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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 – 32<sup>nd</sup> ISE Topical Meeting

Timothee Drugeot<sup>1,2</sup>, Fabrice Micoud<sup>1</sup>, Eric Pinton<sup>1</sup>, Jean-Phillippe Poirot-Crouvezier<sup>1</sup>, Sébastien Rosini<sup>1</sup>, Laure Guetaz<sup>1</sup>, Lucas Poupin<sup>1</sup> and Yann Bultel<sup>2</sup>

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<sup>2</sup>Univ. Grenoble Alpes, Univ. Savoie Mont Blanc, CNRS, Grenoble INP, LEPMI, 38000 Grenoble, France

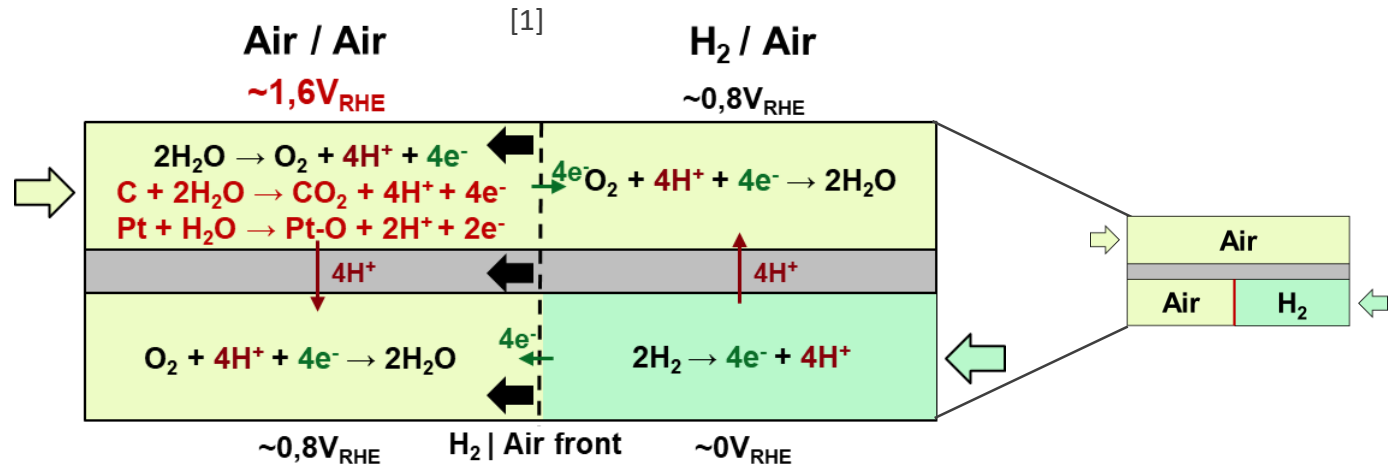
Email: [timothee.drugeot@cea.fr](mailto:timothee.drugeot@cea.fr)







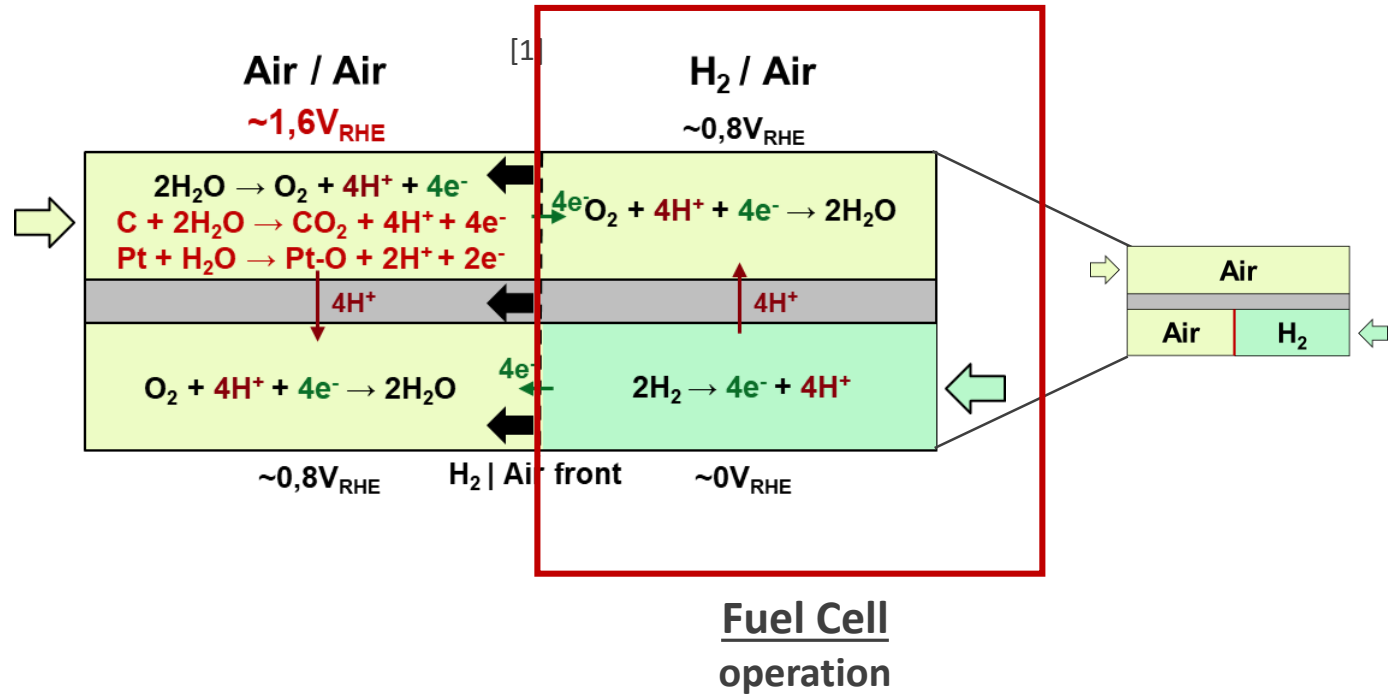
## Reverse Current Decay mechanism



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

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

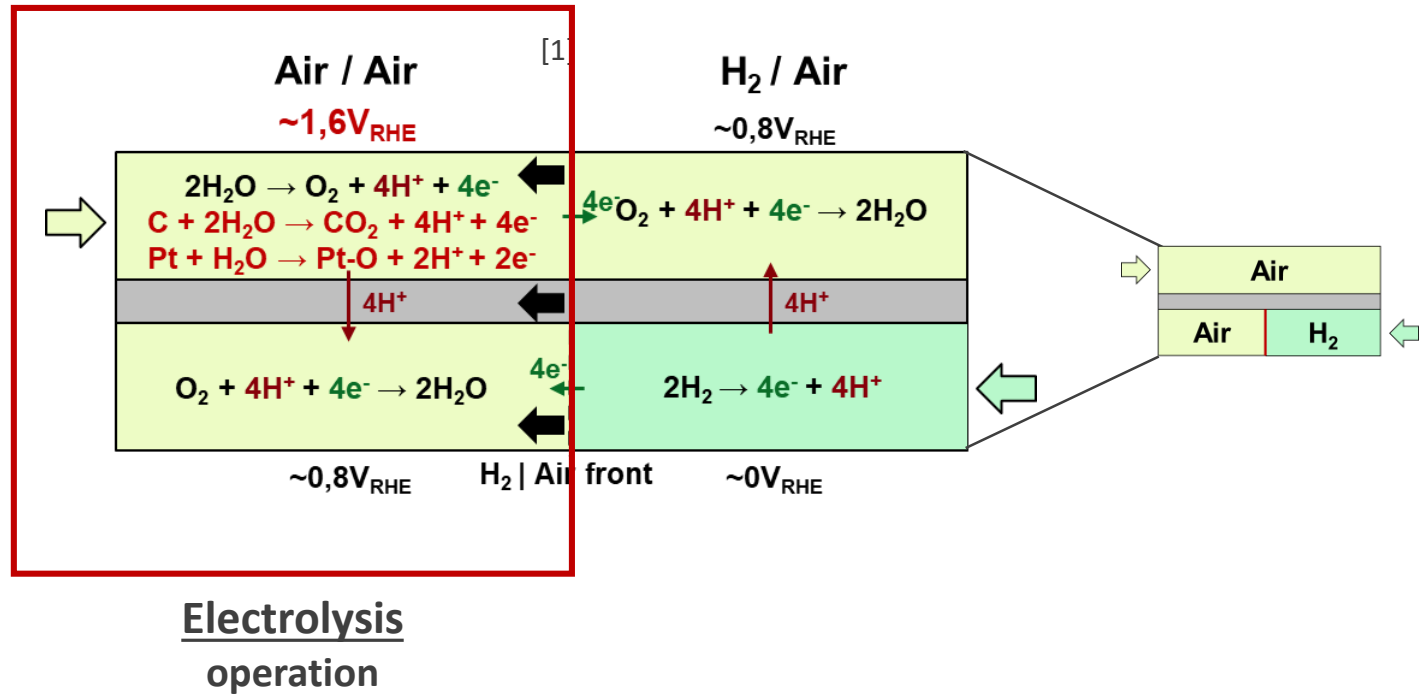
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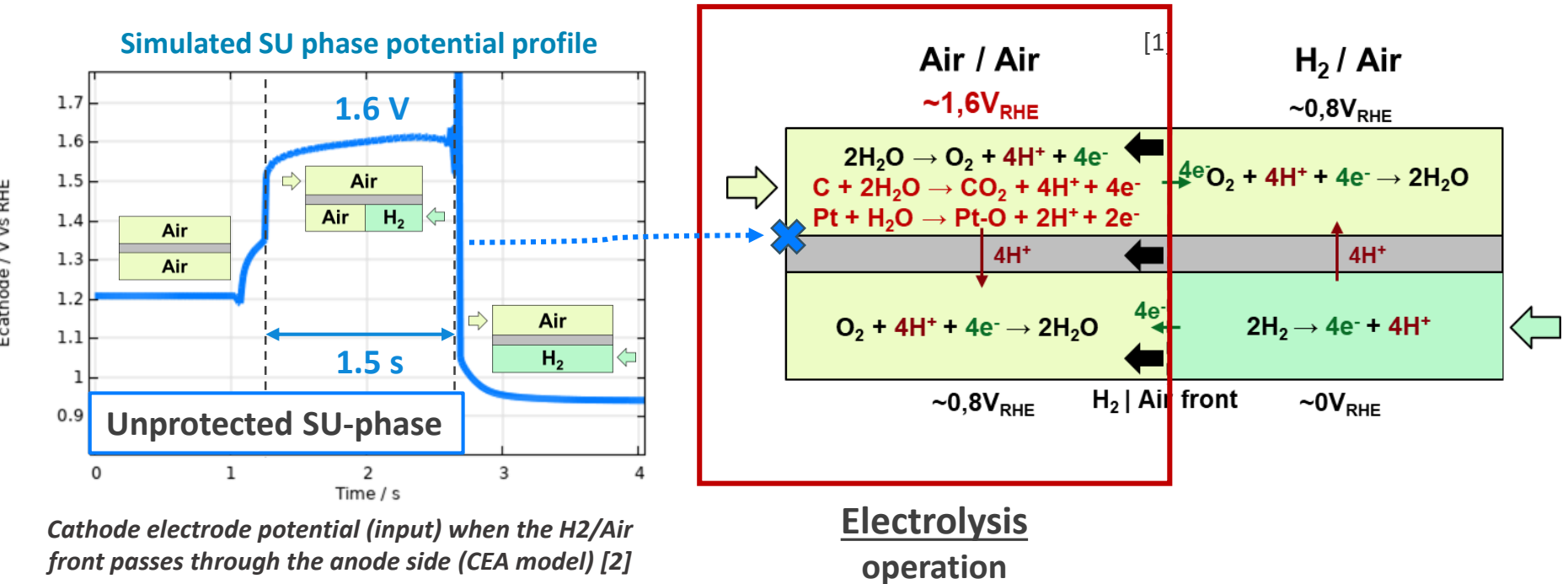


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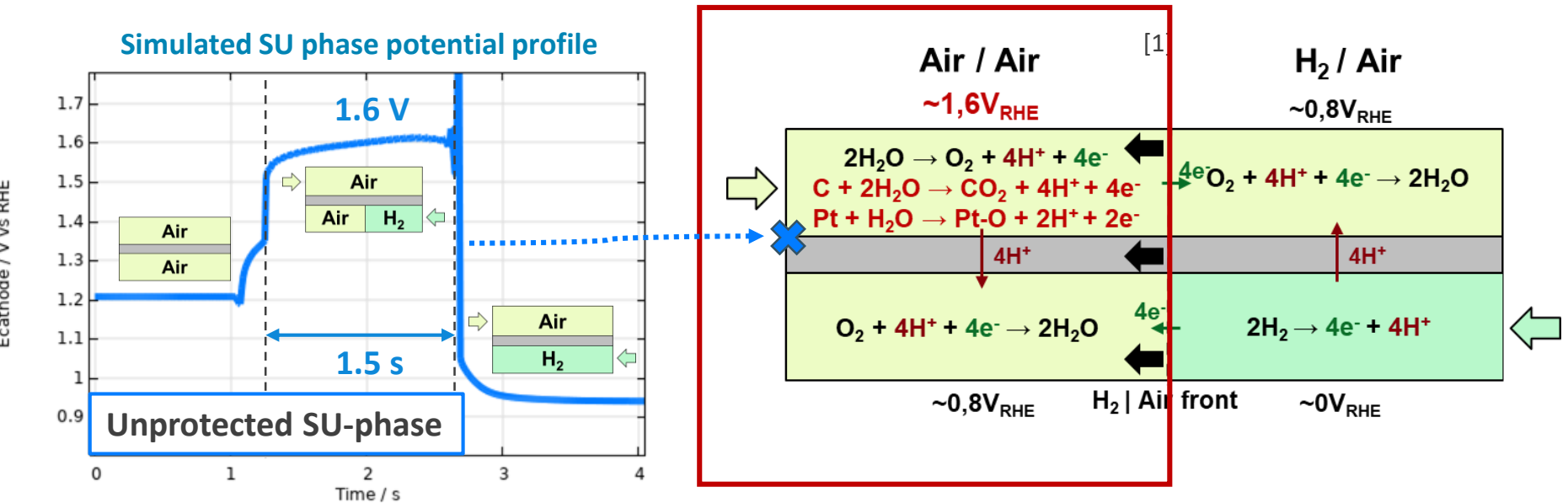
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## Reverse Current Decay mechanism



*Cathode electrode potential (input) when the H<sub>2</sub>/Air front passes through the anode side (CEA model) [2]*



