Development and validation of single-cell AST‘s and correlation to real ageing

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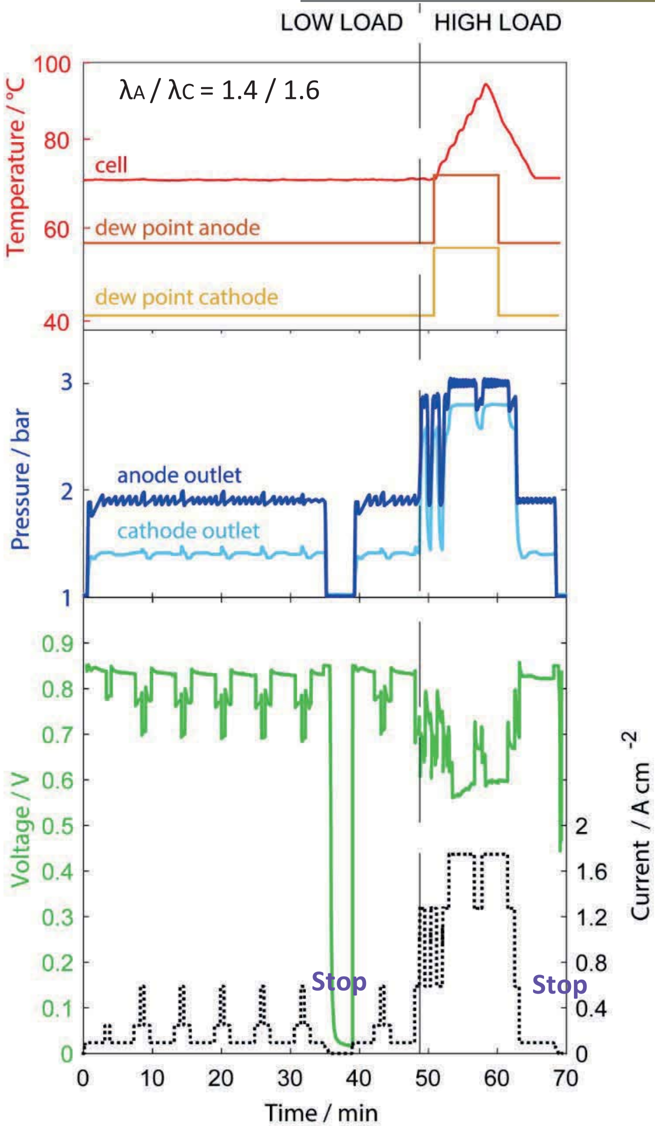
ID-FAST driving cycle adapted for single cell



Cell temperature:

- Assumed as uniform over the cell (no difference between inlet and outlet)
- It ranges between 71 °C and 90 °C

Dew points:

- Dew point changes are obtained through a gas switch (for both A/C)

Pressure:

- Pressure transitions are respected

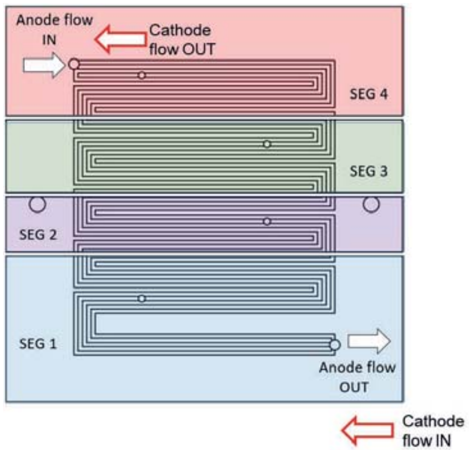
Stops specifications:

- **2 short stops** (5 minutes each)
- Cold soak: every 5 cycles
- Long stop: every 200 cycles

At BoT **voltage** ranges between

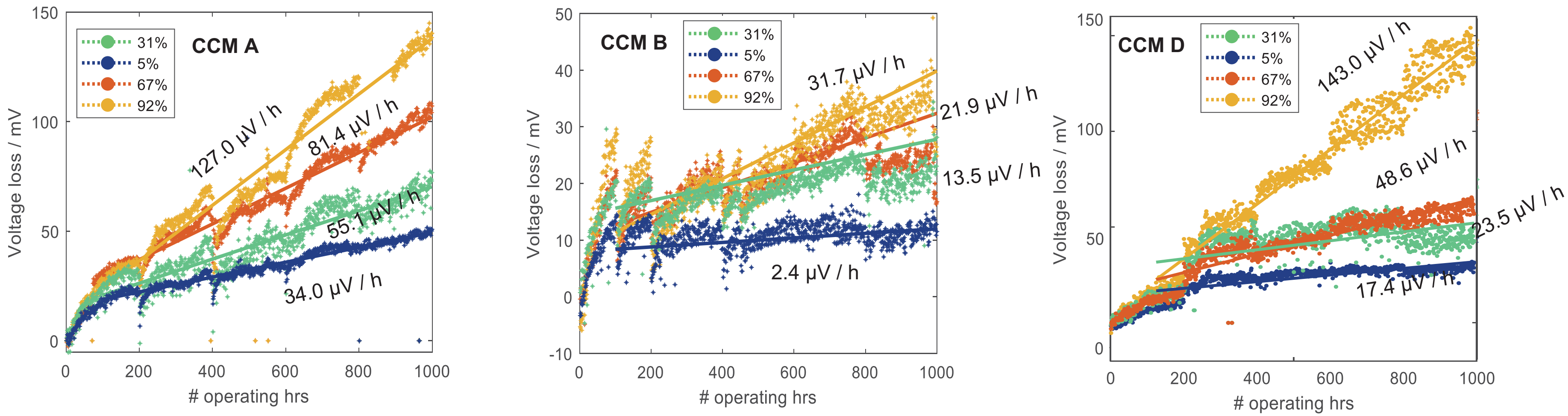
- 0.6 V, at maximum current
- 0.85 V, at minimum current

