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AST PROTOCOLS FOR PEM WATER ELECTROLYIS : INSIGHT ON PERFORMANCES AND COMPONENTS DEGRADATION

2nd international workshop on durabiltiy and degradation issues in PEM electrolysis cells and its components| **Fouda-Onana Frédéric**

NOVEL

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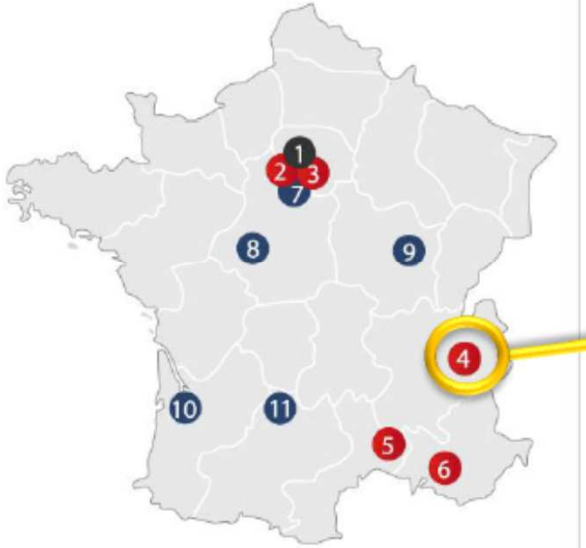

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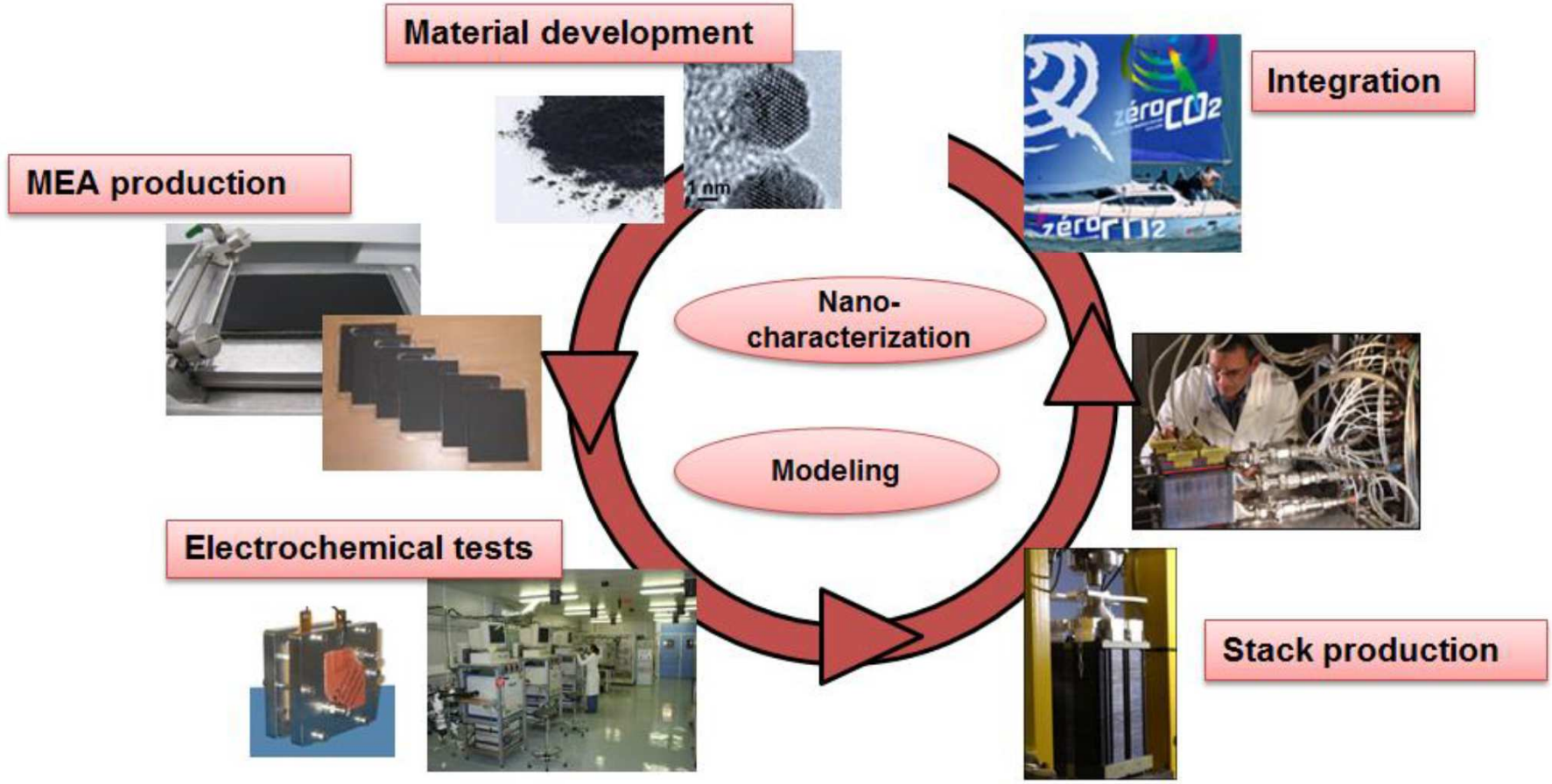
Inks formulation, electrochemical characterisations



CONTEXT

- **High performing and durable PEM WE are need.**

European KPI objectives*

Table 2: Expected evolution of key electrolyser system performance indicators

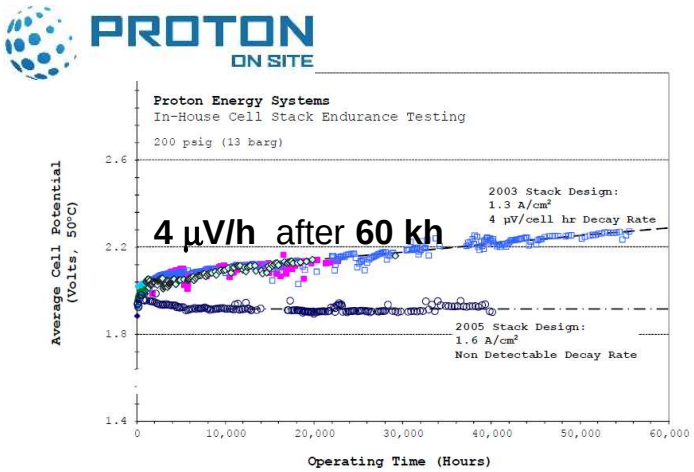
	2015	2020	2025	2030
System cost (€/kW)	950–1,600	600–1,000	600–900	600–800
Indicative stack size (MW)		1-3 MW		2-4 MW
Indicative large system size (MW)	≈3	≈5	≈6	≈7
Electrical input (kWh/kg_{H2})	≈56	≈52	≈51	≈50
Stack life (khr)	65–80	75–95	75–95	80–95

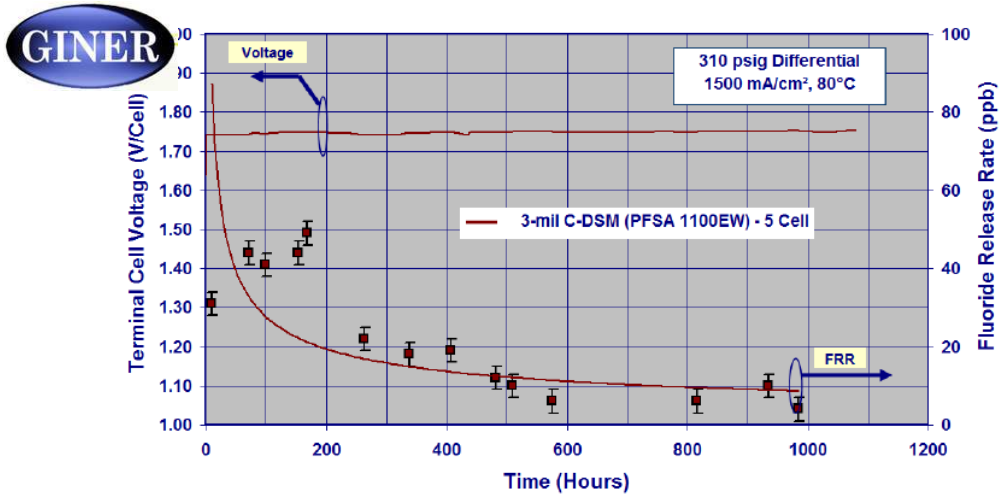
A linear voltage degradation of 1µV/hr translates into an additional electrical energy input of ~2 kWh/kgH_2 after 60,000 hours of continuous operation.

** FCH JU Report « **Development of Water Electrolysis in the European Union » L. Bertuccioli, Feb 2014***

CONTEXT

- **Most of PEM WE show a degradation voltage between 0,5 and 15 µV/h**





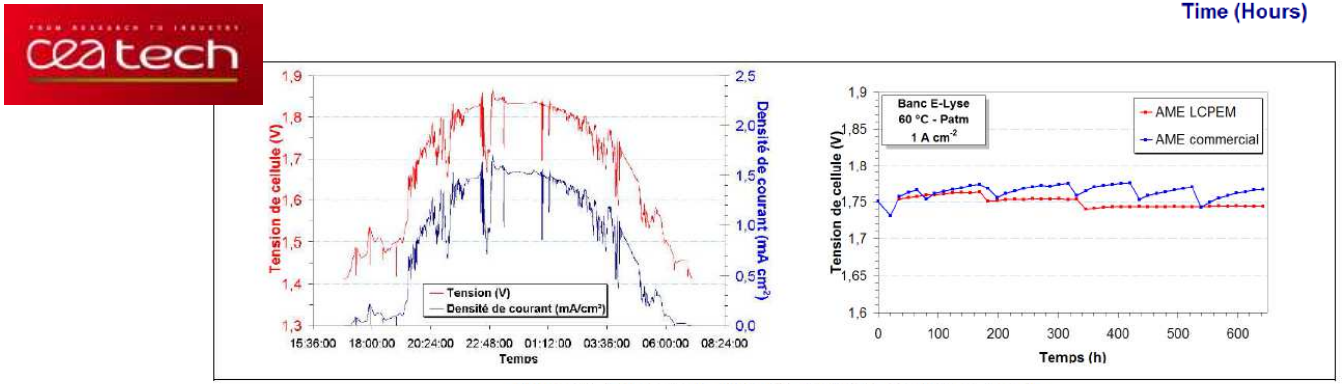
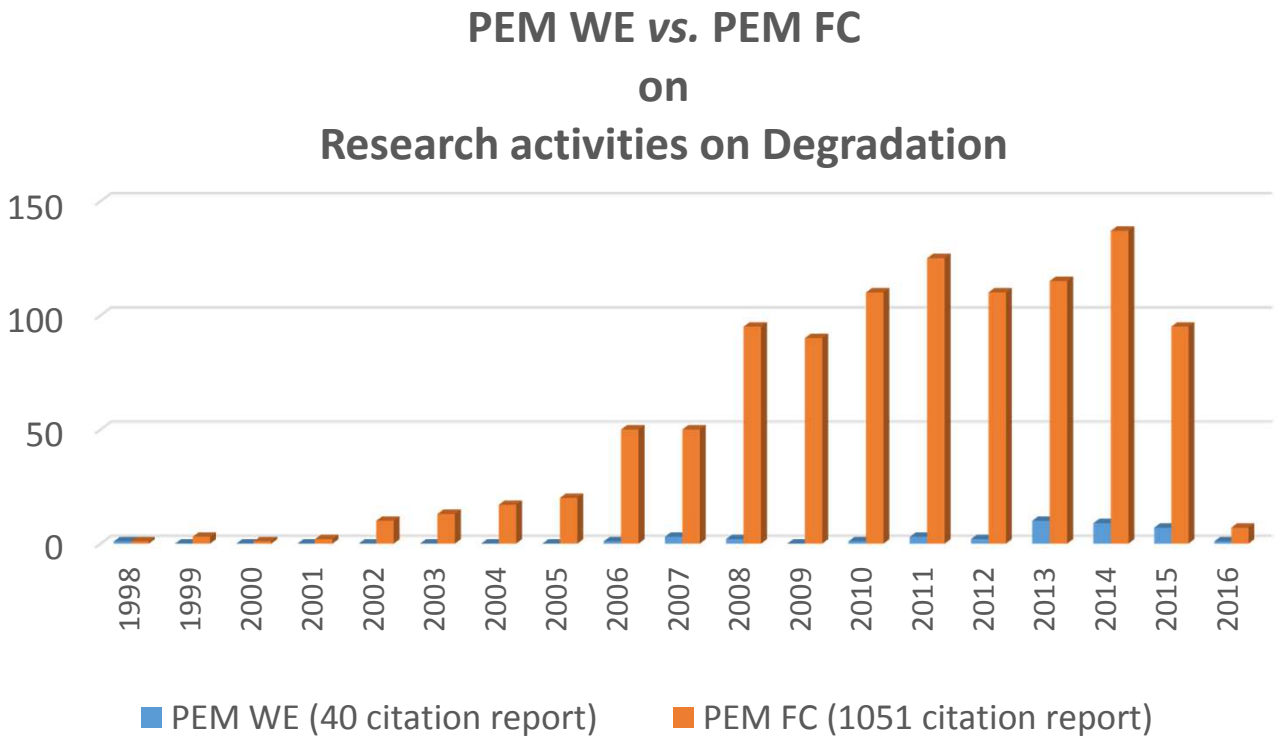


Figure 2. Solar cycle signal for a MEA ageing protocol

- **Highly time consumming to investigate system durability**
- **Need Accelereted stress test (AST)**

CONTEXT

- **PEM WE suffer from less intensive researches on durability and degradation than PEM FC**



Keywords: degradation (PEM WE or PEM FC)

Web of science:
Citation report on 01/27/2016

OUTLINE

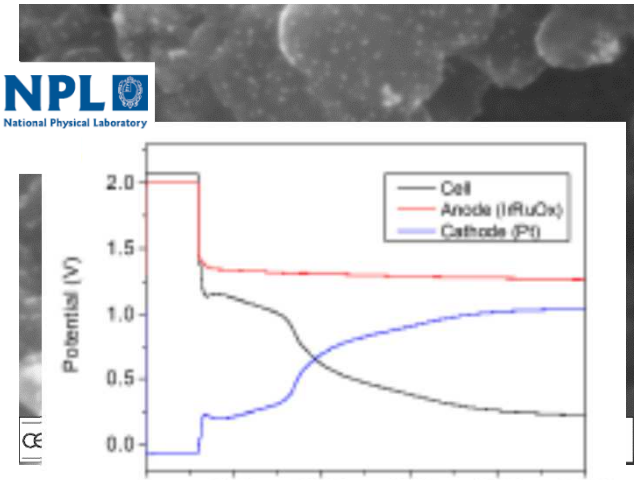
Short introduction on main degrading components in PEM WE

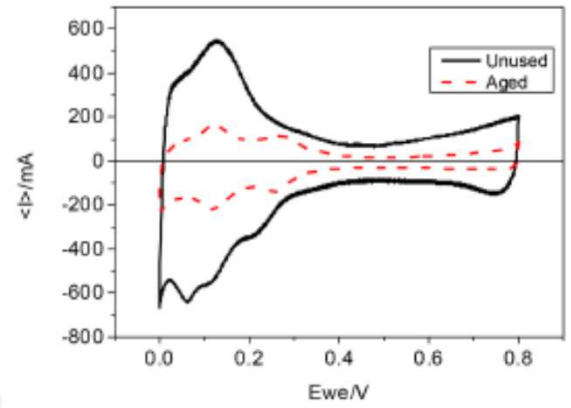
Analytical Methods and main outcomes

Summary

Short introduction on main degrading components in PEM WE

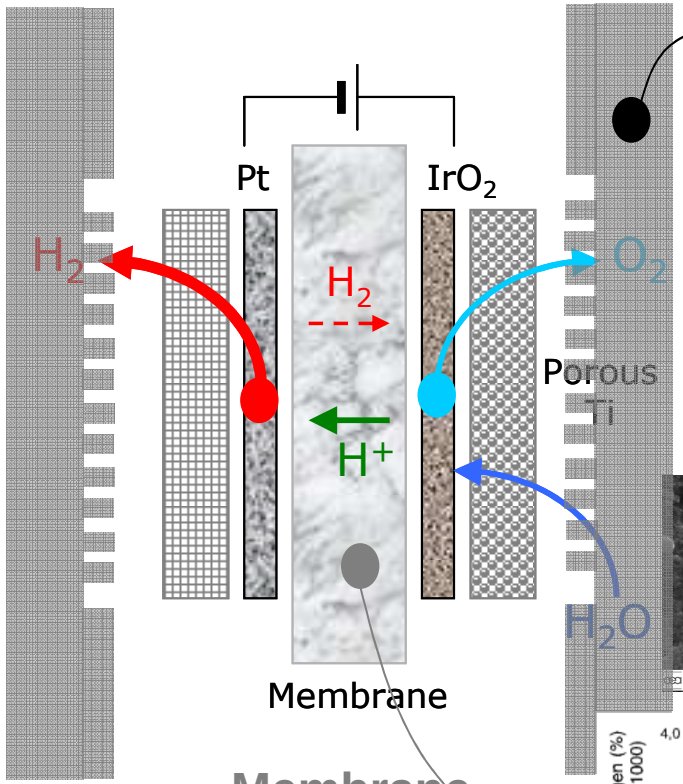
Cathode catalyst degradation





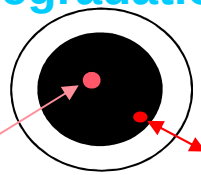
CV of unused (black, solid) and aged (red, dashed) Pt electrodes in situ.
Scan rate = 100 mV/s.