**Cathod Catalyst Layer (CCL) degradation:**

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



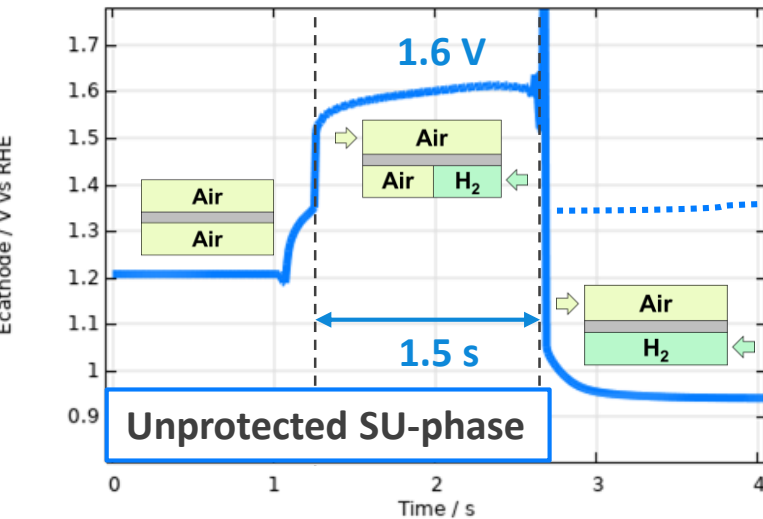
**IRREVERSIBLE loss of cell performance**

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

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

## Reverse Current Decay mechanism

## Simulated SU phase potential profile



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

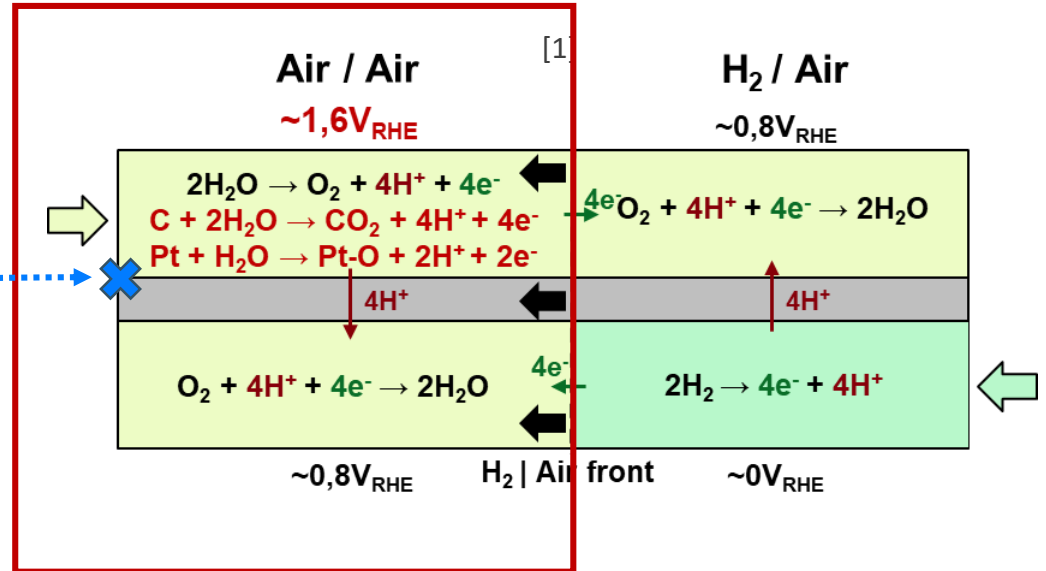


Cathod Catalyst Layer (CCL) degradation:

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



**IRREVERSIBLE** loss of cell performance



### Electrolysis operation

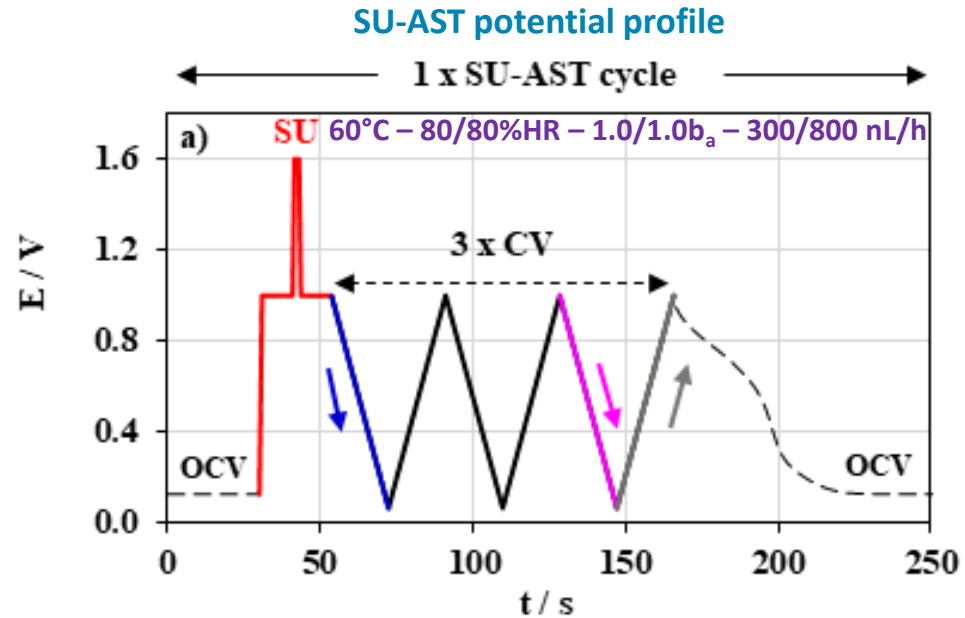
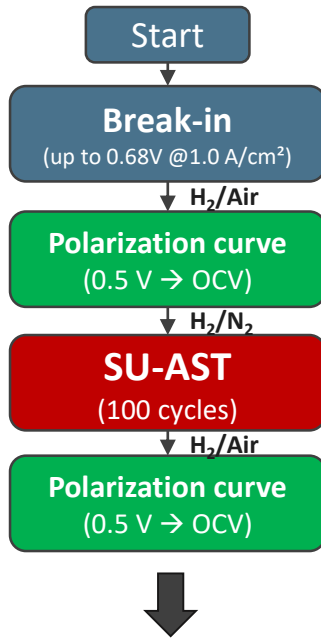
#### Objectives

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

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

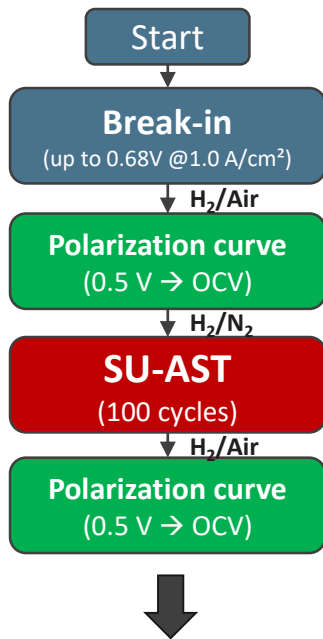
[2] Radriarazafy et al. "Modelling Carbon Corrosion during a PEMFC Startup: Simulation of Mitigation Strategies" (2020)

## Emulation of realistic cathode potential profile

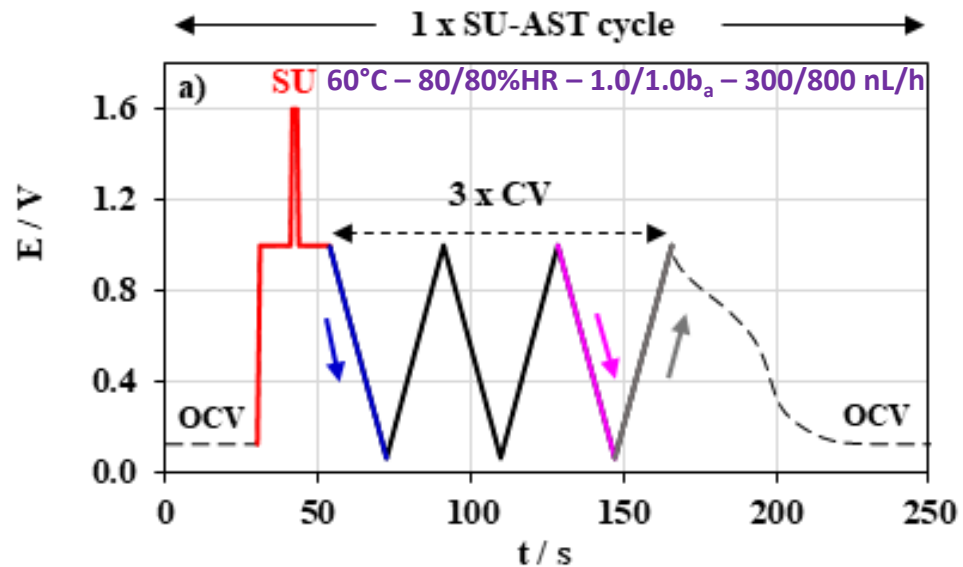
Coupling monitoring techniques

- Cell performance decay (polarization)
- ECSA losses along AST (CV)
- CO<sub>2</sub> emission rate along AST

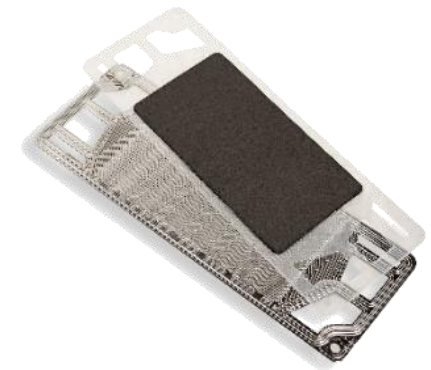
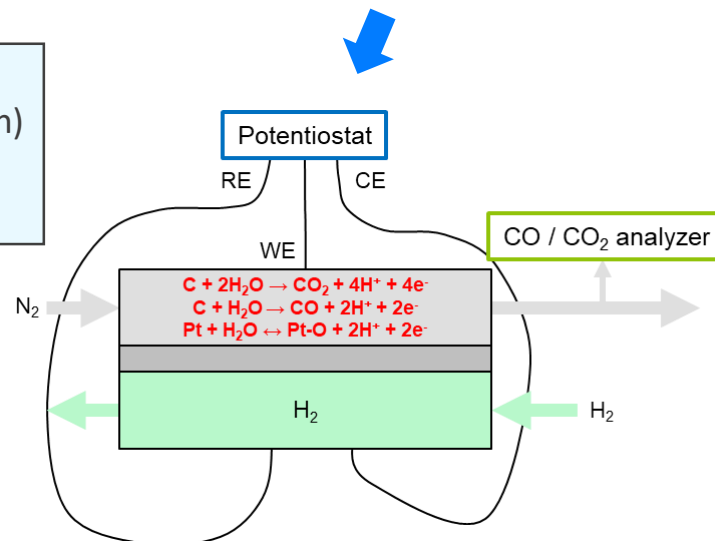
## Emulation of realistic cathode potential profile



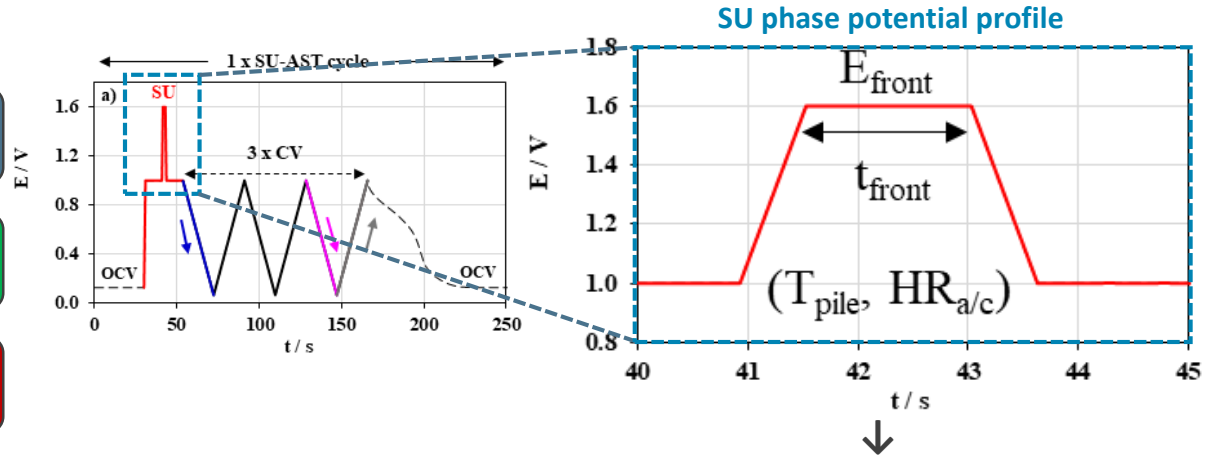
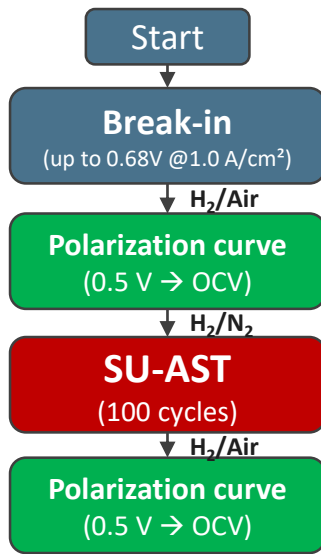
## SU-AST potential profile

Coupling monitoring techniques

- Cell performance decay (polarization)
- ECSA losses along AST (CV)
- CO<sub>2</sub> emission rate along AST



Real stack flow-field design  
100 cm<sup>2</sup> 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*