Performed on a 25 cm^2 segmented cell



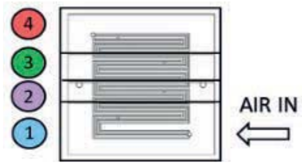
Degradation under driving cycle protocol

Operando voltage losses for the different current setpoints of the driving cycle, expressed as a percentage of the maximum current (1.9 A cm⁻²)

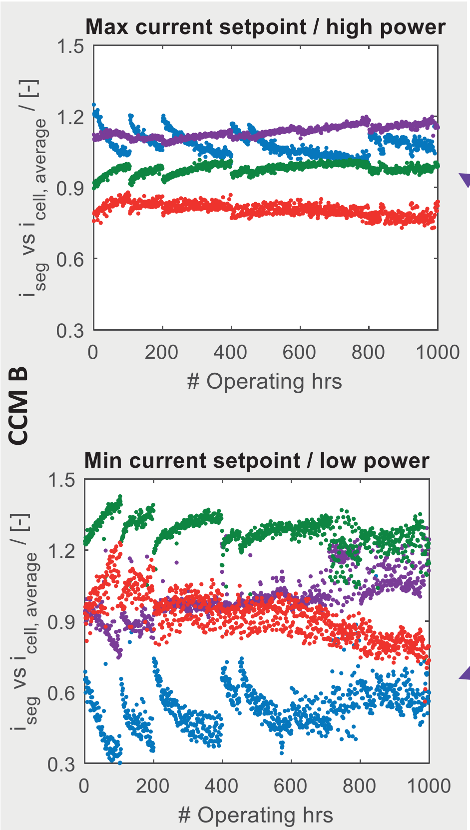


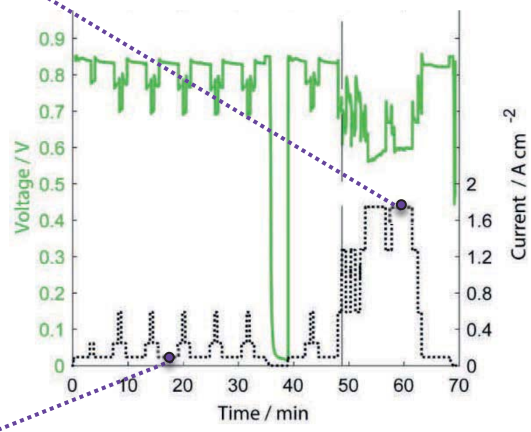
Both reversible and permanent degradation phenomena are present

