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Physicochemical properties evolution of cathodic catalyst layer and cell performance improvement during PEMFC start-up with mitigation strategies

Timothée Drugeot, Fabrice Micoud, Eric Pinton, Jean-Philippe Poirot, Sébastien Rosini, Laure Guetaz, Lucas Poupin, Yann Bultel

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International Society of Electrochemistry

FROM RESEARCH TO INDUSTRY

Physicochemical properties of cathodic catalyst layer and cell performance evolution during PEMFC start-up with mitigation strategies – 32nd ISE Topical Meeting

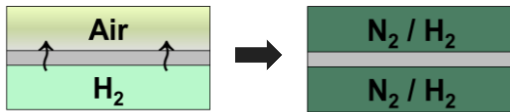
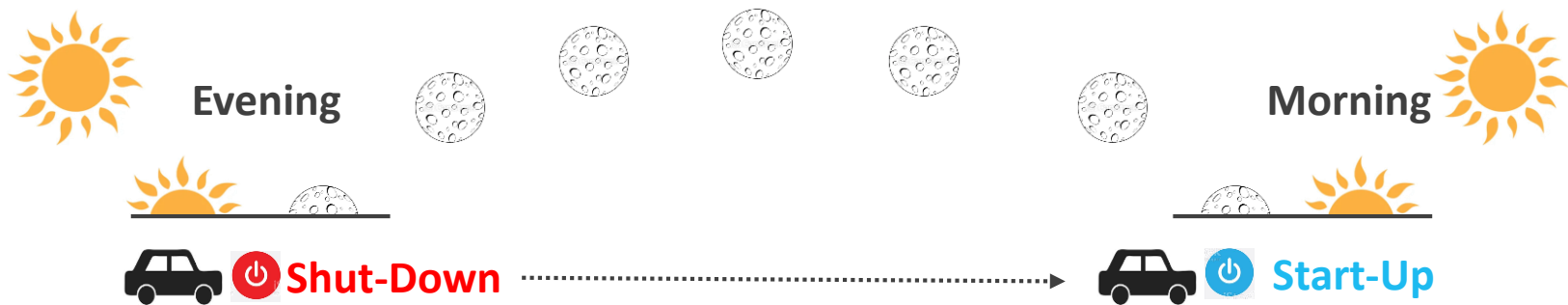
Timothee Drugeot^{1,2}, Fabrice Micoud¹, Eric Pinton¹, Jean-Phillippe Poirot-Crouvezier¹, Sébastien Rosini¹, Laure Guetaz¹, Lucas Poupin¹ and Yann Bultel²

¹Univ. Grenoble Alpes, CEA, LITEN, DEHT 38000 Grenoble, France

²Univ. Grenoble Alpes, Univ. Savoie Mont Blanc, CNRS, Grenoble INP, LEPMI, 38000 Grenoble, France

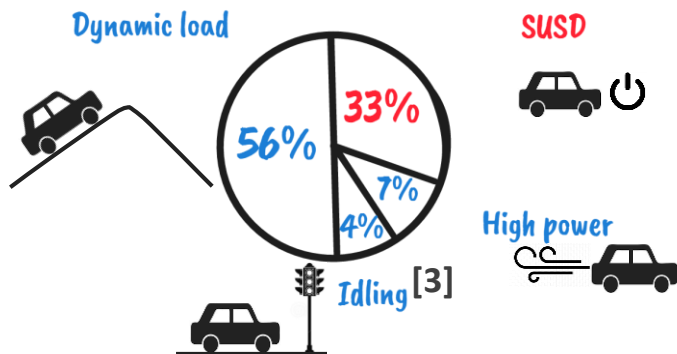
Email: timothee.drugeot@cea.fr

Shut-Down (SD) / Start-Up (SU) process



Oxygen consumption^[1]

Estimation of performance losses [3]

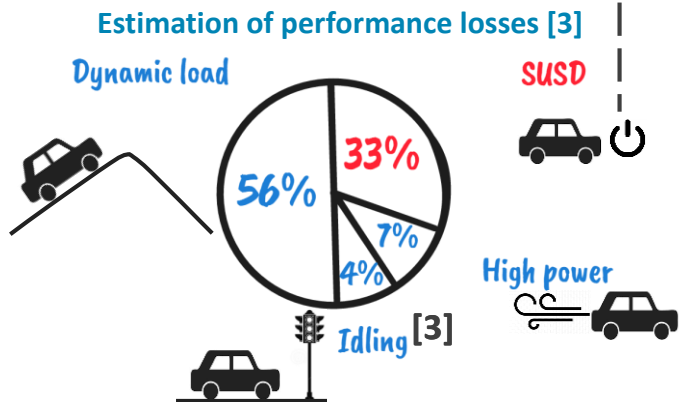
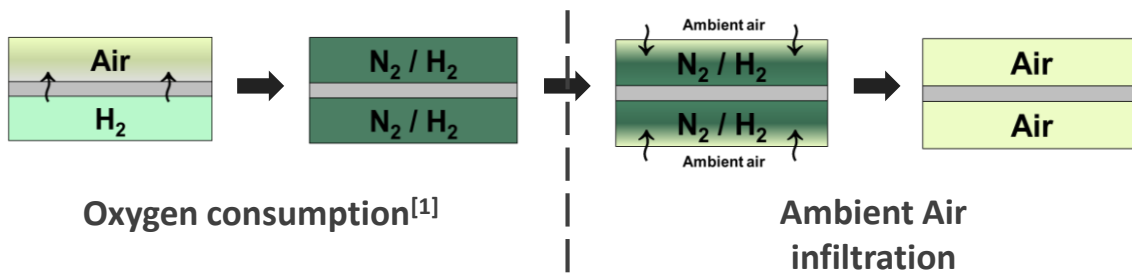
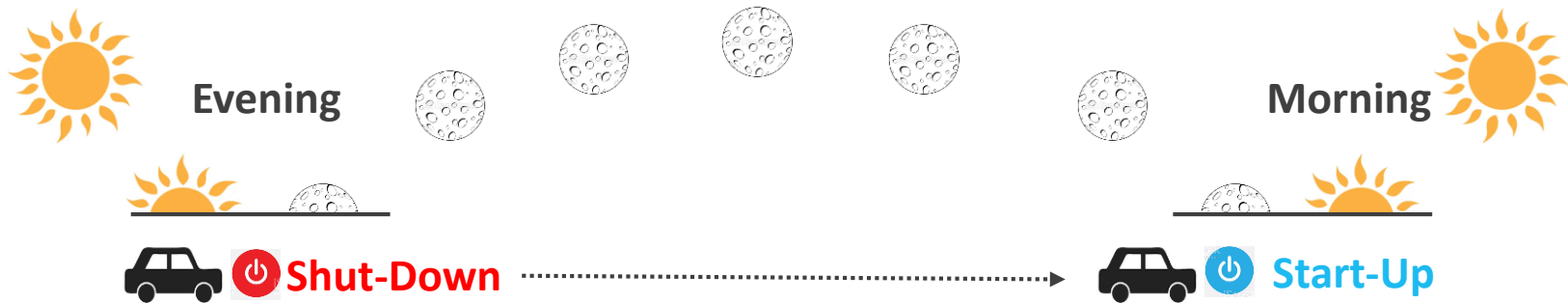


[1] Oyarce et al. "Comparing shut-down strategies for proton exchange membrane fuel cells" (2014)

[2] Reiser et al. "A Reverse-Current Decay Mechanism for Fuel Cells" (2005)

[3] Pei et al. « A quick evaluating method for automotive fuel cell lifetime»

Shut-Down (SD) / Start-Up (SU) process

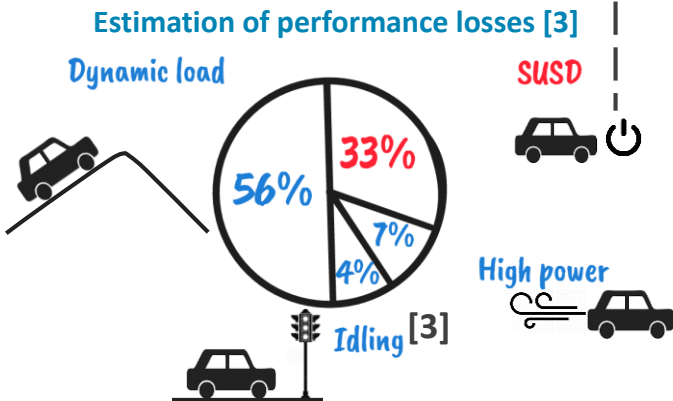
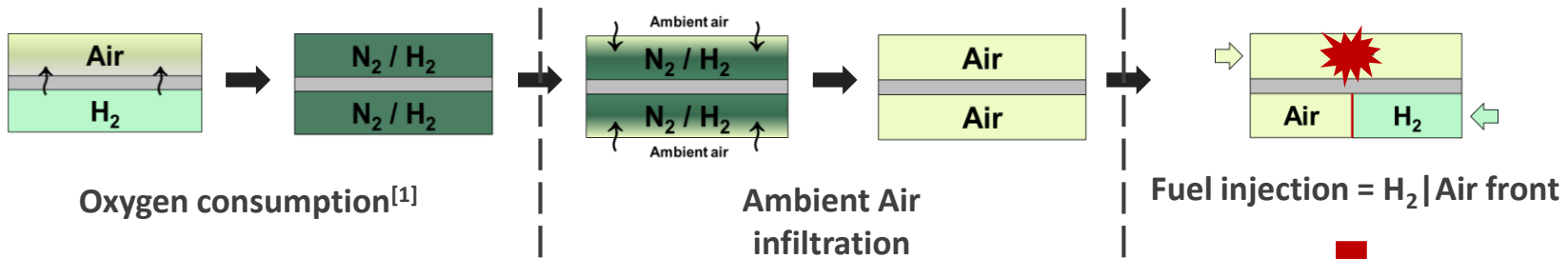
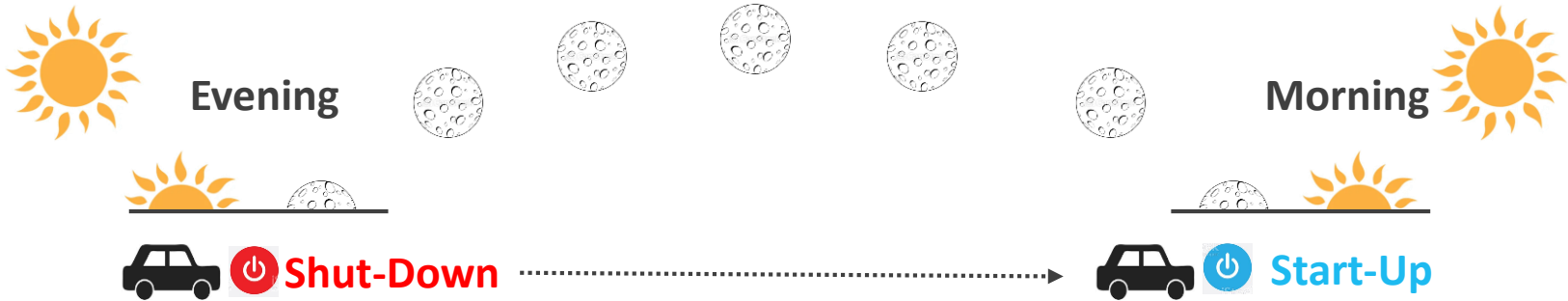


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Shut-Down (SD) / Start-Up (SU) process



Reverse Current Decay mechanism[2]

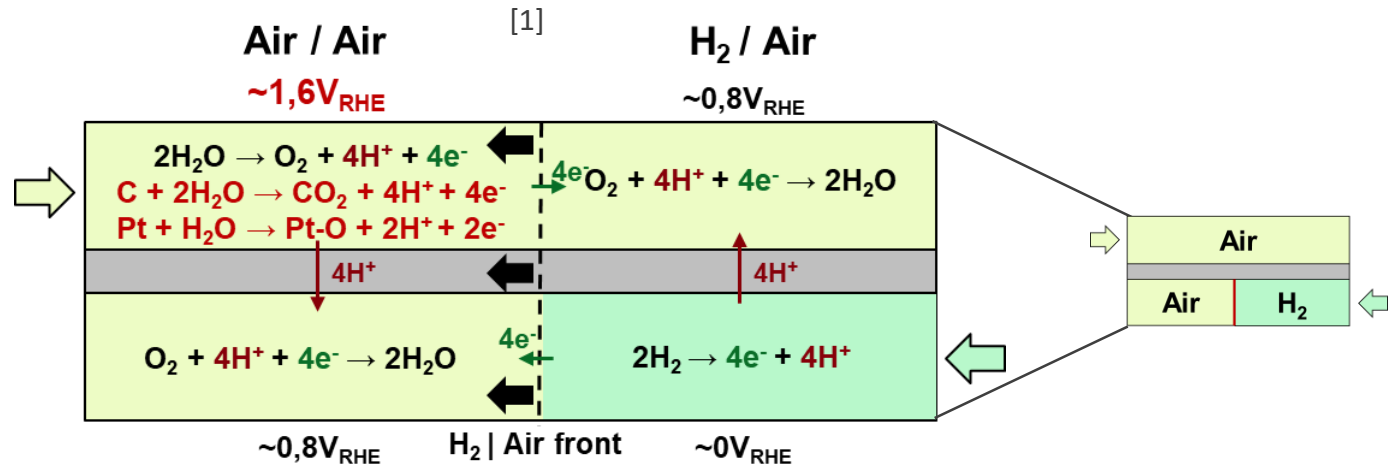
Implementation of mitigation strategies on a system scale

[1] Oyarce et al. "Comparing shut-down strategies for proton exchange membrane fuel cells" (2014)

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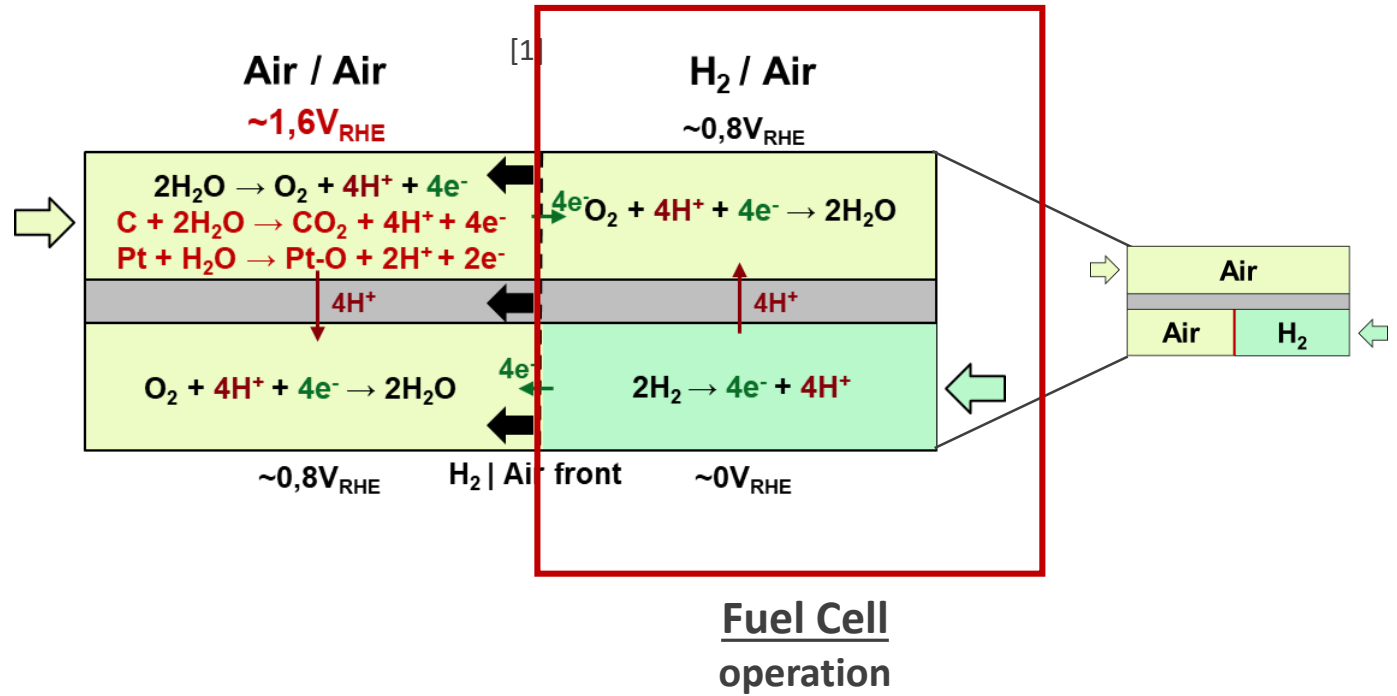
Reverse Current Decay mechanism



