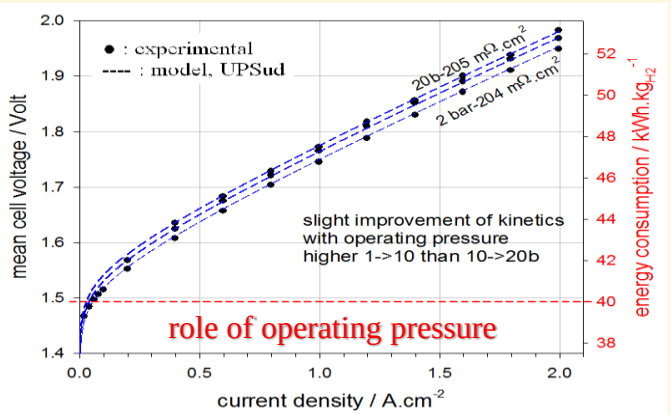
typical iV curves



role of electrocatalysts







The PEM Water Electrolysis stack of cells

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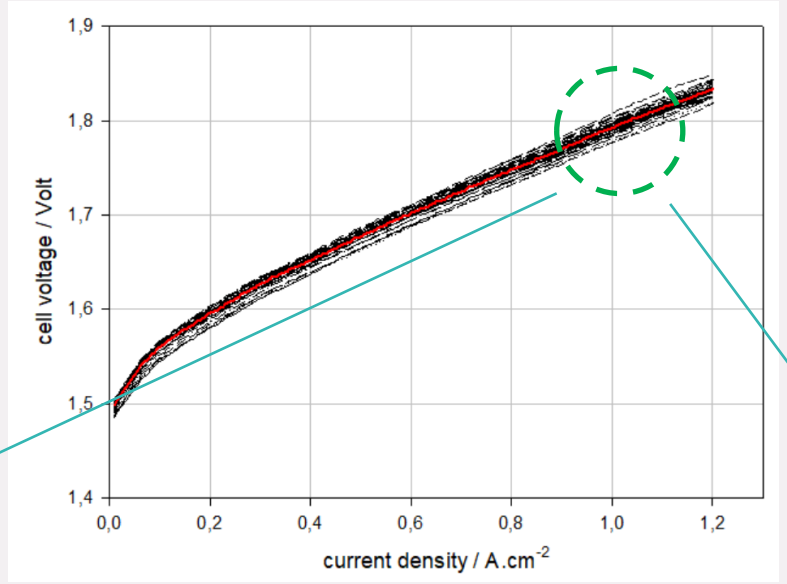
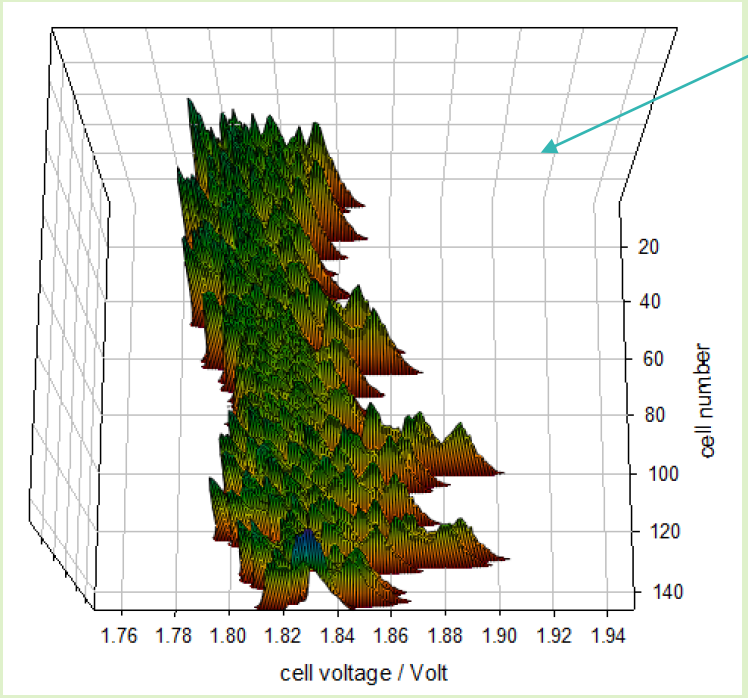