Reversible degradation

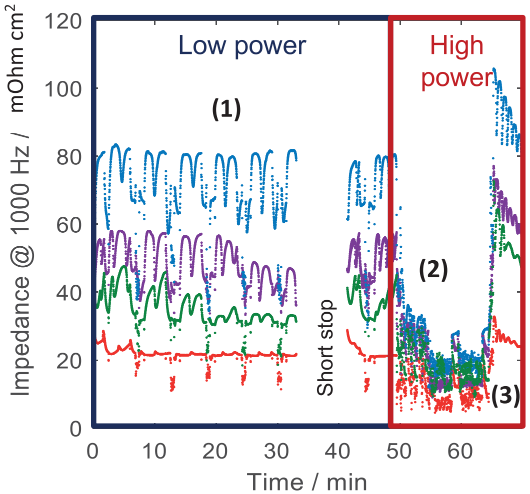


Current distribution among segments



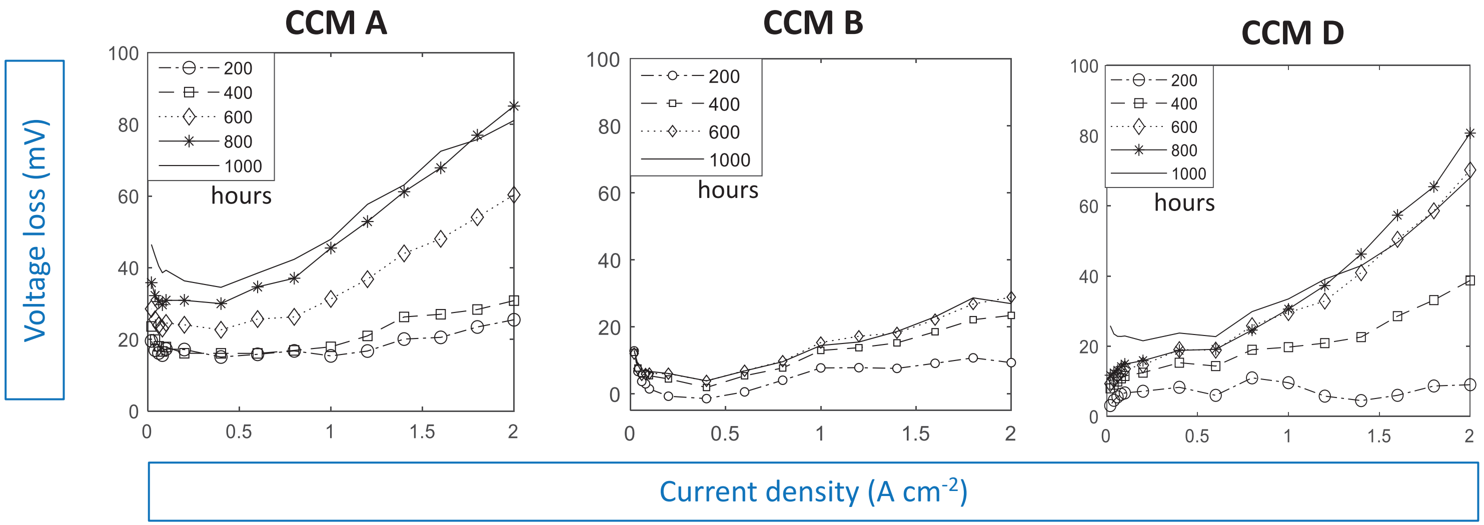


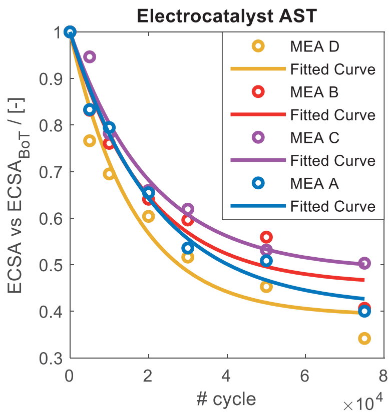
CCM hydration state

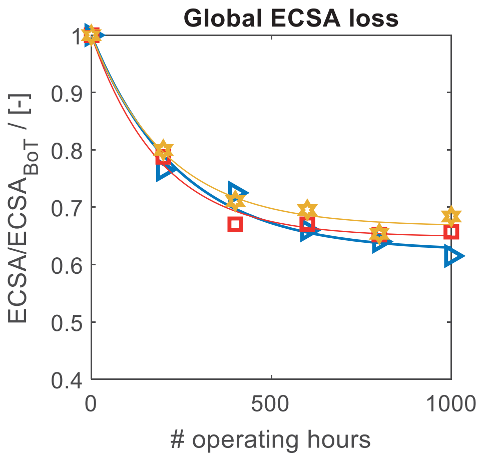


- **Air inlet** suffers of high **reversible losses,** recoverable through **suitable procedures, but further investigation is suggested**
- **Air inlet presents severe dehydration**, that probably contributes to reversible losses, as well as PtOx formation in CCL

Permanent degradation from IV curves







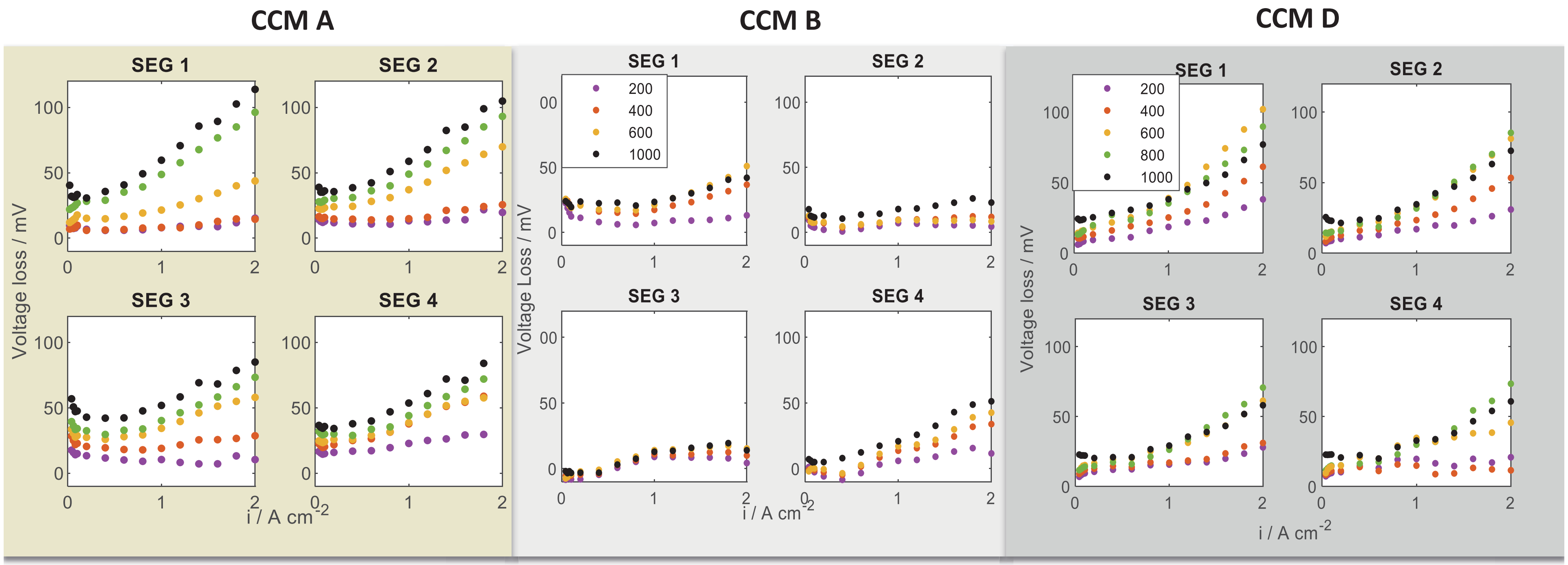
Permanent voltage losses are different in spite of similar ECSA loss