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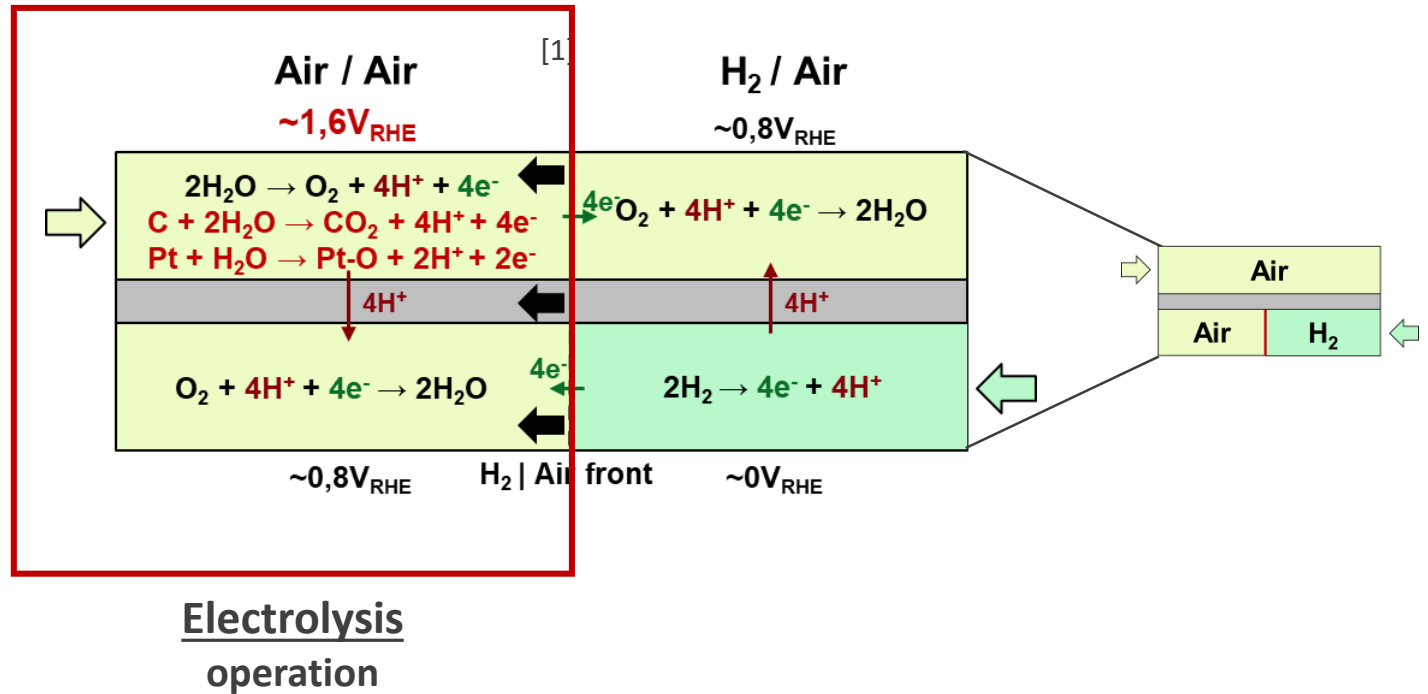
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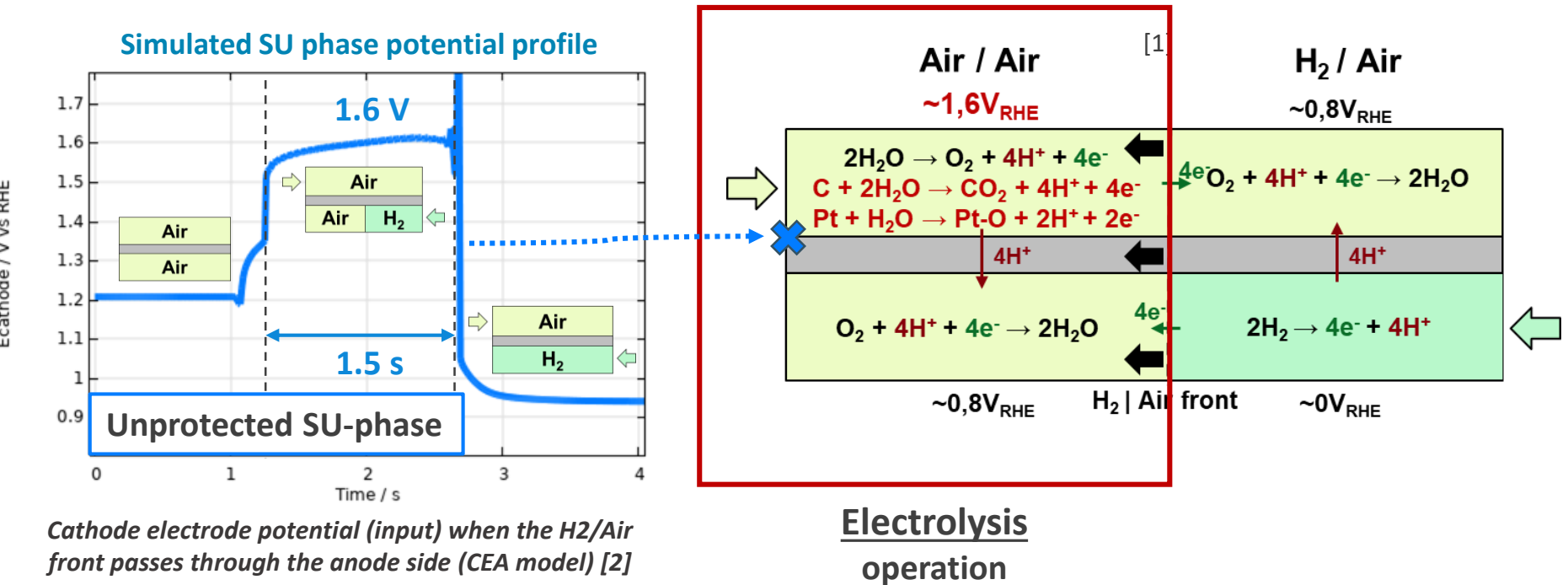
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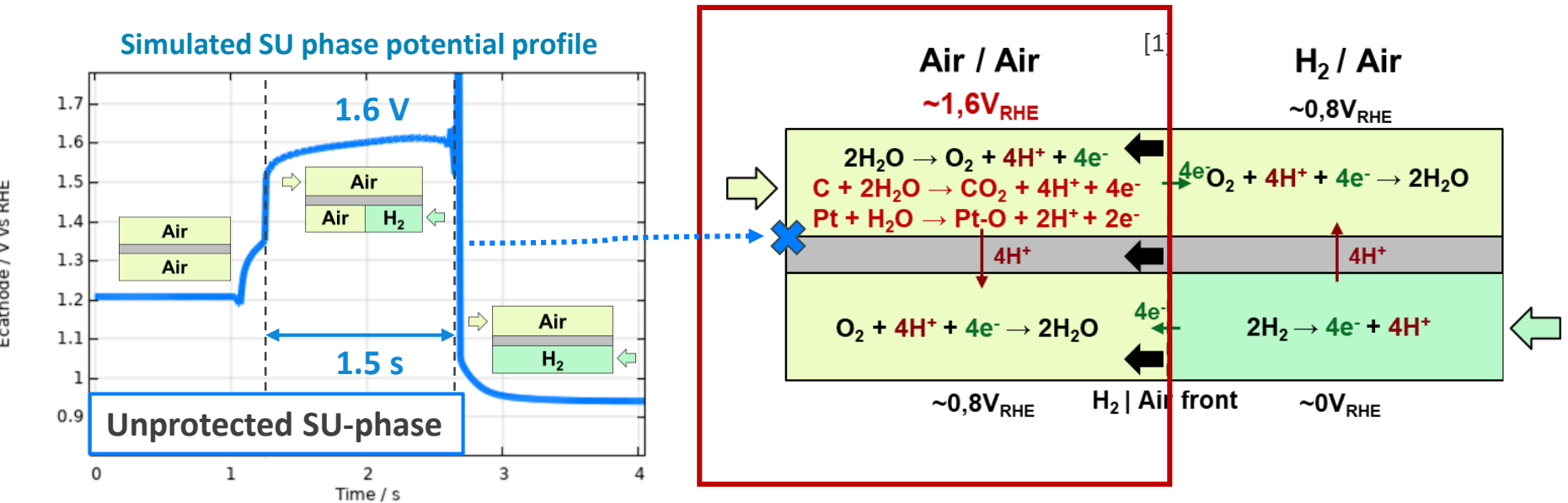
Reverse Current Decay mechanism



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Reverse Current Decay mechanism



Cathode electrode potential (input) when the H₂/Air front passes through the anode side (CEA model) [2]



Cathod Catalyst Layer (CCL) degradation:

- **Carbon Support Corrosion (CSC)**
- **Pt Dissolution/redeposition**

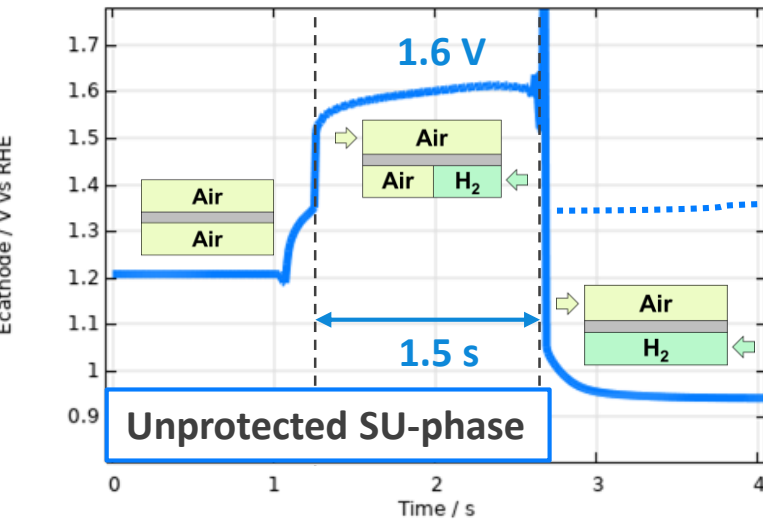


IRREVERSIBLE loss of cell performance

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[2] Radrianarizafy et al. "Modelling Carbon Corrosion during a PEMFC Startup: Simulation of Mitigation Strategies" (2020)

Simulated SU phase potential profile



Cathode electrode potential (input) when the H₂/Air front passes through the anode side (CEA model) [2]

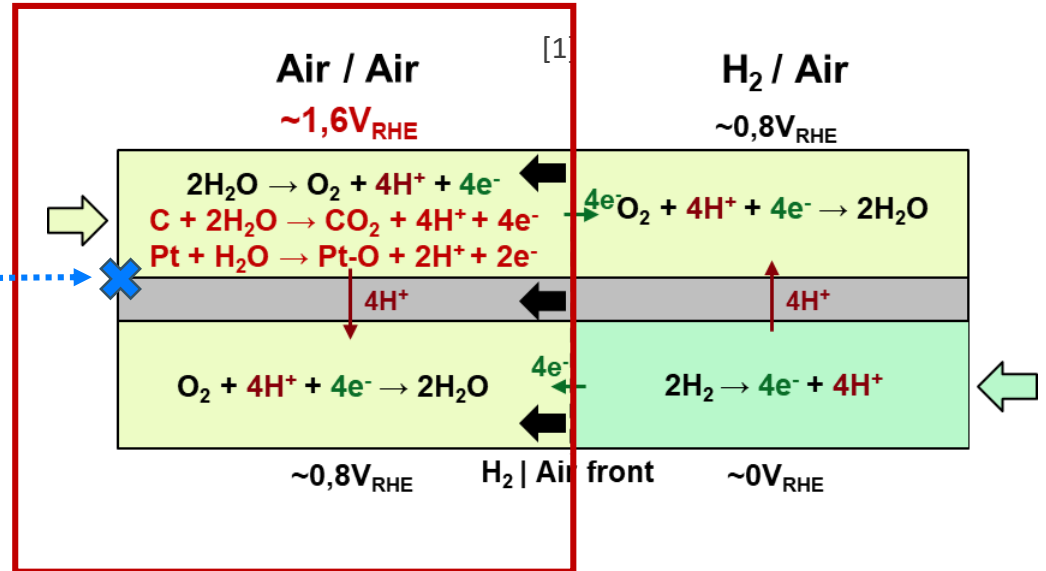


Cathod Catalyst Layer (CCL) degradation:

- Carbon Support Corrosion (CSC)
- Pt Dissolution/redeposition



IRREVERSIBLE loss of cell performance



Electrolysis operation

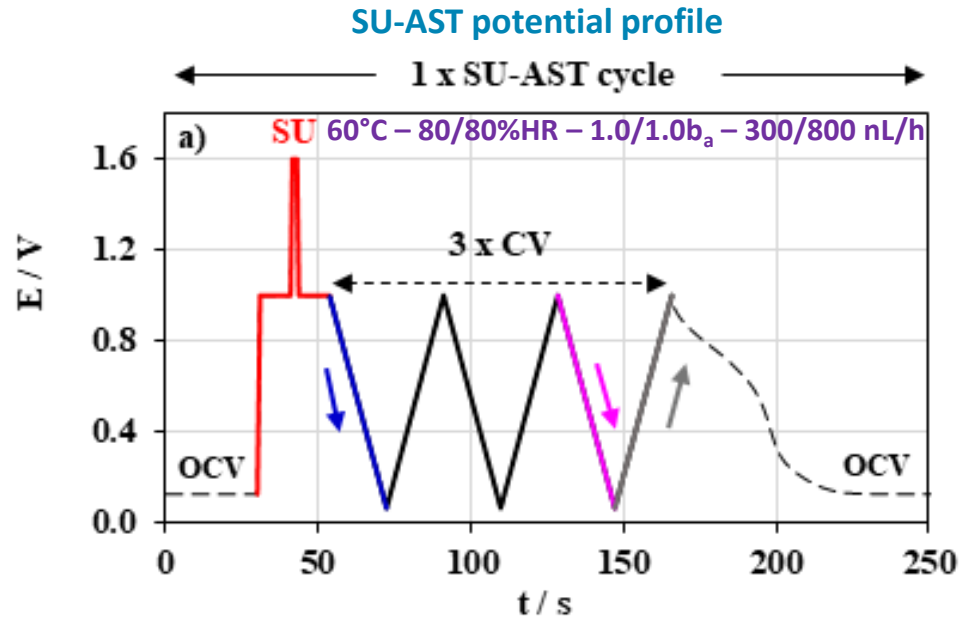
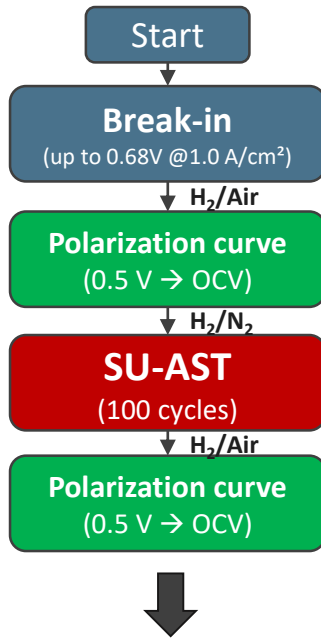
Objectives

1. Better understanding of RCD mechanism and impact on cell performance decay by **sizing of an Accelerated Stress Test** mimicking SU-phase
2. Evaluate the **most impactful mitigating parameters** by coupling several monitoring *in-situ* and *post-mortem* techniques