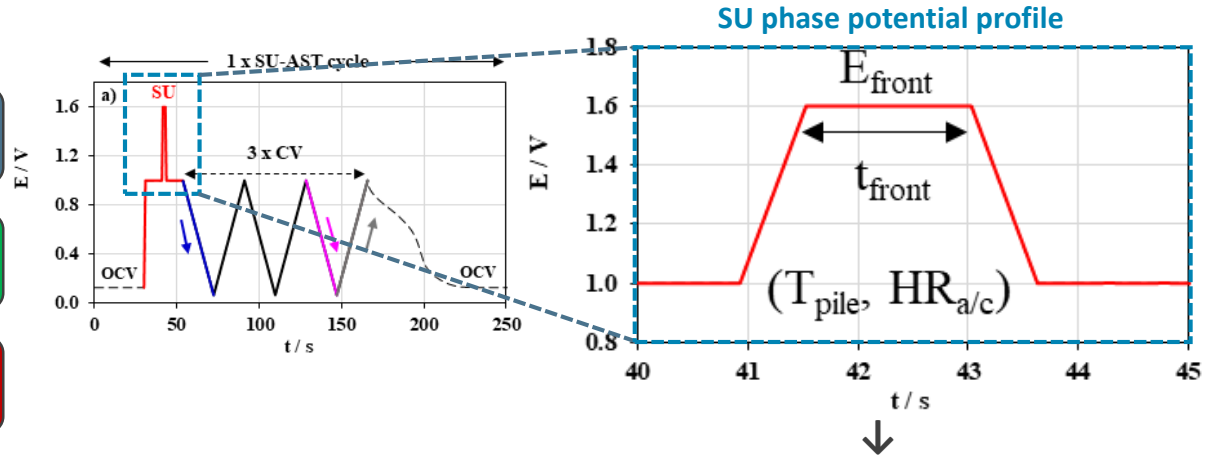
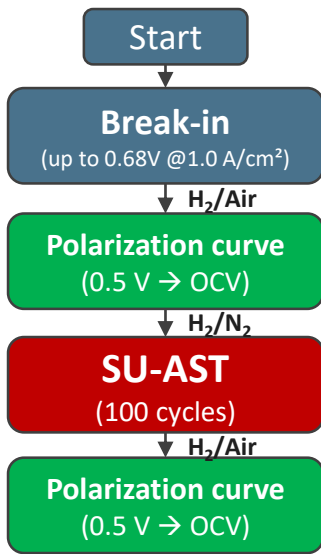
- $RH_{a/c}$  (95 → 50%)

*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**



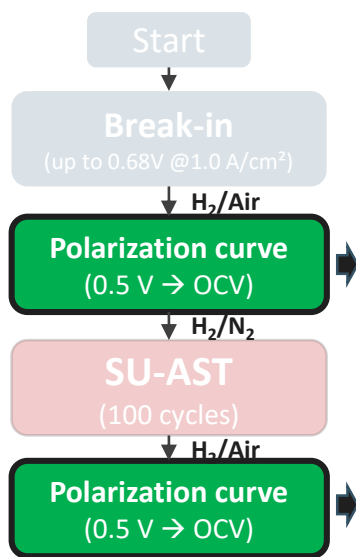
- **1.6V** – 1.5s – 80/80%RH – 60°C (Ref)
- **1.4V** – 1.5s – 80/80%RH – 60°C
- **1.2V** – 1.5s – 80/80%RH – 60°C
- **1.0V** – 1.5s – 80/80%RH – 60°C
- 1.6V – **1.0s** – 80/80%RH – 60°C
- 1.6V – **0.5s** – 80/80%RH – 60°C
- 1.6V – 1.5s – **80/50%RH** – 60°C
- 1.6V – 1.5s – **50/50%RH** – 60°C
- 1.6V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

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

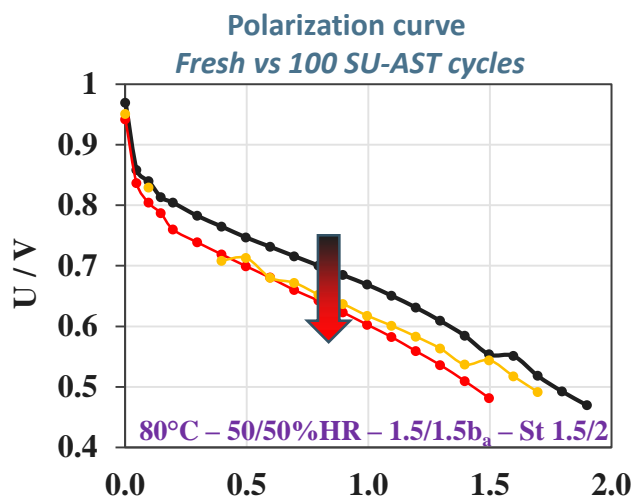
- **$t_{front}$**  (1.5 → 0.5s)  
*relative accelerating  $H_2$  injection in Air-filled anode*

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

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

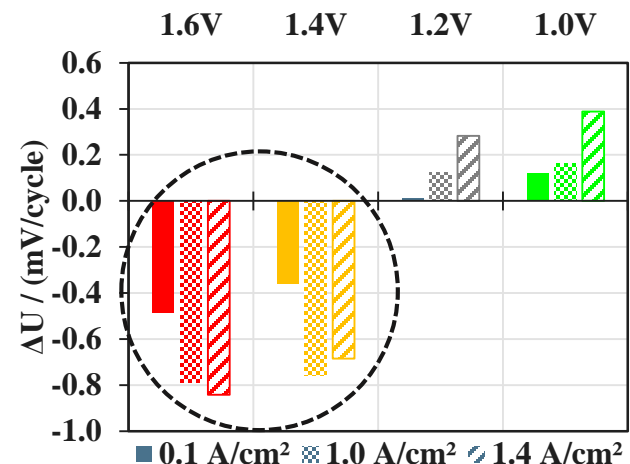
E<sub>front</sub> investigation – Cell voltage evolution

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



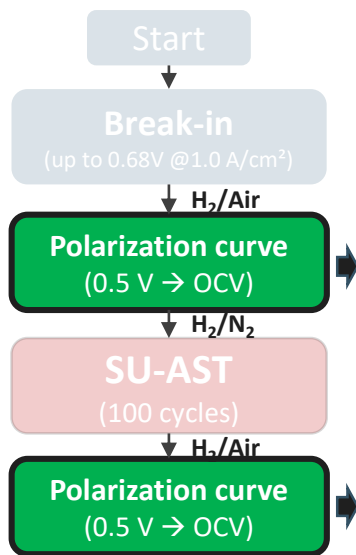
## Performance evolution

Fresh vs 100 SU-AST cycles

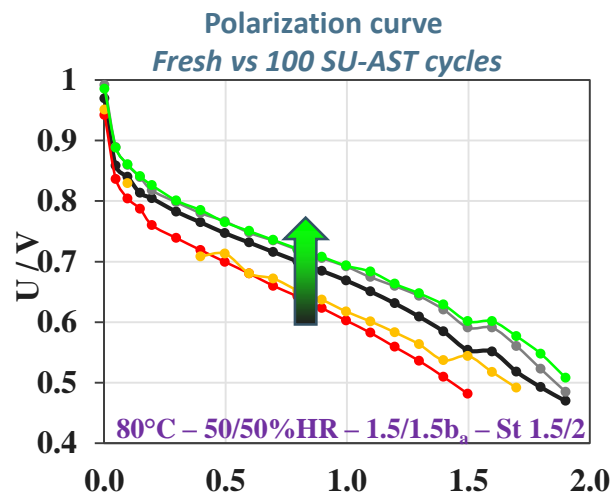
1.4 – 1.6 V range

- Harsh voltage loss along overall polarization curve



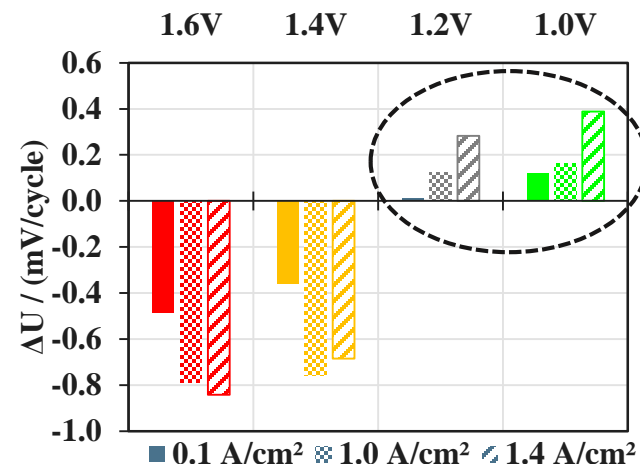
E<sub>front</sub> investigation – Cell voltage evolution

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## Performance evolution

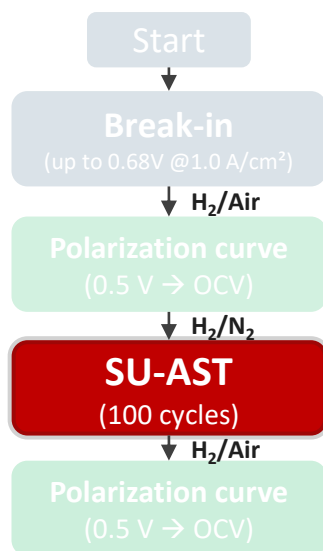
Fresh vs 100 SU-AST cycles

1.0 – 1.2 V range

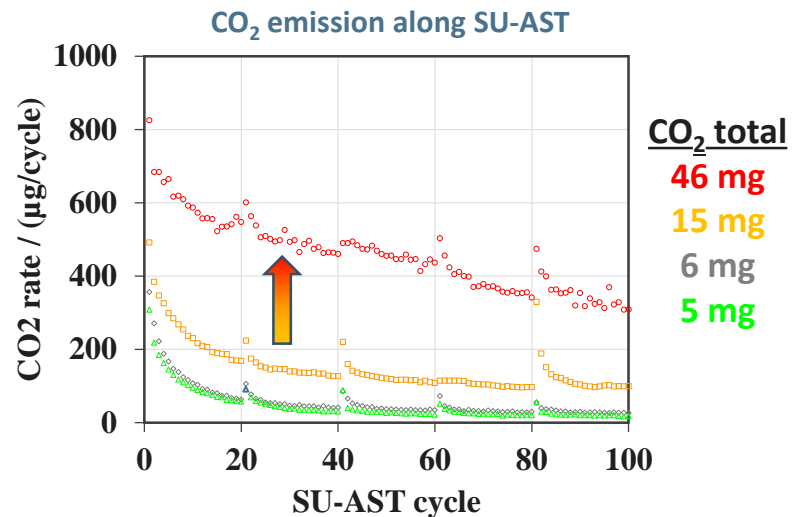
- Unexpected **improvement of cell performance** (even after 100 cycles)

1.4 – 1.6 V range

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



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

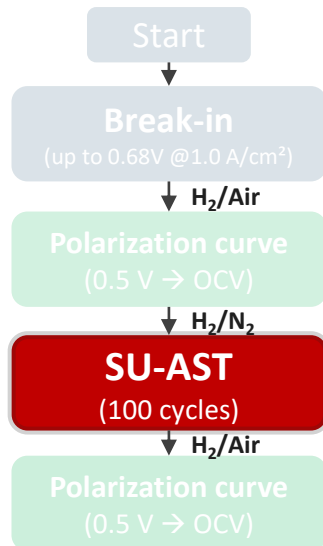


### 1.0 – 1.2 V range

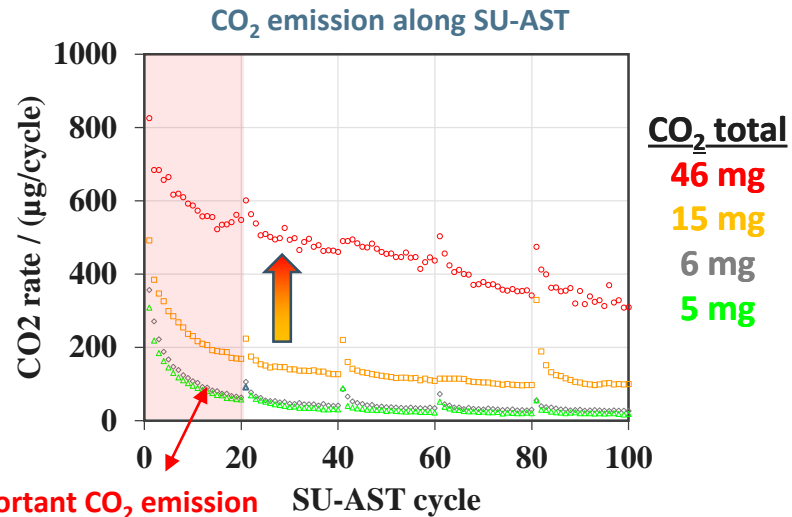
- Unexpected **improvement of cell performance**
- **Low CO<sub>2</sub> emission rate** expected during the first 20 cycles

### 1.4 – 1.6 V range

- **Harsh voltage loss** along overall polarization curve
- **Higher CO<sub>2</sub> emission rate** for 1.6 V case along cycles



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



Important CO<sub>2</sub> emission during the first cycles

### 1.0 – 1.2 V range

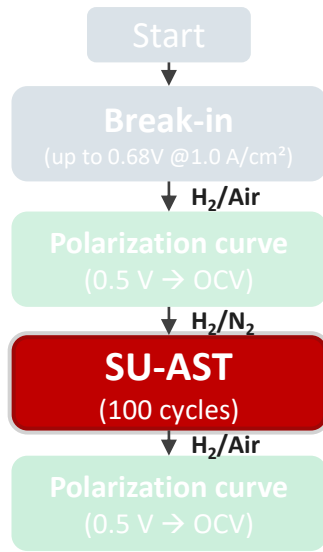
- Unexpected **improvement of cell performance**
- **Low CO<sub>2</sub> emission rate** expected during the first 20 cycles

→ **CSC of only poorly ordered domains**

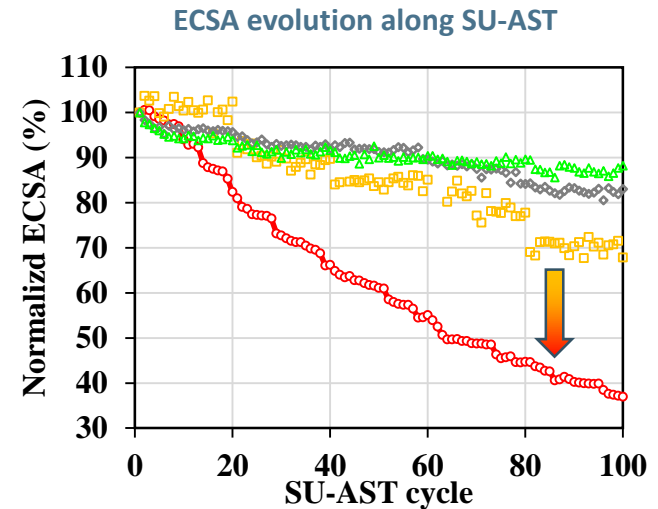
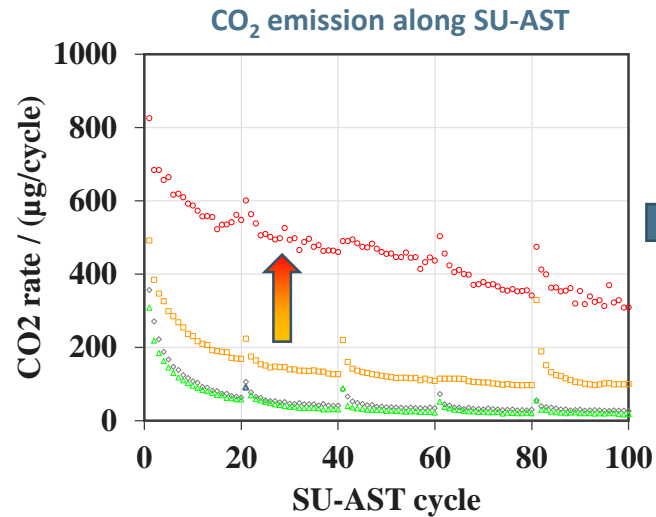
### 1.4 – 1.6 V range