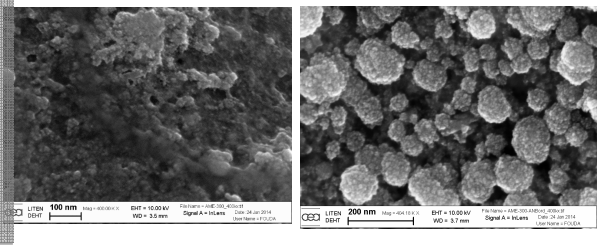
BP degradation



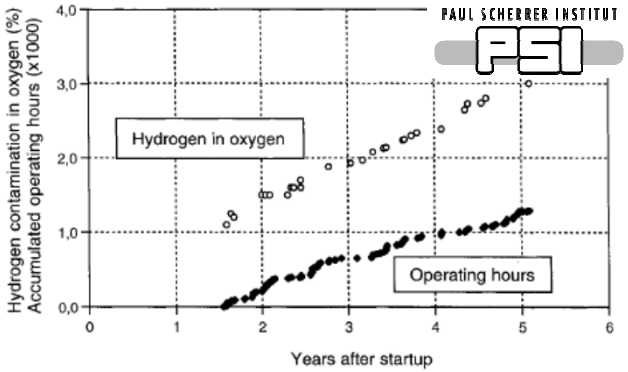
Fraunhofer ISE

Anode catalyst degradation



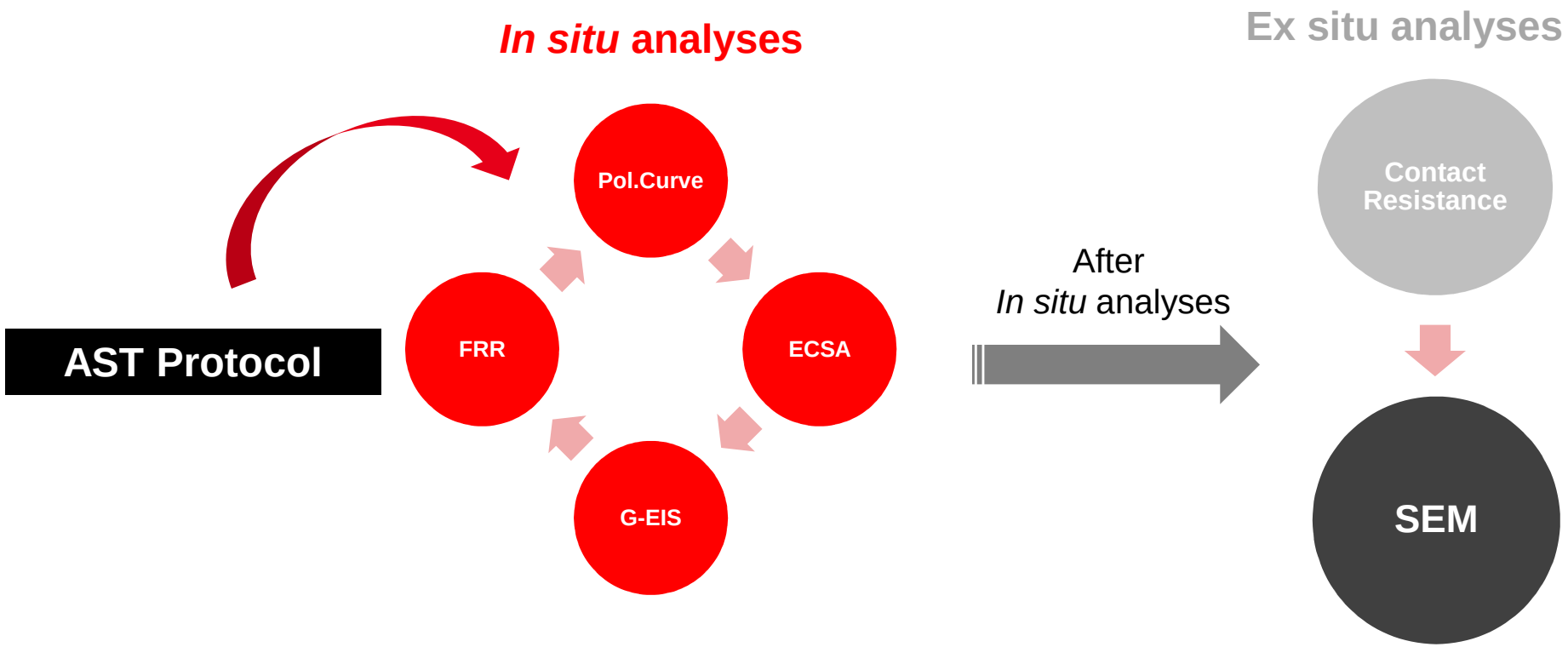


Membrane degradation



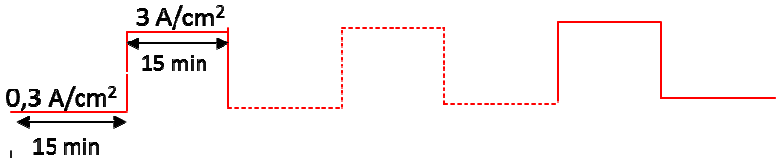
Most of the cell components may age

Analytical Methods and main outcomes



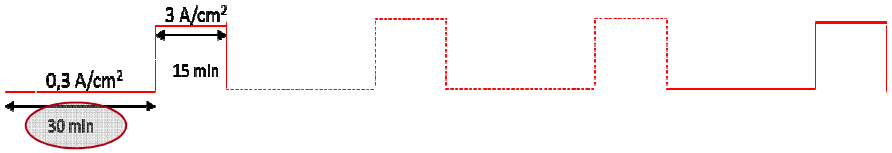
Analytical Methods and main outcomes

AST-1: 48h AST signal @ 90°C repetaed at least 4 times



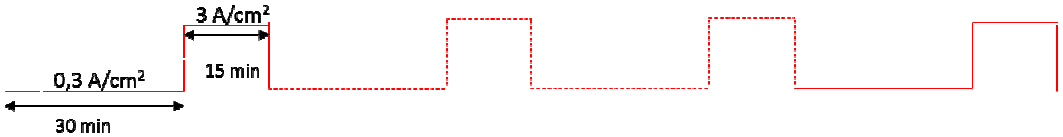
- 3 A/cm² (E > 2V) : speed up BP corrosion
- 0,3 A/cm² : speed up membrane attack

AST-2: 48 h AST@ 90°C repeated at leat 4 times



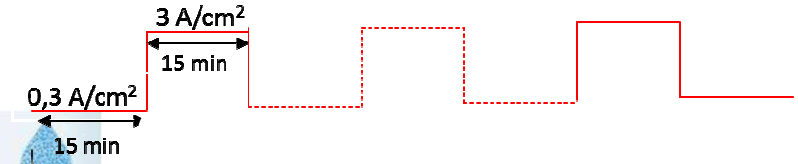
- Longer step time at low current density to amplify the membrane chemical attack

AST-3: : 48 h AST@ 90°C repeated at leat 4 times with ΔP (P_{O2} = 4 bar vs. P_{H2} = 1 bar)



- Suppose to amplify the oxygen permeation and accelerate the membrane attack

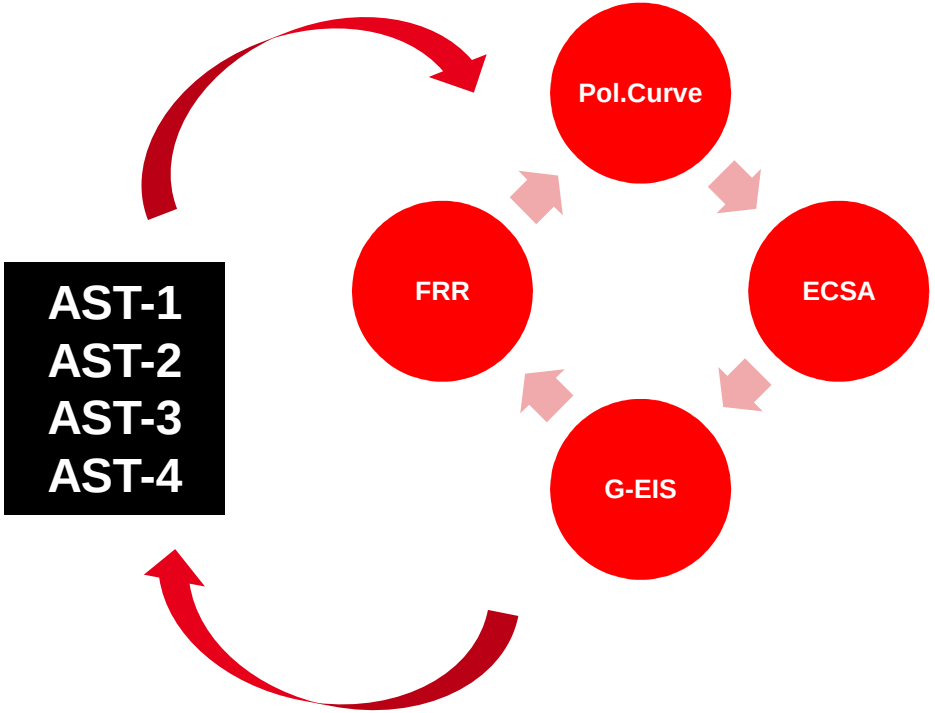
AST- 4: 48 h AST@ 90°C repeated at leat 4 times with 5ppm Fe ions



- Adding metal ion impurities may catalyse the Fenton reaction.

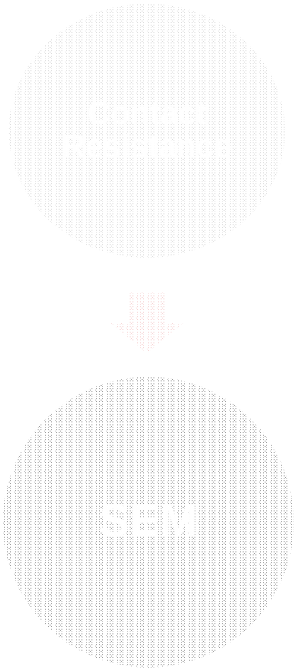
Analytical Methods and main outcomes

In situ analyses

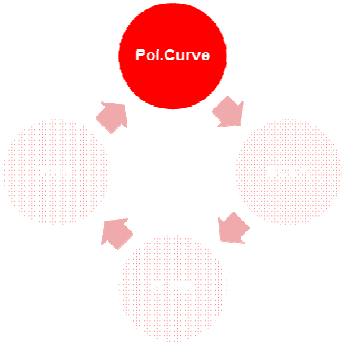


Ex situ analyses

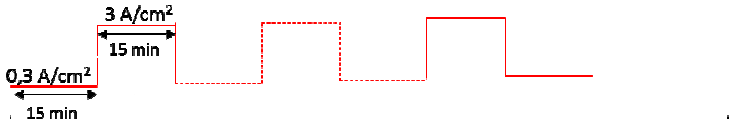
After
In situ analyses

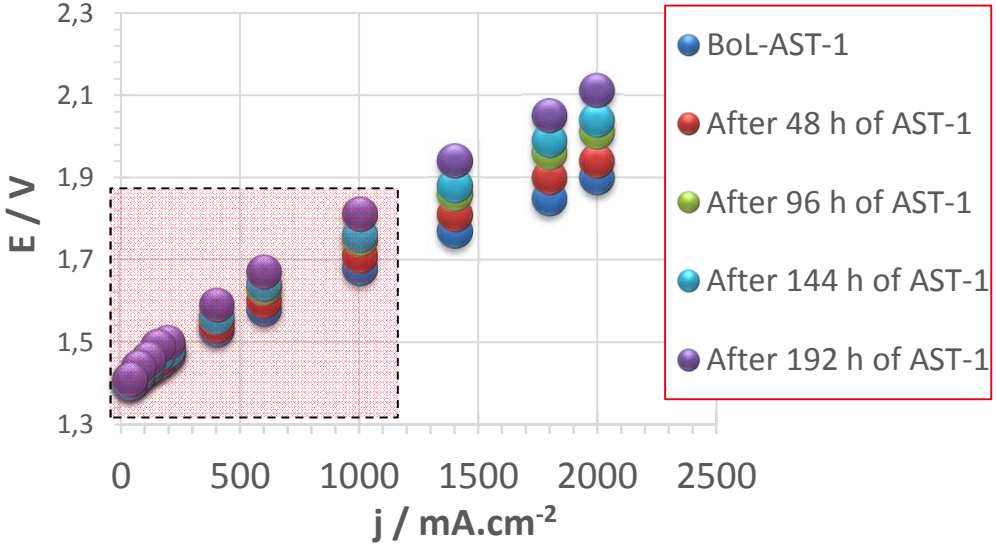


Analytical Methods and main outcomes

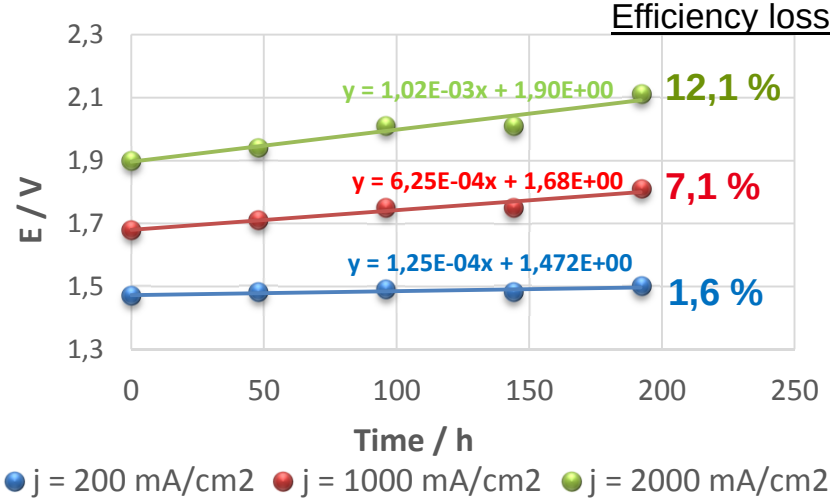


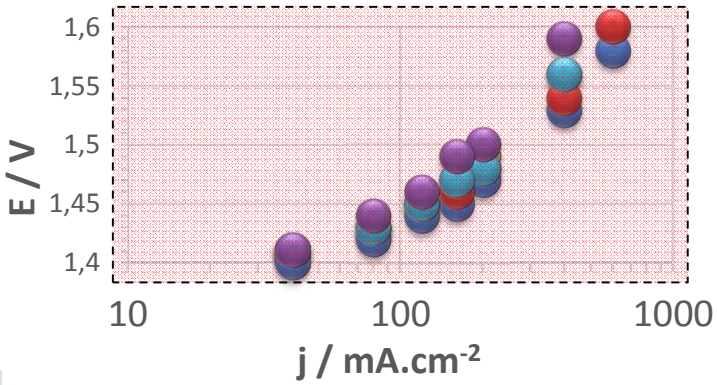
AST-1





Efficiency loss

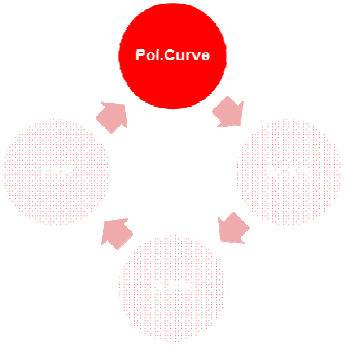




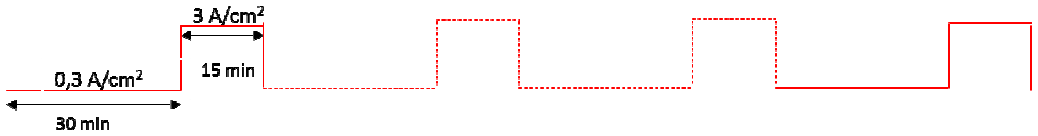
Higher efficiency losses at high current density.