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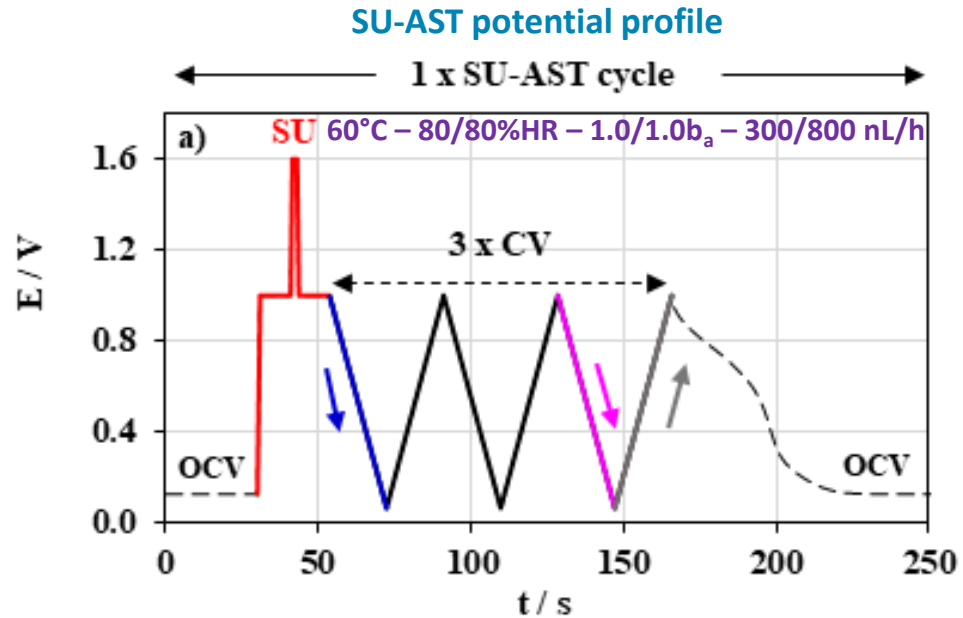
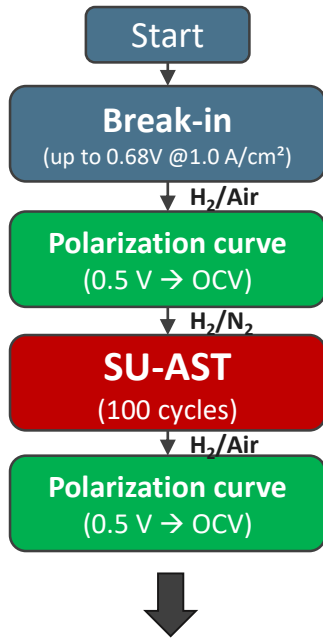
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Emulation of realistic cathode potential profile

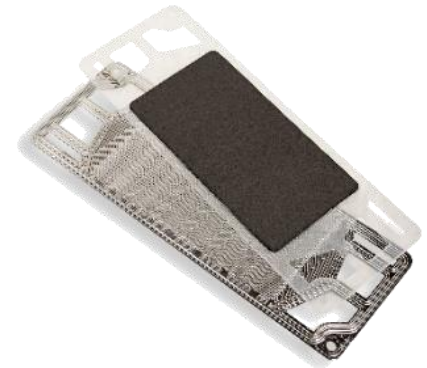
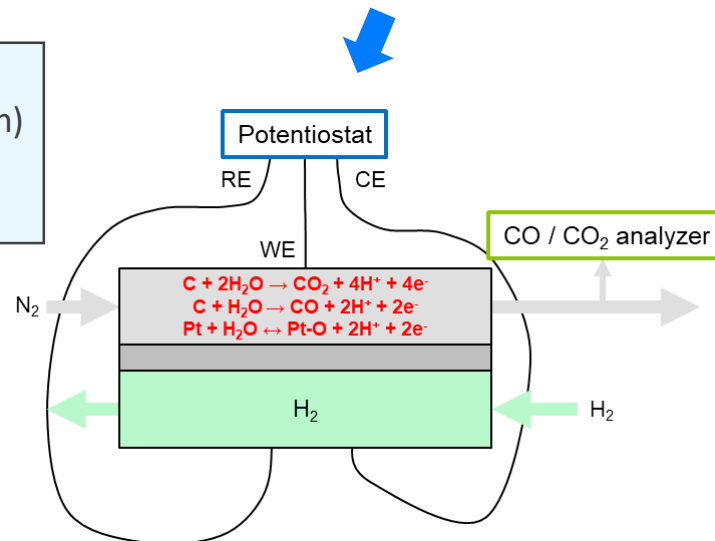
Coupling monitoring techniques

- Cell performance decay (polarization)
- ECSA losses along AST (CV)
- CO₂ emission rate along AST

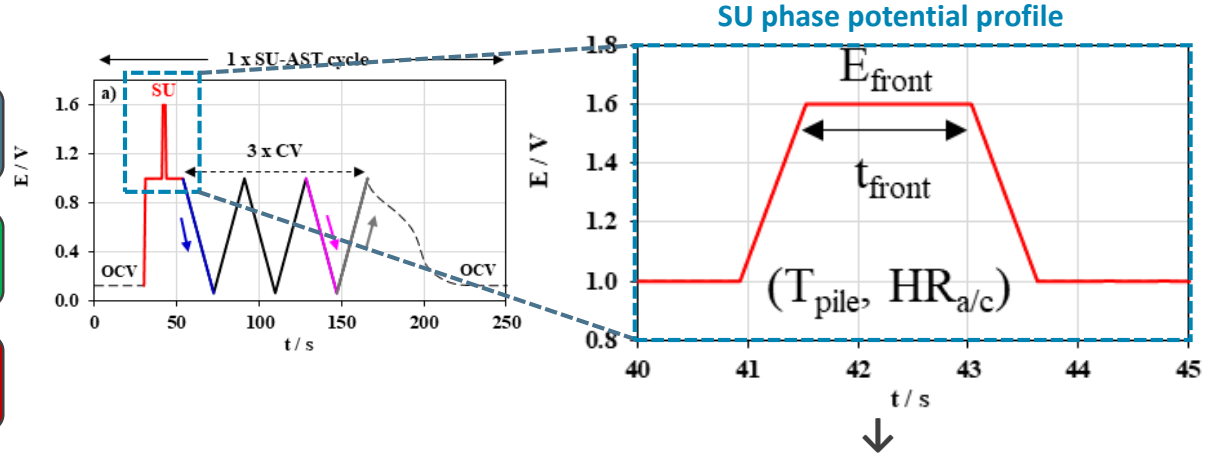
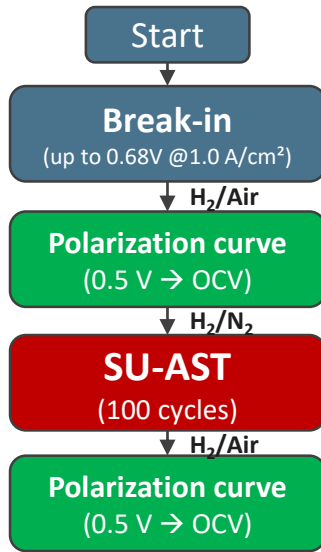
Emulation of realistic cathode potential profile

Coupling monitoring techniques

- Cell performance decay (polarization)
- ECSA losses along AST (CV)
- CO₂ emission rate along AST



Real stack flow-field design
100 cm² MEA single cell



- E_{front} (1.6 → 1.0 V)

relative to electrical current by-passing strategy

- t_{front} (1.5 → 0.5s)

relative accelerating H_2 injection in Air-filled anode

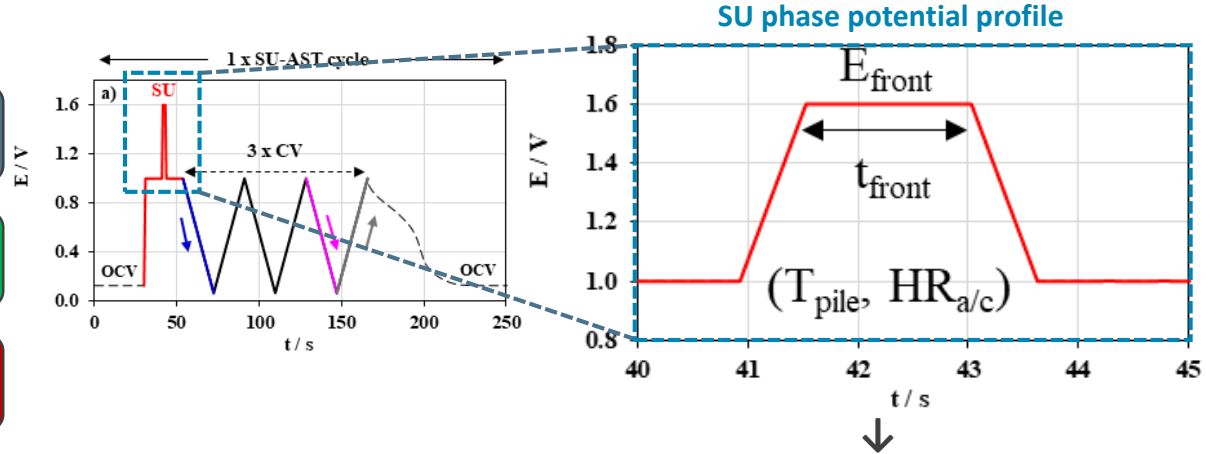
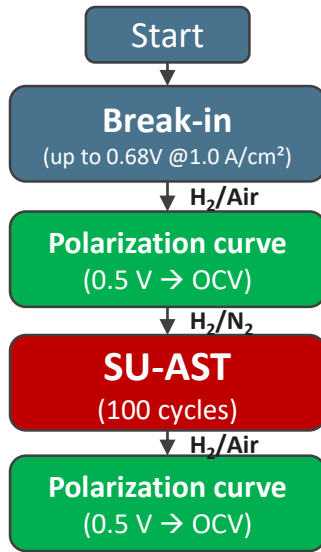
- $RH_{a/c}$ (95 → 50%)

relative to water evaporated at the gas inlet

- T_{cell} (60 → 30°C)

relative to internal cell temperature

- **1.6V** – 1.5s – 80/80%RH – 60°C (Ref)
- **1.4V** – 1.5s – 80/80%RH – 60°C
- **1.2V** – 1.5s – 80/80%RH – 60°C
- **1.0V** – 1.5s – 80/80%RH – 60°C
- 1.6V – **1.0s** – 80/80%RH – 60°C
- 1.6V – **0.5s** – 80/80%RH – 60°C
- 1.6V – 1.5s – **80/50%RH** – 60°C
- 1.6V – 1.5s – **50/50%RH** – 60°C
- 1.6V – 1.5s – **80/95%RH** – 60°C
- 1.6V – 1.5s – 80/80%RH – **45°C**
- 1.6V – 1.5s – 80/80%RH – **30°C**



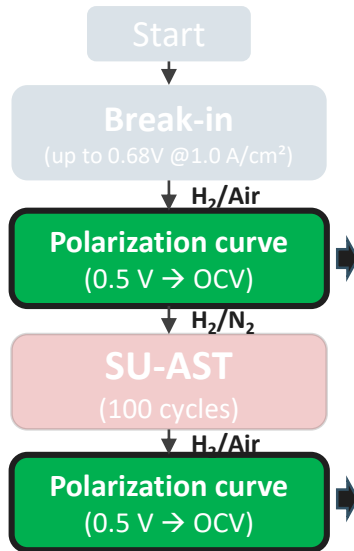
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- **1.2V** – 1.5s – 80/80%RH – 60°C
- **1.0V** – 1.5s – 80/80%RH – 60°C
- 1.6V – **1.0s** – 80/80%RH – 60°C
- 1.6V – **0.5s** – 80/80%RH – 60°C
- 1.6V – 1.5s – **80/50%RH** – 60°C
- 1.6V – 1.5s – **50/50%RH** – 60°C
- 1.6V – 1.5s – **80/95%RH** – 60°C
- 1.6V – 1.5s – 80/80%RH – **45°C**
- 1.6V – 1.5s – 80/80%RH – **30°C**

• **E_{front}** (1.6 → 1.0 V)
relative to electrical current by-passing strategy

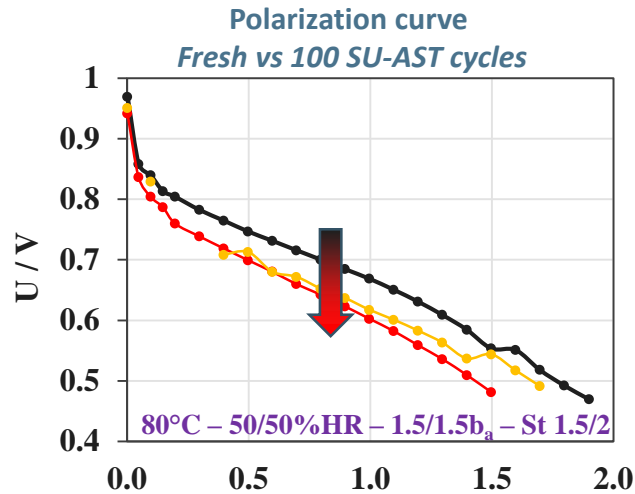
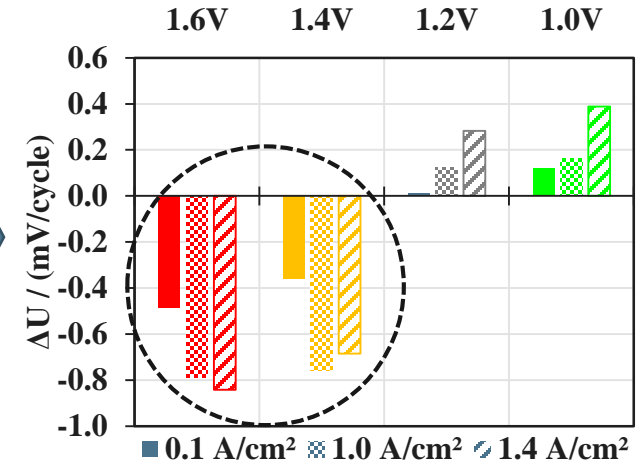
• **t_{front}** (1.5 → 0.5s)
relative accelerating H_2 injection in Air-filled anode

• **$RH_{a/c}$** (95 → 50%)
relative to water evaporated at the gas inlet

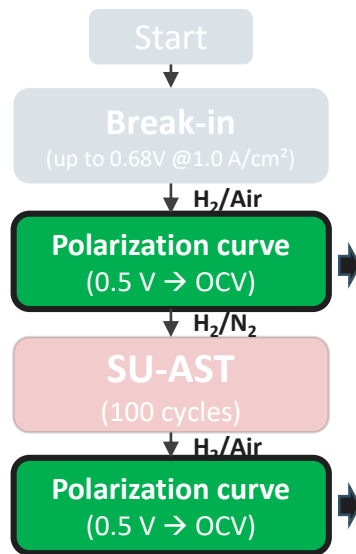
• **T_{cell}** (60 → 30°C)
relative to internal cell temperature

E_{front} investigation – Cell voltage evolution

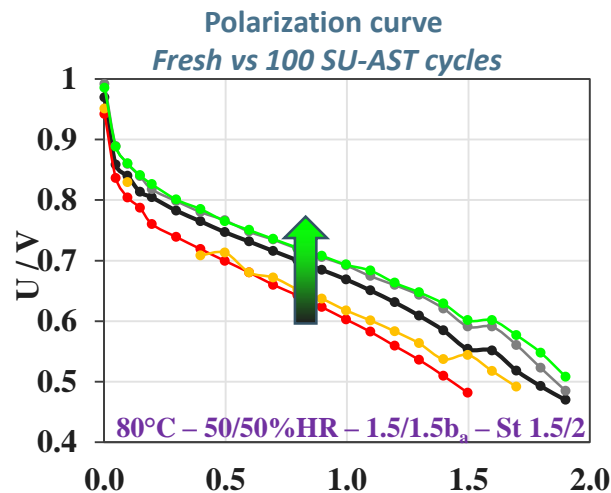
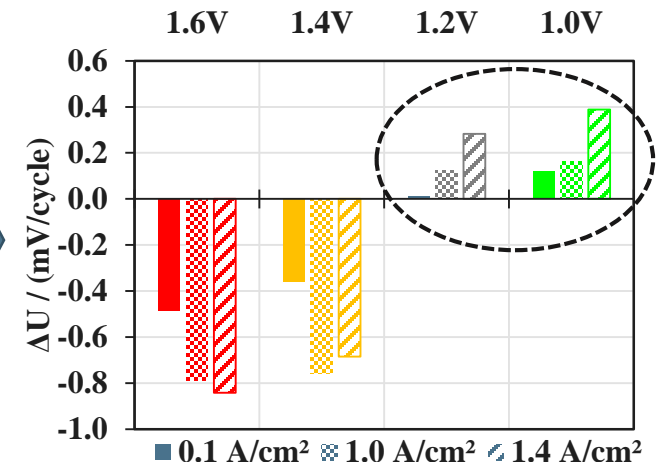
Fresh – 1.0V – 1.2V – 1.4V – 1.5V – 1.6V

Performance evolution
Fresh vs 100 SU-AST cycles1.4 – 1.6 V range

- Harsh voltage loss along overall polarization curve

E_{front} investigation – Cell voltage evolution

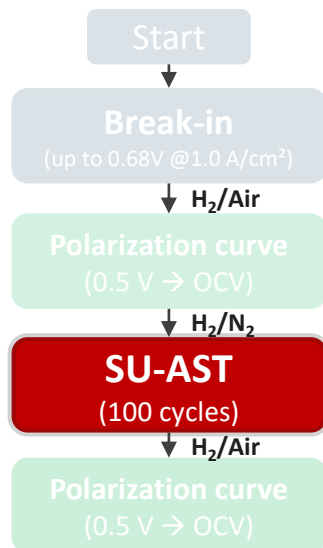
Fresh – 1.0V – 1.2V – 1.4V – 1.5V – 1.6V