- **Harsh voltage loss** along overall polarization curve
- **Higher CO<sub>2</sub> 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

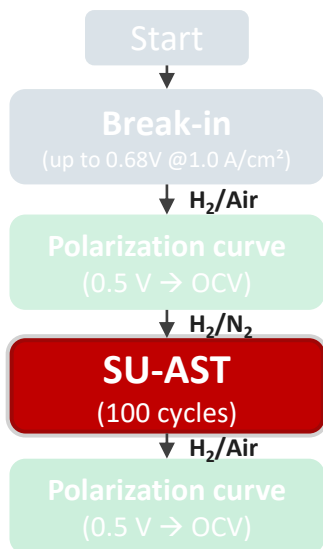
- Unexpected **improvement of cell performance**
- **Low CO<sub>2</sub> emission rate** expected during the first 20 cycles

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

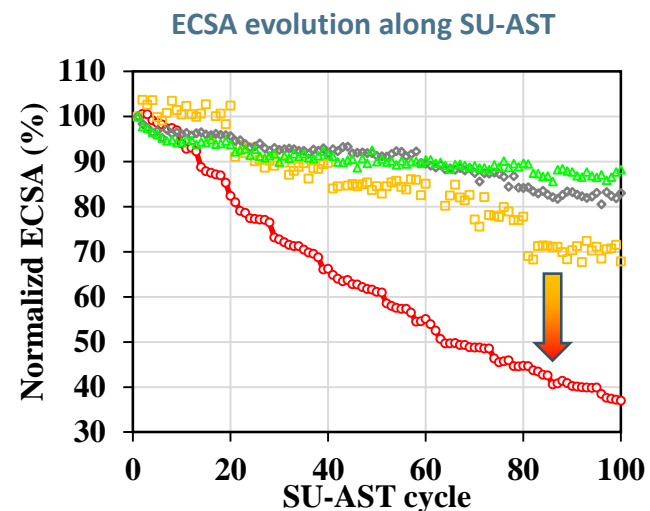
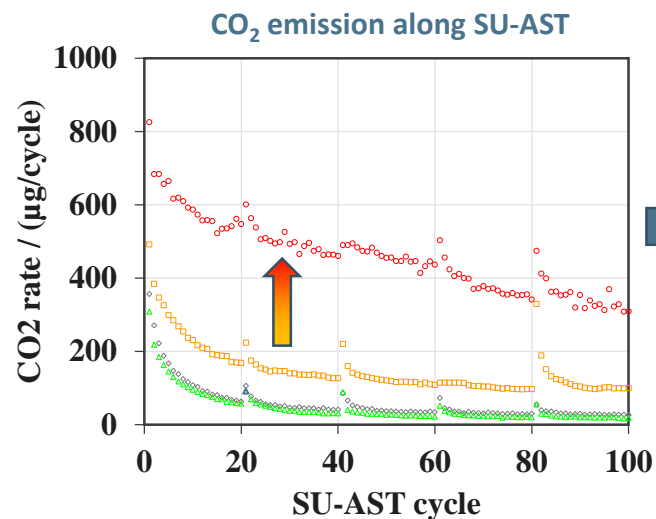
### 1.4 – 1.6 V range

- **Harsh voltage loss** along overall polarization curve
- **Higher CO<sub>2</sub> 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 CO<sub>2</sub> emission rate** expected during the first 20 cycles

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

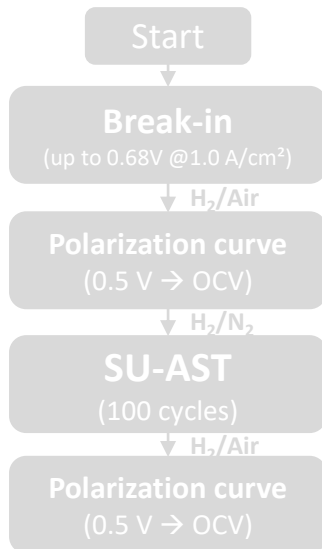
### 1.4 – 1.6 V range

- **Harsh voltage loss** along overall polarization curve
- **Higher CO<sub>2</sub> emission rate** for 1.6 V case along cycles

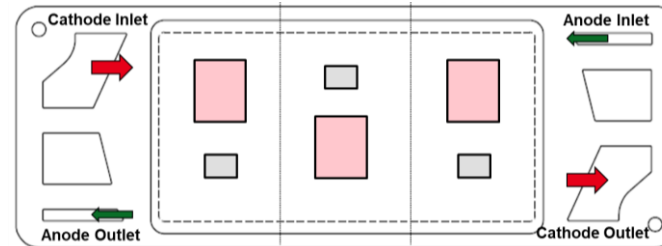
→ **CSC of poorly and more ordered domains [1]**  
→ **Pt dissolution/reposition + Pt detachment/agglomeration (linked to CSC)**

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

## In-situ AST



## Cutting sample of fresh / aged MEA

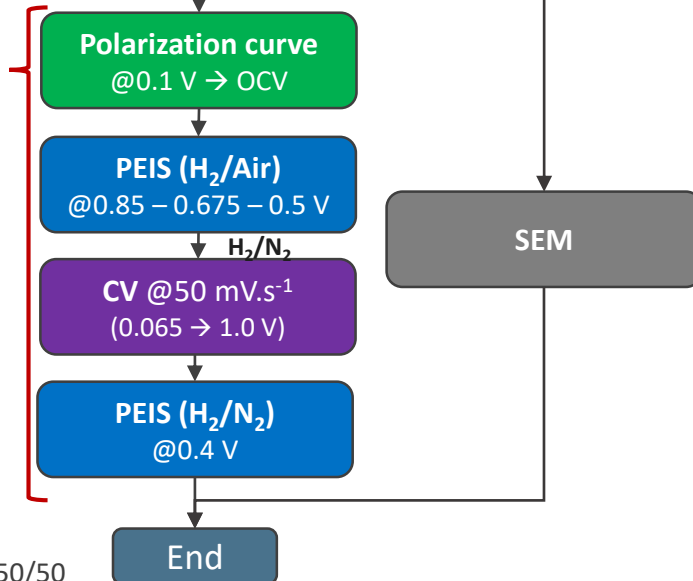


## Post-mortem AST

**X3**  
operating  
conditions

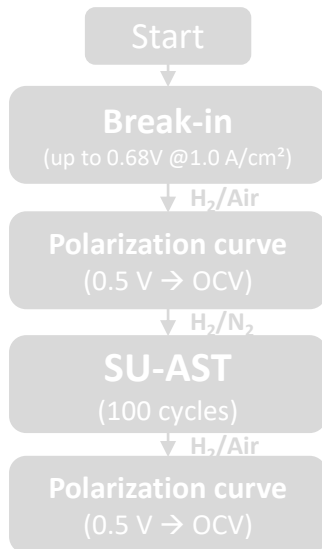


80°C - 50%HR\*  
80°C - 80%HR\*  
80°C - 100%HR\*

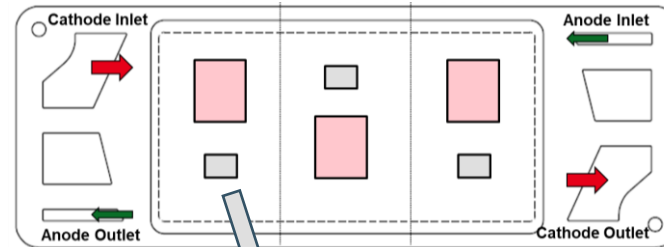


\*1.5/1.5 bar<sub>a</sub> - St 50/50

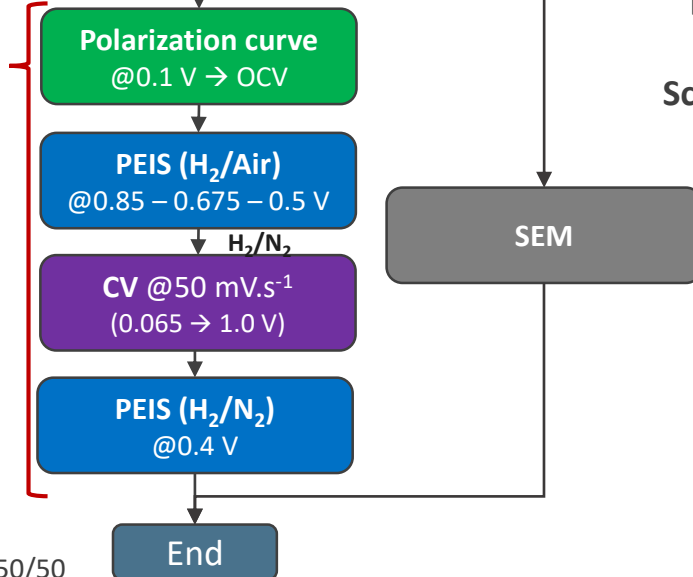
## In-situ AST



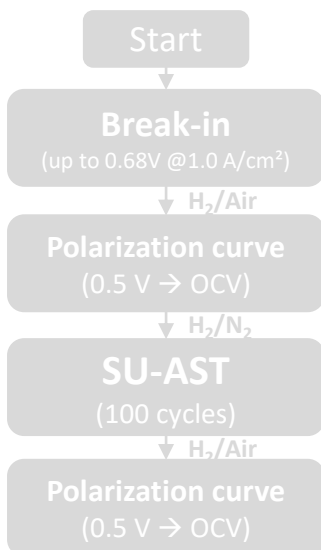
## Cutting sample of fresh / aged MEA

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

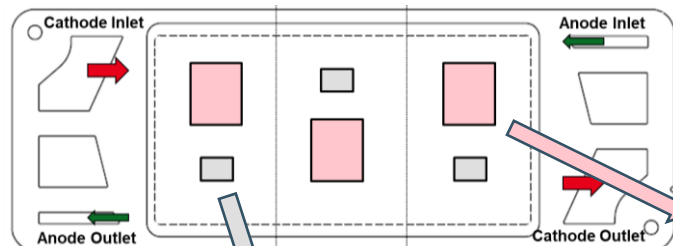
## Post-mortem AST

**X3**  
operating  
conditions80°C - 50%HR\*  
80°C - 80%HR\*  
80°C - 100%HR\*\*1.5/1.5 bar<sub>a</sub> - St 50/50

## In-situ AST



## Cutting sample of fresh / aged MEA

7-layer MEA  
(front view)1.8 cm<sup>2</sup> MEA sample7-layer MEA  
(side view)Local structural analysis  
By  
Scanning Electron Microscopy  
(SEM)Local EC analysis  
By

- Polarization
- CV
- Impedance Spectroscopy (PEIS)

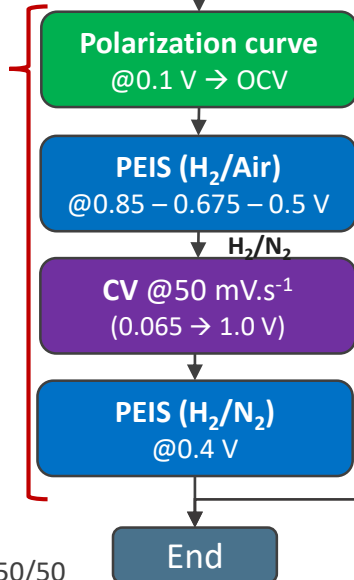
SEM

## Post-mortem AST

**X3**  
operating  
conditions

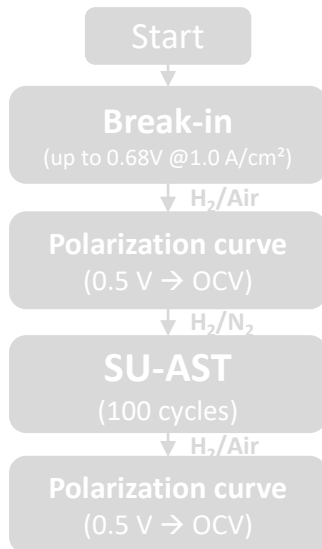


80°C - 50%HR\*  
80°C - 80%HR\*  
80°C - 100%HR\*

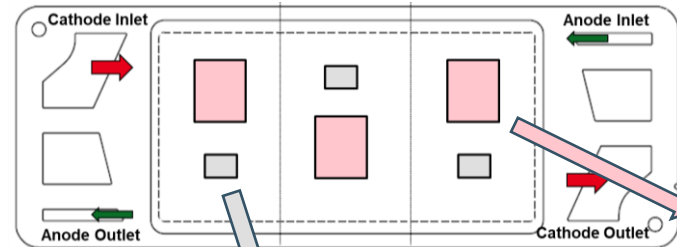
\*1.5/1.5 bar<sub>a</sub> – St 50/50



## In-situ AST



## Cutting sample of fresh / aged MEA

7-layer MEA  
(front view)7-layer MEA  
(side view)1.8 cm<sup>2</sup> MEA sample

Local structural analysis  
By  
Scanning Electron Microscopy  
(SEM)

Local EC analysis  
By

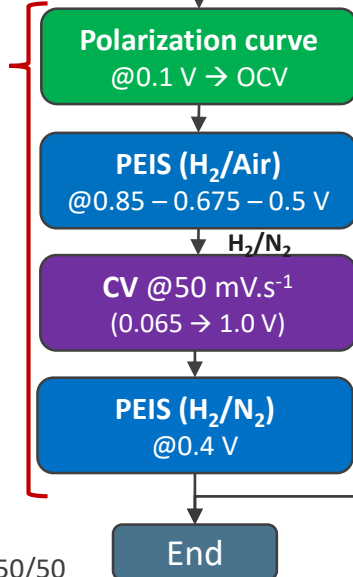
- Polarization
- CV

- Impedance Spectroscopy (PEIS)