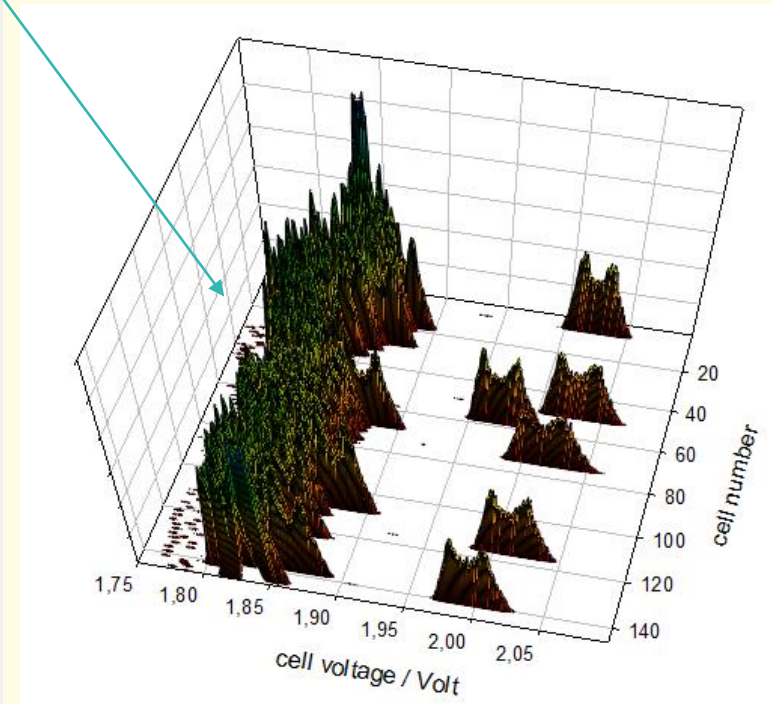
Stacks in operation are more stressed than laboratory cells …

early age stack distributions



- under stationnary operating conditions, individual cell voltages are not constants.
- better to use cell voltage distributions.
- the homogeneity of cell voltage distributions is the KPI of interest
- aged cells see their mean voltage increase faster than others.

aged stack distributions



Durability data

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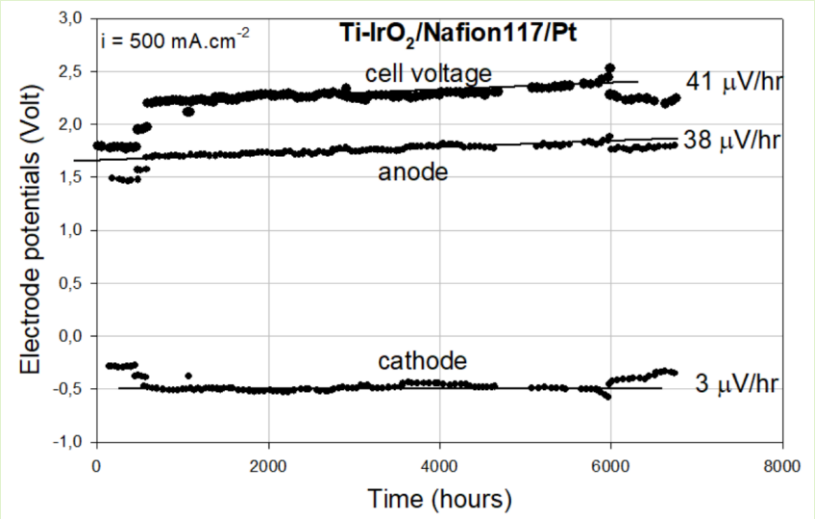
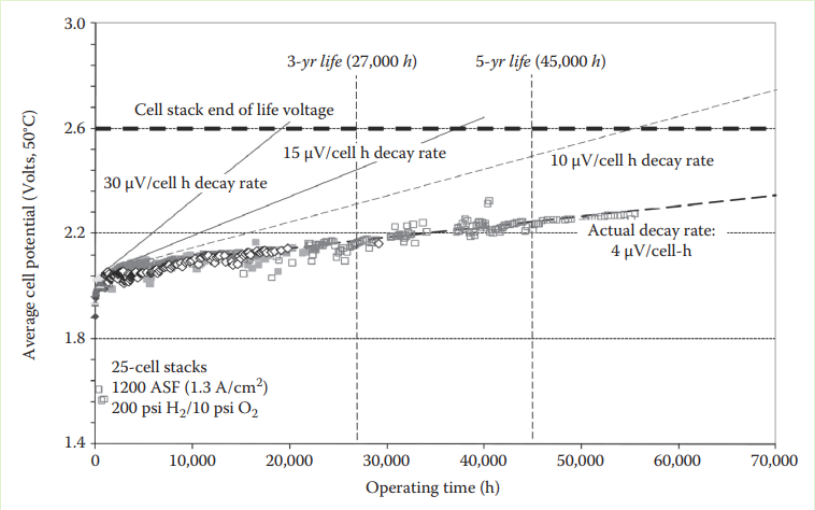
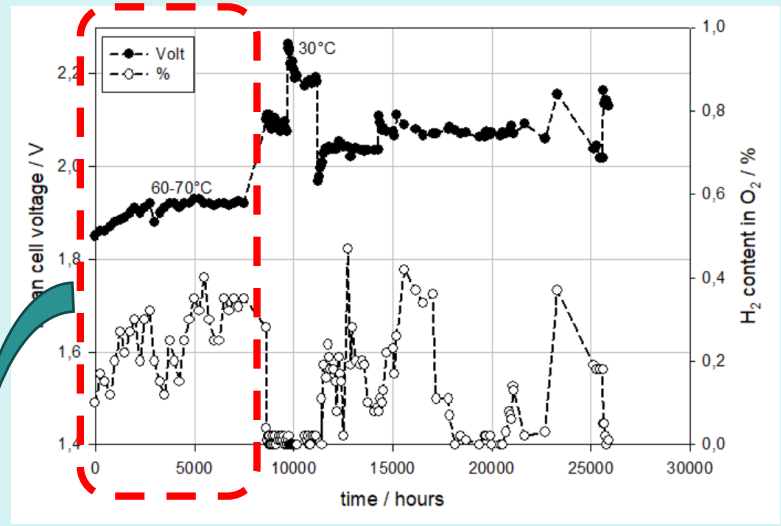
some literature data