Performance evolution
Fresh vs 100 SU-AST cycles1.0 – 1.2 V range

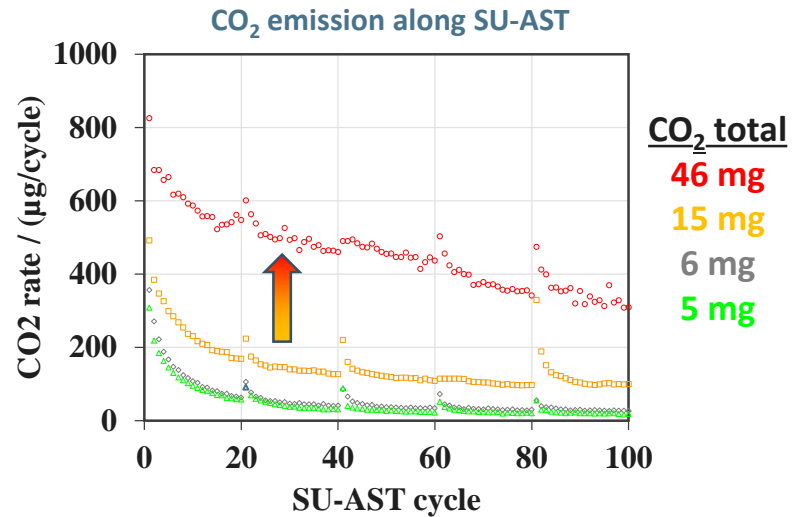
- Unexpected **improvement of cell performance** (even after 100 cycles)

1.4 – 1.6 V range

- **Harsh voltage loss** along overall polarization curve



Fresh – 1.0V – 1.2V – 1.4V – 1.5V – 1.6V

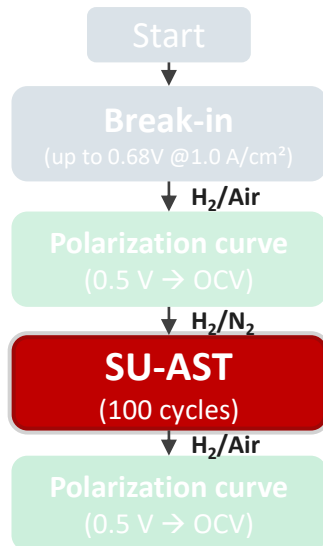


1.0 – 1.2 V range

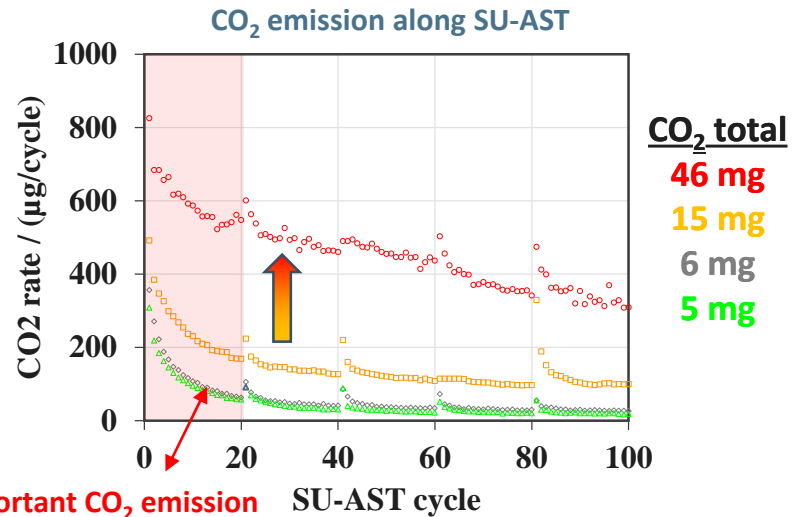
- Unexpected **improvement of cell performance**
- **Low CO₂ emission rate** expected during the first 20 cycles

1.4 – 1.6 V range

- **Harsh voltage loss** along overall polarization curve
- **Higher CO₂ emission rate** for 1.6 V case along cycles



Fresh – 1.0V – 1.2V – 1.4V – 1.5V – 1.6V



Important CO₂ emission during the first cycles

1.0 – 1.2 V range

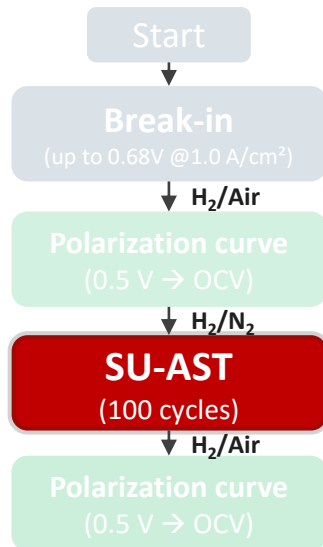
- Unexpected **improvement of cell performance**
- **Low CO₂ emission rate** expected during the first 20 cycles

→ **CSC of only poorly ordered domains**

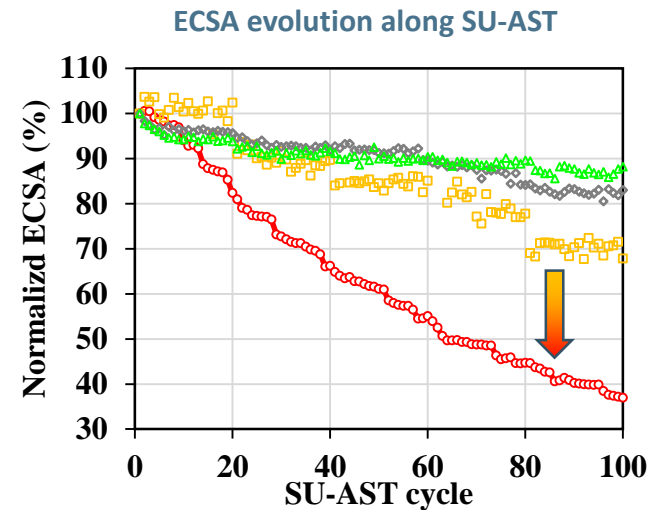
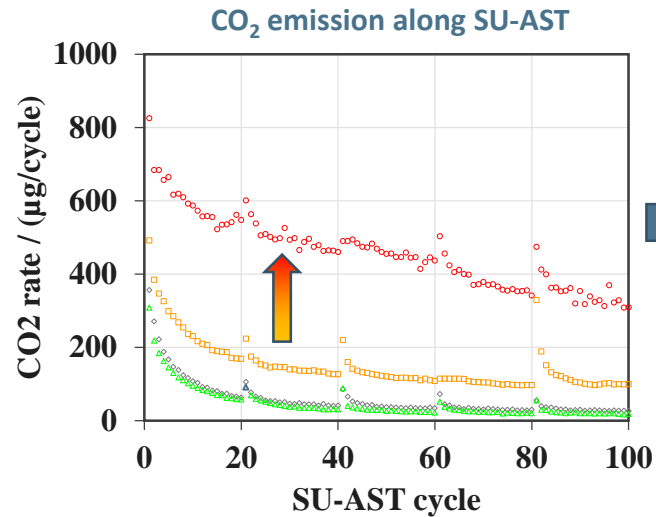
1.4 – 1.6 V range

- **Harsh voltage loss** along overall polarization curve
- **Higher CO₂ emission rate** for 1.6 V case along cycles

→ **CSC of poorly and more ordered domains**



Fresh – 1.0V – 1.2V – 1.4V – 1.5V – 1.6V



1.0 – 1.2 V range

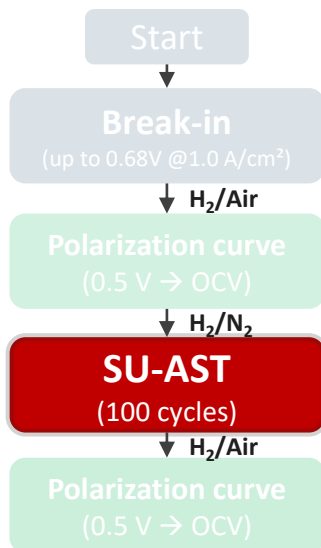
- Unexpected **improvement of cell performance**
- **Low CO₂ emission rate** expected during the first 20 cycles

→ **CSC of poorly ordered domains**
→ **Pt Dissolution/redeposition**

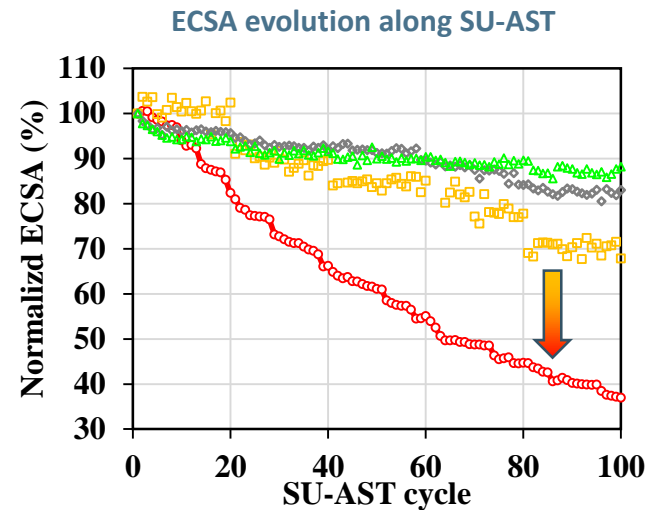
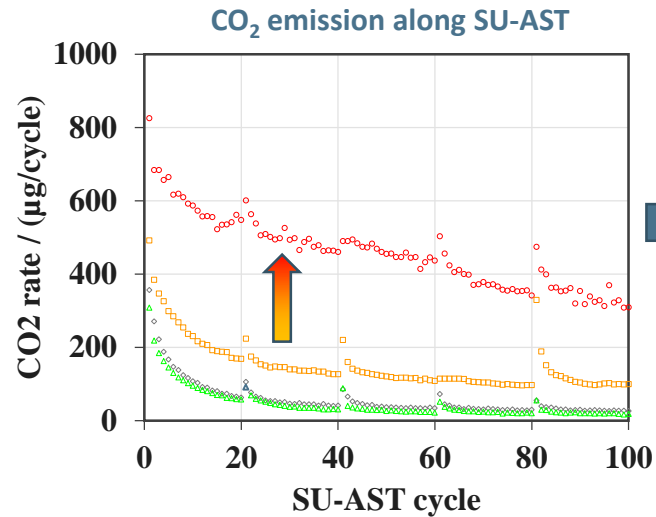
1.4 – 1.6 V range

- **Harsh voltage loss** along overall polarization curve
- **Higher CO₂ emission rate** for 1.6 V case along cycles

→ **CSC of poorly and more ordered domains [1]**
→ **Pt dissolution/reposition +
Pt detachment/agglomeration (linked to CSC)**



Fresh – 1.0V – 1.2V – 1.4V – 1.5V – 1.6V



1.0 – 1.2 V range

- Unexpected **improvement of cell performance**
- **Low CO₂ emission rate** expected during the first 20 cycles

- **CSC of poorly ordered domains**
- **Pt Dissolution/redeposition**

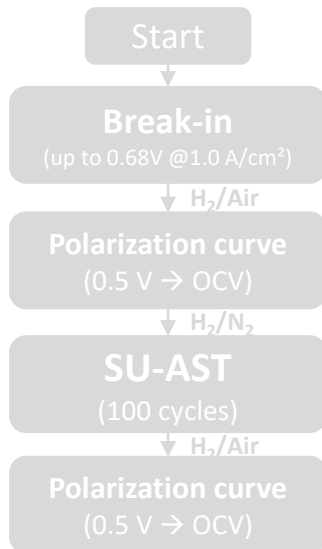
1.4 – 1.6 V range

- **Harsh voltage loss** along overall polarization curve
- **Higher CO₂ emission rate** for 1.6 V case along cycles

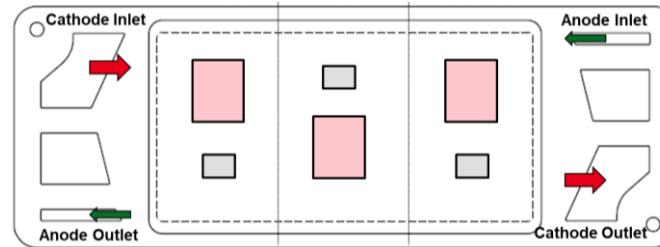
- **CSC of poorly and more ordered domains [1]**
- **Pt dissolution/reposition + Pt detachment/agglomeration** (linked to CSC)

- Validation & Quantification of the **mitigation of performance decay by lowering E_{front} potential**
- Further insights on degradation mechanisms through a **post-mortem study**

In-situ AST



Cutting sample of fresh / aged MEA

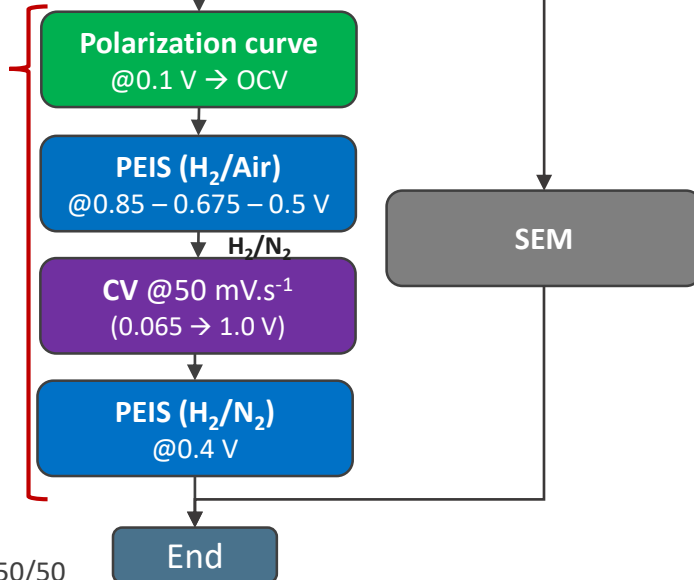


Post-mortem AST

X3
operating
conditions

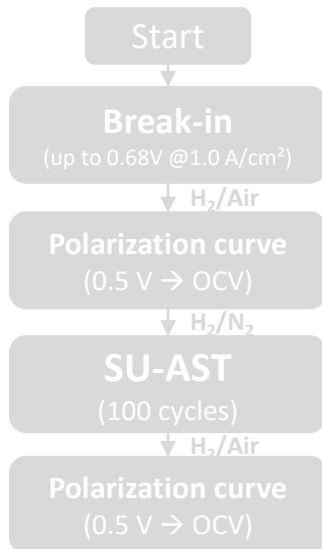


80°C - 50%HR*
80°C - 80%HR*
80°C - 100%HR*

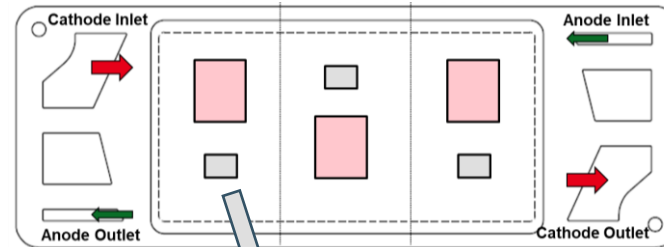


*1.5/1.5 bar_a - St 50/50

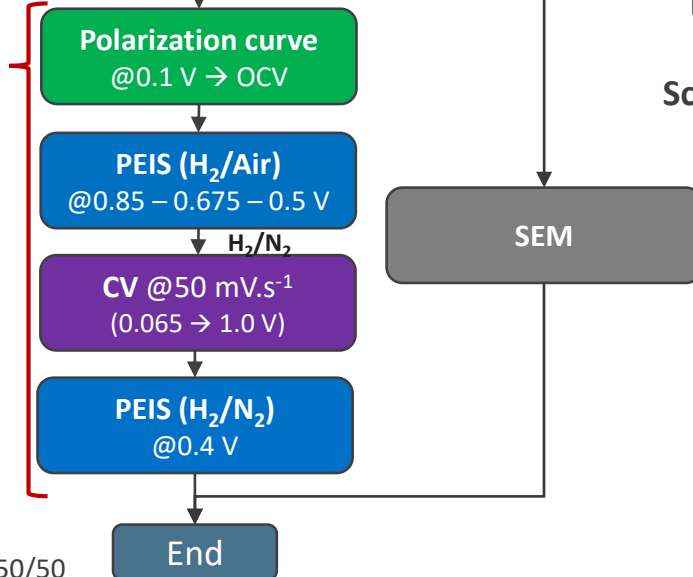
In-situ AST



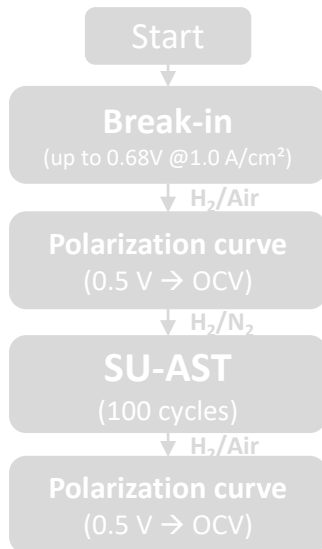
Cutting sample of fresh / aged MEA

7-layer MEA
(side view)Local structural analysis
By
Scanning Electron Microscopy
(SEM)