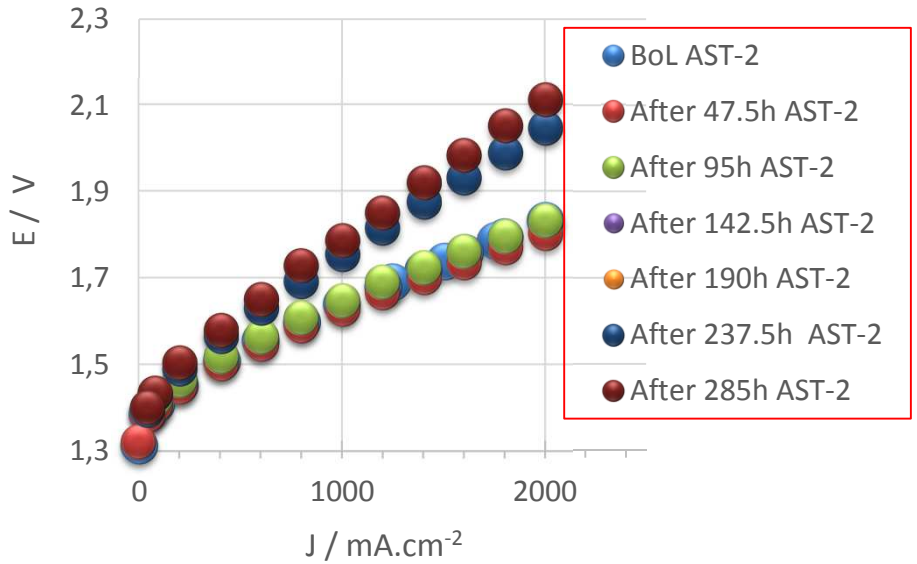
No clear impact in the « activation zone » of the Pol.Curv.

Analytical Methods and main outcomes

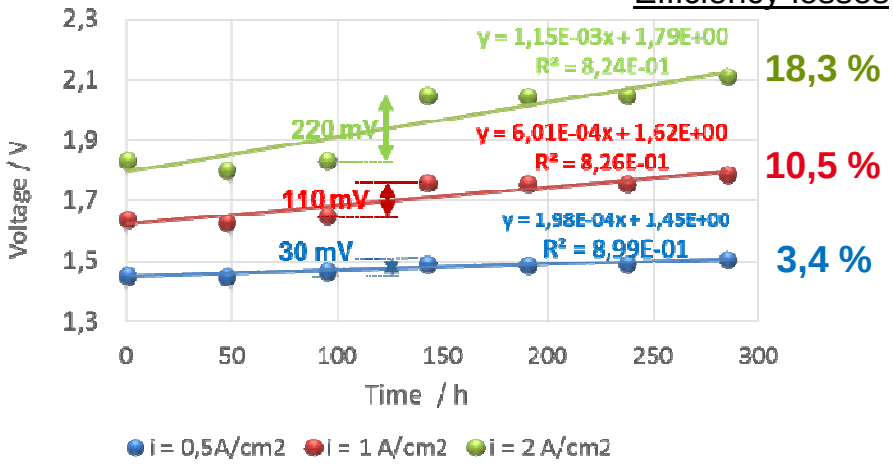


AST-2





Efficiency losses



18,3 %

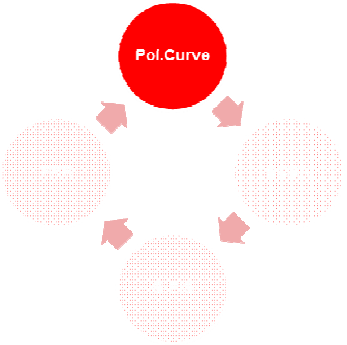
10,5 %

3,4 %

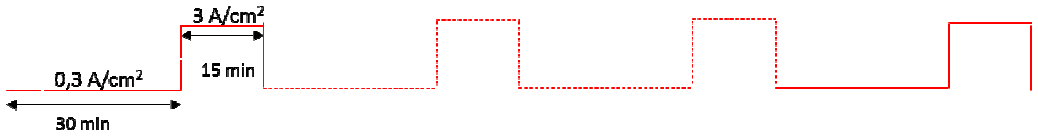
Efficiency losses every 100h

Again higher efficiency losses at high current density

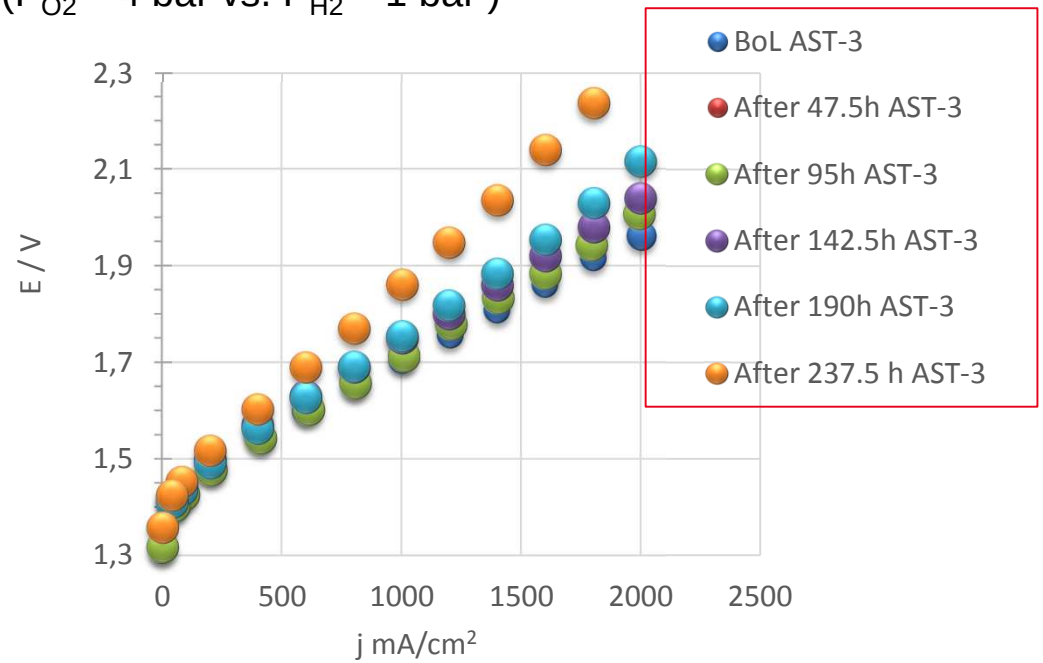
Analytical Methods and main outcomes



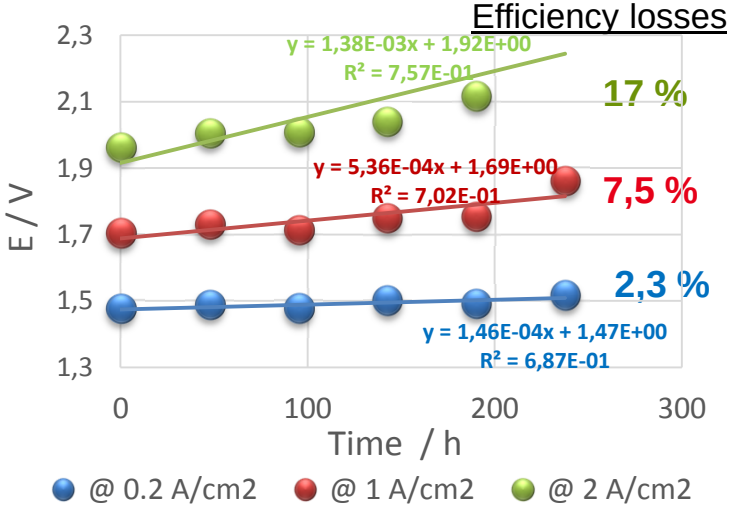
AST-3



ΔP (P_{O2} = 4 bar vs. P_{H2} = 1 bar)



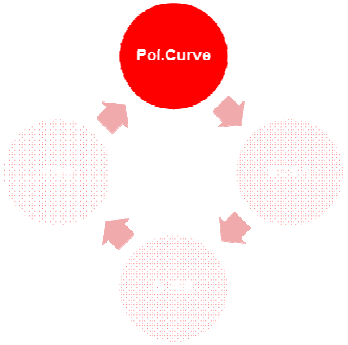
Efficiency losses



Efficiency losses every 100h (close to AST-2)

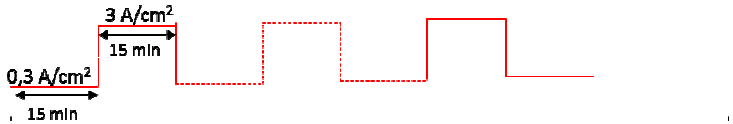
Again higher efficiency losses at high current density

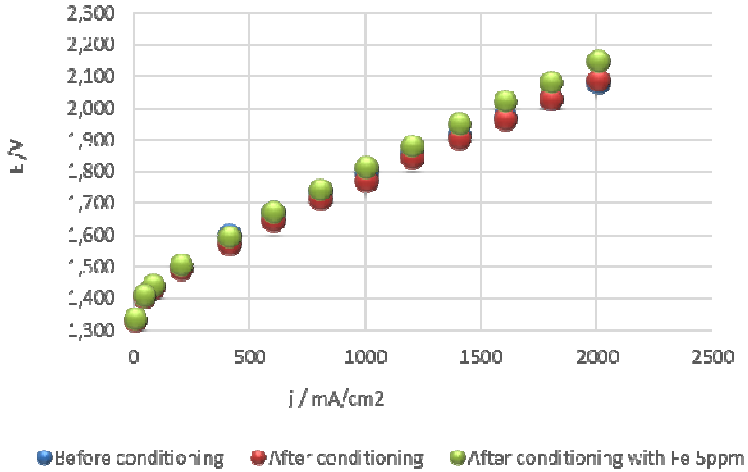
Analytical Methods and main outcomes

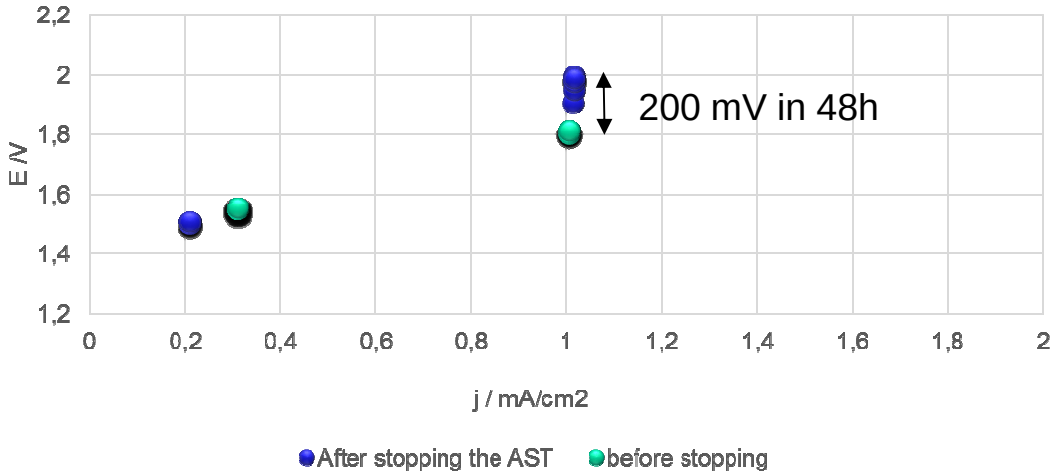


AST-4

H_2O + 5 ppm Fe







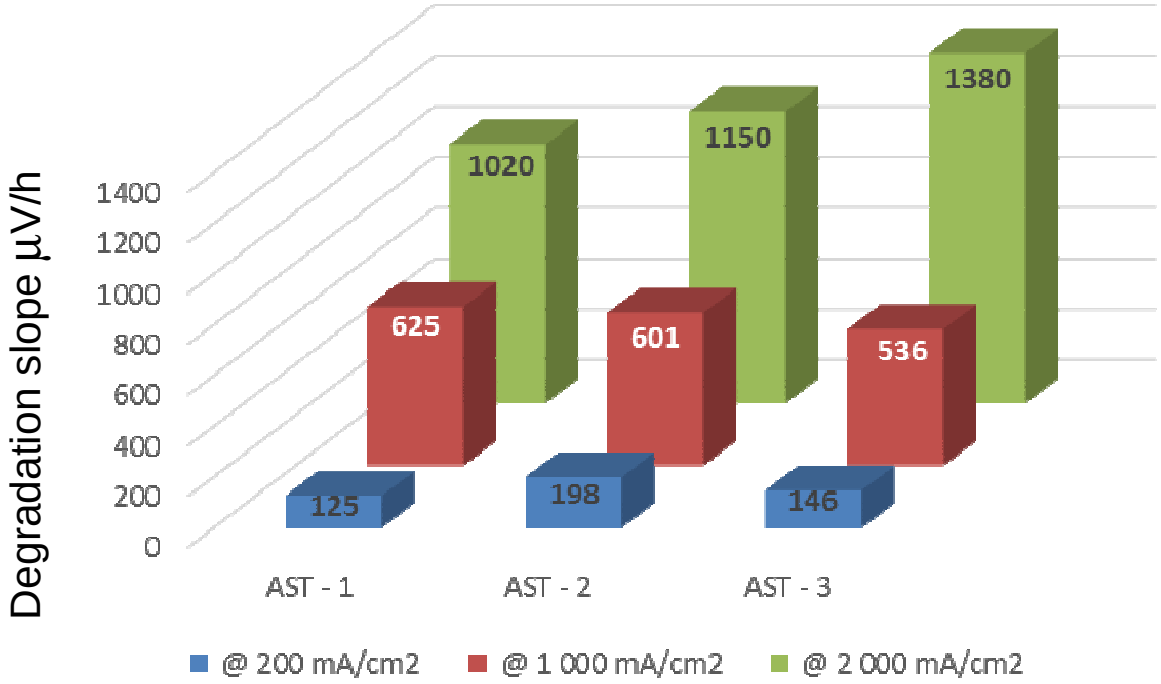
AST-4 : was stopped earlier

5 ppm Fe^{3+} is a too high concentration

Few tens of ppb might be enough

Analytical Methods and main outcomes

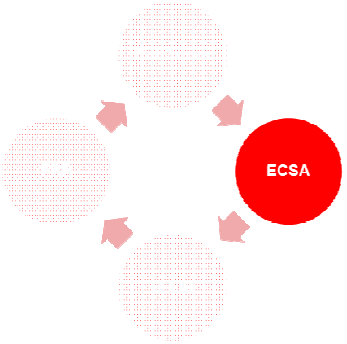
Conclusion from Pol.Curve



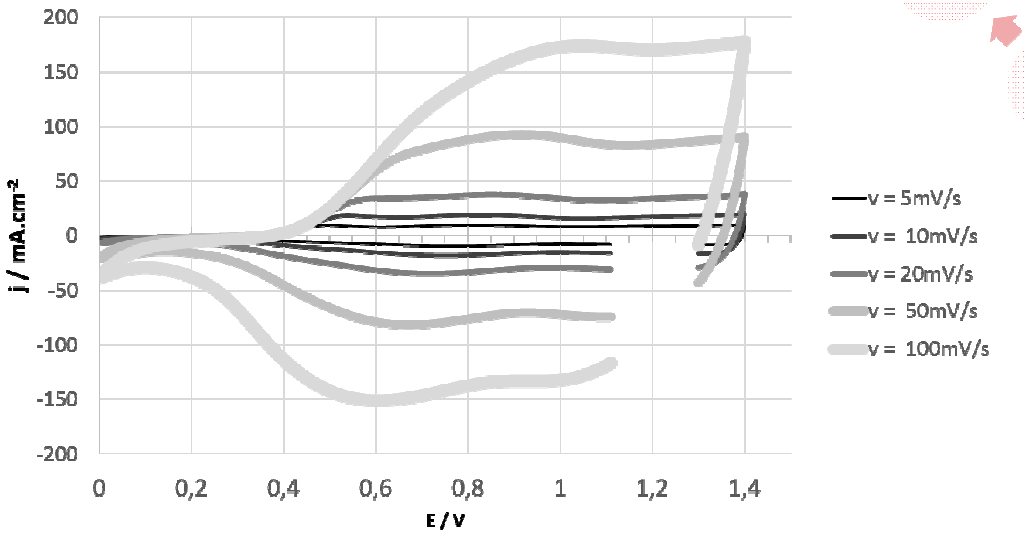
Ageing more important at high current (caused by the resistance).