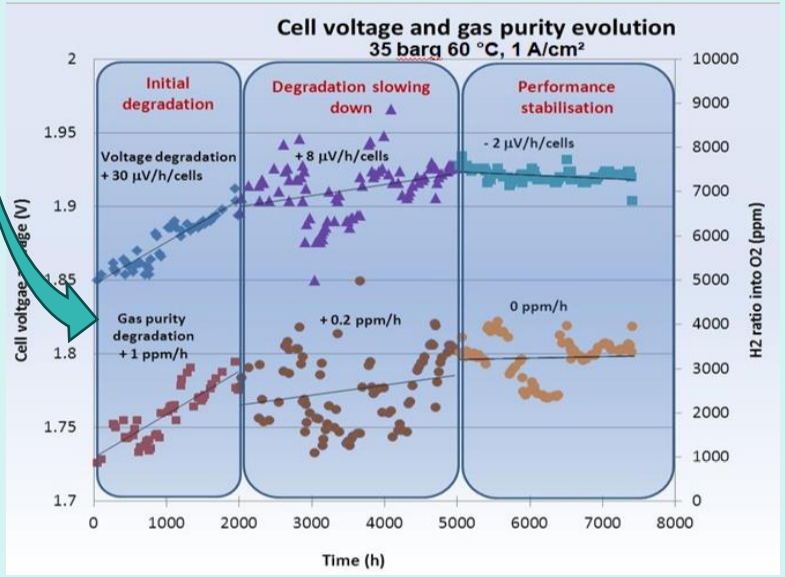




J. Renner et al., in: 'PEM water Electrolysis for hydrogen production: Principles and Applications', D. Bessarabov, H. Wand, H. Li, N. Zhao, CRC Press (2015).

some corporate data





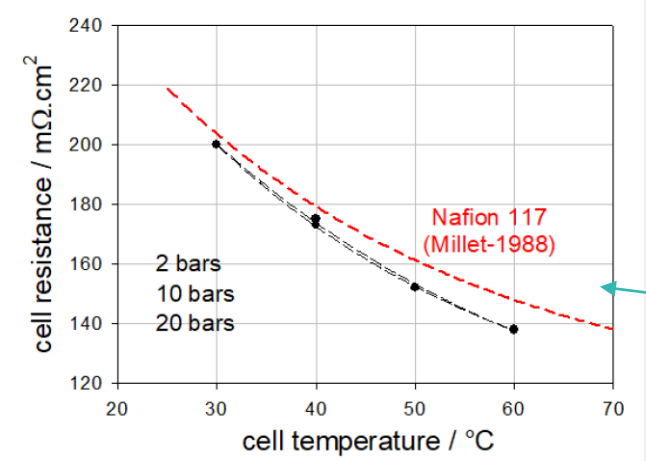
some key facts

- PEM water electrolysers can be operated up to 70-80 khrs.
- the mean cell voltage increases with time.
- as a result, the mean energy consumption in kWh/kg$_{H2}$ also increases.
- some cells age quicker than others.
- the H_2 content in O_2 also tends to increase if not properly mitigated.
- the cell voltage at which the stack is stopped and replaced depends on several technical/cost factors.