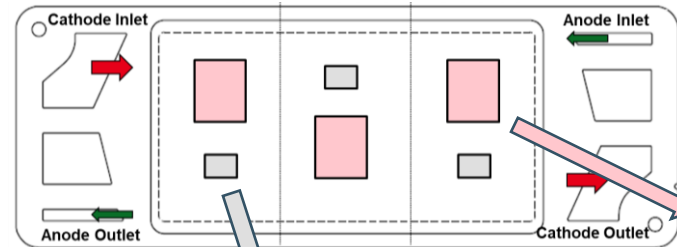
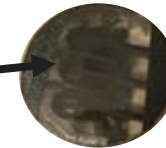
Post-mortem AST

X3
operating
conditions80°C - 50%HR*
80°C - 80%HR*
80°C - 100%HR**1.5/1.5 bar_a - St 50/50

In-situ AST



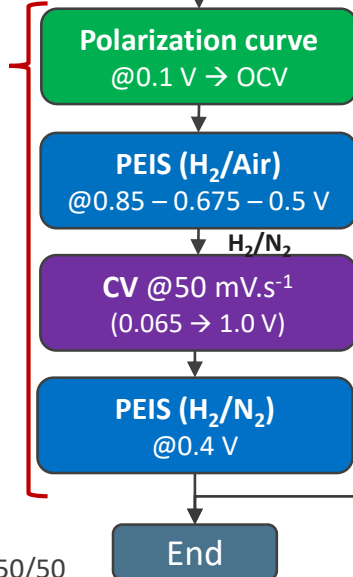
Cutting sample of fresh / aged MEA

7-layer MEA
(front view)1.8 cm² MEA sample7-layer MEA
(side view)Local structural analysis
By
Scanning Electron Microscopy
(SEM)Local EC analysis
By

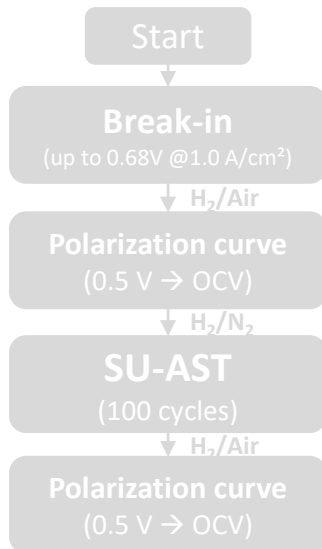
- Polarization
- CV
- Impedance Spectroscopy (PEIS)

SEM

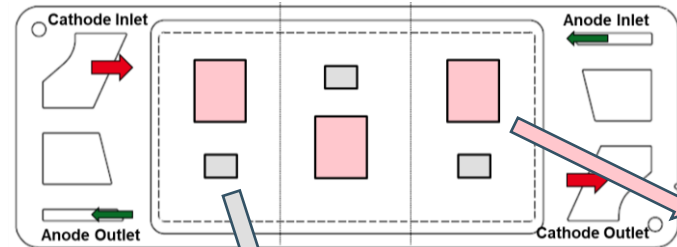
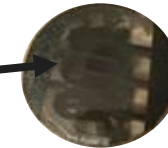
Post-mortem AST

X3
operating
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In-situ AST



Cutting sample of fresh / aged MEA

7-layer MEA
(front view)1.8 cm² MEA sample7-layer MEA
(side view)

Local structural analysis
By
Scanning Electron Microscopy
(SEM)

Local EC analysis
By

- Polarization
- CV
- Impedance Spectroscopy (PEIS)

- *Reproducibility on fresh MEA* ✓

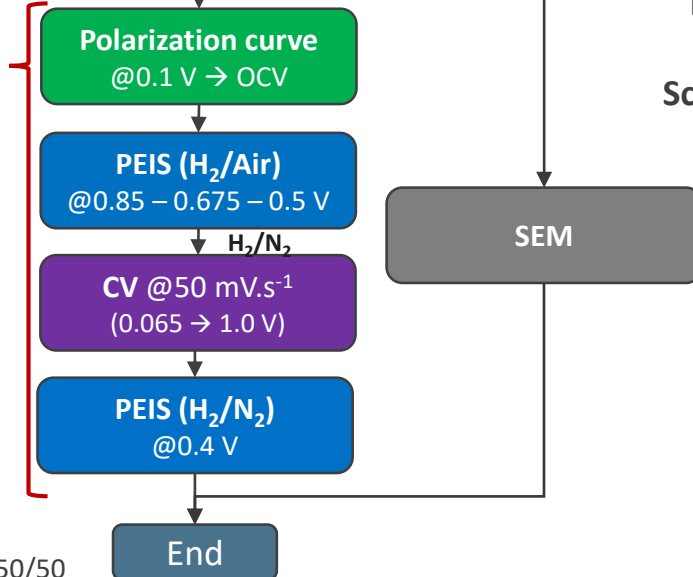
- *Homogeneity (inlet – middle – outlet) on aged MEA @ 1.6 – 1.4 V* ✓

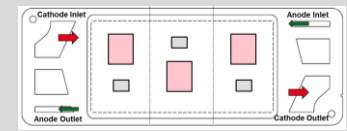
Post-mortem AST

X3
operating
conditions



80°C - 50%HR*
80°C - 80%HR*
80°C - 100%HR*

*1.5/1.5 bar_a – St 50/50

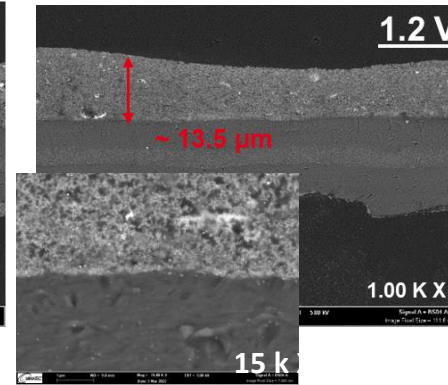
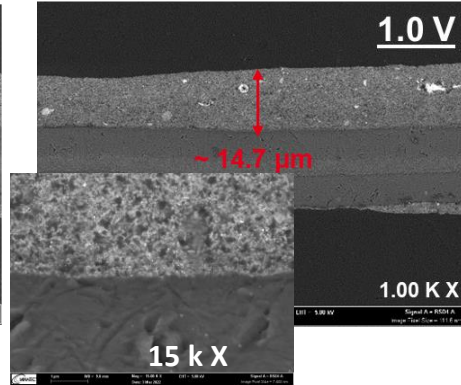
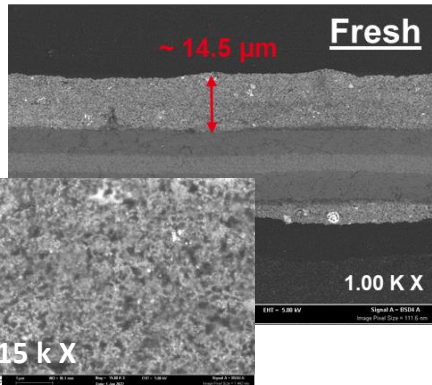


Low thinning from fresh to 1.2 V aged commercial MEA

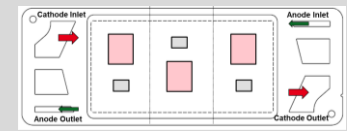
Fresh

1.0 V

1.2 V



- No CCL structural modification from fresh to aged MEA at 1.2 V

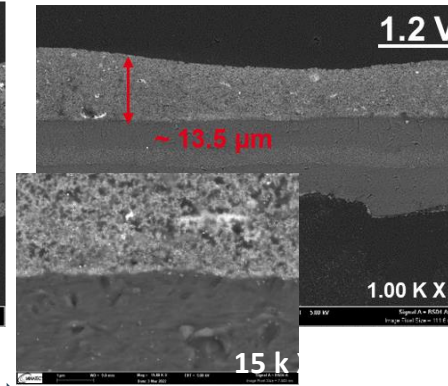
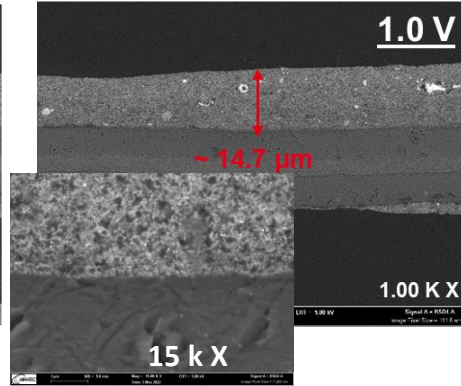
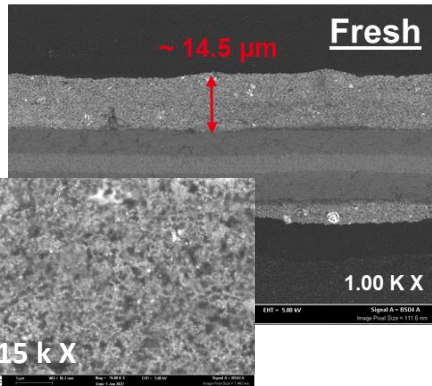


Low thinning from fresh to 1.2 V aged commercial MEA

Fresh

1.0 V

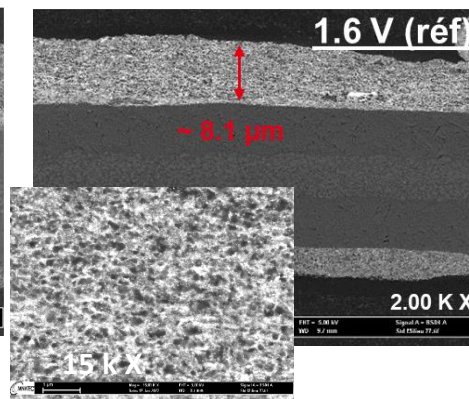
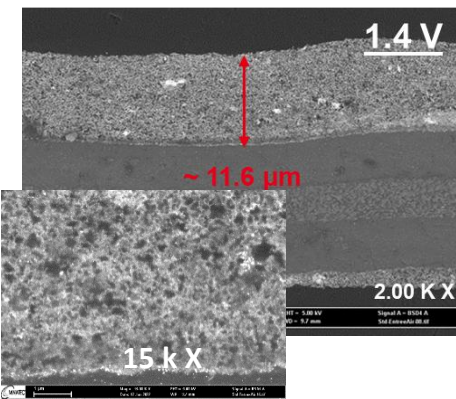
1.2 V



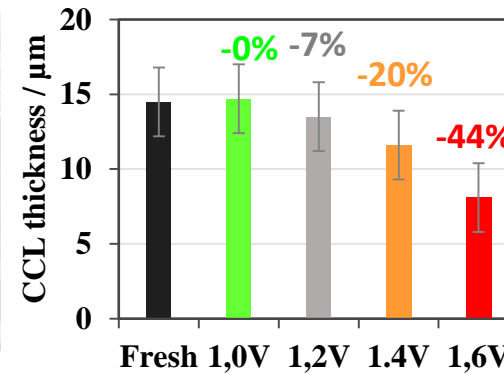
High thinning beyond 1.4 V

1.4 V

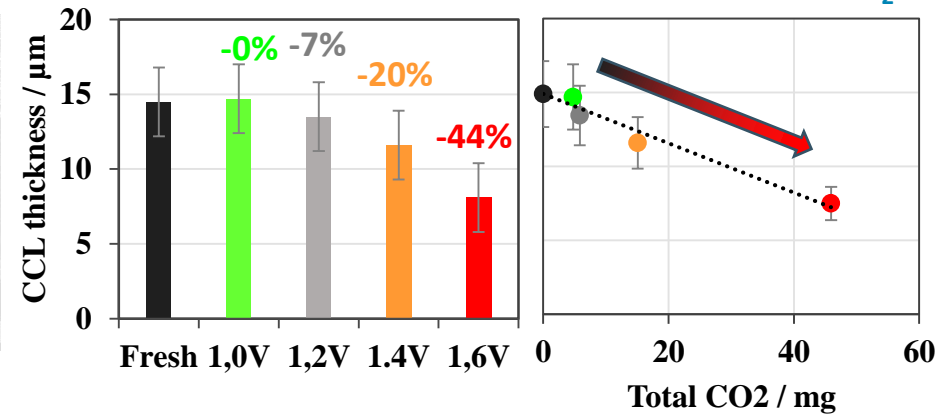
1.6 V



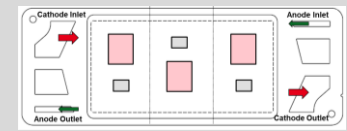
Estimated CCL thickness



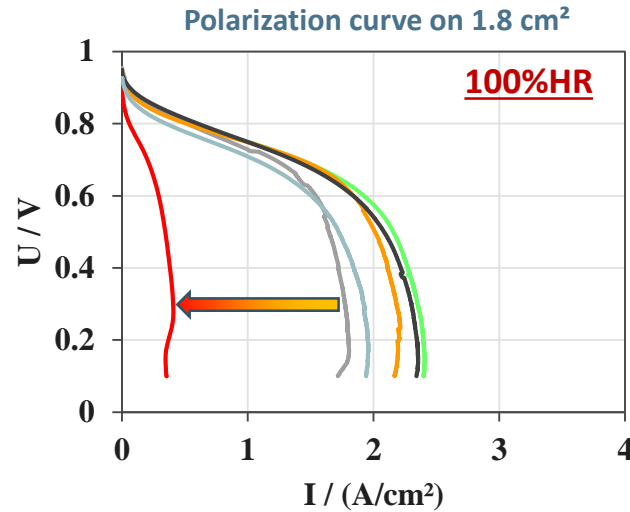
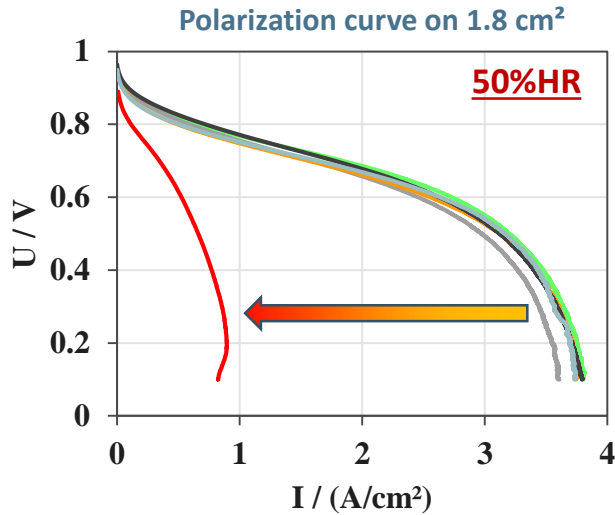
CCL thickness VS CO₂



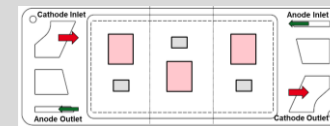
- No CCL structural modification from fresh to aged MEA at 1.2 V
- Low compaction of CCL and densification of Pt nanoparticles at 1.4 V and **harsher at 1.6 V**
 → **Linear correlation with CSC mechanisms**



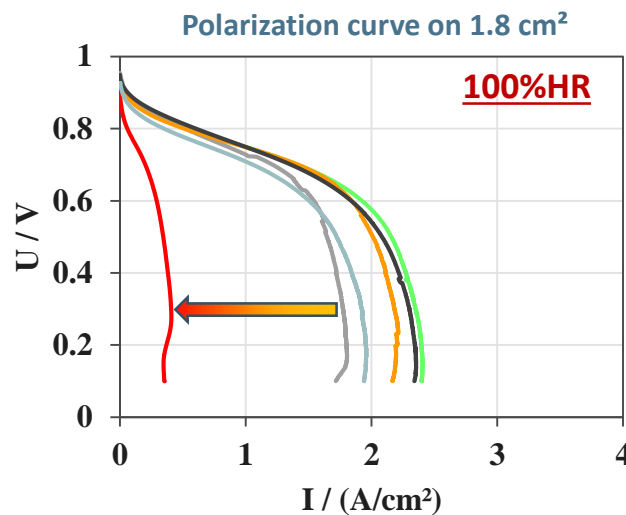
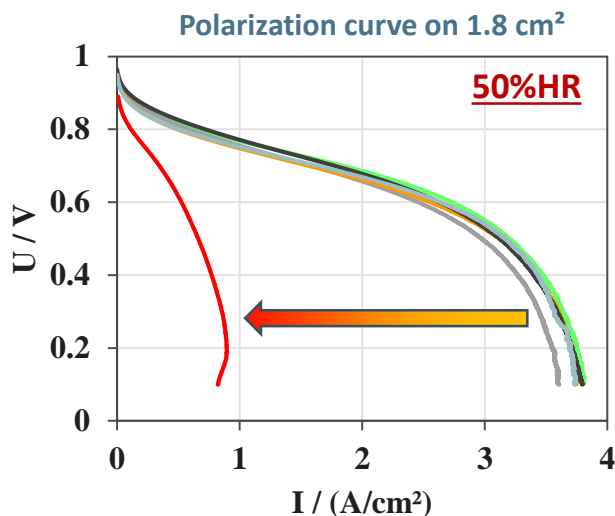
Fresh – 1.0V – 1.2V – 1.4V – 1.5V – 1.6V