Cannot conclude without further analyses

Analytical Methods and main outcomes



Cyclic voltammetry



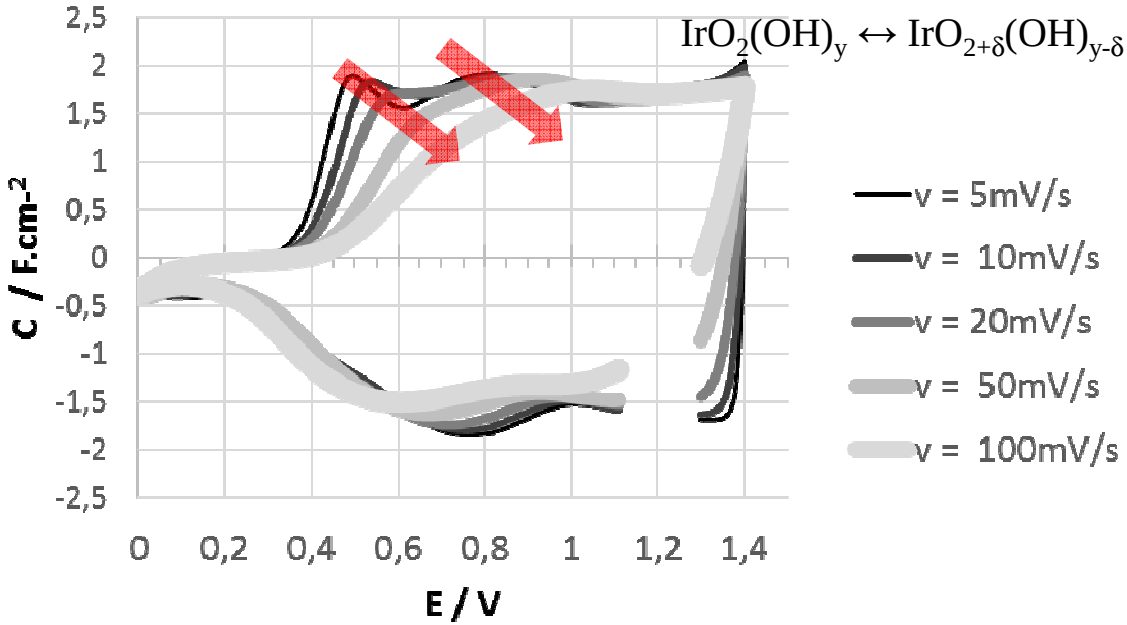
$$IrO_2(OH)_y \leftrightarrow IrO_{2+\delta}(OH)_{y-\delta} + \delta\,(H^+ + e^-)$$

$$i = \frac{dQ}{dt} = C\frac{dV}{dt}$$

$$V = E_{OCV} \pm \nu \times t$$

$$\frac{dV}{dt} = \pm \nu$$

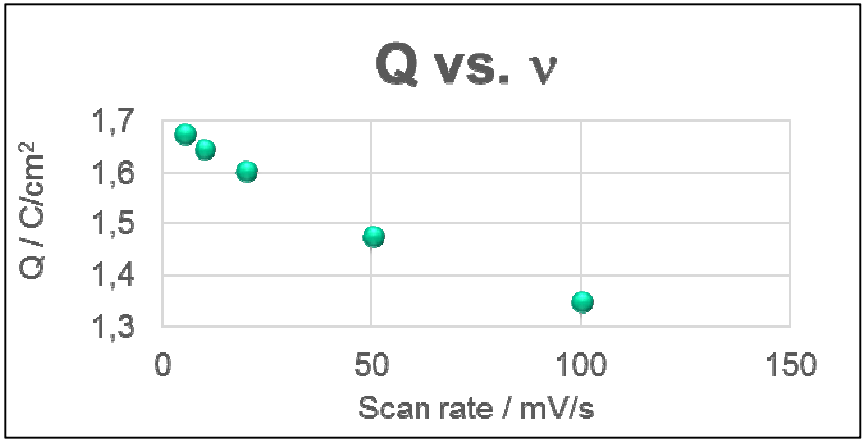
$$i = \frac{dQ}{dt} = \pm(C \times \nu)$$

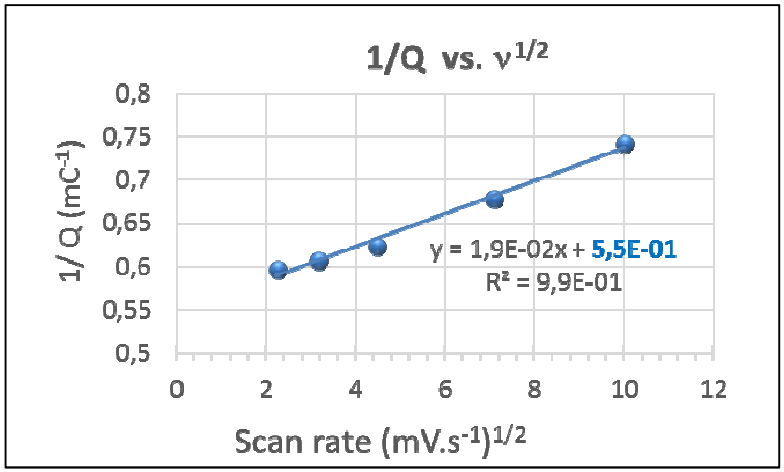


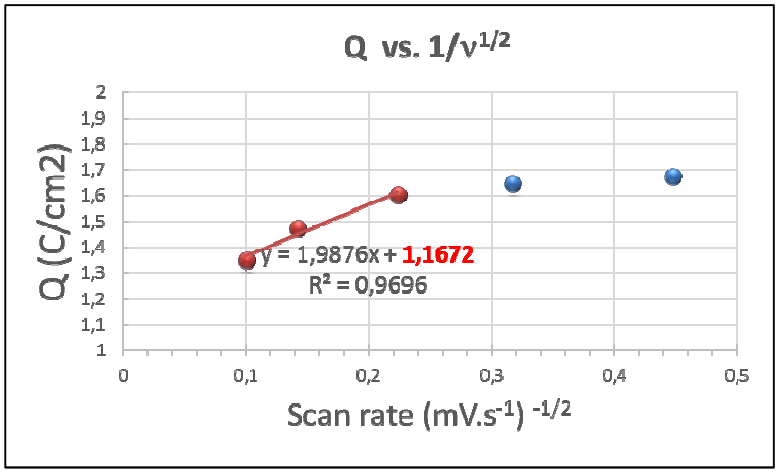
Analytical Methods and main outcomes

ECSA

Cyclic voltammetry







$Q_{tot} = Q_{inner} + Q_{outer}$

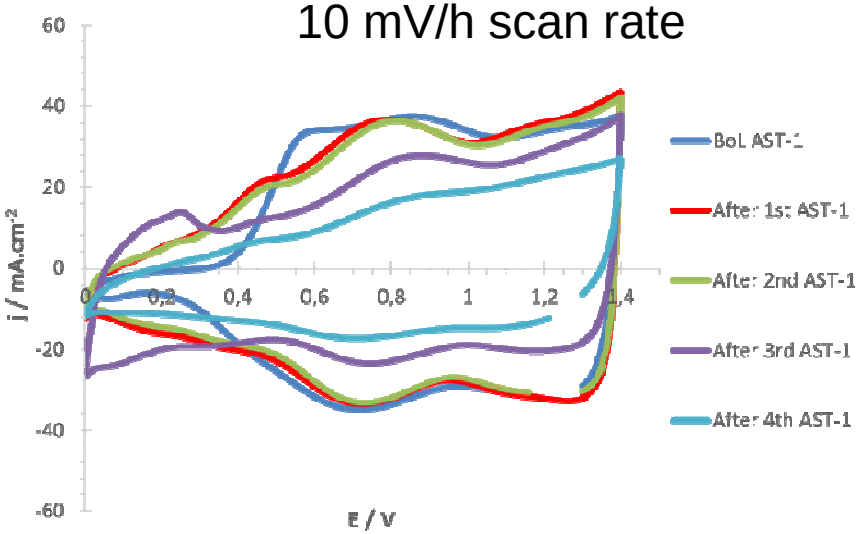
Ardizzone et al. Electrochimica acta vol 35 n° 1- 263-267 (199

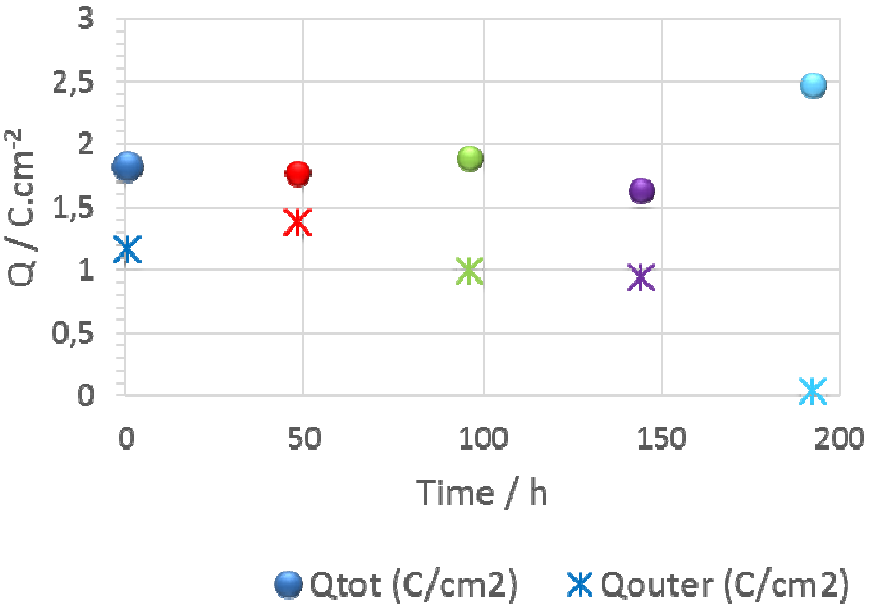
Analytical Methods and main outcomes

ECSA

Cyclic voltammetry

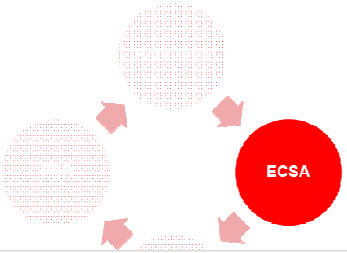
10 mV/h scan rate



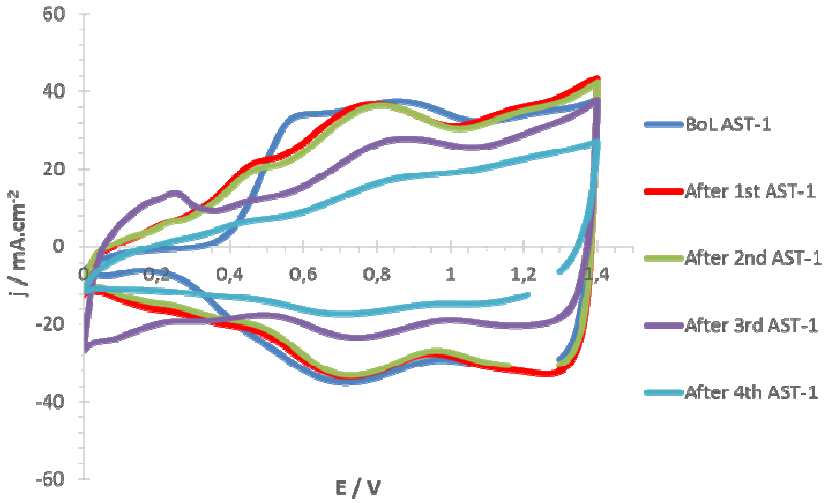


- **The different shapes of CV do not affect the Pol.Curve (activation part)**
- **After 196 h(EoL) CV unusal shape, probably too resitive contact resistance**
- **After 144 h appearence of Hupd peak (0 < E < 0,3 V_{RHE})**