Section 2

Review of main cell **ageing processes**

The PEM Water Electrolysis iV curve
(simple 1D model)



ohmic losses

$$i\sum_{k=1}^{n} R_k = \lim_{\omega \to 10kHz} Z^{cell}(\omega, T, P)$$

OER overvoltage

$$\eta_{O_2} \approx \frac{R\ T}{\overleftarrow{\alpha}_a\ F} Ln\left(\frac{j^a}{j_0^a\ r_f^a}\right)$$

$$U_{cell}(T,P,j) = E_{T,P} + i\sum_{k=1}^{n} R_k(T,P,j) + \eta_{H_2}(T,P,j) + \eta_{O_2}(T,P,j) + \eta_{H_2O}(T,P,j)$$

thermodynamics

$$E_{T,P} = \frac{\Delta G(T,P)}{2F}$$

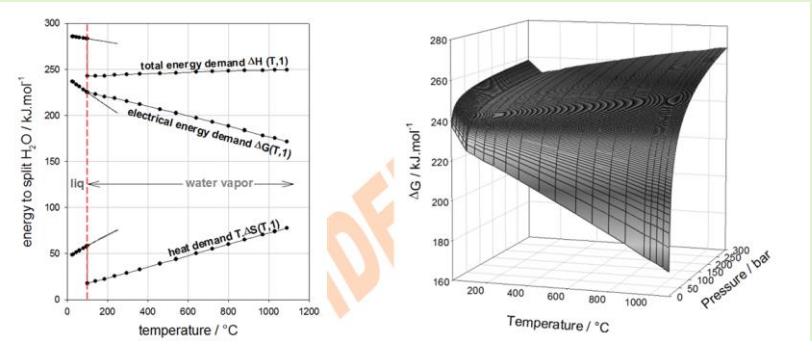


Figure 3 : graphs of $w_{H_2}^{rev}$ (T,1b), $q_{H_2}^{rev}$ (T,1b) and ΔH(T,1b) for water dissociation at 1b. (—) data for liquid water up to 250°C.

Figure 4 : Plot of $w_{H_2}^{rev}(T,p)$ (Eq. 3).

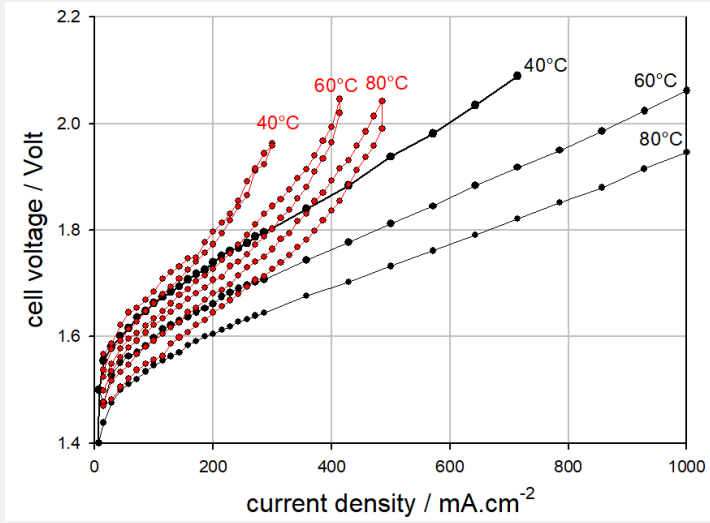
P. Millet et al., 'Handbook of H_2 Energy', C10, *H_2 production using high pressure water electrolysers*, WoodHead Science (**2015**).

HER overvoltage

$$\eta_{H2} \approx \frac{R\ T}{\overrightarrow{\alpha}_c\ F} Ln\left(\frac{-j^c}{j_0^c\ r_f^c}\right)$$