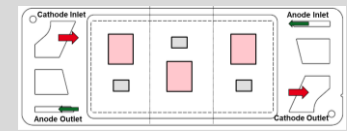
- **At 50 %HR** : No performance decay excepted for 1.6 V case
↓
- **At 100 %HR** : Emergence of progressive performance decay



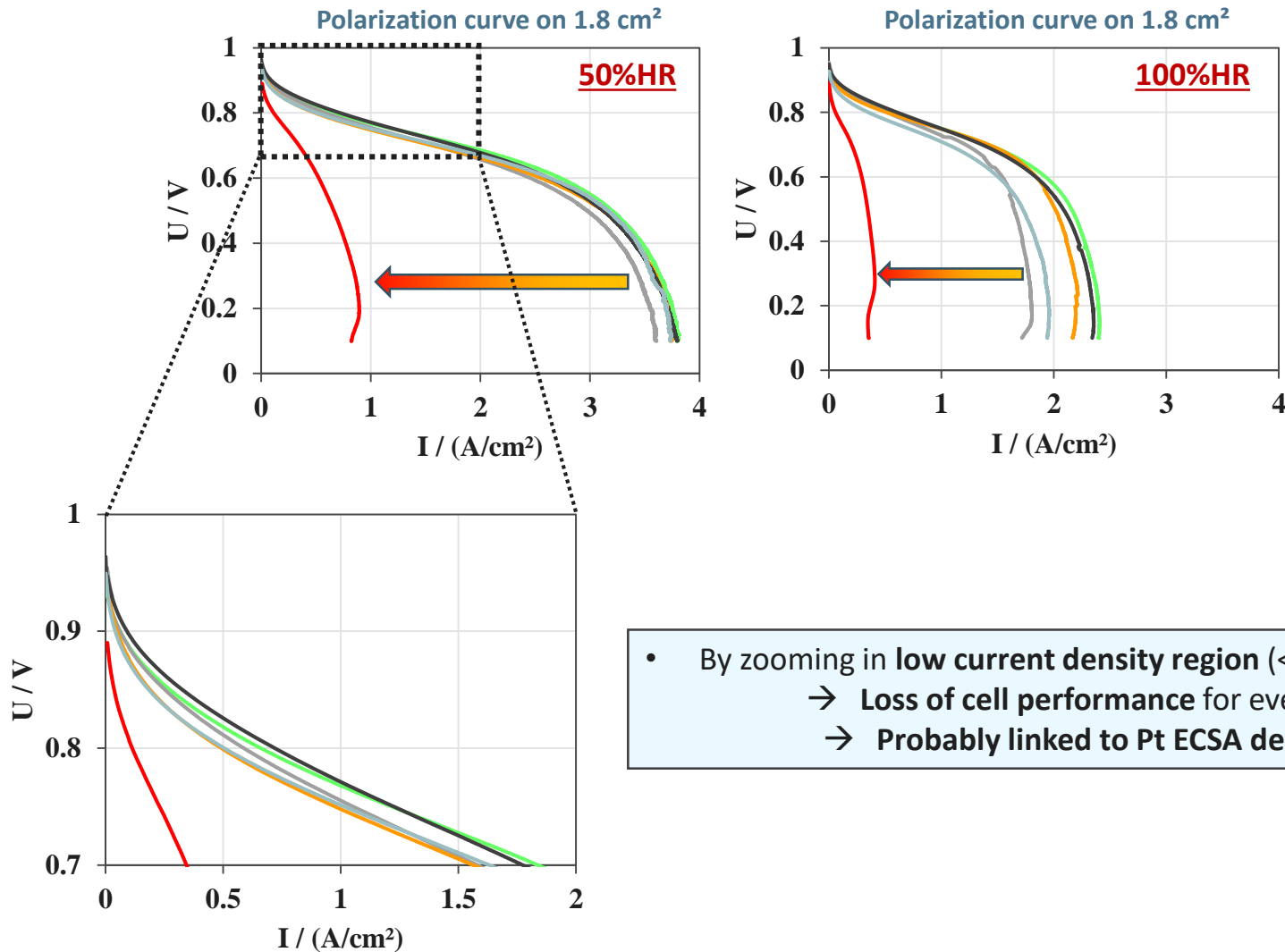
Fresh – 1.0V – 1.2V – 1.4V – 1.5V – 1.6V



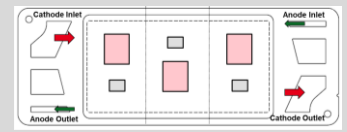
- **At 50 %HR** : No performance decay excepted for 1.6 V case
↓
- **At 100 %HR** : Emergence of progressive performance decay
- **Improvement of performance for 1.0 V** case similar as in previous in-situ SU-AST (98 cm²)
→ **Mass transport limitation is more pronounced At higher RH**
↓
- **Water management is altered** due to **CCL chemical and/or electrochemical modifications**:
 - Loss of hydrophobicity
 - Modification of carbon surface properties
 - Higher Pt/C loading ratio due to carbon support corrosion



Fresh – 1.0V – 1.2V – 1.4V – 1.5V – 1.6V



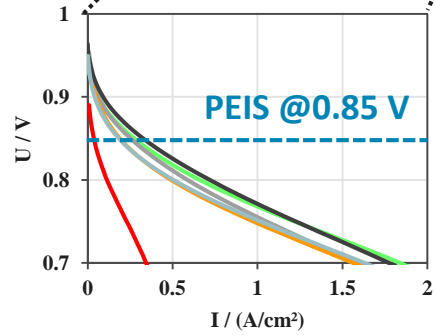
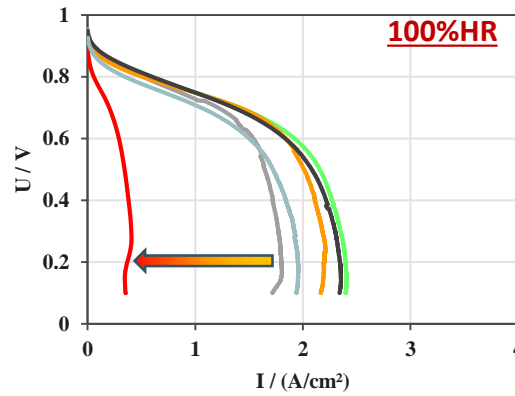
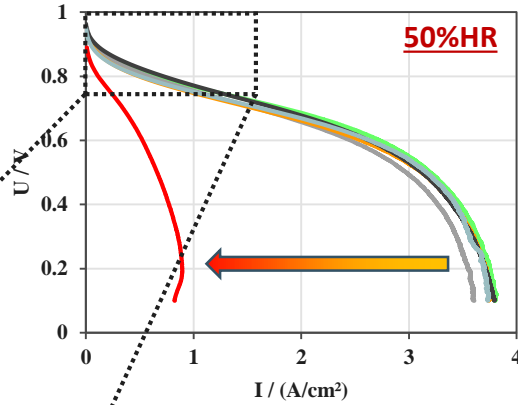
- By zooming in **low current density region** (< 2 A/cm²)
 - **Loss of cell performance** for every case
 - **Probably linked to Pt ECSA decrease**



Fresh – 1.0V – 1.2V – 1.4V – 1.5V – 1.6V (ref)

Polarization curve on 1.8 cm²

Polarization curve on 1.8 cm²



PEIS model (H_2 /Air)

Ionic transport resistance through MB

$R_{H^+, MB}$

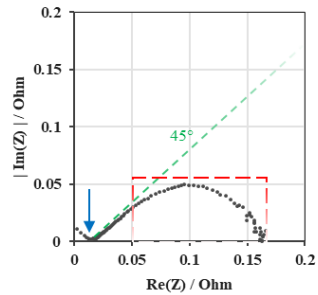
R_{tc}

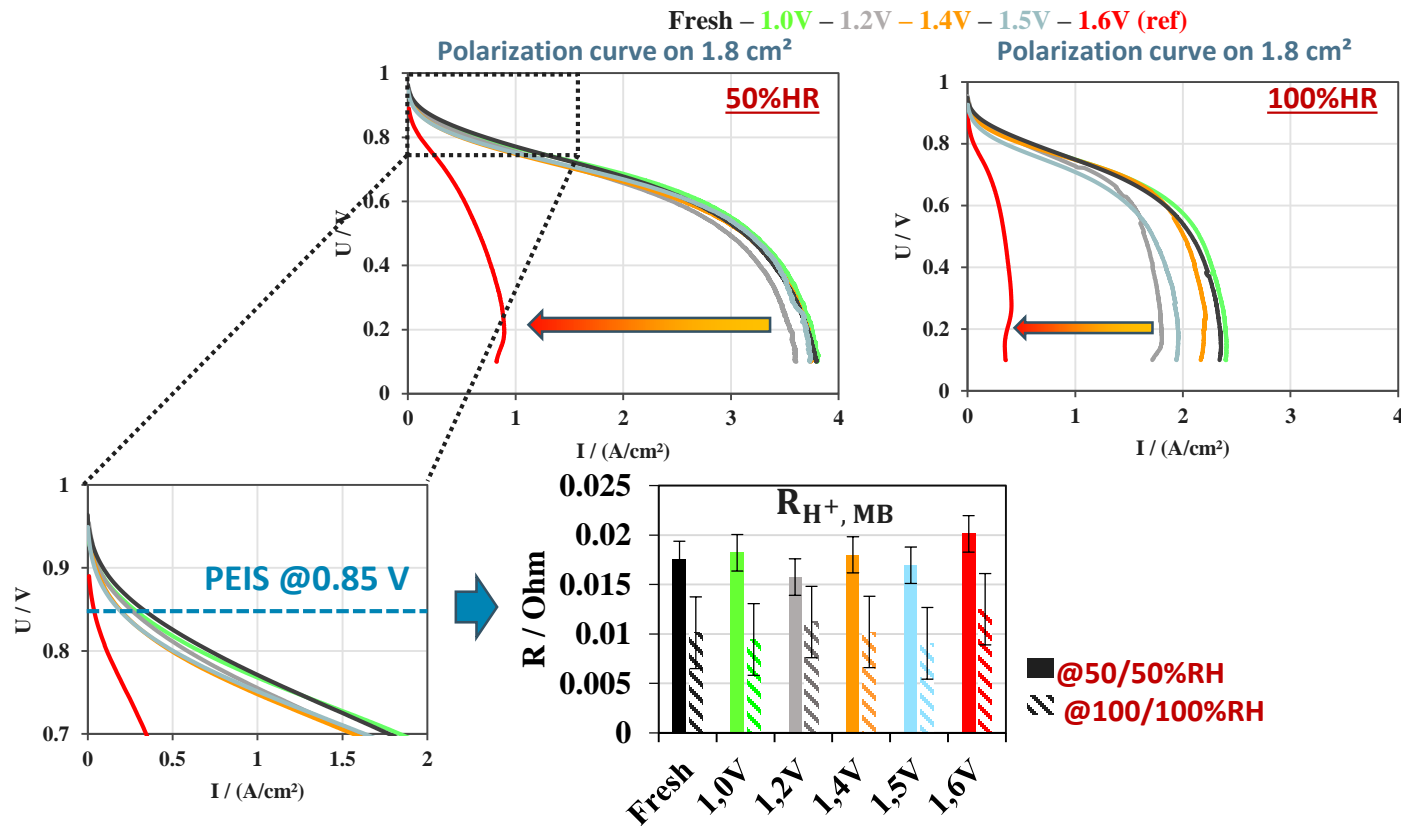
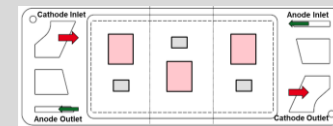
C_{tc}

$R_{H^+, CCL}$

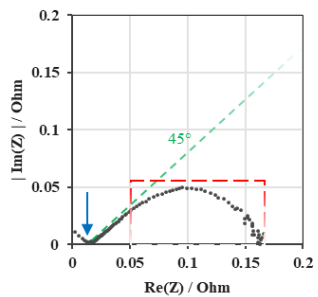
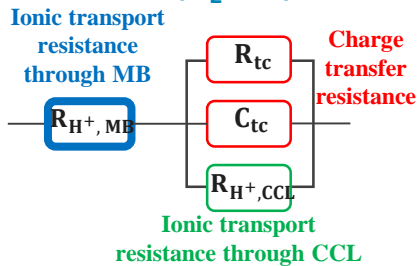
Ionic transport resistance through CCL

Charge transfer resistance



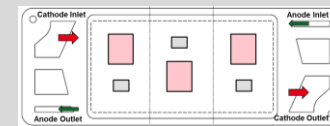


PEIS model (H₂/Air)



No high frequency resistance variation

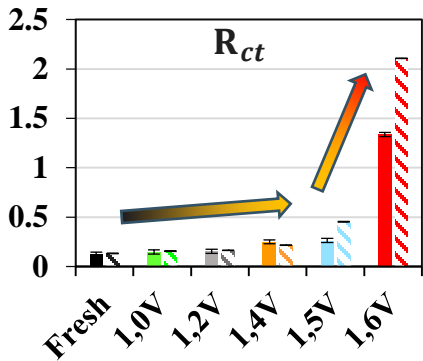
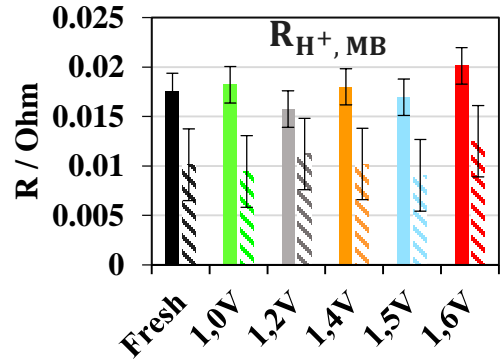
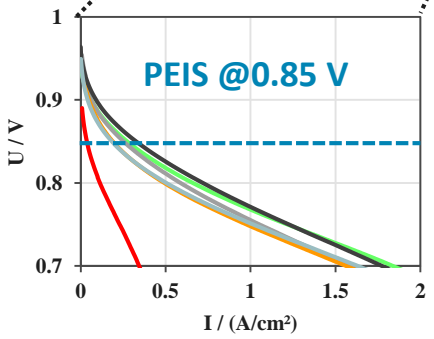
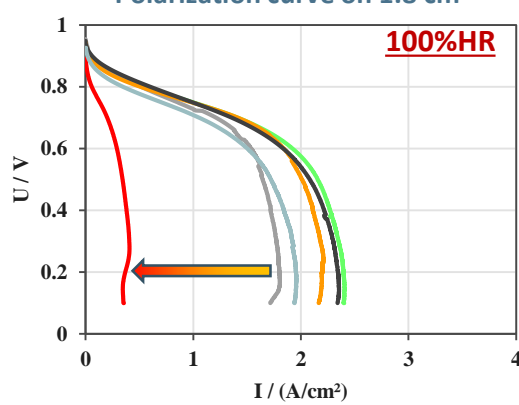
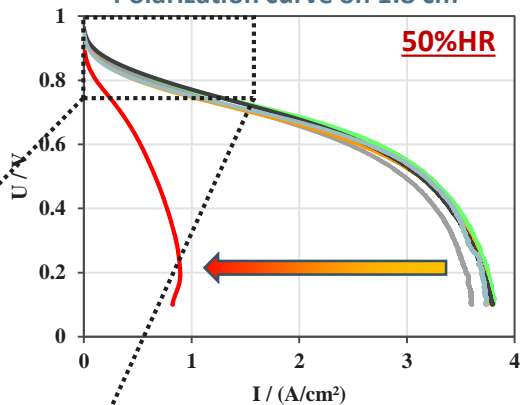
→ Protonic conductivity of the membrane is conserved during SU-AST