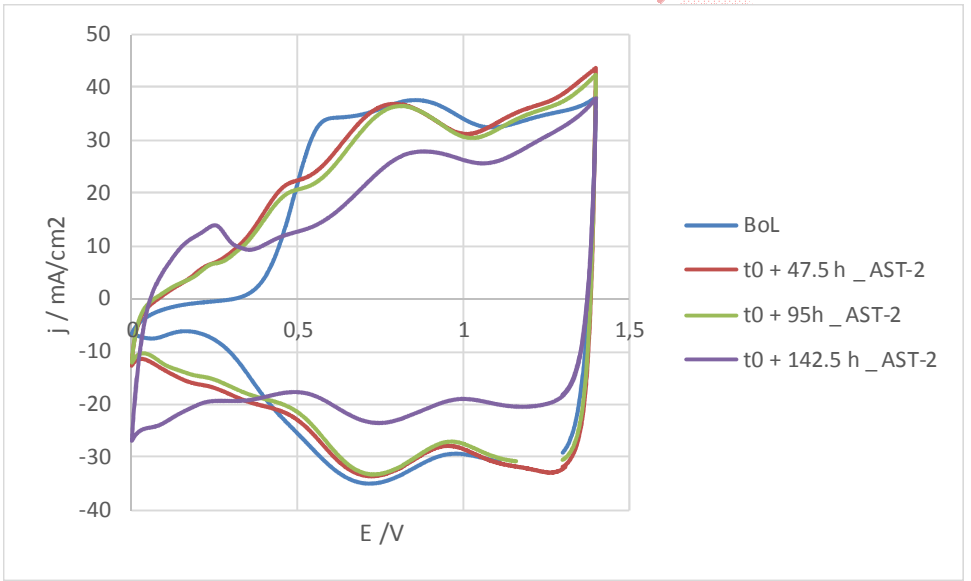
Analytical Methods and main outcomes



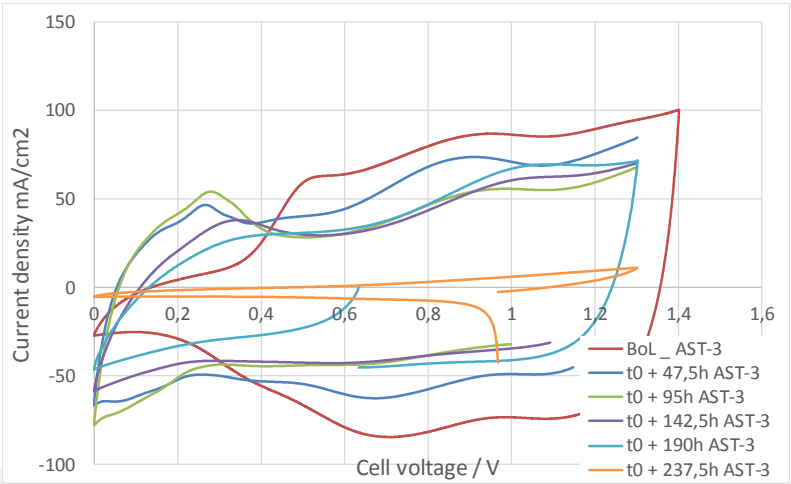
AST – 1



AST – 2

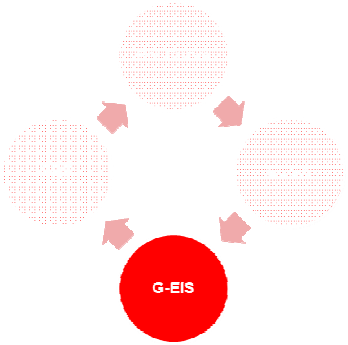


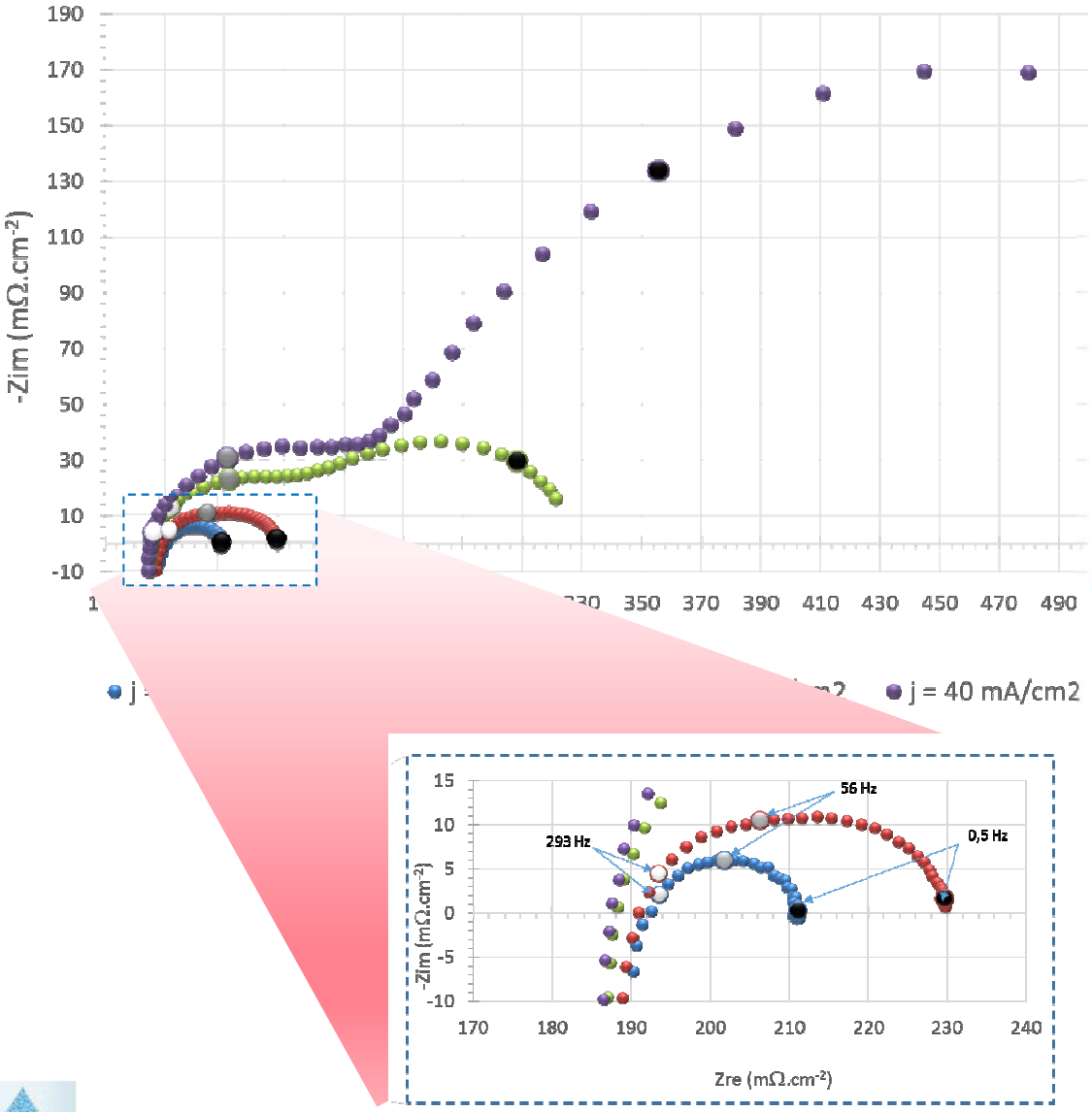
AST – 3

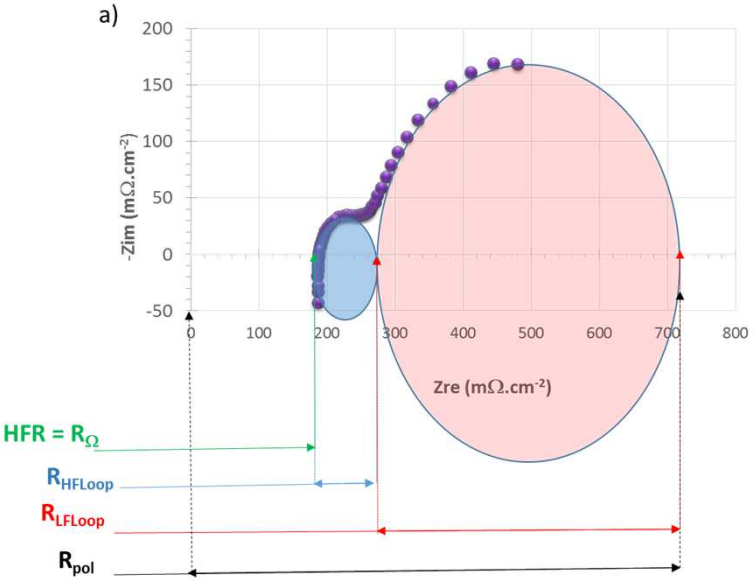


- **Same conclusion for AST2 and AST-3 than AST-1**
- **No effect of the active surface area change on the Pol.Curves**
- **With ageing, appears H_{upd} peak**

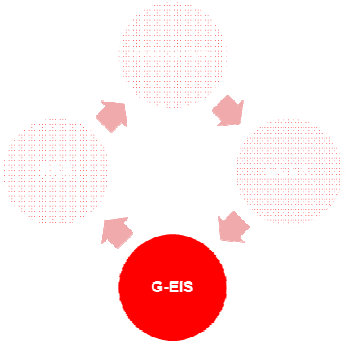
Analytical Methods and main outcomes

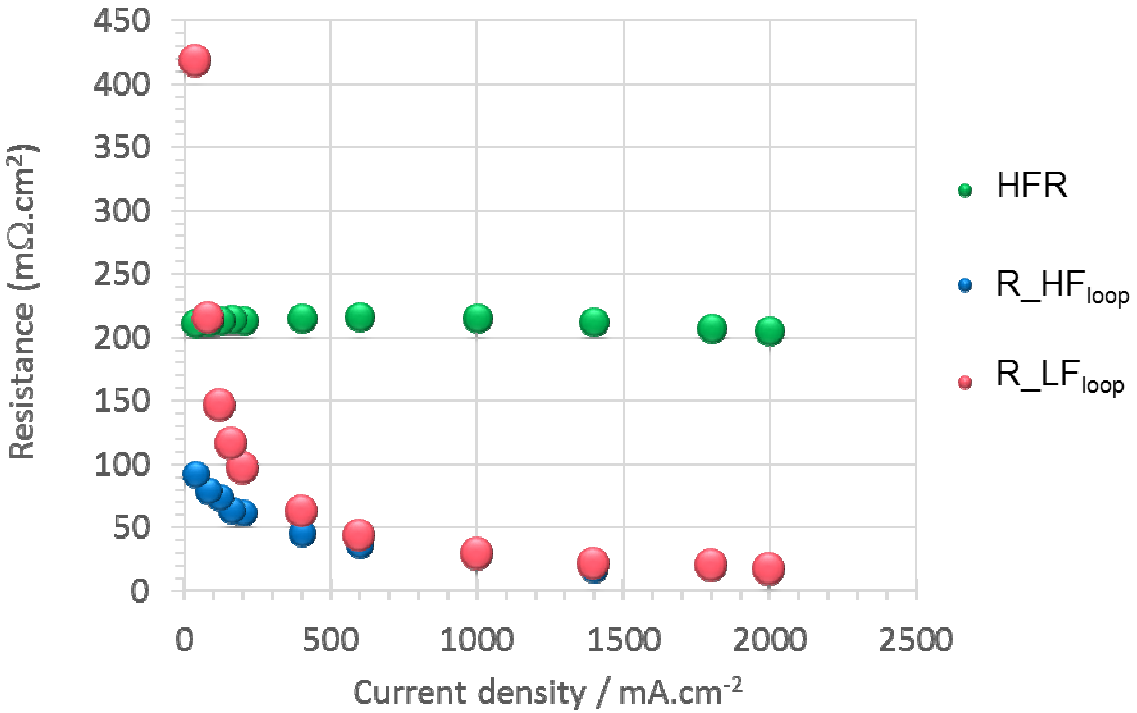


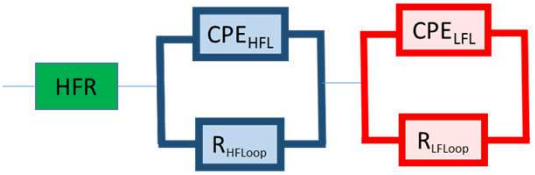




Analytical Methods and main outcomes

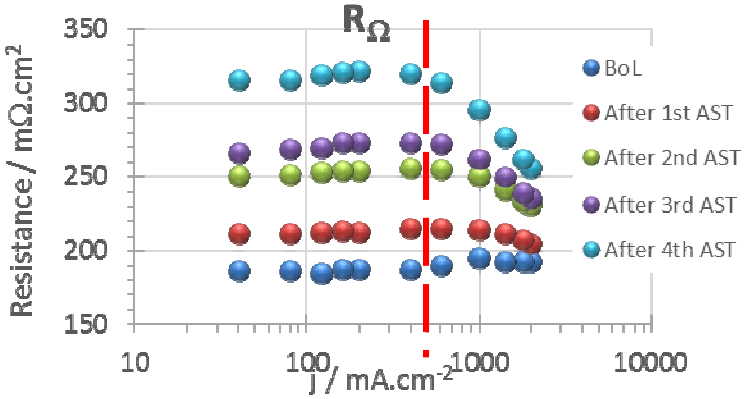


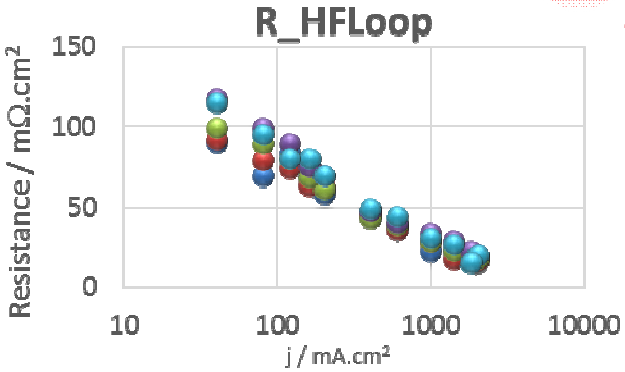


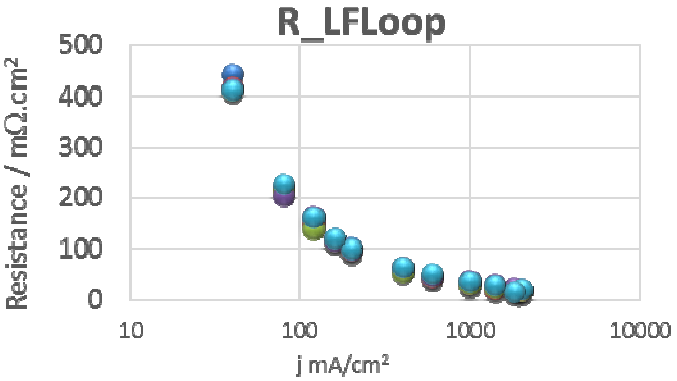


- R_{Ω} independant of the current density (ohmic behaviour)
- R_{HFLoop} decrease with polarization (charge transfert behaviour)
- R_{LFLoop} decreases with polarization (charge transfert behaviour)

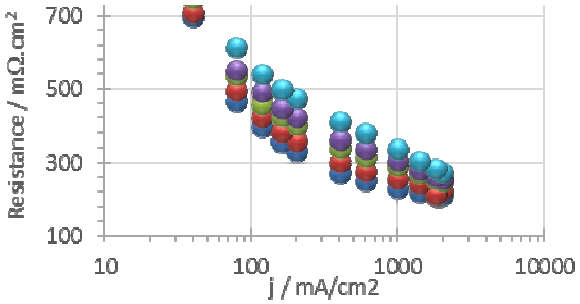
Analytical Methods and main outcomes





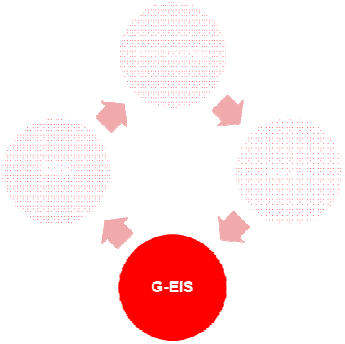


$R_{pol} = R_\Omega + R\_HFLoop + R\_LFLoop$



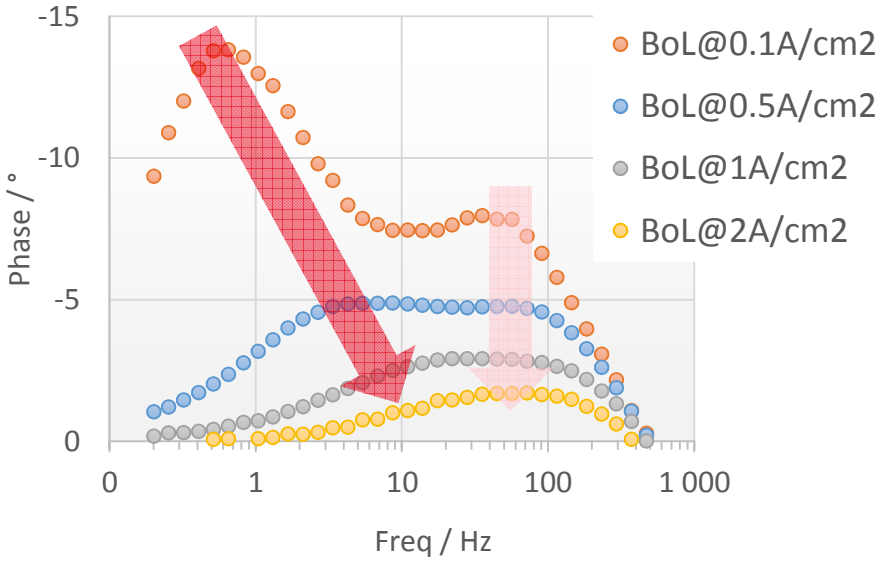
- **With ageing R_Ω decrease at high current density**
- **R_{HFLoop} and R_{LFLoop} do not change with ageing *(consistent with activation part Pol.curves)***
- **The increase of R_{pol} is due to R_Ω**