mass transport

$$\eta_{H_2O} \approx \frac{R\ T}{n\ F} Ln\left(\frac{j}{j_L - j}\right)$$



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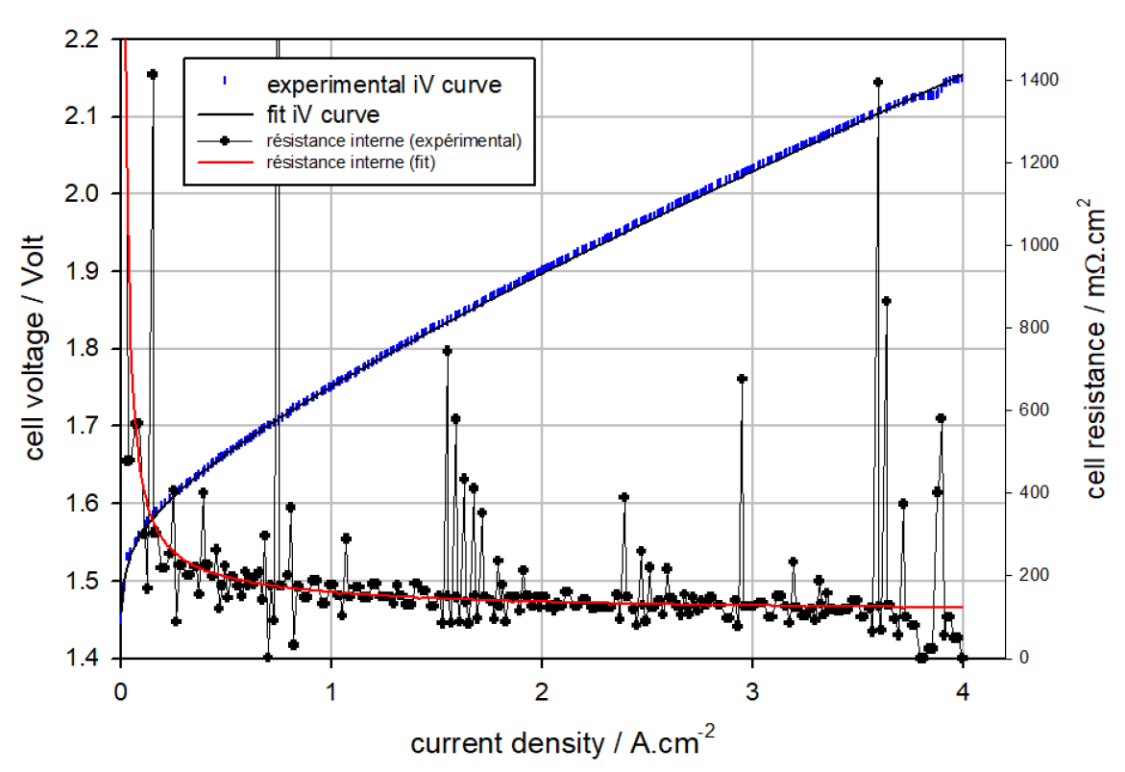
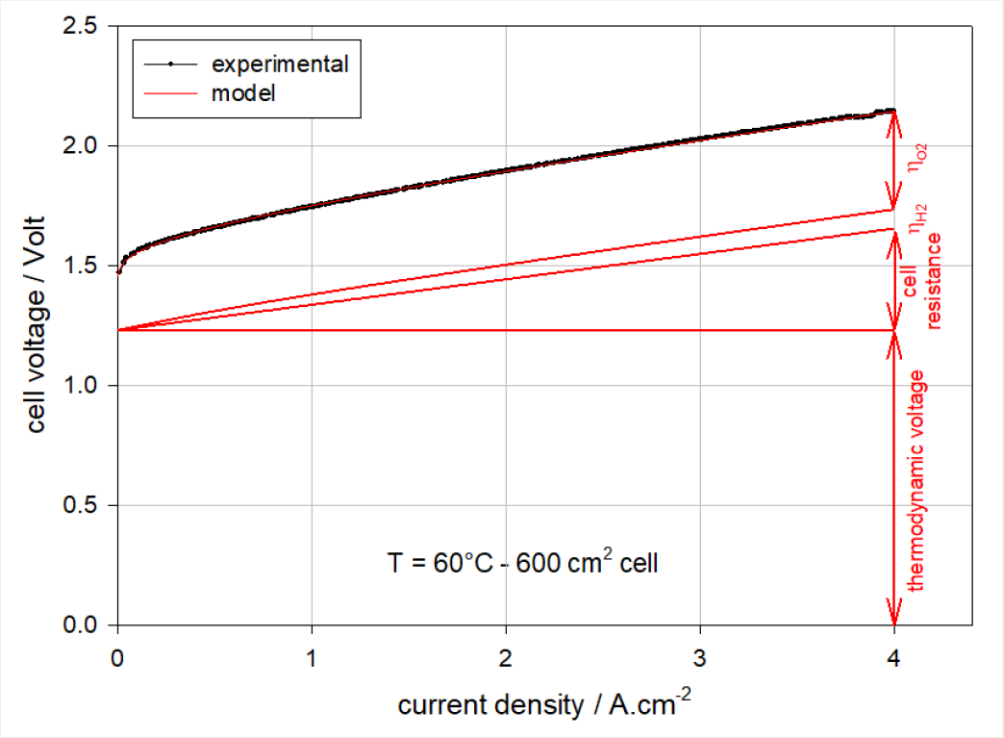
Cell voltage contributing terms





Ranking cell voltage terms in descending order (using Nafion 115, without mass transport issues):