ECSA decrease tends to stabilise around 600-800 h, as well as performance one

Global polarization curve under ageing

POLA P: T = 80 °C, RH $_{A/C}$ = 100%, P_A/P_C = 250/230 kPa

Permanent degradation from IV curves

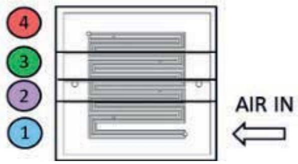


Higher degradation at inlet and outlet regions

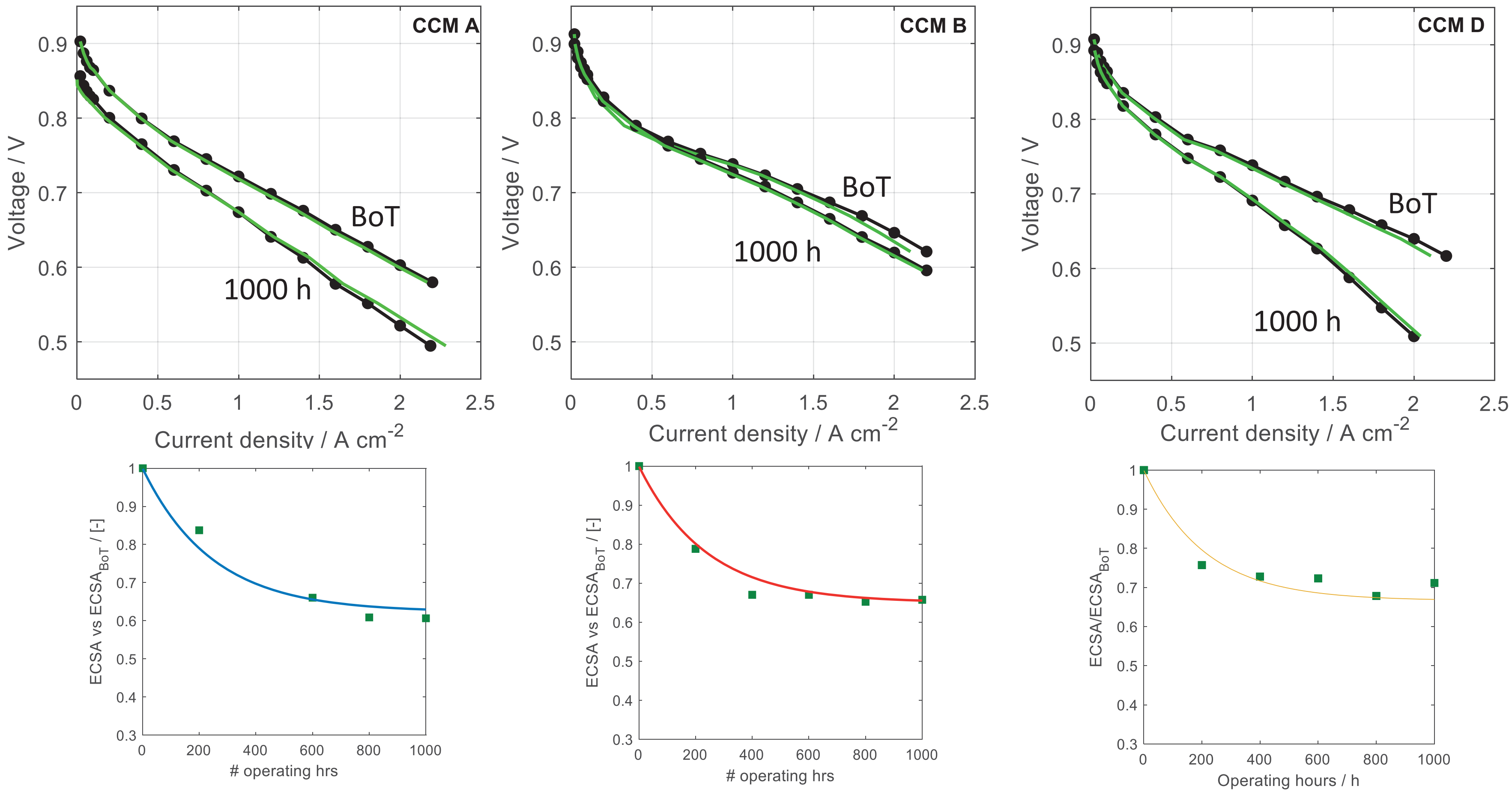
Global polarization curve under ageing

POLA P: T = 80 °C, RH $_{A/C}$ = 100%, P_A/P_C = 250/230 kPa

Middle region representativeness



The middle region is representative of the whole cell



Degradation origins

In-situ characterizations reveal

Major Catalyst layer ageing

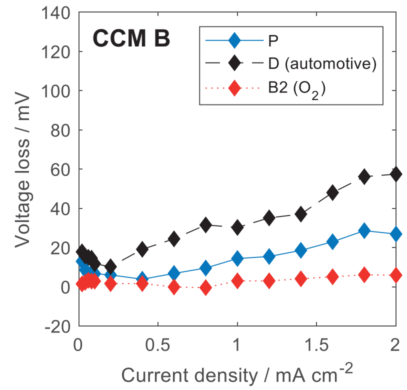
- ECSA loss
- mass transport resistance: *pressure independent component increases*
- probable ionomer alteration

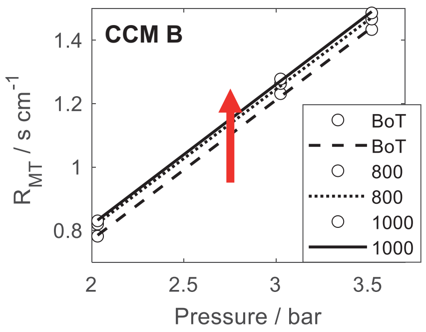
Minor Membrane ageing:

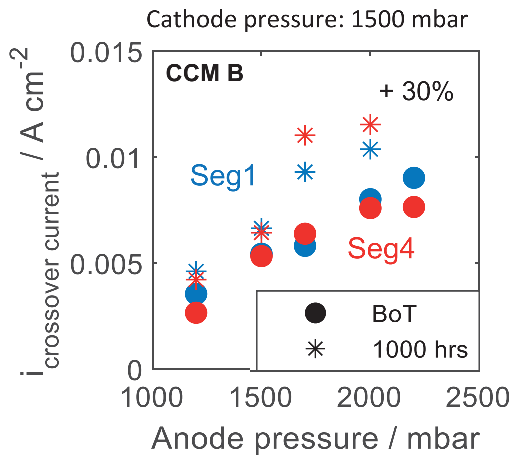
- HFR keeps constant
- minor increase of crossover current for CCM B and C
- membrane failure for CCM A.