Analytical Methods and main outcomes

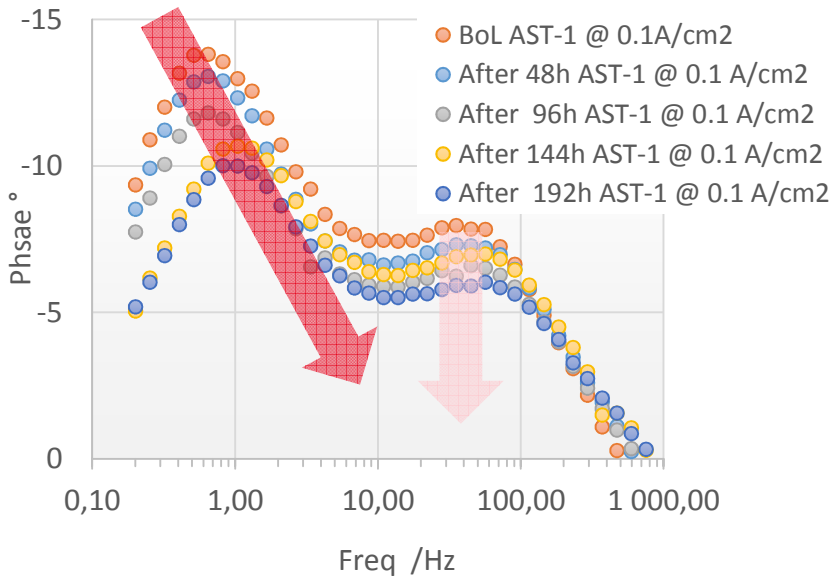


Analyses from Bode representation

$$f_c = 1 / (2\pi RC)$$



Effect of the polarization reduces the charge transfer resistance (LF_{loop}) that increases Cutt-off Frequency

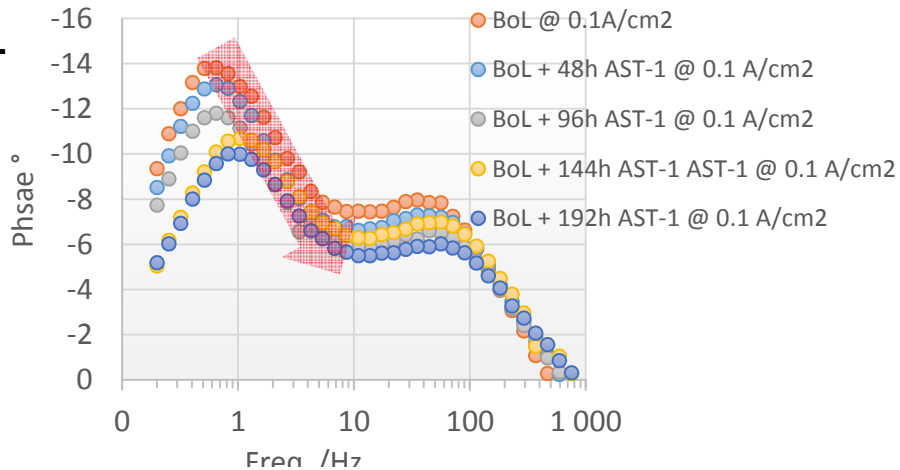


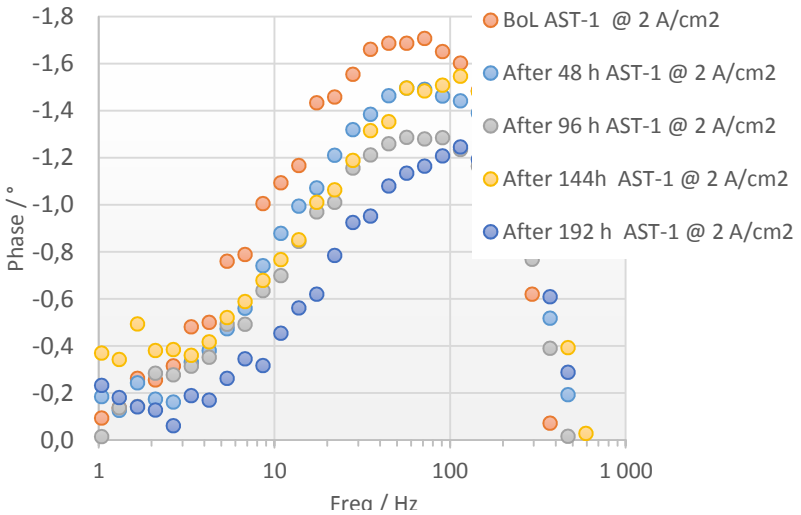
Effect of the ageing reduces the Cdl that increases Cutt-off frequency
(consistent with the outer capacitance diminution with the ageing)

Analytical Methods and main outcomes

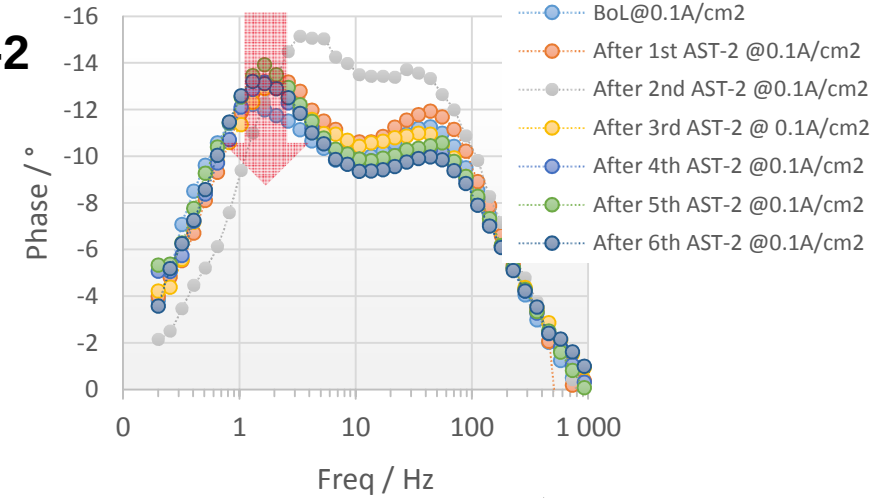
Analyses from Bode representation

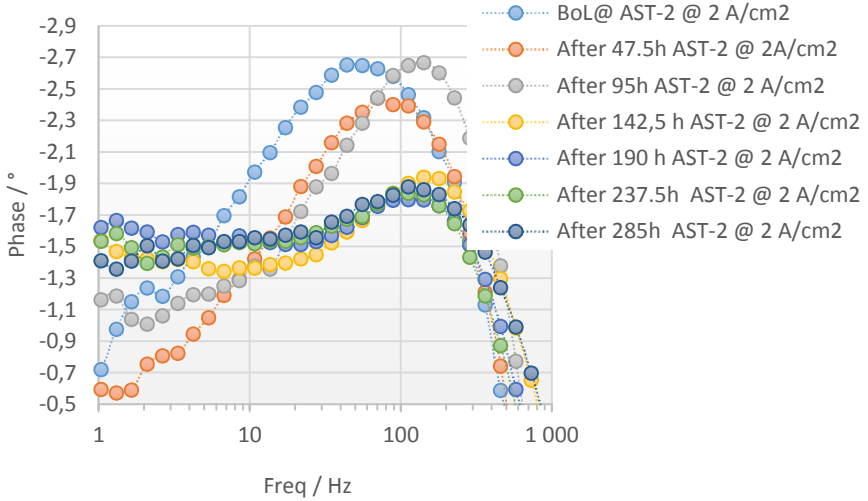
AST-1





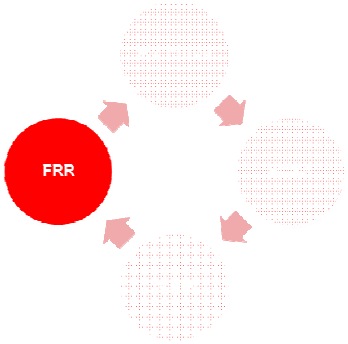
AST-2

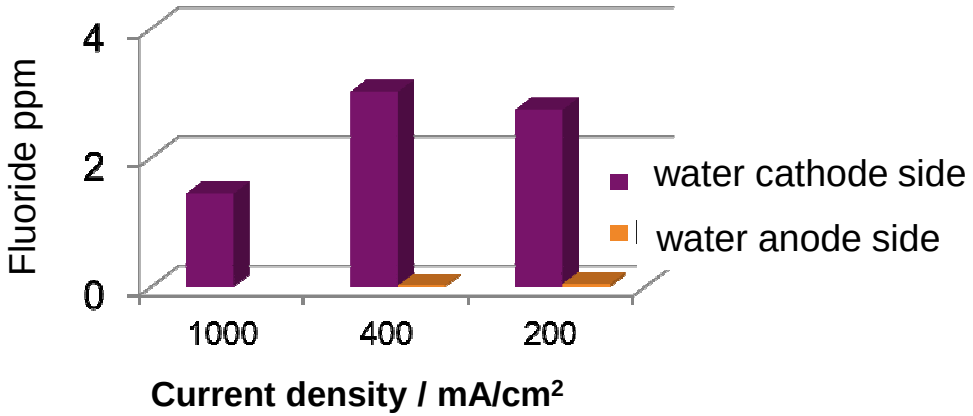




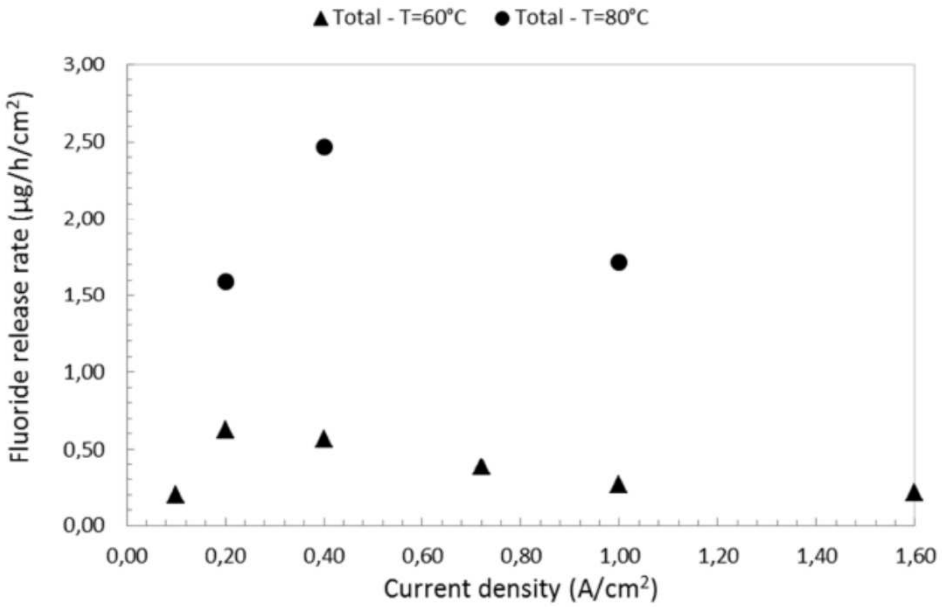
Cut-off frequency shitf might be linked to the electrode degradation

Analytical Methods and main outcomes





Fluoride is found mainly on the cathode side

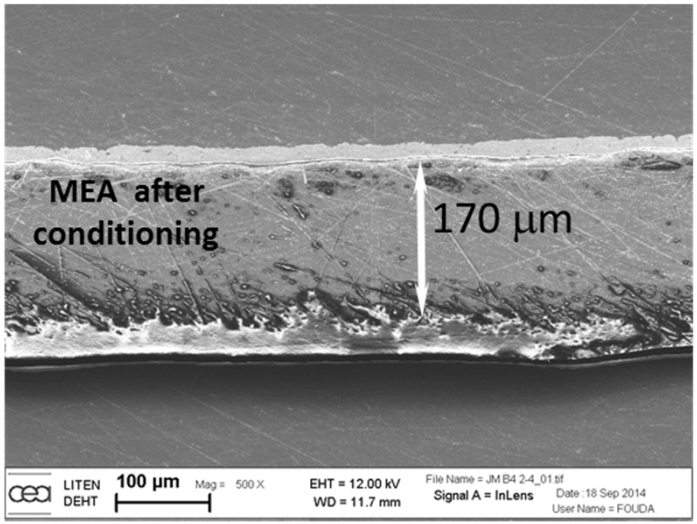


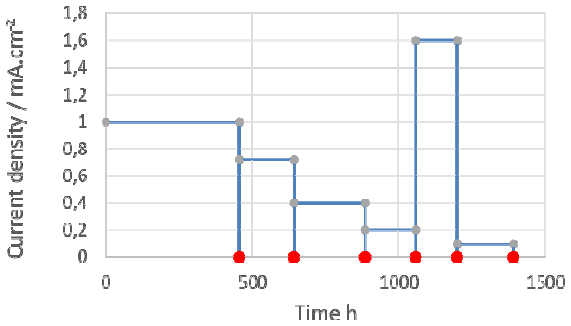
Temperature and Setting current effect on FRR*

These results lead us to define AST parameters
(0,3 A/cm² and high temeprature 90°C)

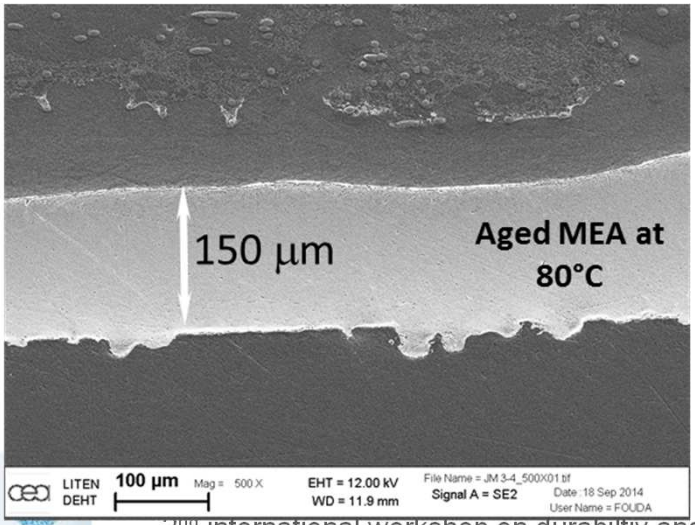
* M.Chandesris *et al.* Int.J.Hyd. Energy, 40 (2015) 1353 - 1366

Analytical Methods and main outcomes

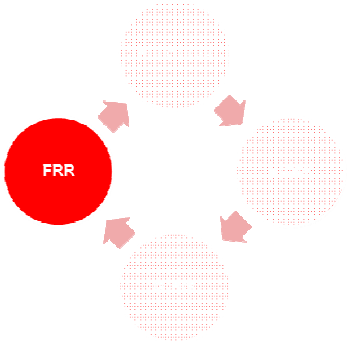




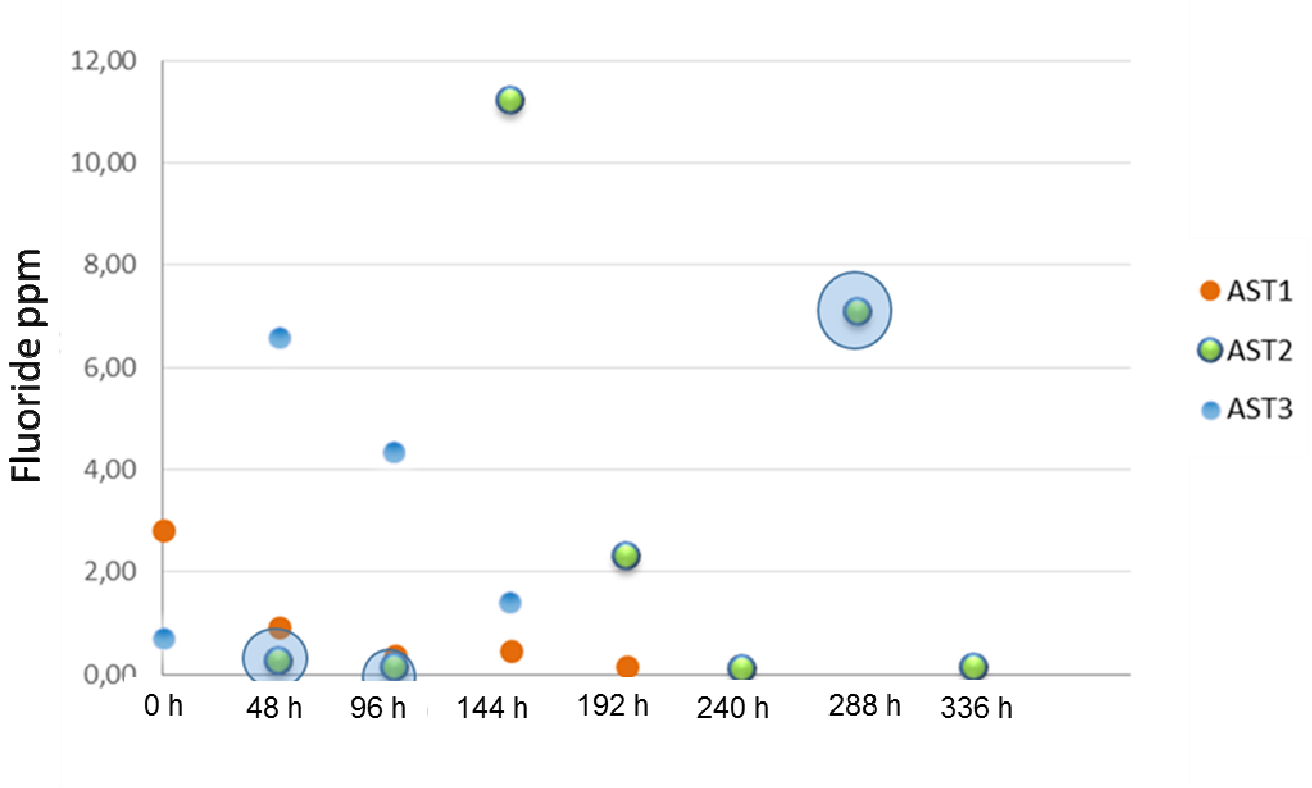
30 µm lost 1500 h (20 nm/h)