- *Reproducibility on fresh MEA* ✓

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

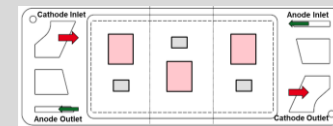
## Post-mortem AST



SEM

End

\*1.5/1.5 bar<sub>a</sub> – St 50/50

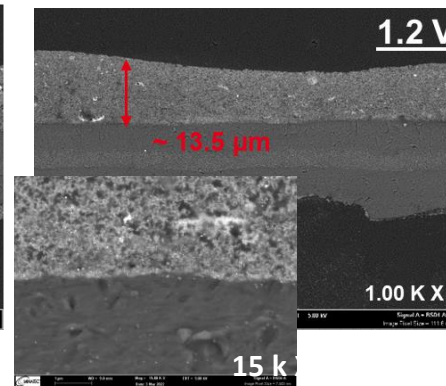
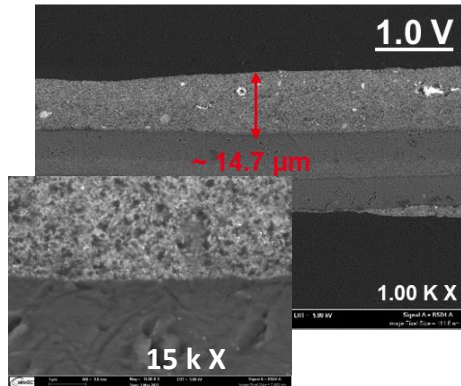
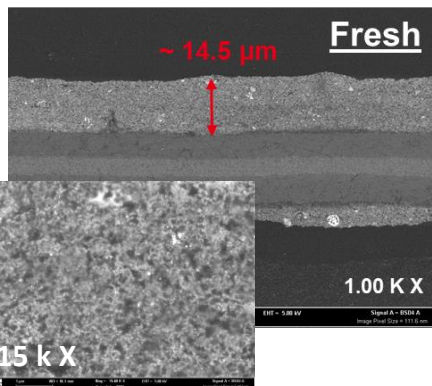


Low thinning from fresh to 1.2 V aged commercial MEA

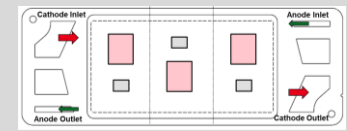
Fresh

1.0 V

1.2 V



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

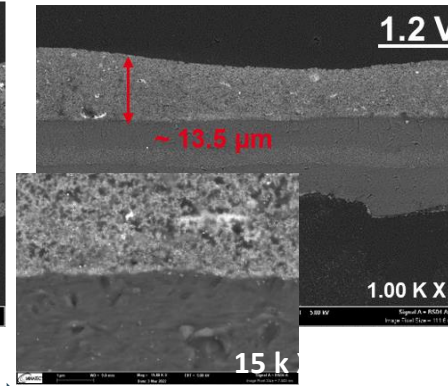
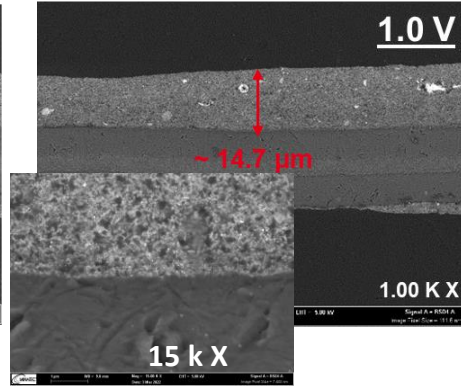
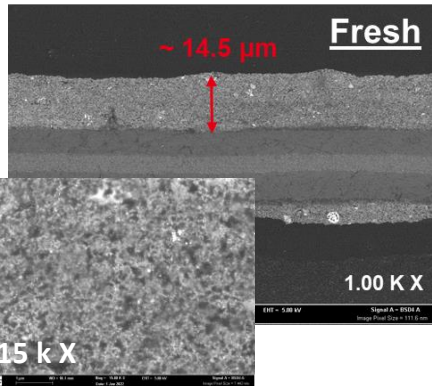


Low thinning from fresh to 1.2 V aged commercial MEA

Fresh

1.0 V

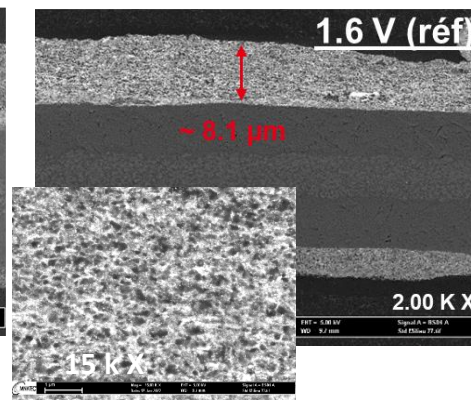
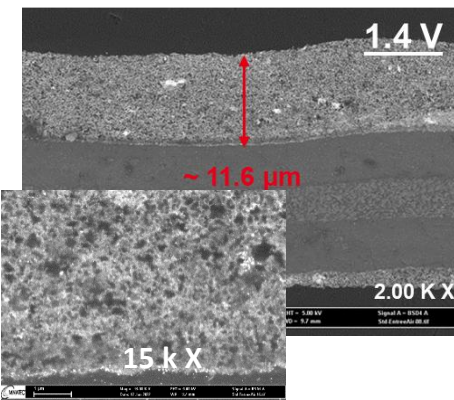
1.2 V



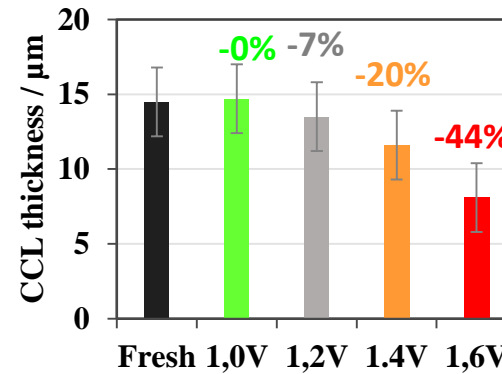
High thinning beyond 1.4 V

1.4 V

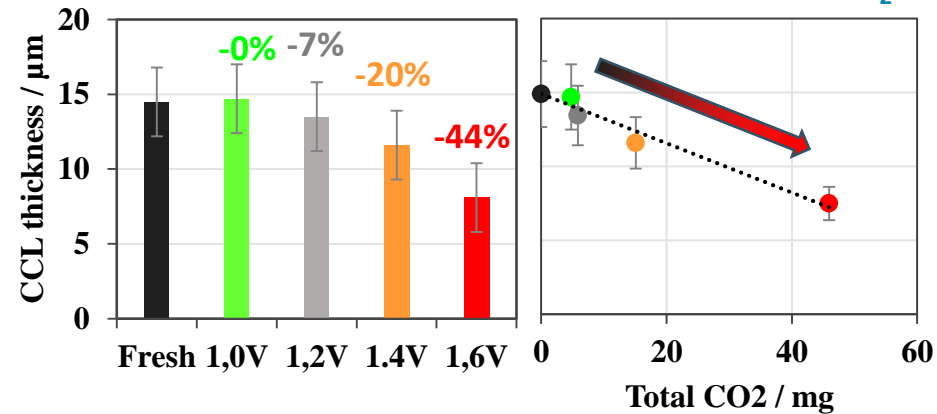
1.6 V



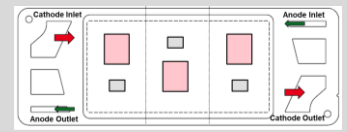
Estimated CCL thickness



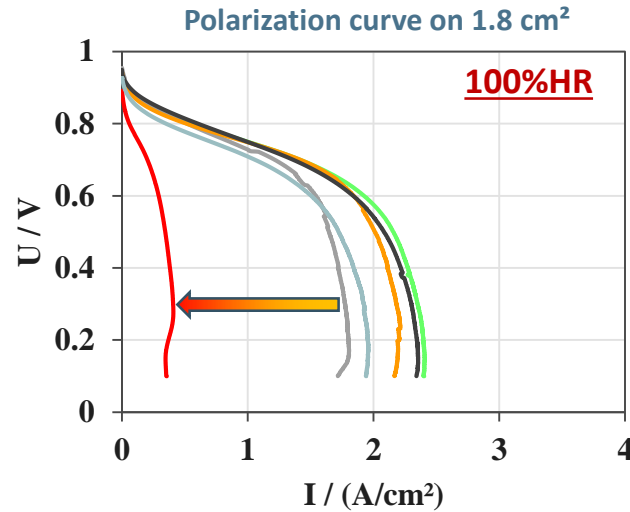
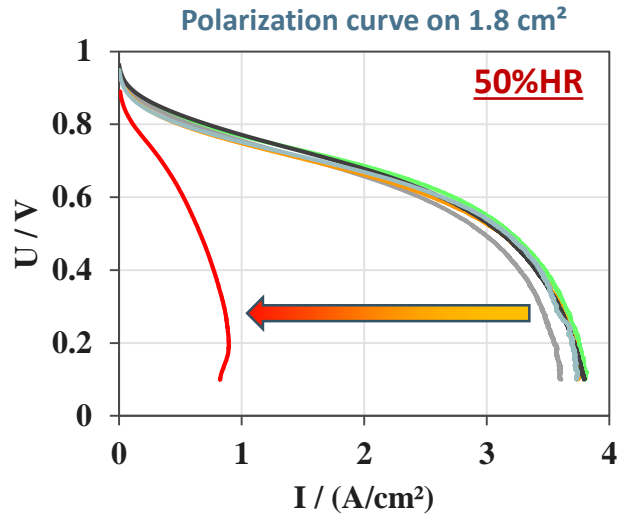
CCL thickness VS CO<sub>2</sub>



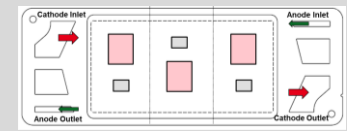
- No CCL structural modification from fresh to aged MEA at 1.2 V
- Low compaction of CCL and densification of Pt nanoparticles at 1.4 V and **harsher at 1.6 V**  
 → **Linear correlation with CSC mechanisms**



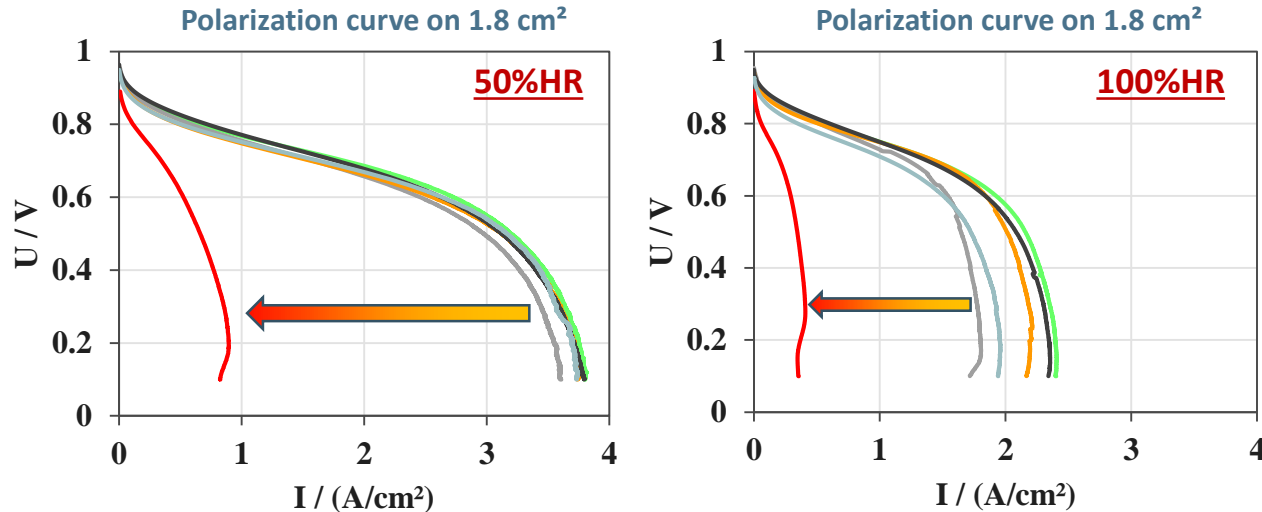
Fresh – 1.0V – 1.2V – 1.4V – 1.5V – 1.6V



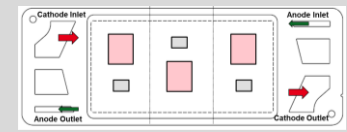
- **At 50 %HR** : No performance decay excepted for 1.6 V case  
↓
- **At 100 %HR** : Emergence of progressive performance decay



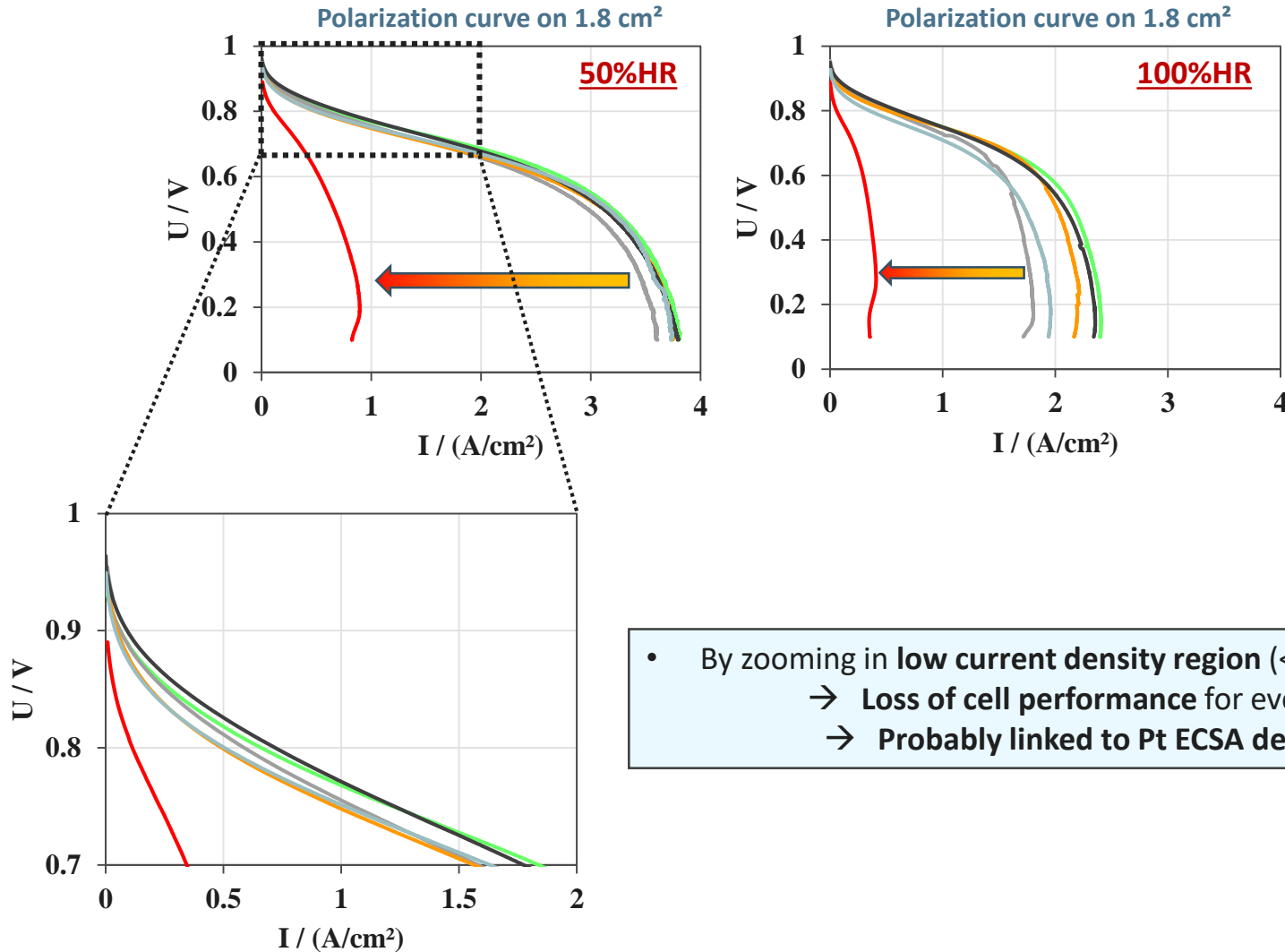
Fresh – 1.0V – 1.2V – 1.4V – 1.5V – 1.6V