Fresh – 1.0V – 1.2V – 1.4V – 1.5V – 1.6V (ref)

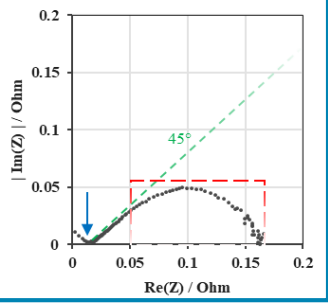
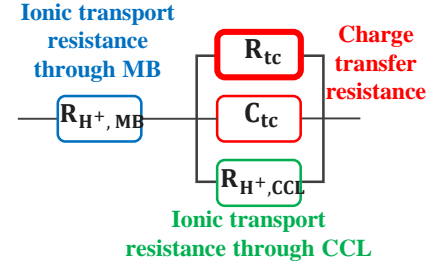
Polarization curve on 1.8 cm²

Polarization curve on 1.8 cm²

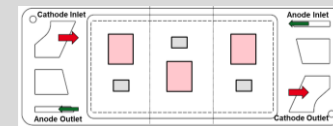


■ @50/50RH
 ▨ @100/100RH

PEIS model (H₂/Air)



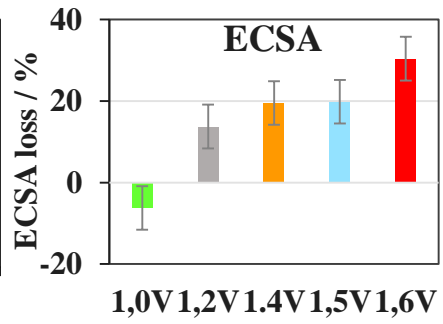
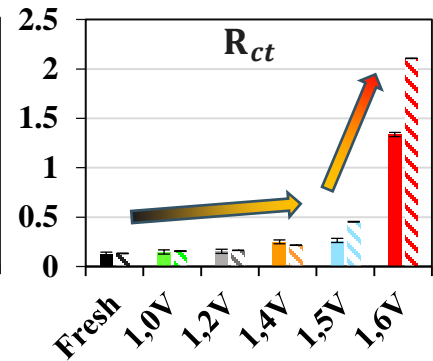
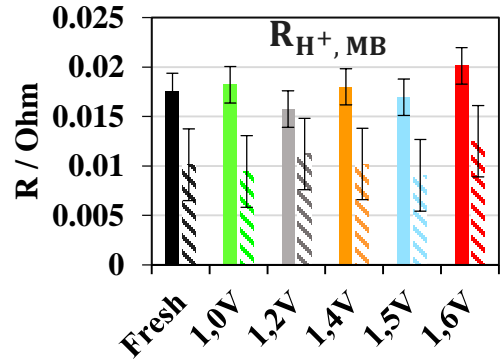
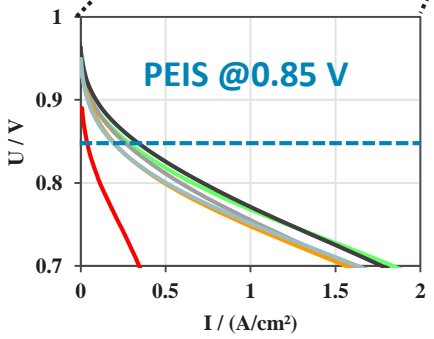
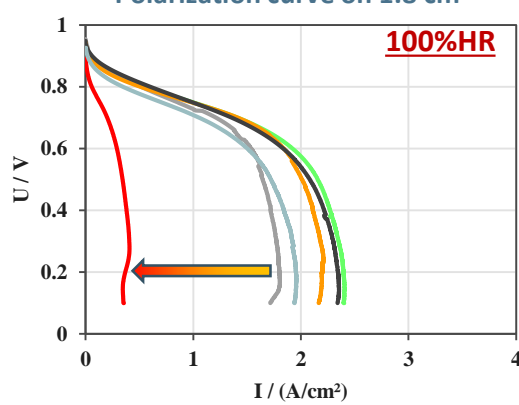
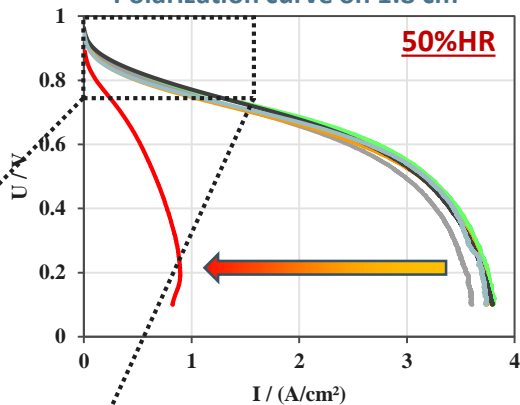
- Slight increase of charge transfer resistance from fresh up to aged MEA at 1.4 V
- High increase of R_{ct} value above 1.5 V



Fresh – 1.0V – 1.2V – 1.4V – 1.5V – 1.6V (ref)

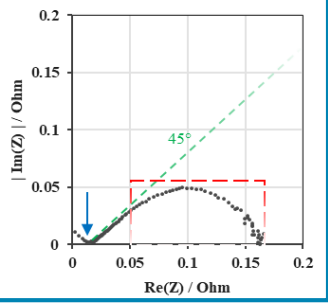
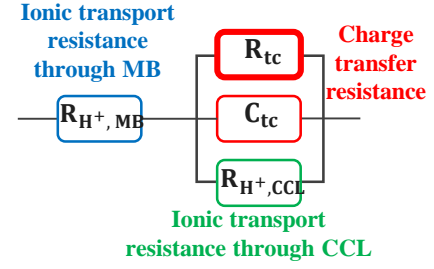
Polarization curve on 1.8 cm²

Polarization curve on 1.8 cm²



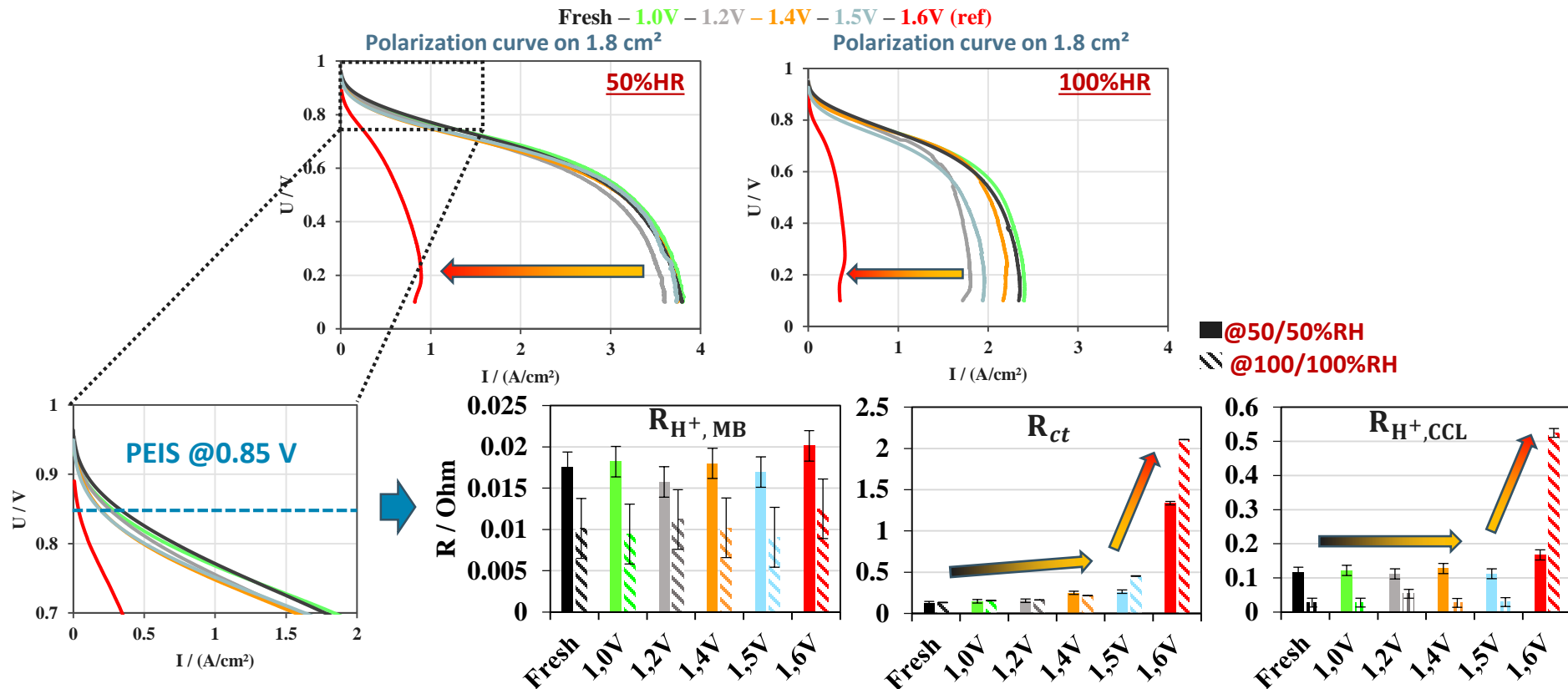
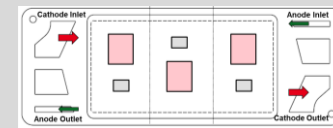
■ @50/50RH
 ▨ @100/100RH

PEIS model (H_2 /Air)

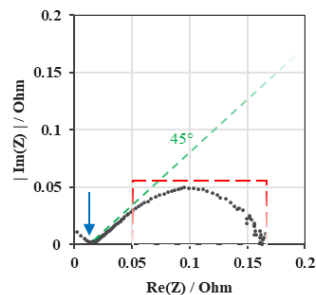
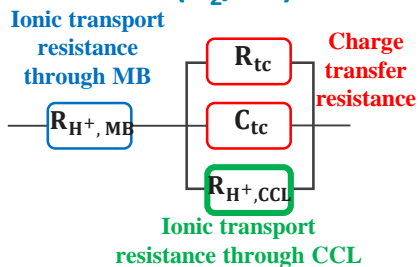


→ R_{ct} evolution cannot be fully linked to ECSA loss and thus Pt degradations

→ Other limiting mechanisms above 1.5 V

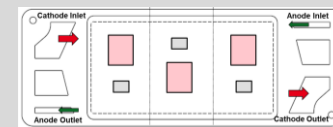


PEIS model (H₂/Air)



- No significant variation for CCL protonic transport resistance from fresh up to aged MEA at 1.5 V
- Drastic R_{H⁺, CCL} increase for 1.6 V case in FC operation

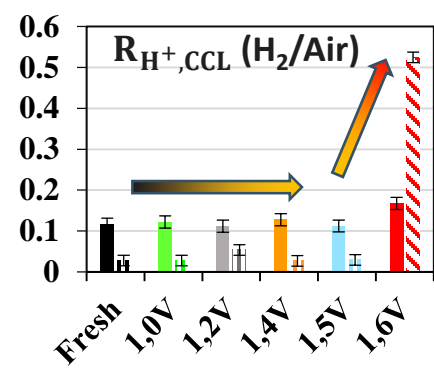
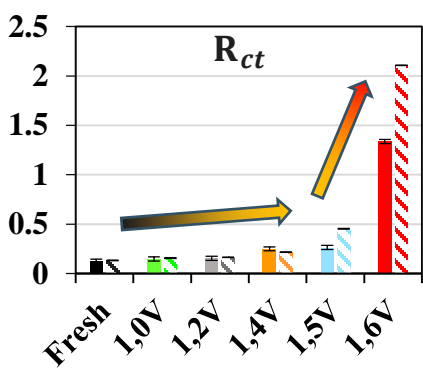
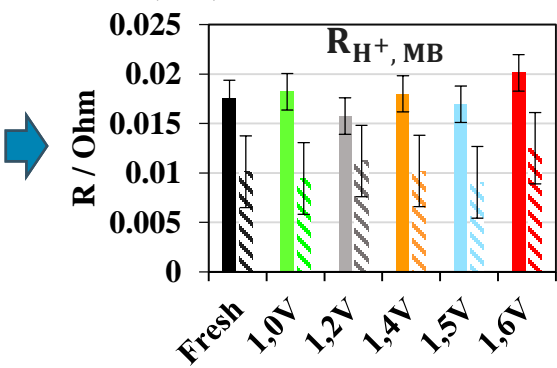
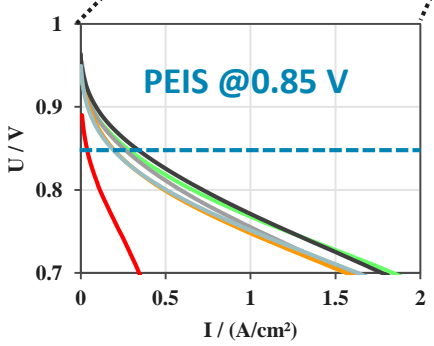
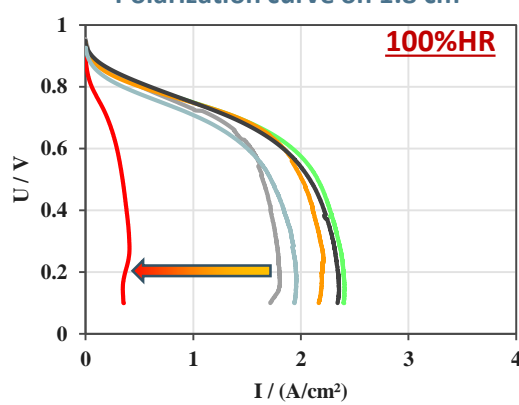
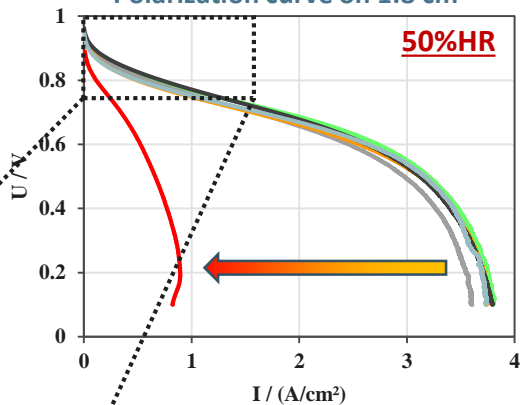
→ Modification of proton transport properties in CCL due to carbon support collapse ?