No GDL ageing

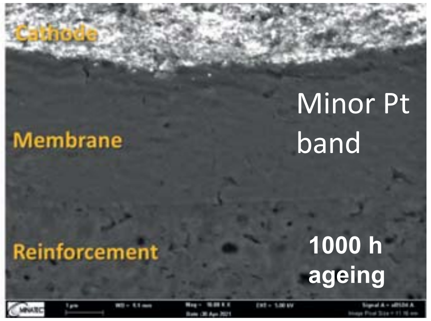
- consistently with a wide investigation on GDL

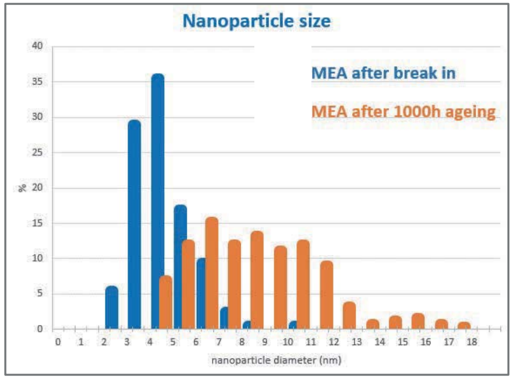




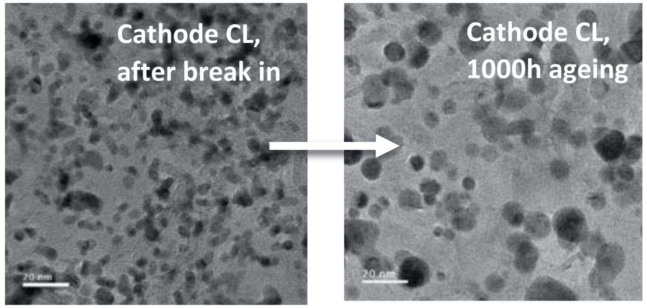


Degradation origins



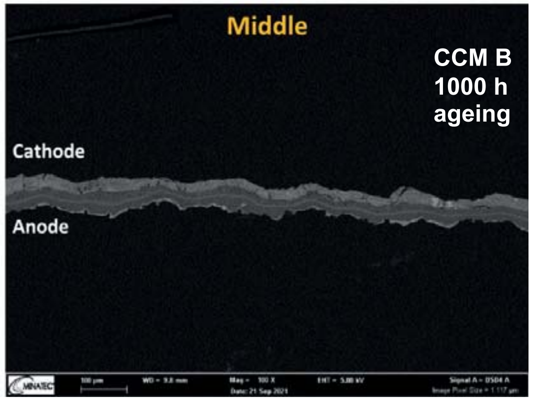


Ex-situ characterizations reveal



Major Catalyst layer ageing

- Particle growth -> ECSA loss
- Minor Pt band formation



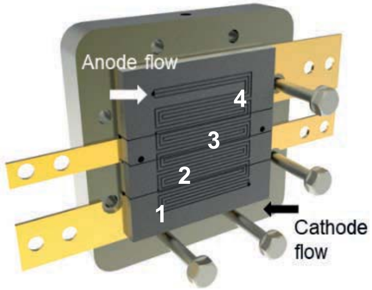
Minor Membrane ageing:

- CCM deformation -> increase of crossover

AST development

Driving cycle

Segmented hardware

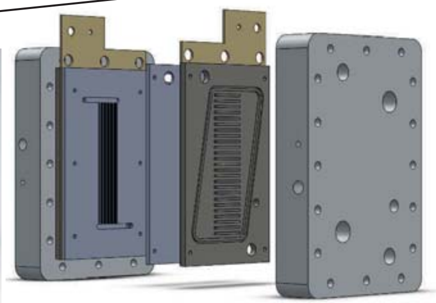


25 cm² CCM

Rabissi C. et al 2018.
Journal of Power Sources, 397, 361–373

Accelerated Stress Tests

Zero-Gradient hardware (Baltic, JRC, Polimi, …)