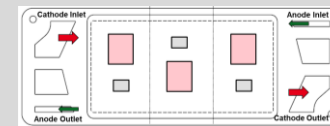
- **At 50 %HR** : No performance decay excepted for 1.6 V case  
↓
- **At 100 %HR** : Emergence of progressive performance decay
- **Improvement of performance for 1.0 V** case similar as in previous in-situ SU-AST (98 cm<sup>2</sup>)  
→ **Mass transport limitation is more pronounced At higher RH**  
↓
- **Water management is altered** due to **CCL chemical and/or electrochemical modifications**:
  - i. Loss of hydrophobicity
  - ii. Modification of carbon surface properties
  - iii. Higher Pt/C loading ratio due to carbon support corrosion



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



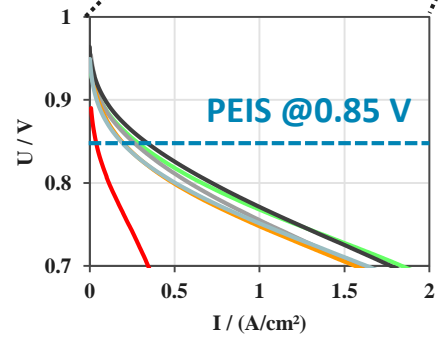
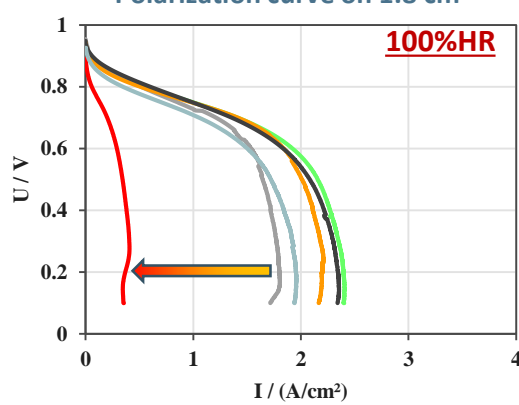
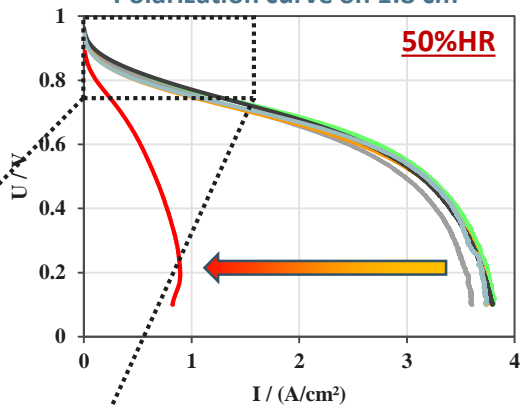
- By zooming in **low current density region** ( $< 2 \text{ A/cm}^2$ )
  - **Loss of cell performance** for every case
  - **Probably linked to Pt ECSA decrease**



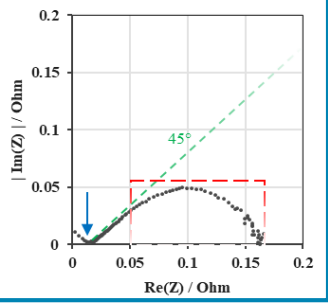
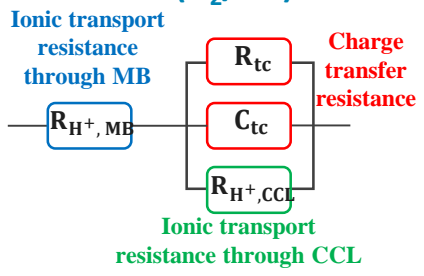
Fresh – 1.0V – 1.2V – 1.4V – 1.5V – 1.6V (ref)

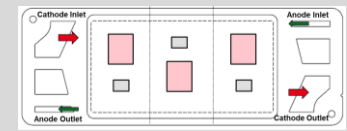
Polarization curve on 1.8 cm<sup>2</sup>

Polarization curve on 1.8 cm<sup>2</sup>



### PEIS model ( $H_2$ /Air)

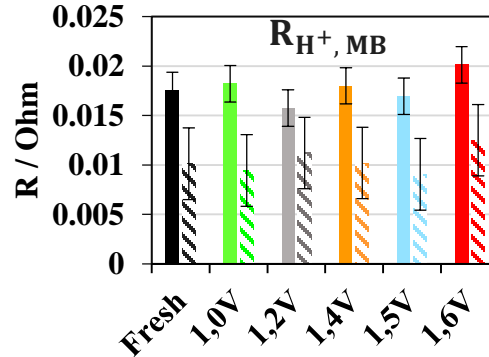
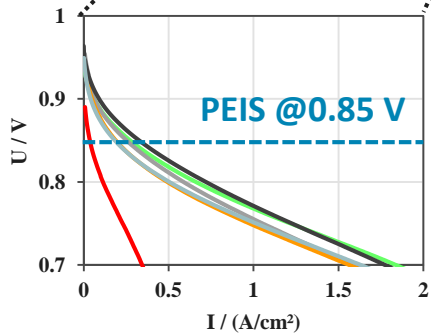
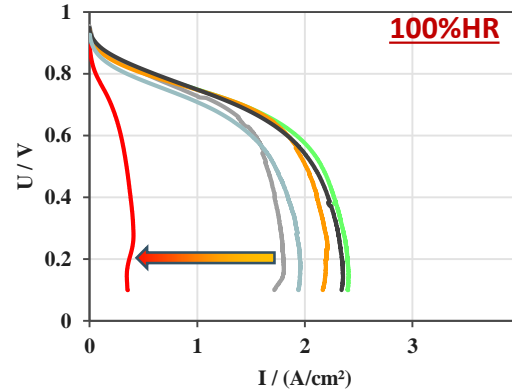
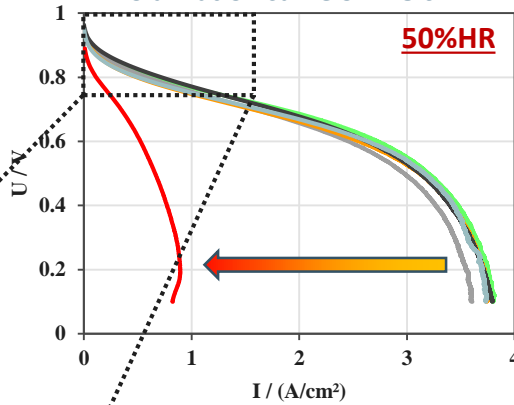




Fresh – 1.0V – 1.2V – 1.4V – 1.5V – 1.6V (ref)

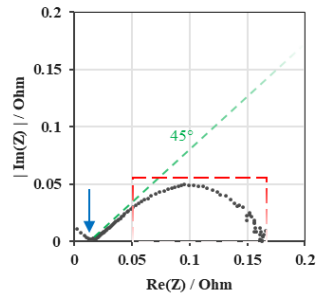
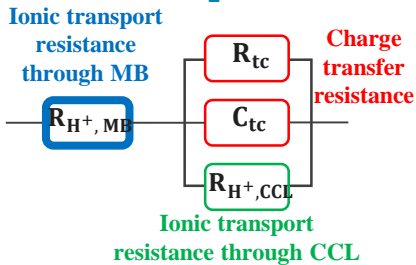
Polarization curve on 1.8 cm<sup>2</sup>

Polarization curve on 1.8 cm<sup>2</sup>



■ @50/50RH  
▨ @100/100RH

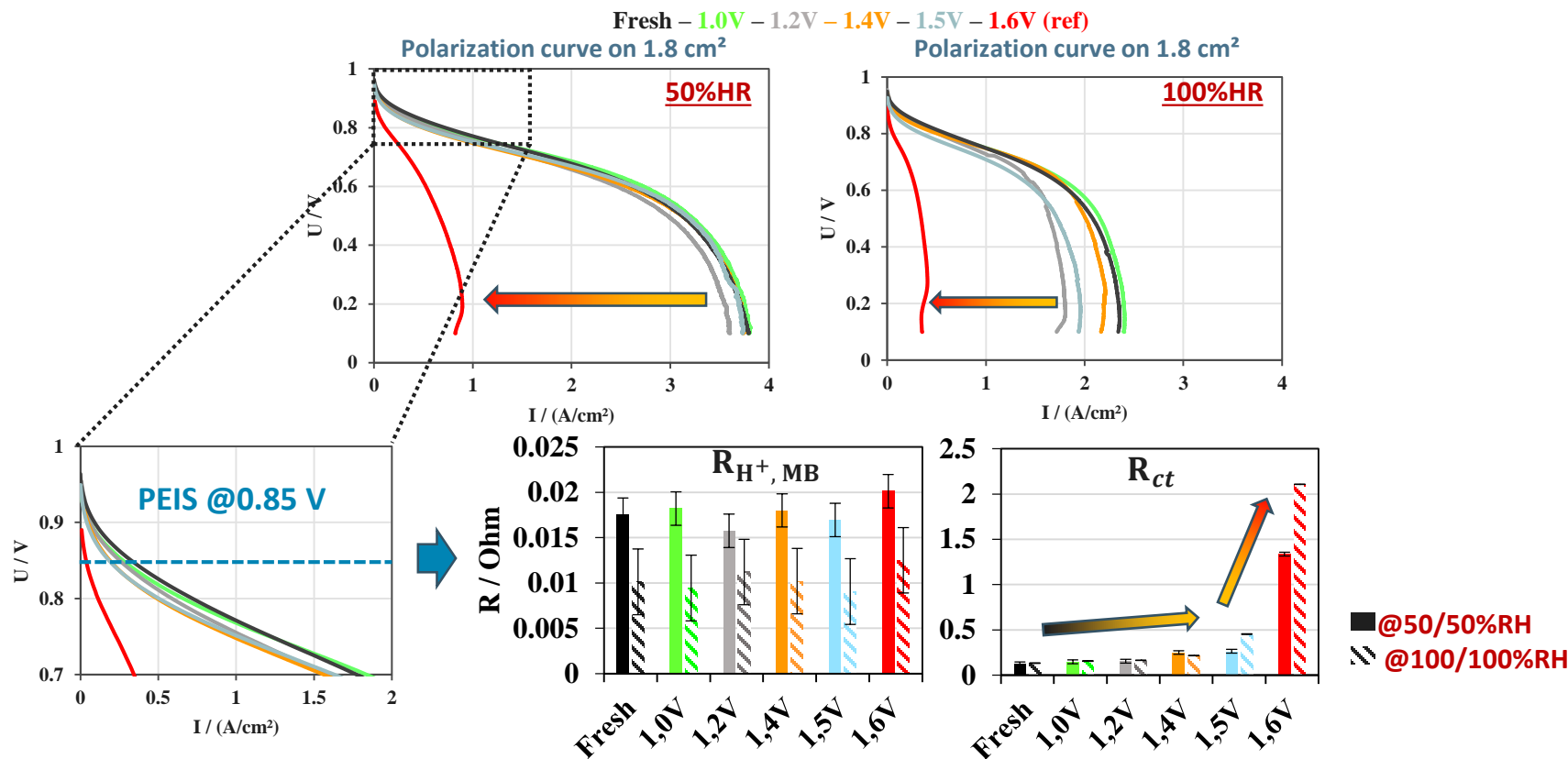
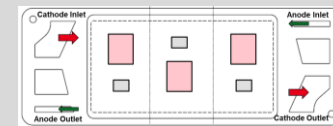
### PEIS model (H<sub>2</sub>/Air)



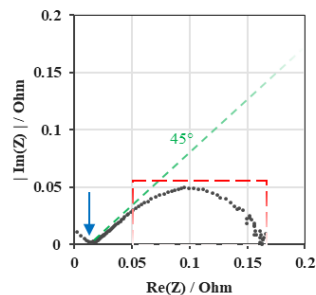
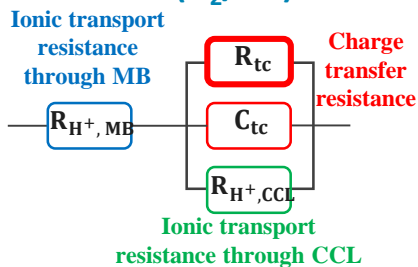
No high frequency resistance variation