1. the thermodynamic cell voltage (E° = 1.23 V)
2. the OER overvoltage
3. the ohmic cell resistance (metallic + ionic)
4. the HER overvoltage

iV curve degradation phenomena

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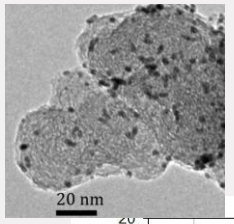
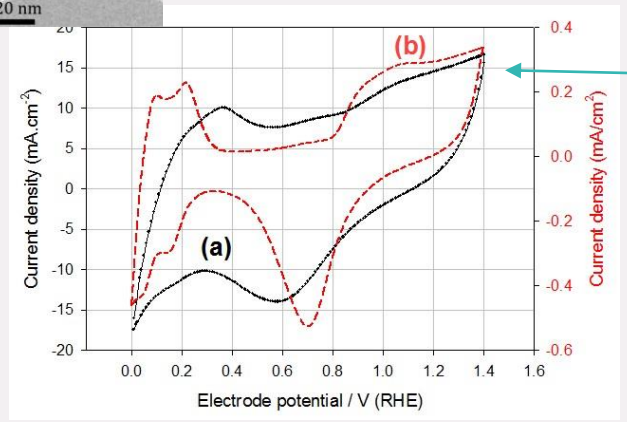
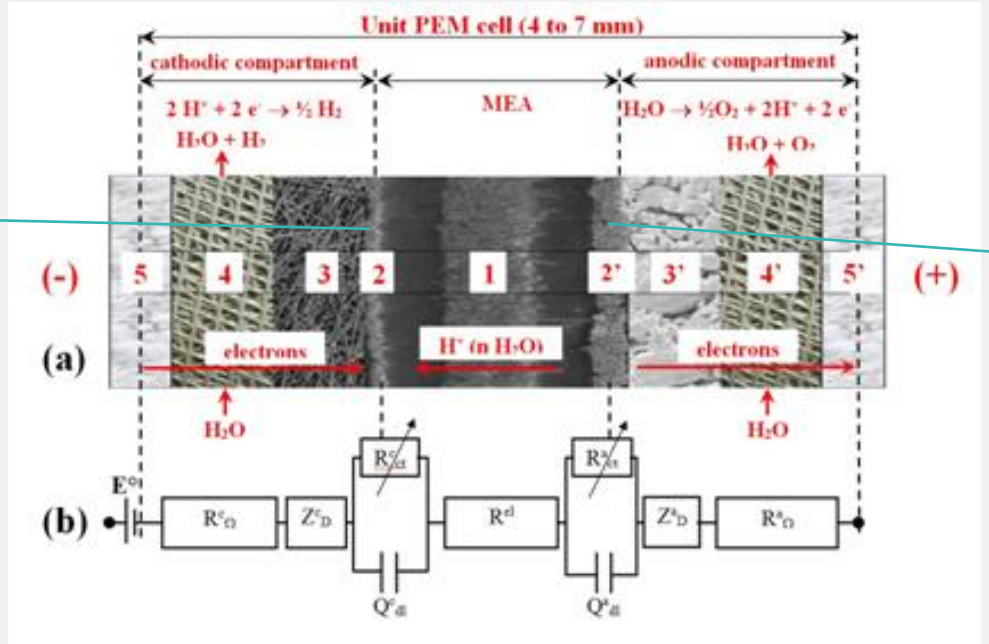
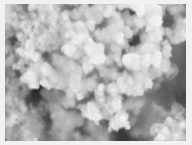


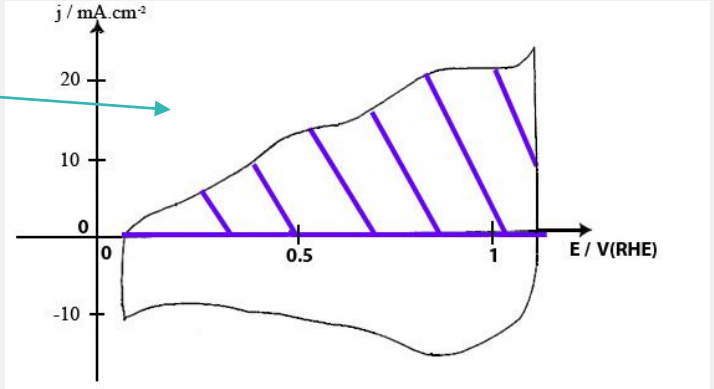
HER: Pt or Pt/C





OER: IrO_2





type of ageing process

- external CCM contamination, ion-exchange
- oxidation of internal cell components
- loss of HER active sites
- loss of OER active sites
- PFSA membrane degradation
- mass transport issues
- deactivation of H2 recombiner (pressurized)

ageing mechanism & consequences

- increased resistivity and HER overvoltage
- increasing contact resistance and Z_{cell}
- increasing HER overvoltage
- increasing OER overvoltage
- impact on conductivity, stability, H_2 cross-over
- reduced water supply, limiting current density
- dissolution/contamination

possible mitigation measures

- monitoring of process water quality
- use of protective coatings
- *increase initial loadings*
- *increase initial loadings*
- use of additives
- management of cell design/hydrodynamics