Andrea Bisello et al 2021
J. Electrochem. Soc. 168 054501

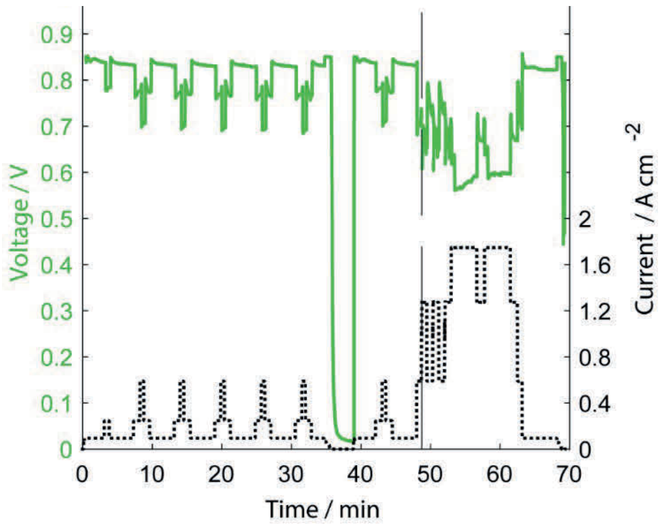
Drivers

Representativeness

ΔV profile similar to real cycle
Conditions of middle region

Acceleration

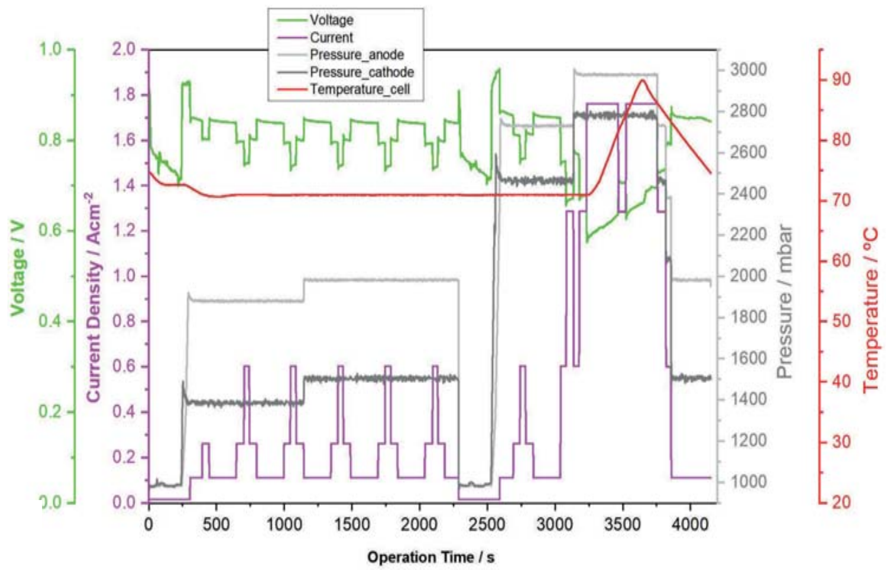
Simplicity

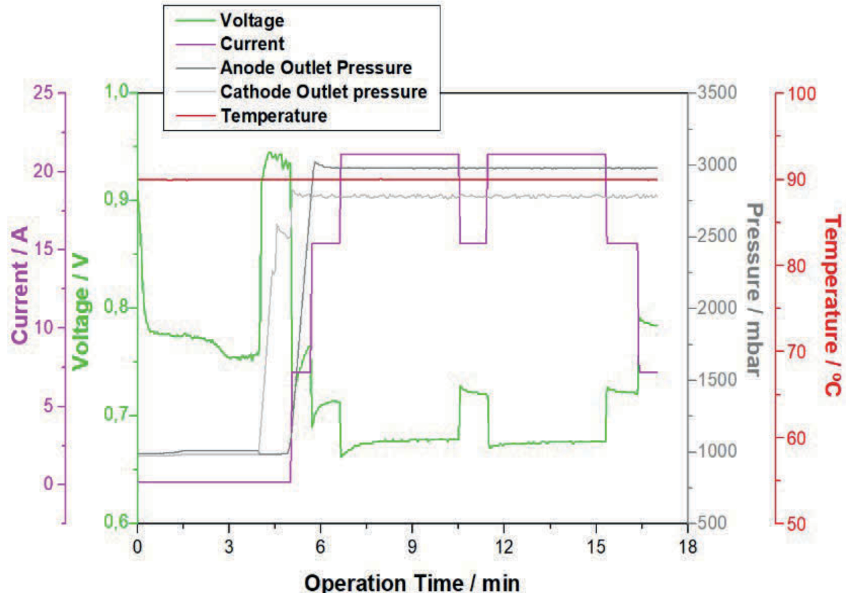


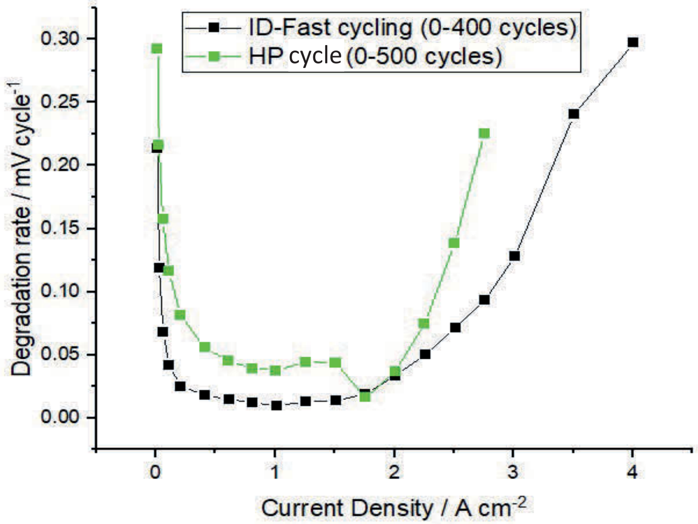
ID-Fast cycling at High Power

- Analysis of only HP period
- Baltic Differential Cell
- Middle conditions (15%O_2)
- Fixed Temperature at 90°C
- Including stops

Comparable degradation rate,
HP period major cause of degradation



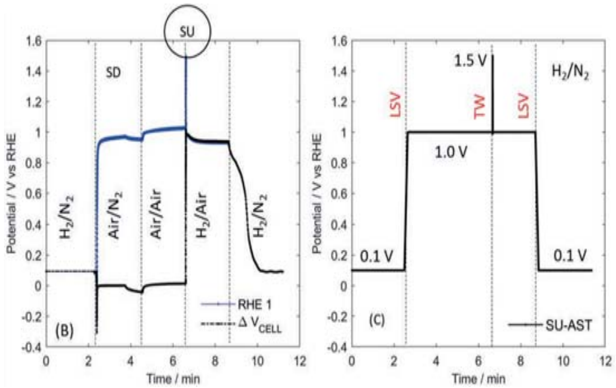




Define ASTs that mimic the driving cycle

1

Mitigated air start-up AST



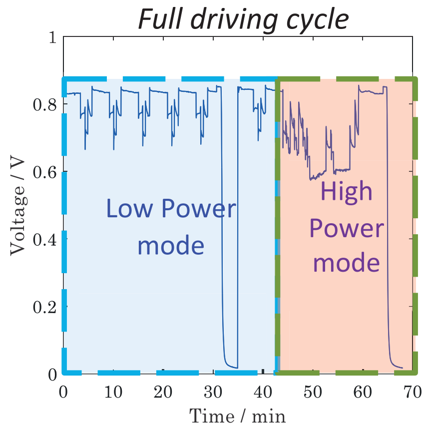
Mitigated air start-up in segmented cell with RHE