Analytical Methods and main outcomes



Erratic points



AST-2 and AST-3 more degrading than AST-1

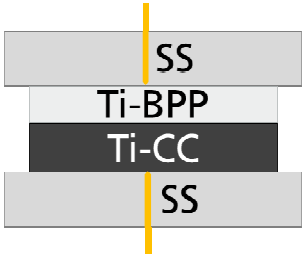
AST-3 do not age more the membrane than AST-2 (contrary to expectations)

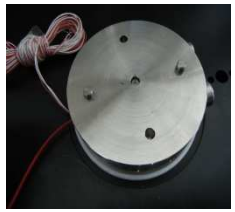
Analytical Methods and main outcomes

Analytical Methods and main outcomes

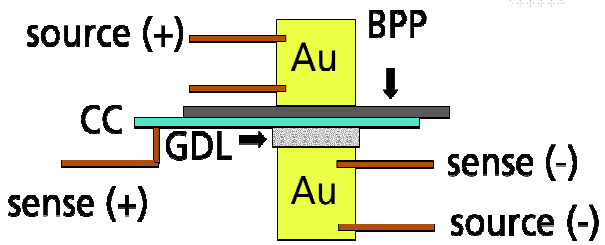
Contact Resistance

Contact Resistance





Contact resistance BPP/Curr.Coll



Résistance de contact « soft material » // Curr.Coll

	Bulk measurement	Interfacial Contact Resistance
Aged CC	20 $\mu\Omega.cm^2$	
Fresh CC	20 $\mu\Omega.cm^2$	
Aged (CC/IrO_2) // BP		13,9 $m\Omega.cm^2$
Aged (IrO_2/CC) // BP		22,6 $m\Omega.cm^2$
Fresh CC // BP		***1 m Ω .cm2***
GDL // aged (IrO_2/CC) // BP		68 $m\Omega.cm^2$
GDL // aged (CC/IrO_2) // BP		426 $m\Omega.cm^2$
GDL // fresh CC) // BP		***79 m Ω .cm²***

No bulk resistance difference

IrO_2 remaining particles improve interface resistance BP/Curr Coll.

Higher contact resitance with a «soft material ».

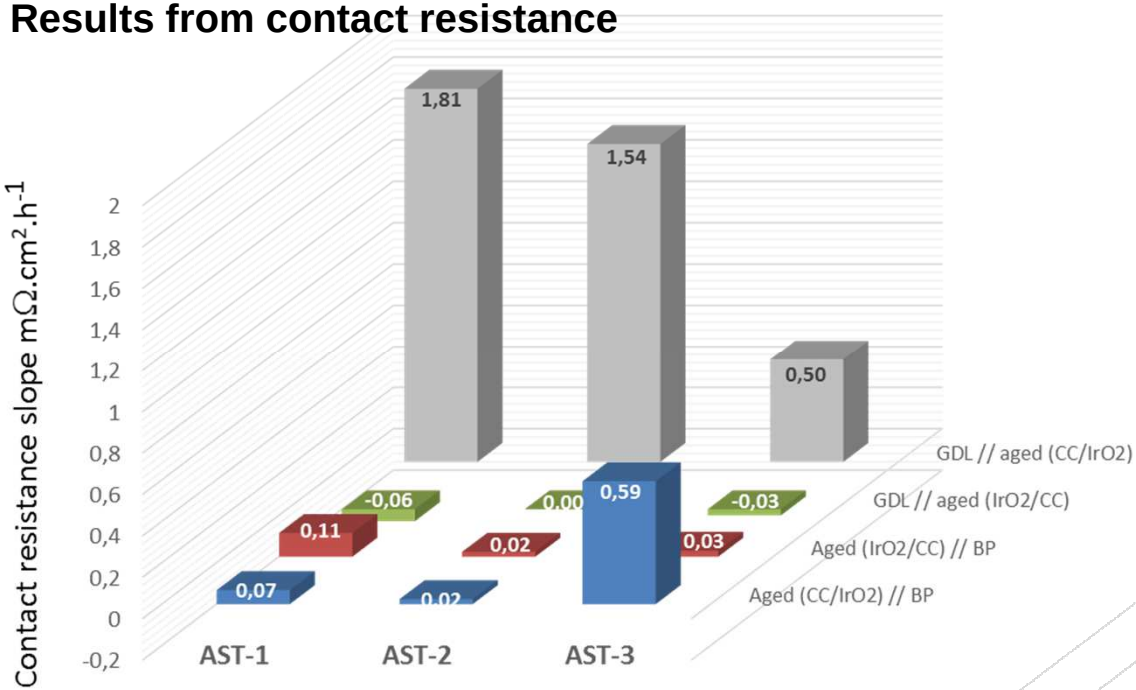
// Interface

CC/IrO_2 // BP: IrO_2 facing CC in contact with the BP

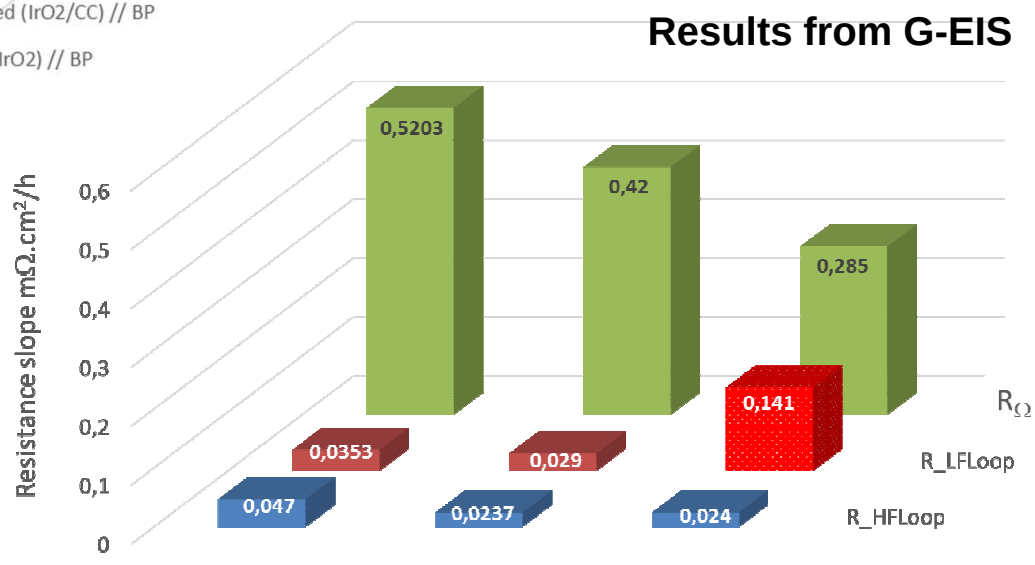
Analytical Methods and main outcomes

Contact Resistance

Results from contact resistance



Results from G-EIS



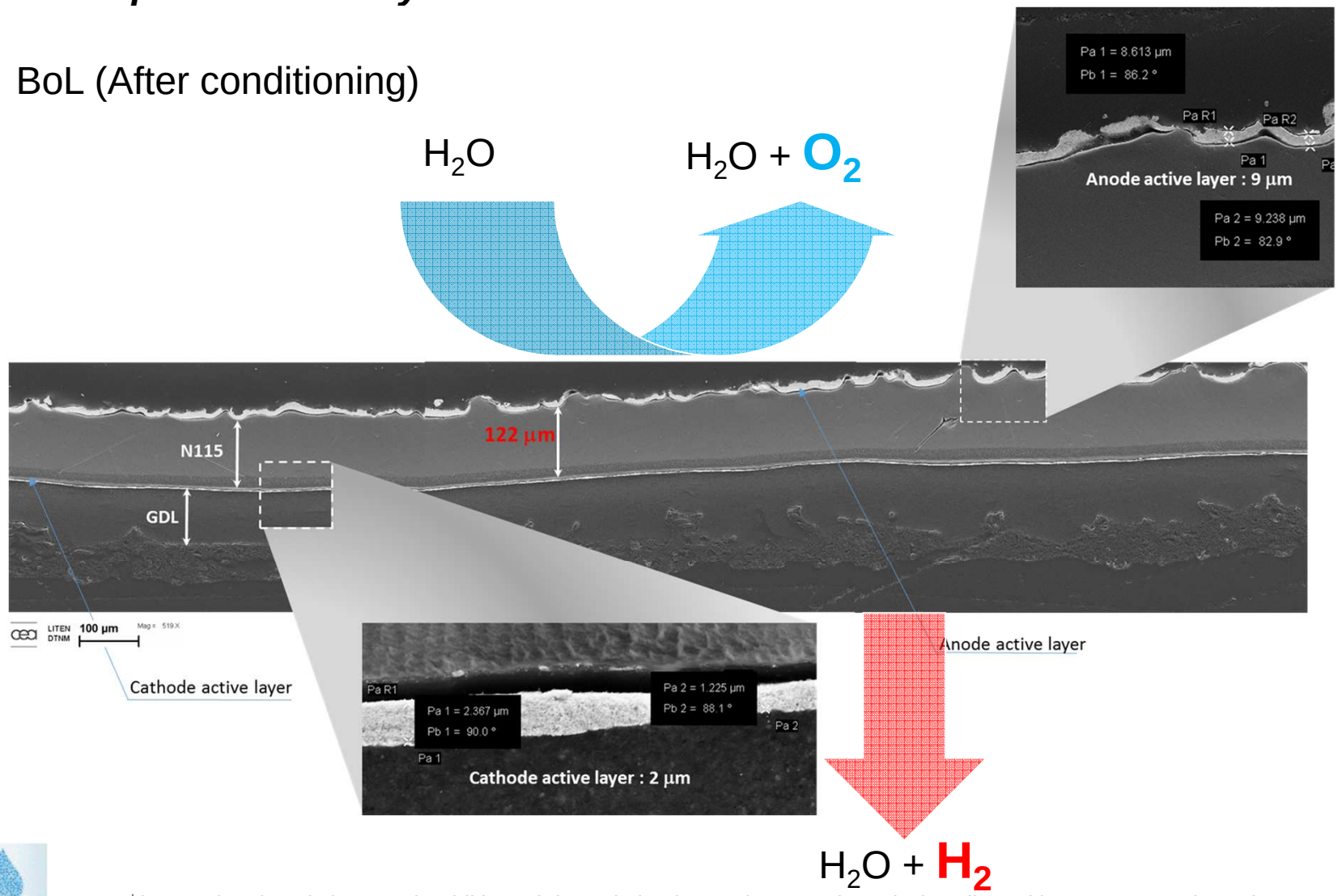
Increase of R_Ω is mainly caused by the interface « soft material »// Curr.Coll.

Analytical Methods and main outcomes

SEM

SEM qualitative analyses

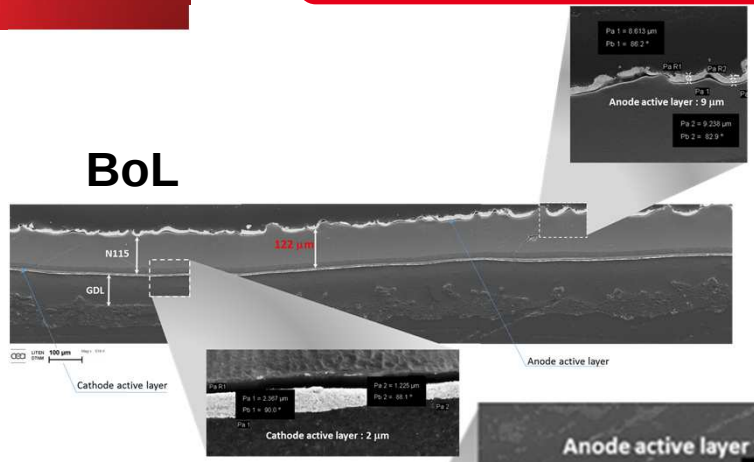
BoL (After conditioning)