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

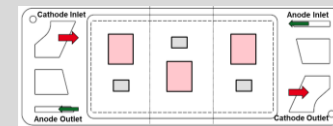




### PEIS model (H<sub>2</sub>/Air)



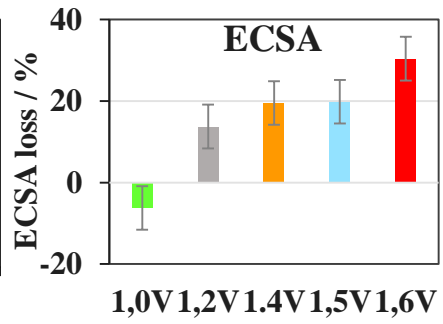
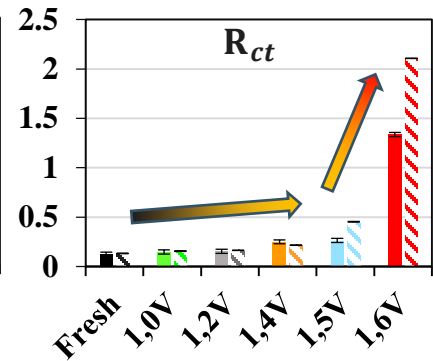
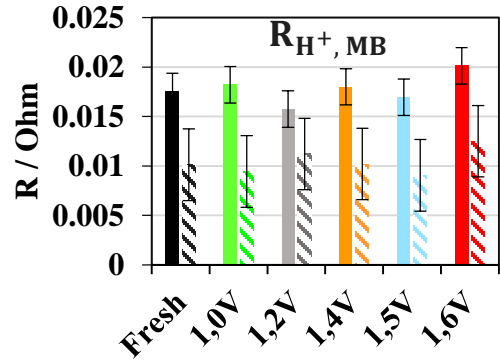
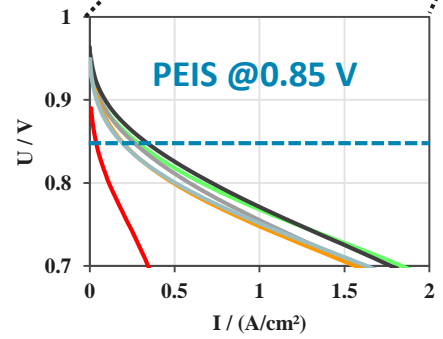
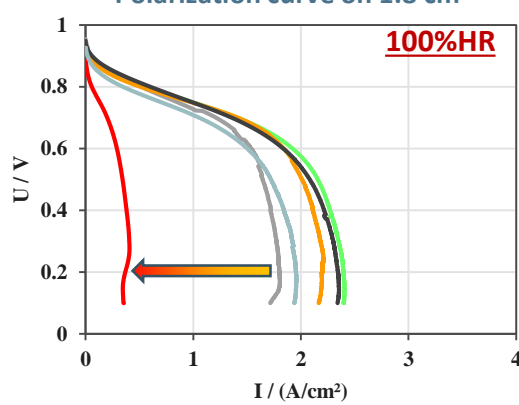
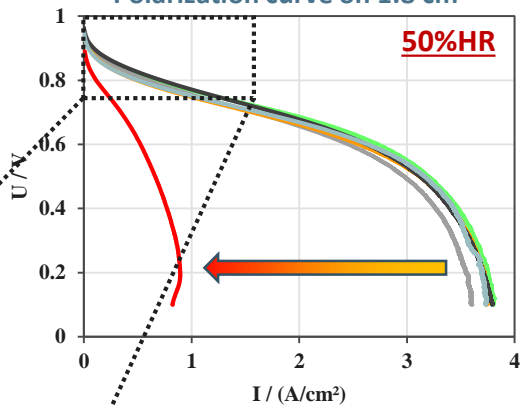
- Slight increase of charge transfer resistance from fresh up to aged MEA at 1.4 V
- High increase of R<sub>ct</sub> value above 1.5 V



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

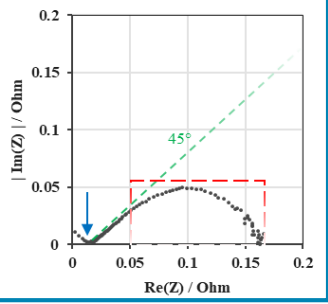
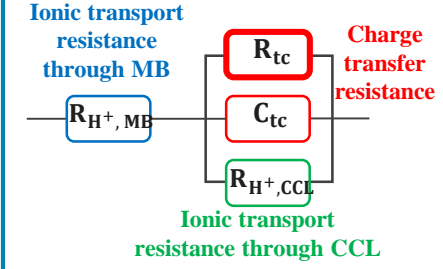
Polarization curve on 1.8 cm<sup>2</sup>

Polarization curve on 1.8 cm<sup>2</sup>



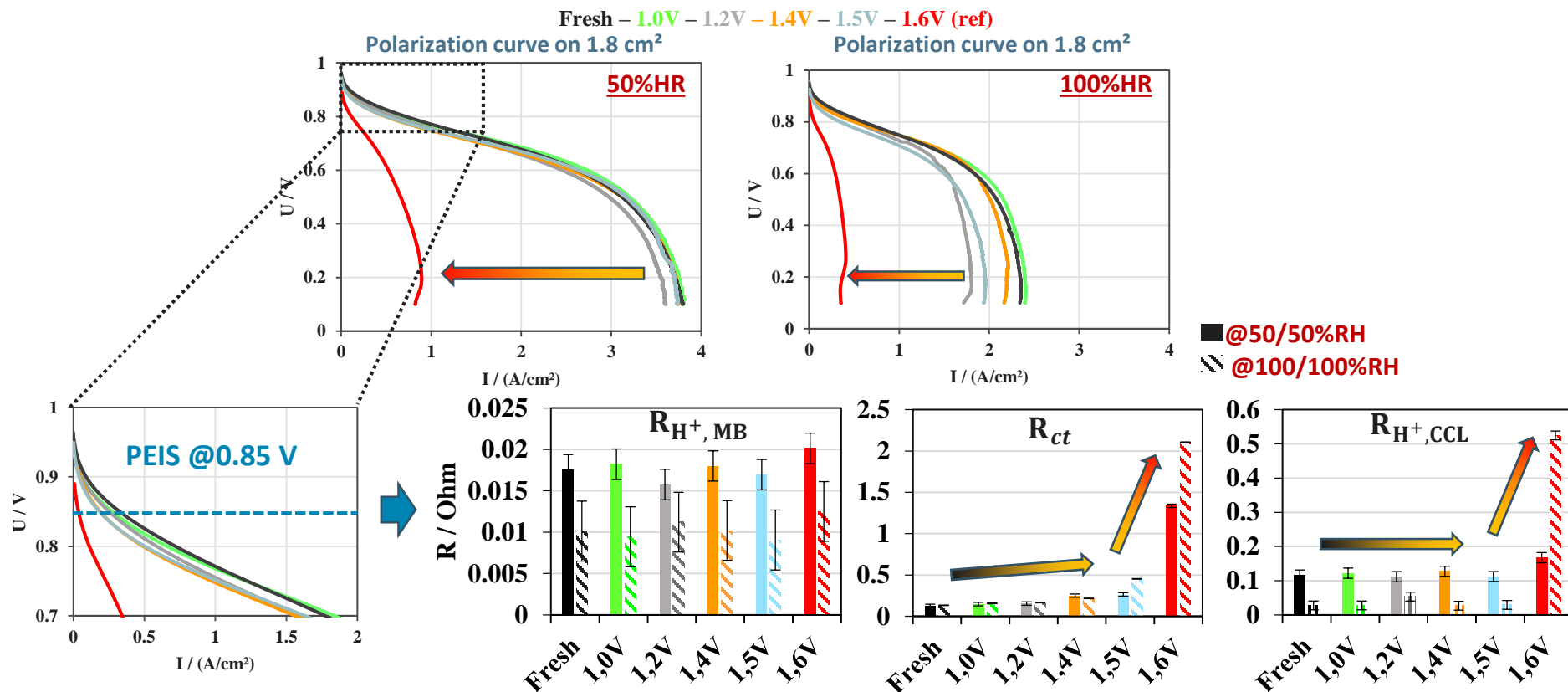
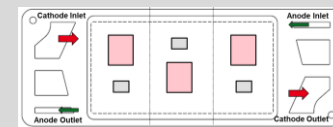
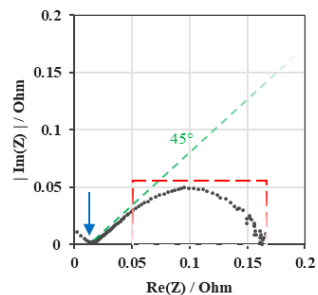
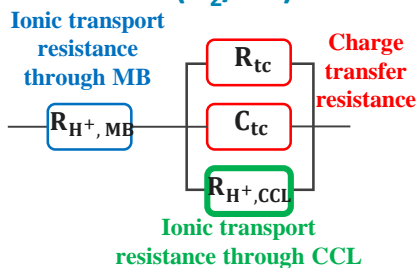
■ @50/50RH  
▨ @100/100RH

### PEIS model (H<sub>2</sub>/Air)

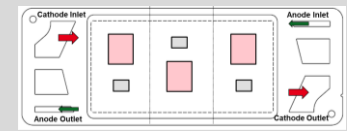


→ R<sub>ct</sub> evolution cannot be fully linked to ECSA loss and thus Pt degradations

→ Other limiting mechanisms above 1.5 V

PEIS model (H<sub>2</sub>/Air)

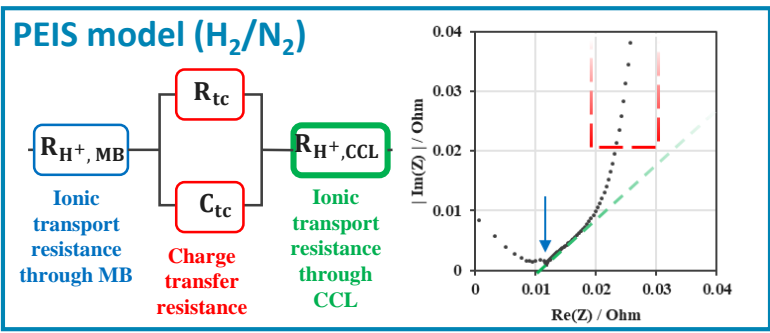
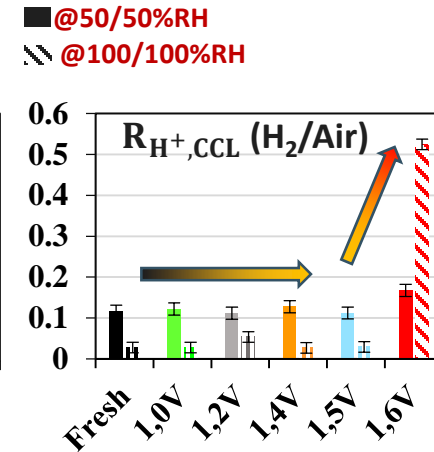
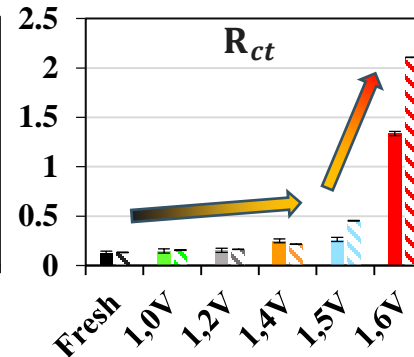
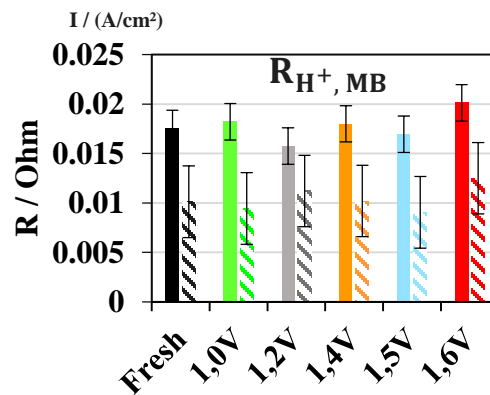
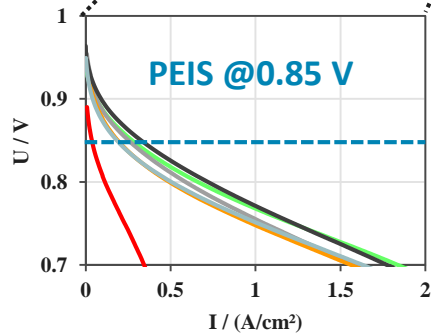
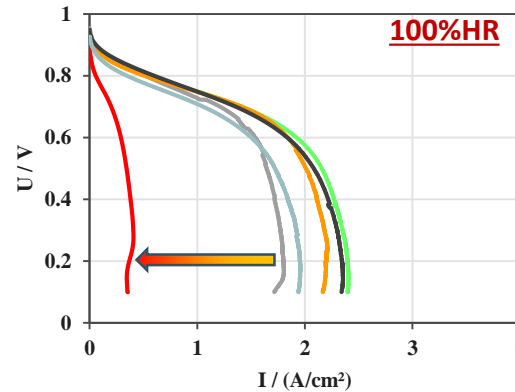
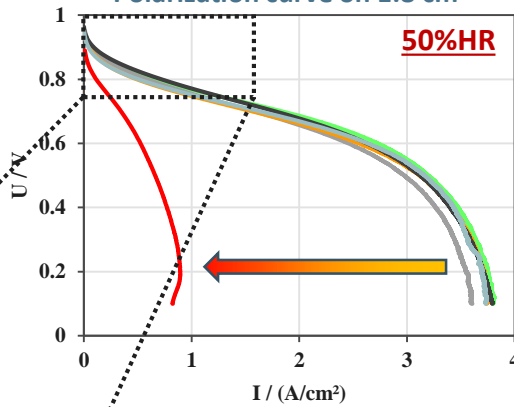
- No significant variation for CCL protonic transport resistance from fresh up to aged MEA at 1.5 V
  - Drastic  $R_{H^+, CCL}$  increase for 1.6 V case in FC operation
- Modification of proton transport properties in CCL due to carbon support collapse ?



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

Polarization curve on 1.8 cm<sup>2</sup>

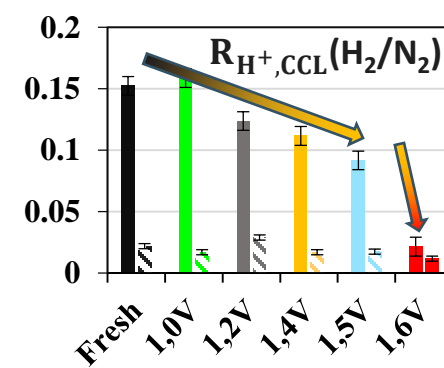
Polarization curve on 1.8 cm<sup>2</sup>



- 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



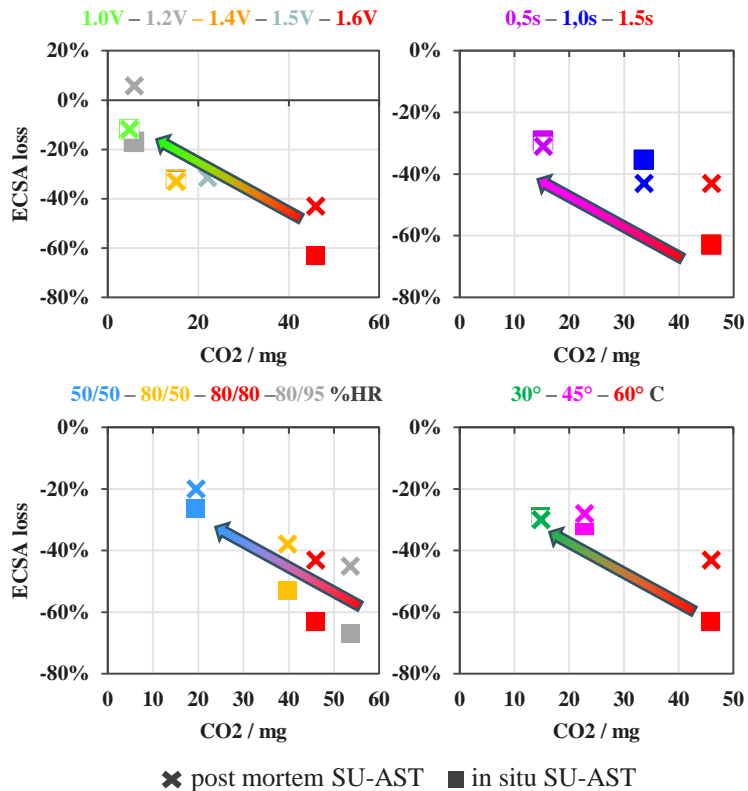
- **Validation of complete *in-situ* & *post-mortem* investigation by:**
  - Electrochemical and physico-chemical analysis on large (98 cm<sup>2</sup>) and localized small (1.8 cm<sup>2</sup>) MEA areas
  