AST in Zero-Gradient

- simulate degradation after long stops, when air start-up occurs under mitigated conditions
  (low temperature, fast residence time, mitigated shut-down)

2

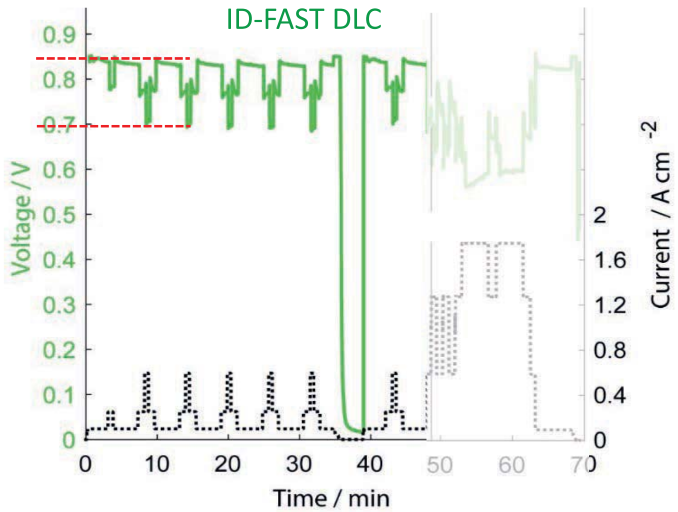
Combined AST

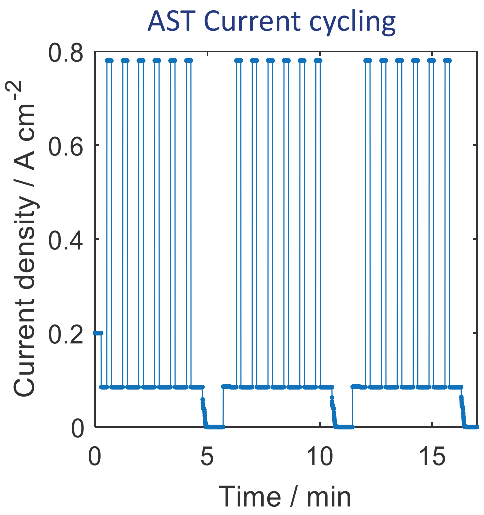


- reproducing voltage and HFR cycling
- short and long stops present
- middle region conditions
- high stoichiometry (8/20)

Andrea Bisello et al 2021 J. Electrochem. Soc. 168 054501, doi:10.1149/1945-7111/abf77b
Elena Colombo et al 2021 J. Electrochem. Soc. 168 054508, doi: 10.1149/1945-7111/abf4eb

Low Power AST

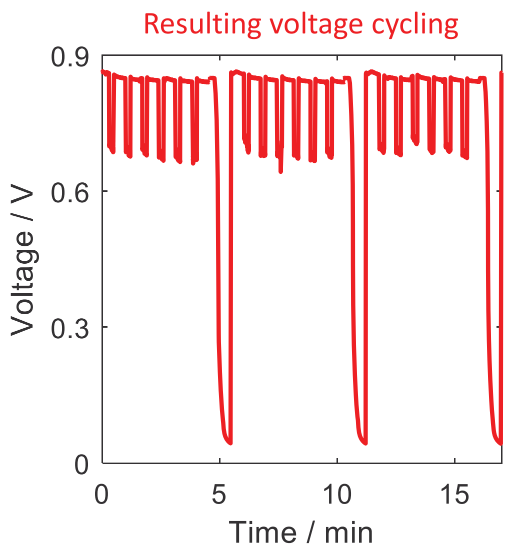


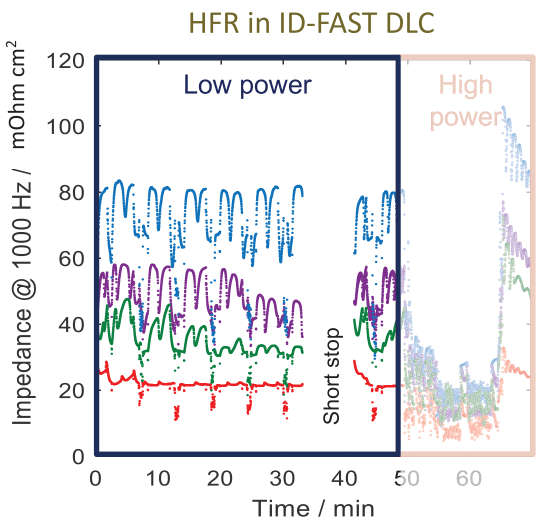


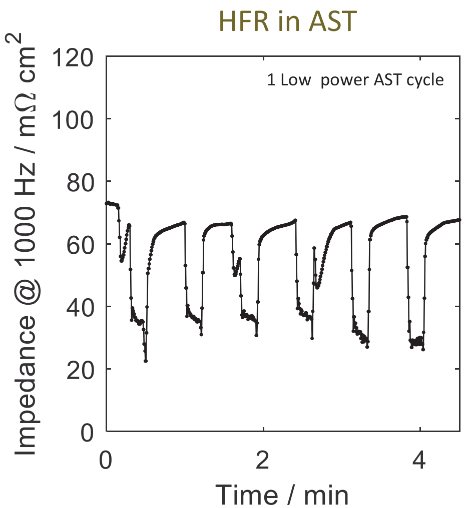
galvanostatic cycles:
2 current setpoints
at 0.7 V – 0.85 V at BoT