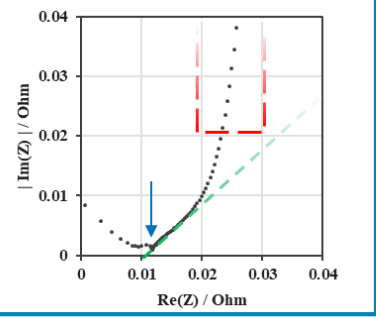
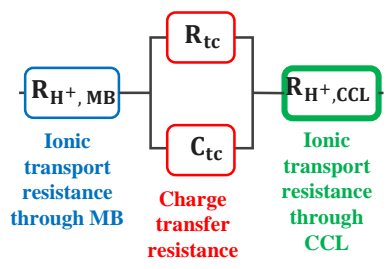
Fresh – 1.0V – 1.2V – 1.4V – 1.5V – 1.6V (ref)

Polarization curve on 1.8 cm²

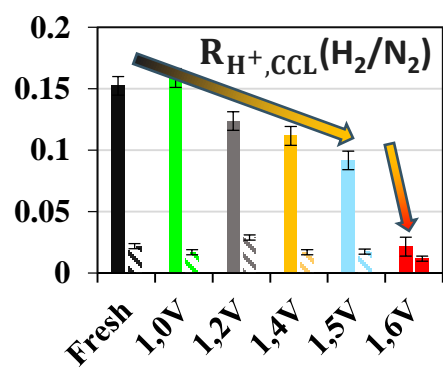
Polarization curve on 1.8 cm²



PEIS model (H_2/N_2)



- Progressive reduction R_{H^+} in CCL under N_2 when E_{front} is increased
 - Drastic decrease in proton resistance at 1.6 V at 50%RH
- Higher water retention in damaged CCL ?
- To be confirmed by additional techniques



- **Validation of complete *in-situ* & *post-mortem* investigation by:**
 - Electrochemical and physico-chemical analysis on large (98 cm²) and localized small (1.8 cm²) MEA areas

- **Mitigating parameters confirmed and quantified** with represented potential profile in real flow field design:
 - **E_{front}**: Lowering cathode potential by by-passing electrical current through dummy load
 - **t_{front}**: Lowering exposure time by accelerating H₂ injection in Air-filled anode
 - **RH_{a/c}**: Flushing cell with dry gas before H₂ injection
 - **T_{cell}**: Lowering stack temperature before H₂ injection

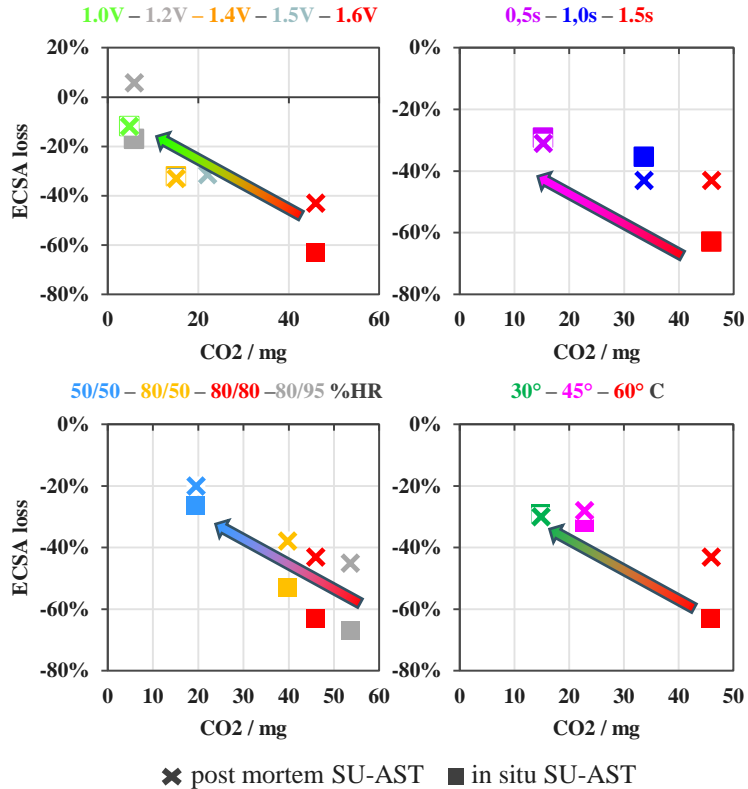
- **Complex degradation mechanism revealed:**
 - Weaker water management for damaged MEA in our SU-AST beyond 1.4 V
 - Better cell performance for damaged MEA at 1.0 V
 - Further insights on degradation mechanisms by using:
 - **Water sorption measurements**
 - **Raman spectroscopy** → Investigation of amorphous and graphitized domains into CCL
 - **XPS technique** → Investigation of functional groups onto carbon surface



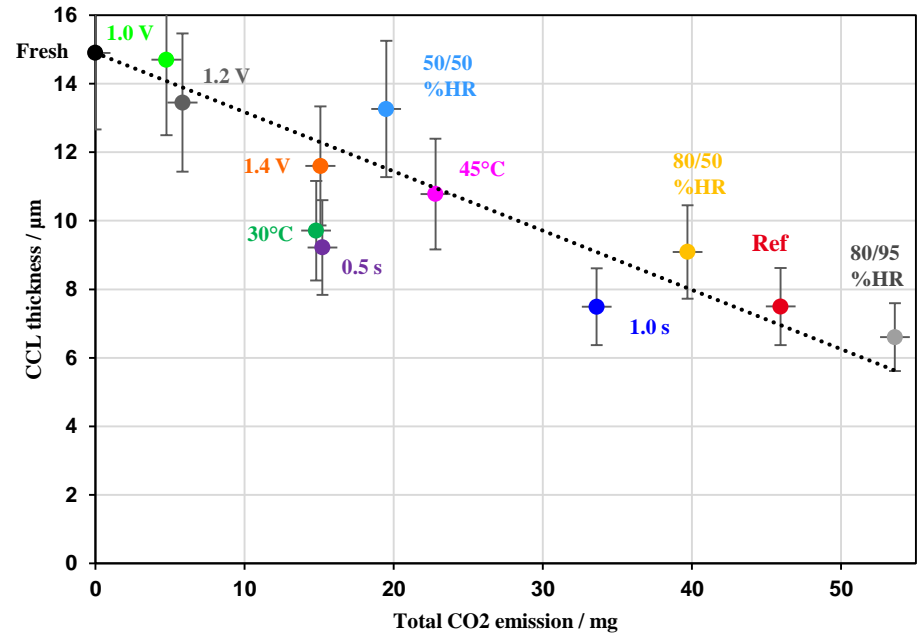
Thank for your attention

Timothée DRUGEOT

ECSA loss VS CO₂ emission



CCL thickness VS CO₂ emission



Lowering $E_{\text{front}} / t_{\text{front}} / \text{HR} / T_{\text{cell}}$

- Reduce CSC mechanism and Pt degradations
- Reduce CCL thinning and thus loss of porosity

→ Require additional post-mortem analysis to validate water retention and degradation mechanisms

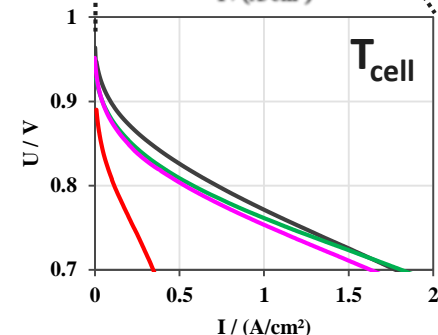
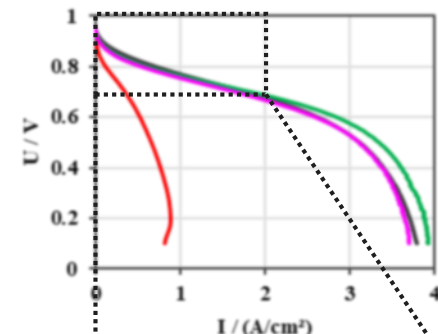
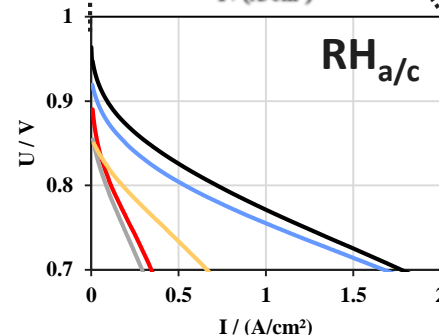
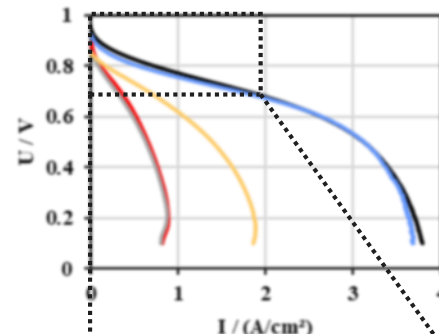
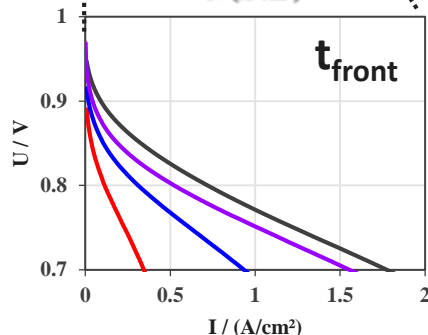
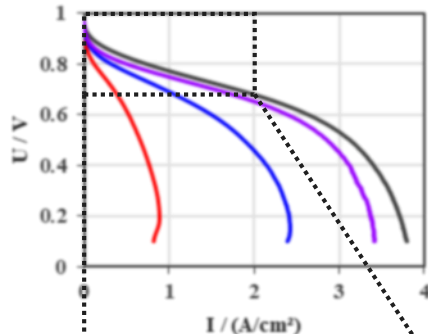
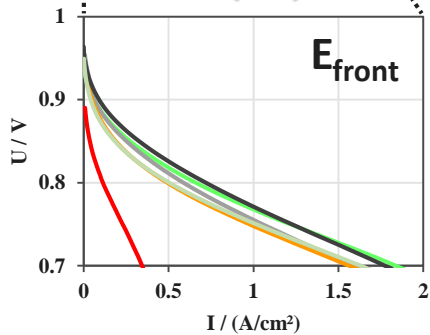
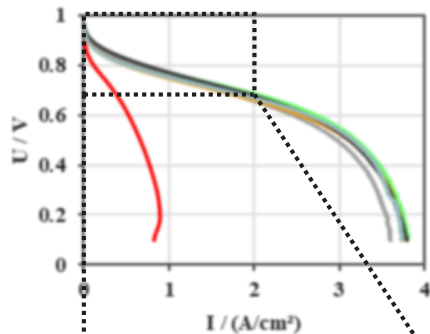
80°C – 50/50HR – 1.5/1.5_a – St 50/50

Fresh – 1.0V – 1.2V – 1.4V – 1.5V – 1.6V (ref)

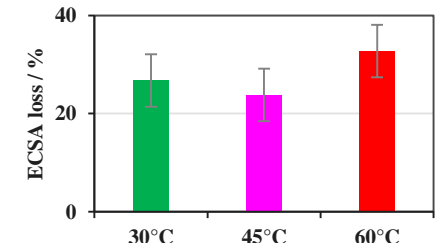
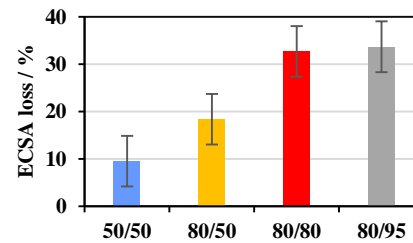
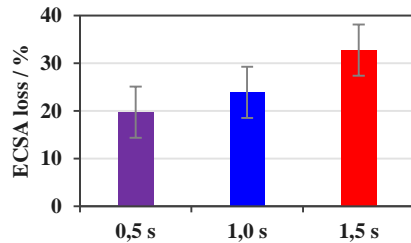
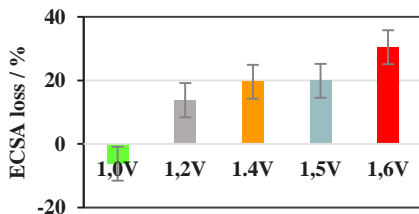
Fresh – 0.5 s – 1.0 s – 1.5 s (ref)

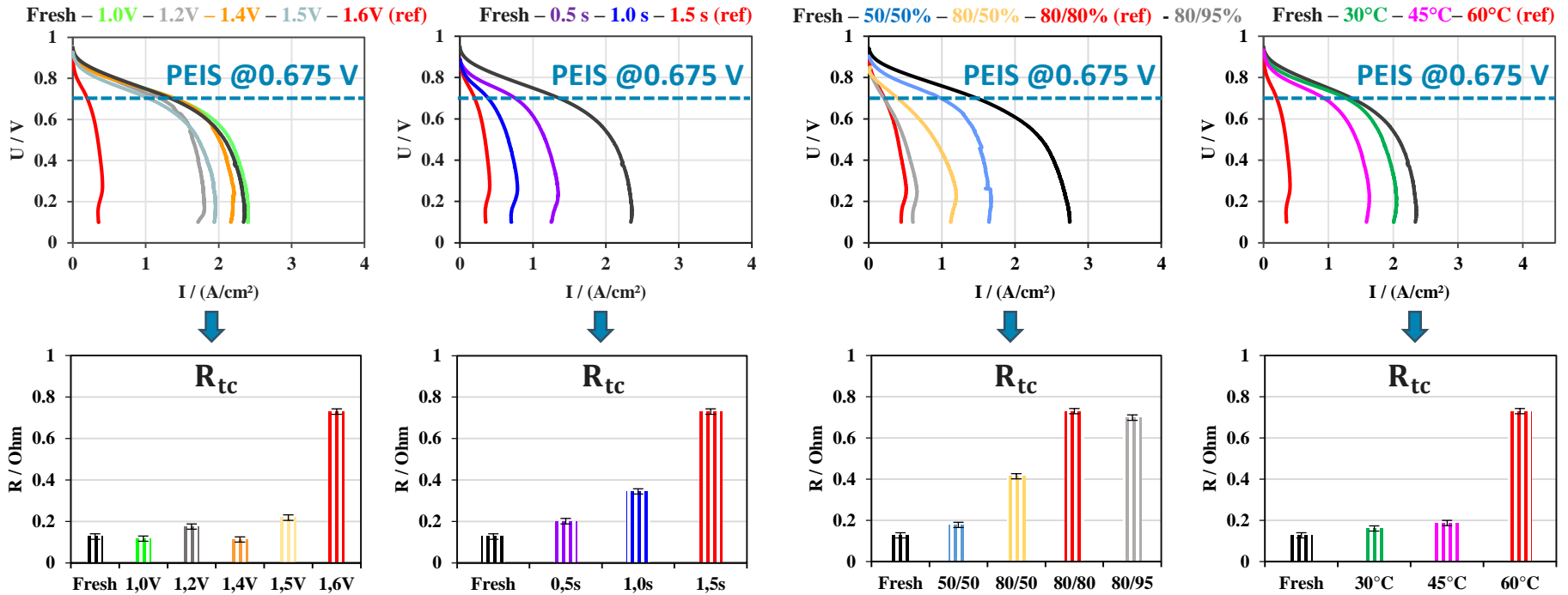
Fresh – 50/50% – 80/50% – 80/80% (ref) – 80/95%

Fresh – 30°C – 45°C – 60°C (ref)



ECSA loss



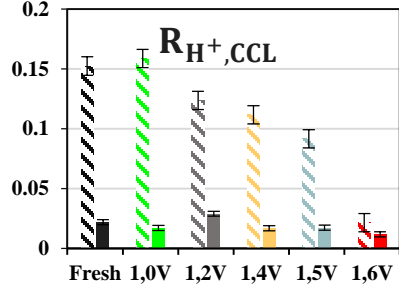
80°C – **95/95%HR** – 1.5/1.5 b_a – St 50/50

80°C – 1.5/1.5b_a – St 50/50

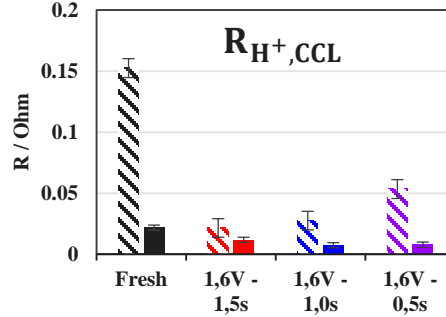
▨ @50/50%RH

■ @100/100%RH

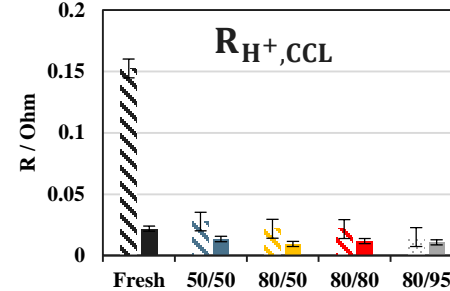
Fresh – 1.0V – 1.2V – 1.4V – 1.5V – 1.6V (ref)



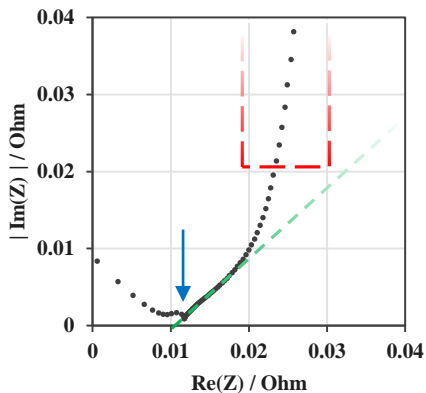
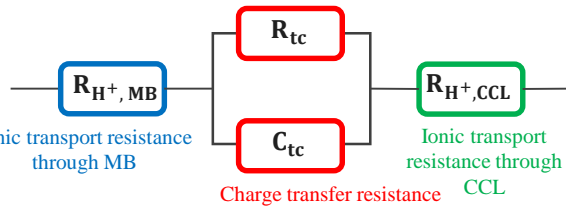
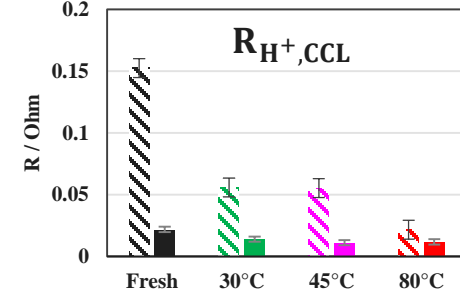
Fresh – 0.5 s – 1.0 s – 1.5 s (ref)



Fresh – 50/50% – 80/50% – 80/80% (ref) – 80/95%



Fresh – 30°C – 45°C – 60°C (ref)



PEIS at high HR condition (95/95% HR)

- Lower resistance with higher RH was expected
 - Lower resistance for more degraded CCL could be explained by :
 - A structural modification of ionomer phases with the carbon support collapse
 - A lower water removal abilities due to loss of hydrophobicity
- Requires additional analysis (water sorption, Raman spectroscopy...)