- **Mitigating parameters confirmed and quantified** with represented potential profile in real flow field design:
  - **E<sub>front</sub>**: Lowering cathode potential by by-passing electrical current through dummy load
  - **t<sub>front</sub>**: Lowering exposure time by accelerating H<sub>2</sub> injection in Air-filled anode
  - **RH<sub>a/c</sub>**: Flushing cell with dry gas before H<sub>2</sub> injection
  - **T<sub>cell</sub>**: Lowering stack temperature before H<sub>2</sub> 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



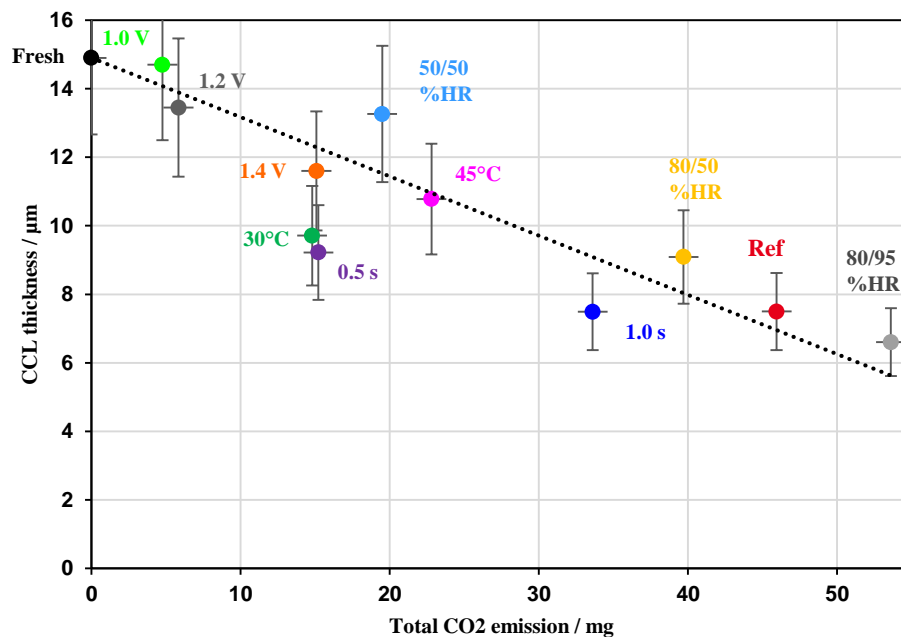
**Thank for your attention**

Timothée DRUGEOT

### ECDSA loss VS CO<sub>2</sub> emission



### CCL thickness VS CO<sub>2</sub> 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**

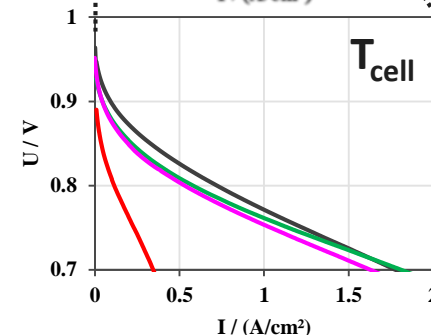
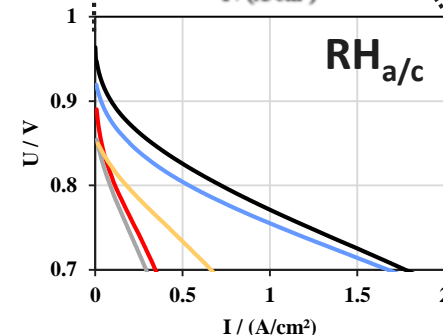
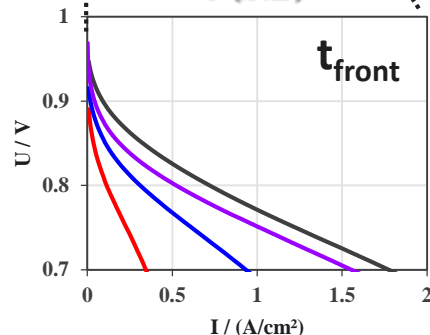
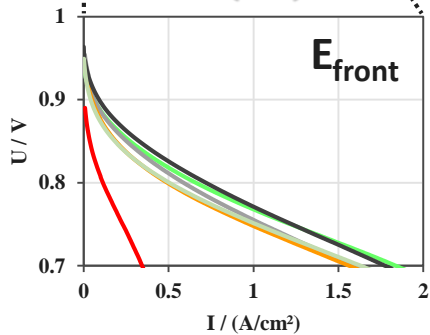
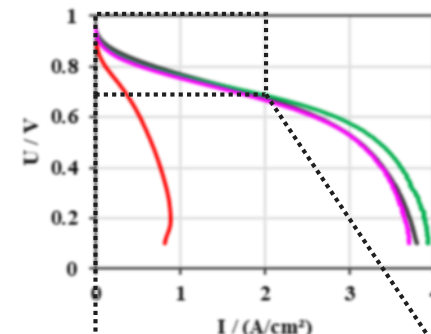
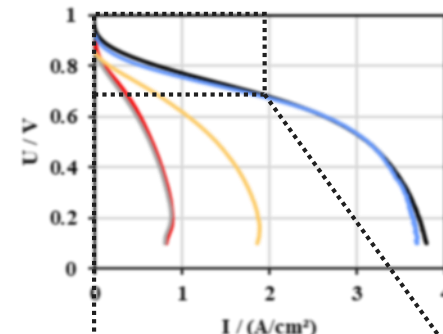
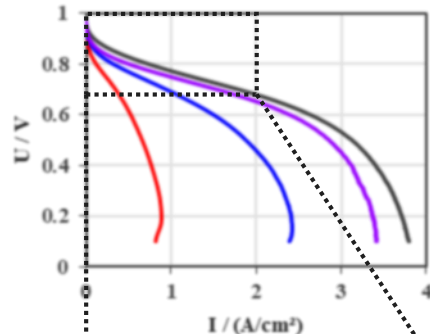
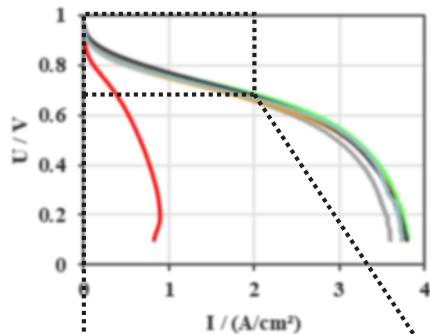
80°C – 50/50HR – 1.5/1.5b<sub>a</sub> – St 50/50

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

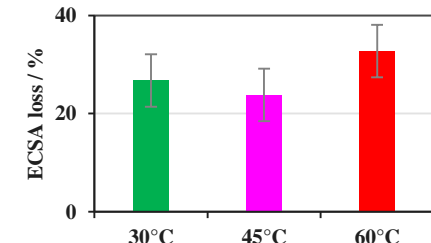
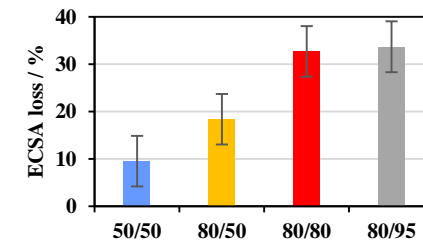
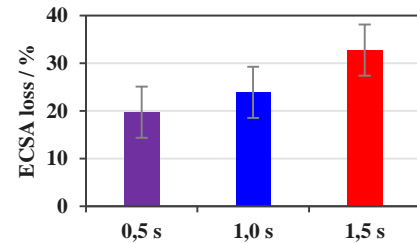
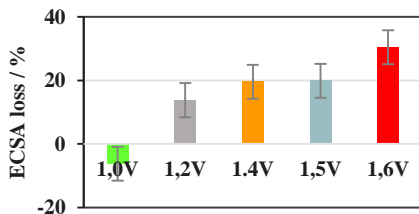
Fresh – 0.5 s – 1.0 s – 1.5 s (ref)

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

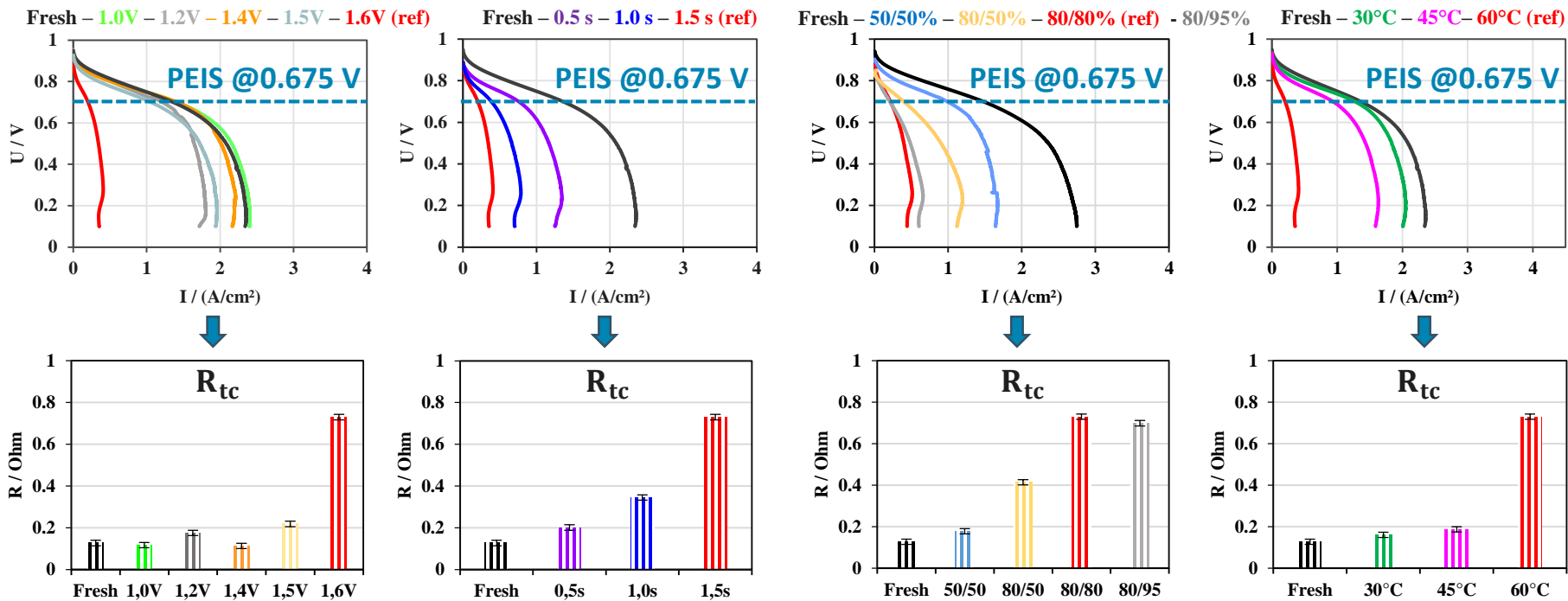
Fresh – 30°C – 45°C – 60°C (ref)



## ECSA loss





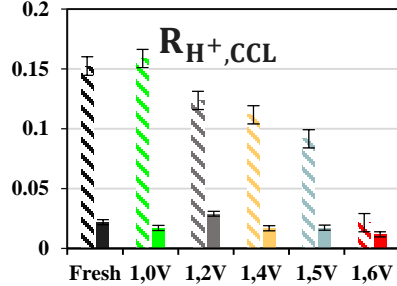
80°C – **95/95%HR** – 1.5/1.5 $b_a$  – St 50/50

80°C – 1.5/1.5b<sub>a</sub> – St 50/50

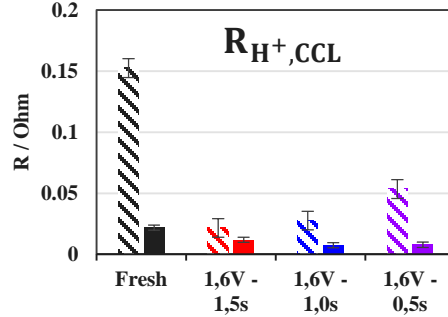
▨ @50/50%RH

■ @100/100%RH

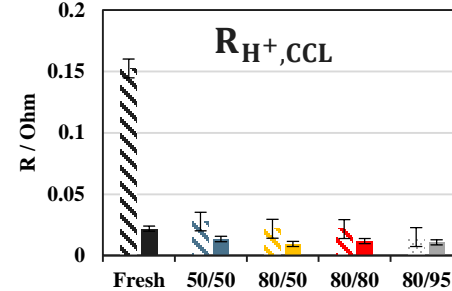
Fresh – 1.0V – 1.2V – 1.4V – 1.5V – 1.6V (ref)



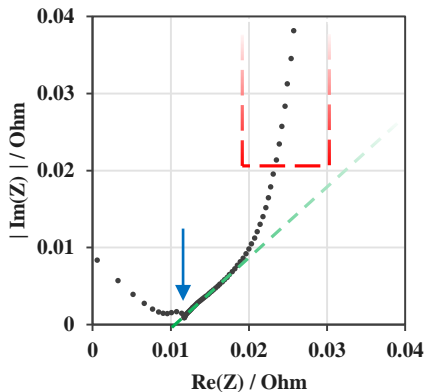
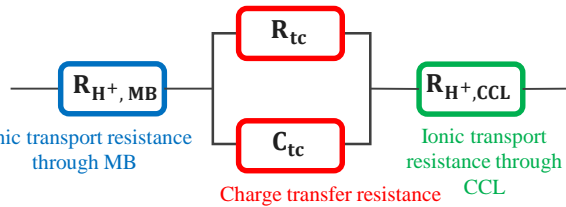
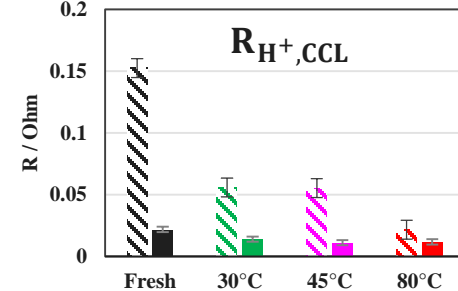
Fresh – 0.5 s – 1.0 s – 1.5 s (ref)



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...)