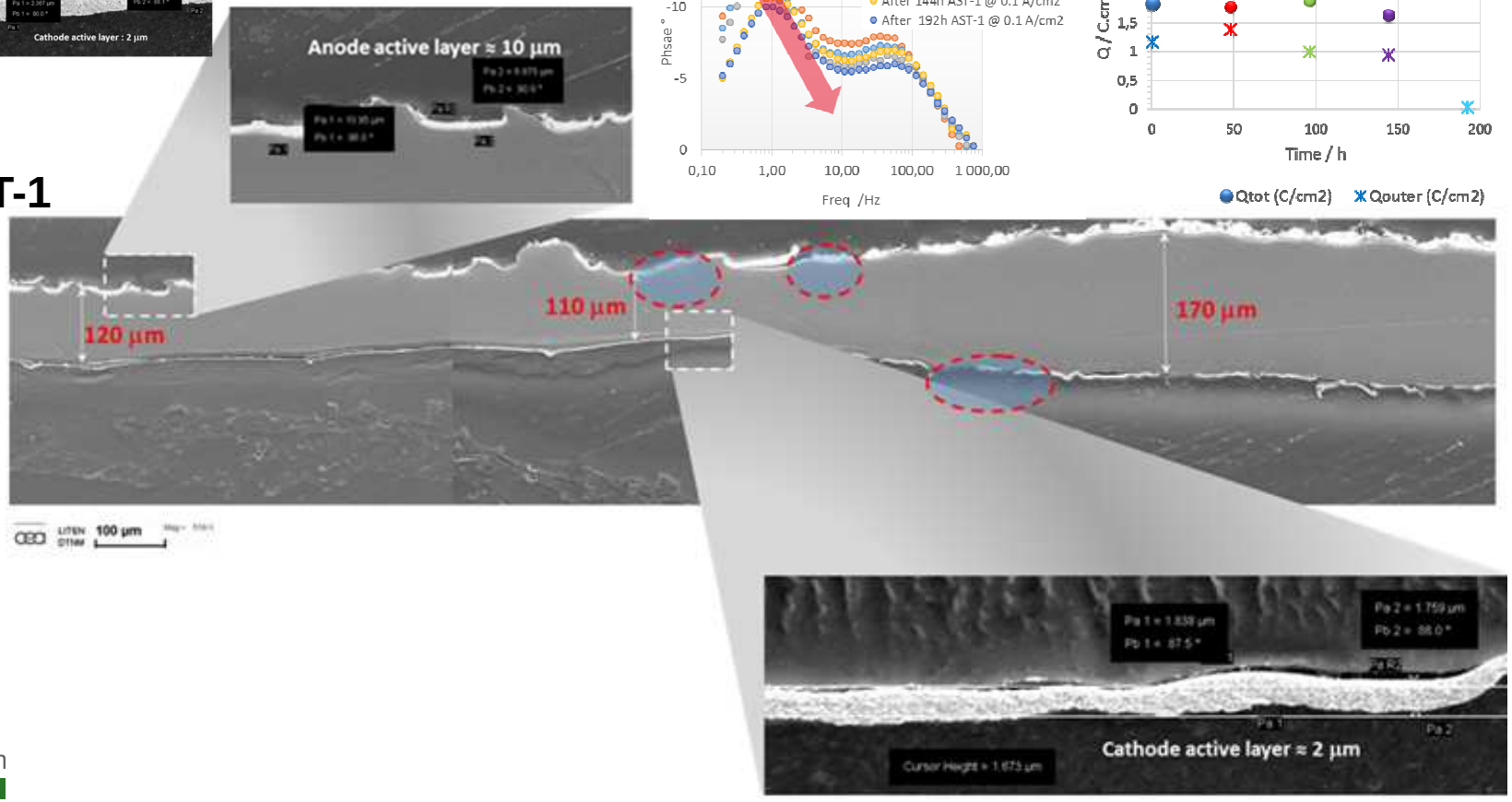
Analytical Methods and main outcomes

SEM

BoL



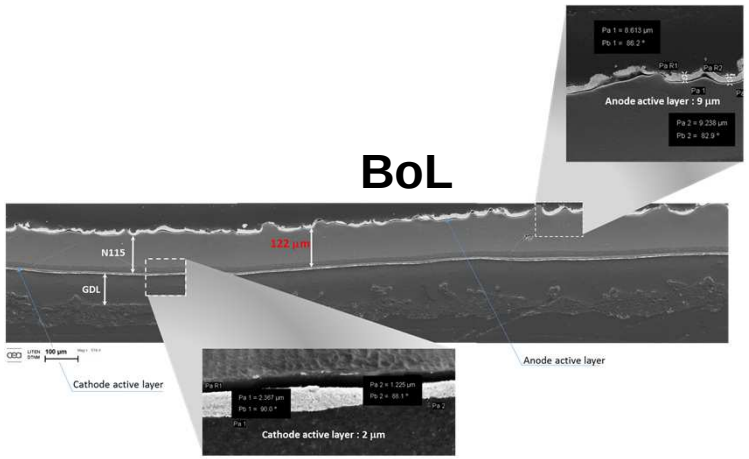
EoL AST-1



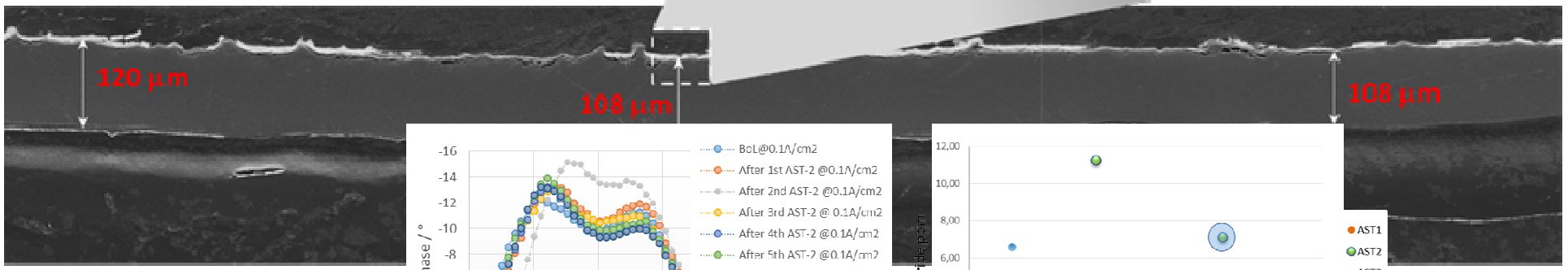
Analytical Methods and main outcomes

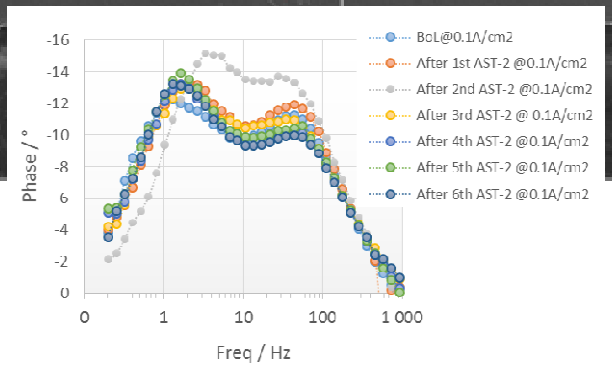
SEM

BoL



EoL AST – 2

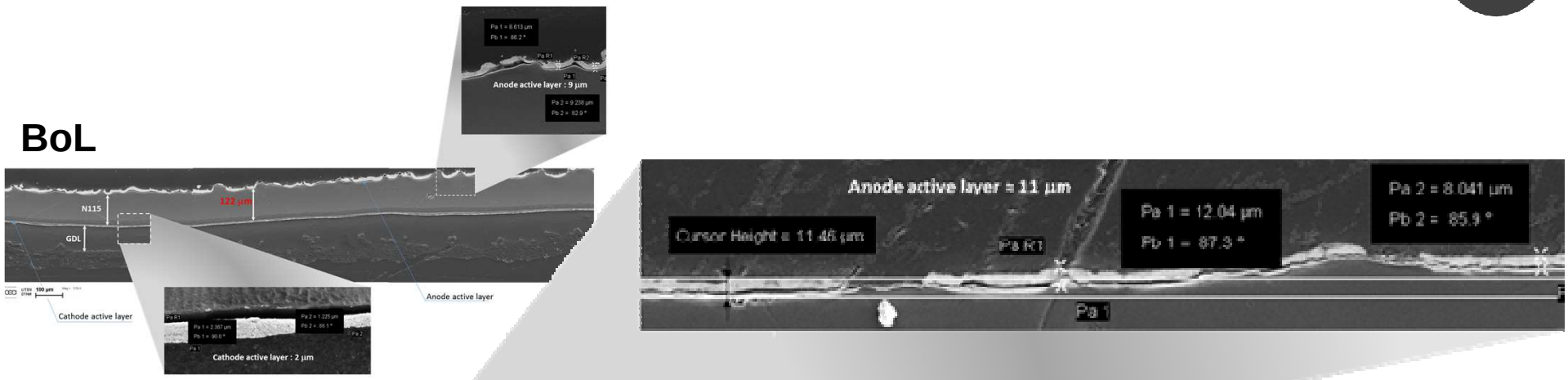




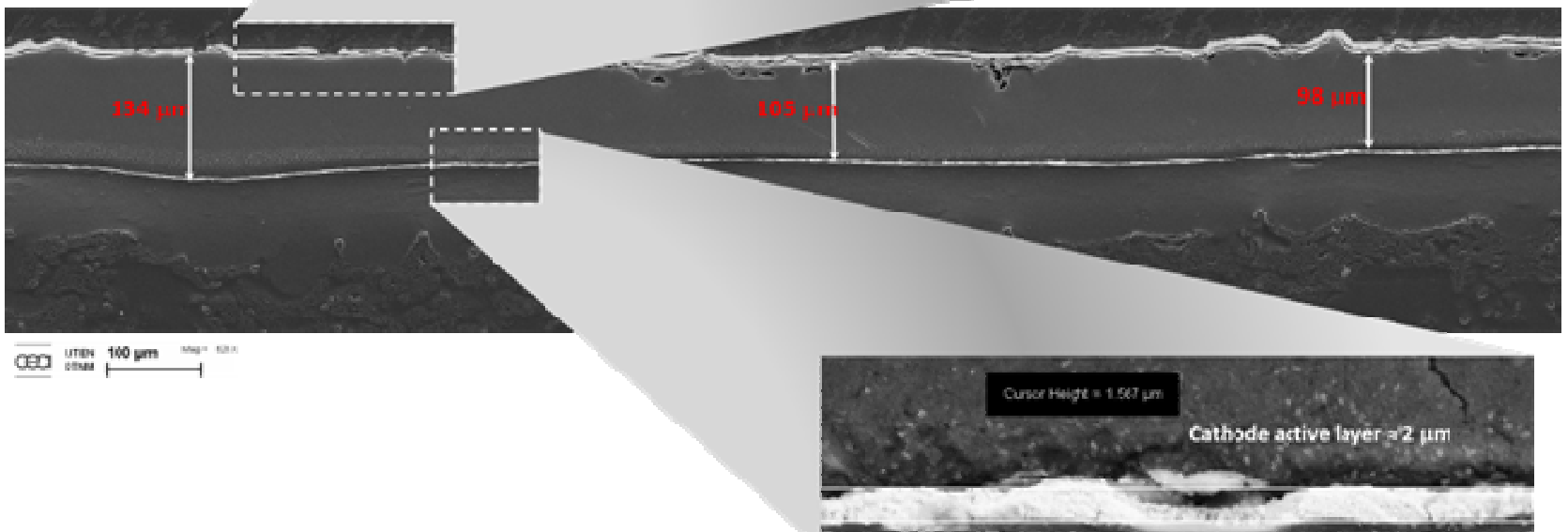
Analytical Methods and main outcomes

SEM

BoL



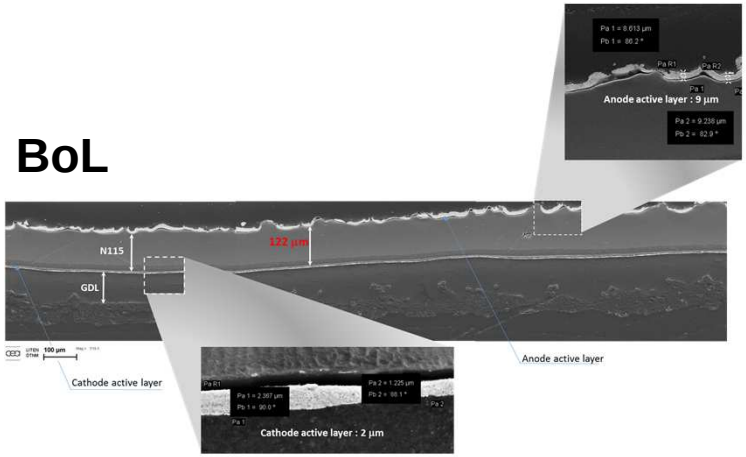
EoL AST-3



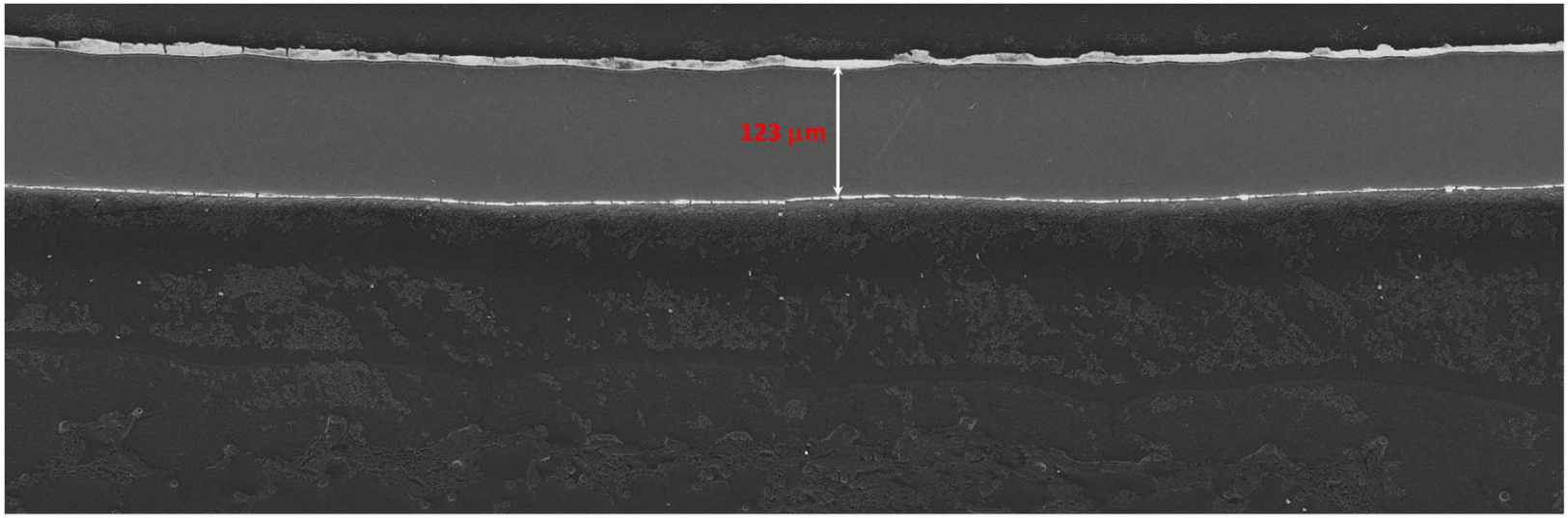
Analytical Methods and main outcomes

SEM

BoL

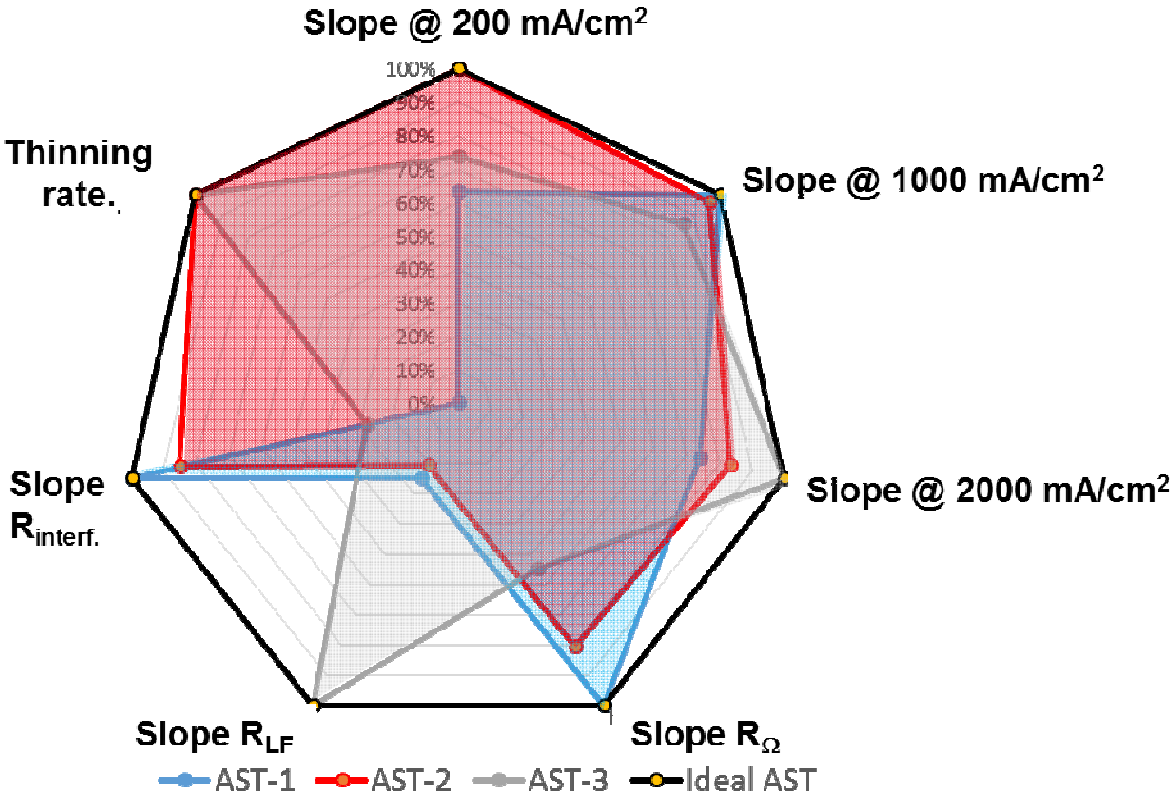


EoL AST-4



Summary

Conclusion



- **AST are more agressive than steady state ageing (40 times faster in comparison with 5 cells – 300 cm² for 4000h)** ✓
- **AST-2 able to thin the membrane and oxidized CC**
  Most complete ageing protocols from those tested ✓

Acknowledgements

CEA :

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liten

cea tech

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AST PROTOCOLS FOR PEM WATER ELECTROLYIS : INSIGHT ON PERFORMANCES AND COMPONENTS DEGRADATION

Thank you for the attention

NOVEL