Section 3

ASTs
ageing stress tests

Chronopotentiometric analysis

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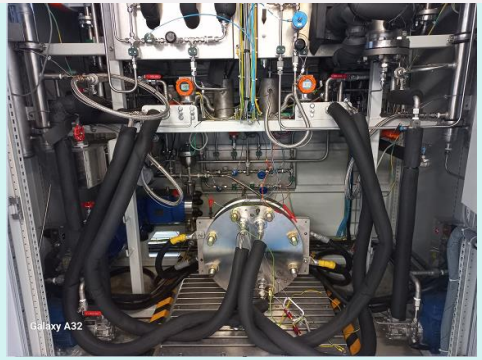
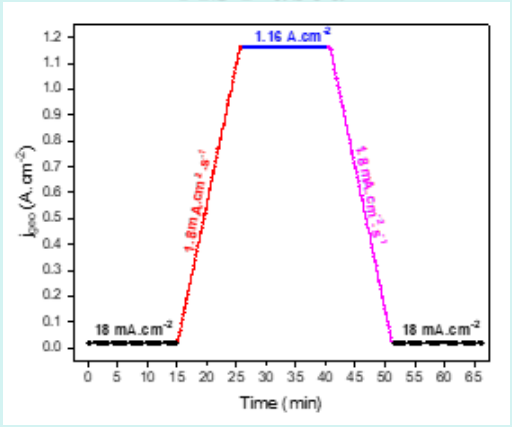
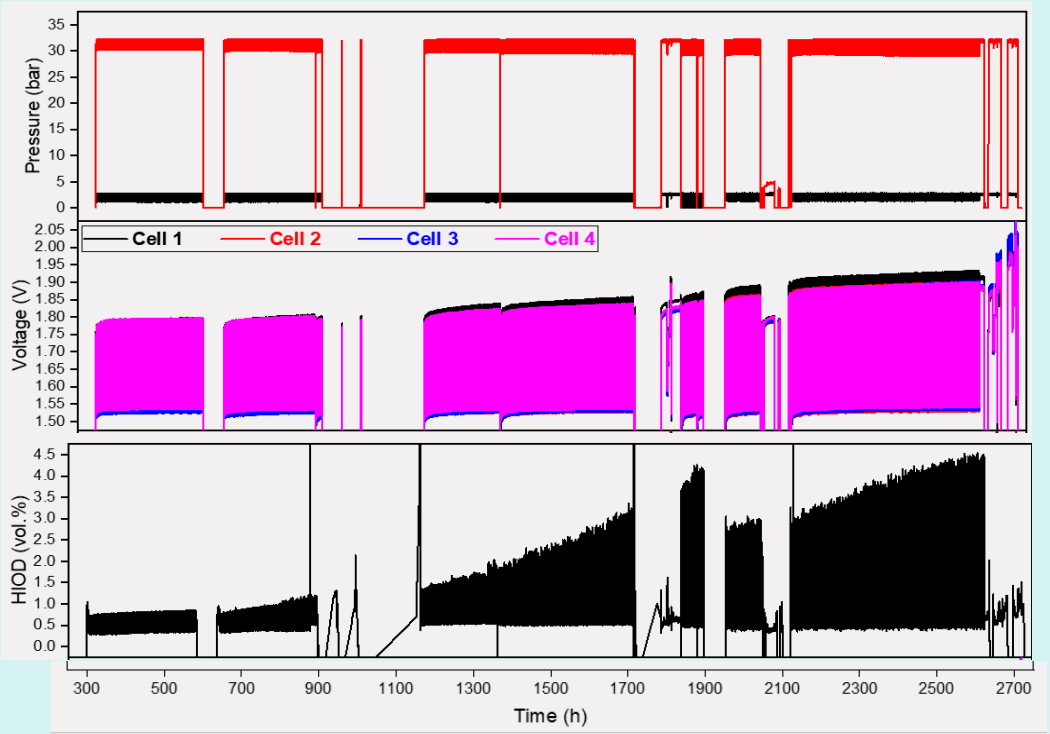
ASTs can be used for R&D or business purposes; business ASTs reflect power input conditions.

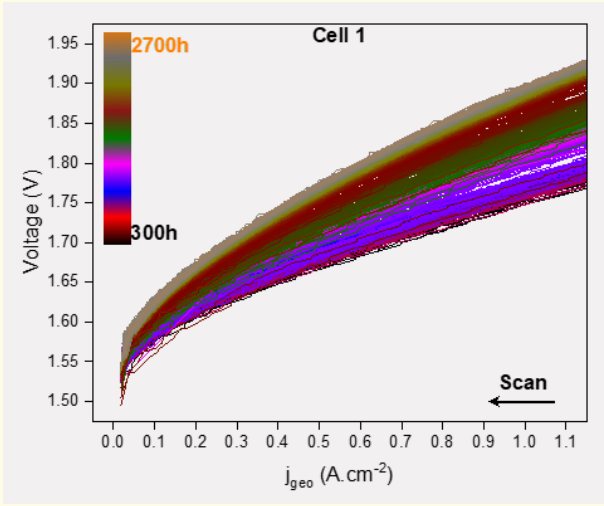


AST used

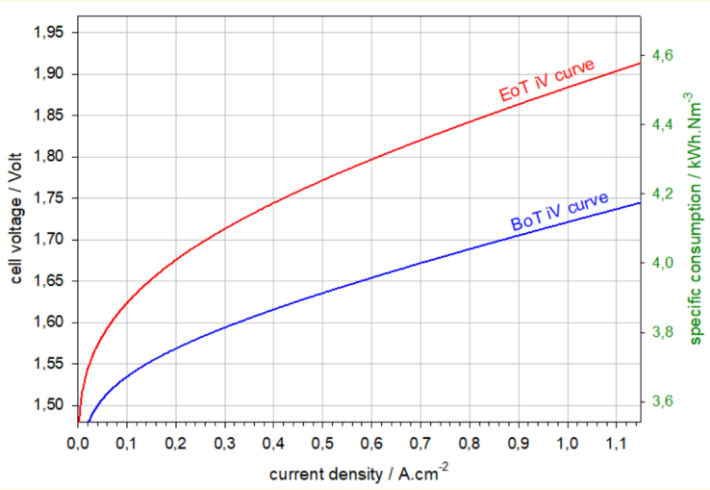


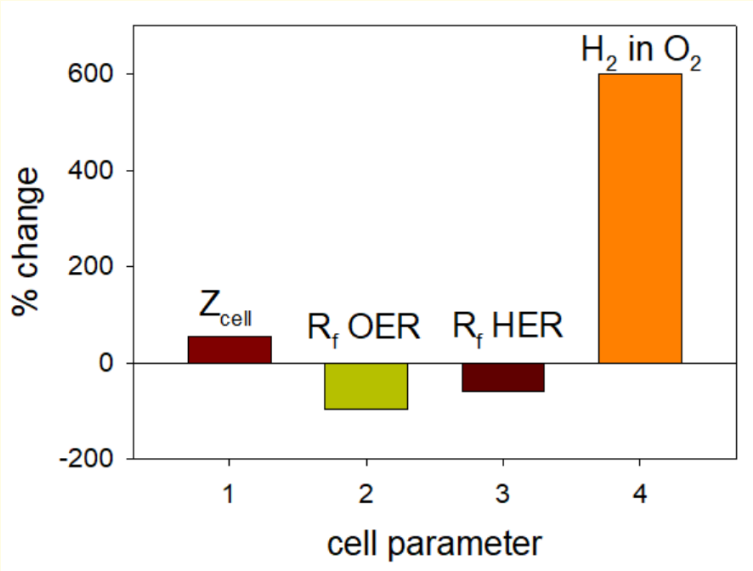


iV curve ageing



BoT -> EoT iV curves





H_2 in O_2 has increased by a factor of 6

Section 4

Conclusions & perspectives

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Conclusions & perspectives

Conclusions

1. some degradation phenomena are reversible (eg, contamination) while some others are irreversible.
2. for individual cells, the analysis of iV curve provides all the necessary information to identify degradation phenomena.
3. complementary techniques (eg, EIS, CV) can also be used but not routinely for stacks.
4. all microkinetic parameters tend to deteriorate with time, in proportions which depend on the operating conditions
5. metallic cations from various sources (eg, process piping) induce low-noise contamination of CCMs:
6. this leads to a progressive increase in membrane resistance, but also to increasing HER overvoltage.
7. IrO_2 corrosion/dissolution can lead to large OER overvoltage increases.

Perspectives

1. PFSA membranes and Pt are higly sensitive to trace amounts of metallic cations that tend to accumulate inside CCMs.
2. degradation mechanisms need to be investigated by taking into account the type of electrical profile used by customers.
3. reducing IrO_2 contents for cost reasons comes up against corrosion processes which tend to consume IrO_2.
4. the ongoing procedures to ban the use of PFAS in the European area pose a threat to investments and the future of the PEM sector.
5. R&D on alternative proton conductors and HER/OER electrocatalysts for acidic media is still needed.

Thank you for your attention

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