H_2/air feeding + stops

x7 acceleration in operating time

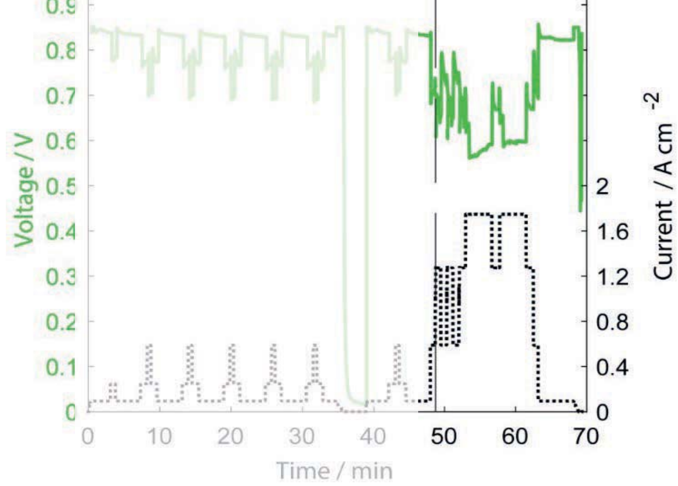




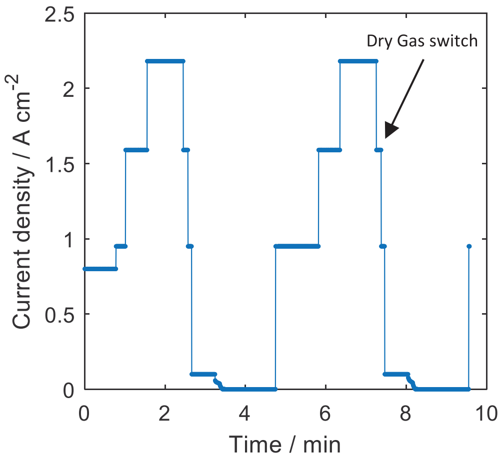


High Power AST

ID-FAST DLC



AST Current cycling

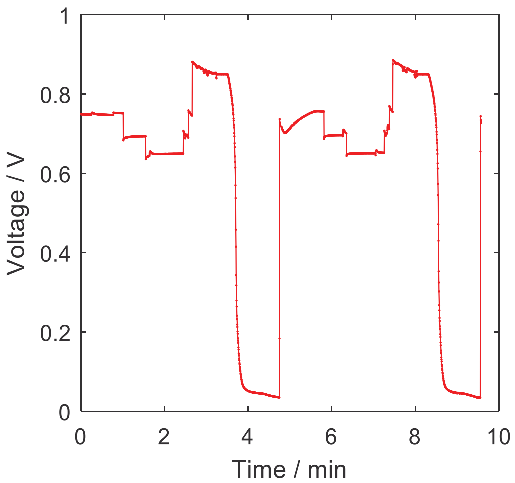


galvanostatic cycles:
4 current setpoints
at 0.85 V - 0.75 V – 0.7 V – 0.65 V at BoT.

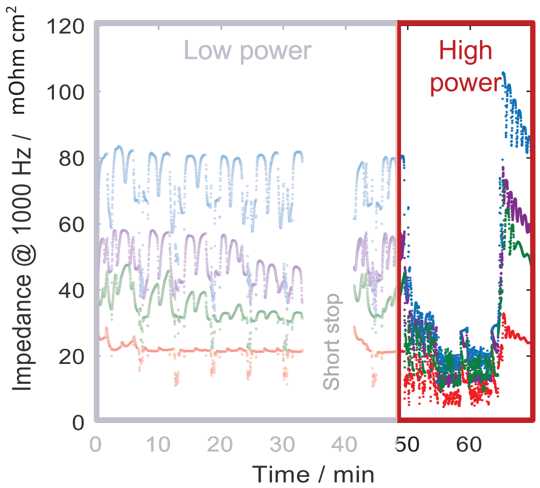
Dry gas switch + stops

x7 acceleration in operating time

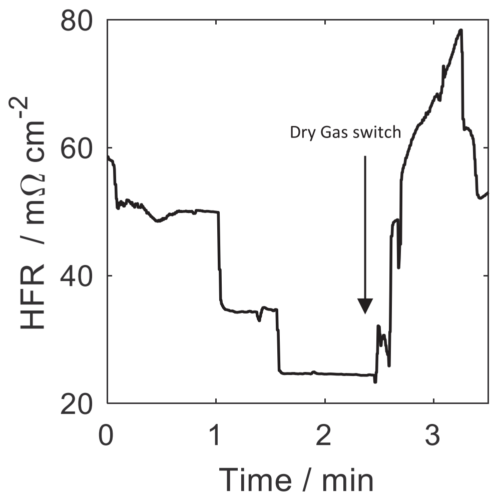
Resulting voltage cycling



HFR in ID-FAST DLC



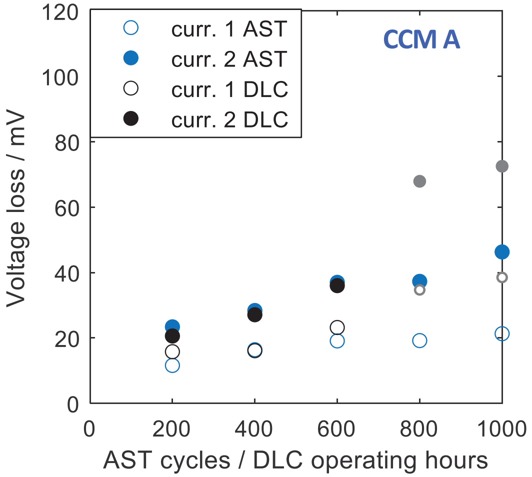
HFR in AST

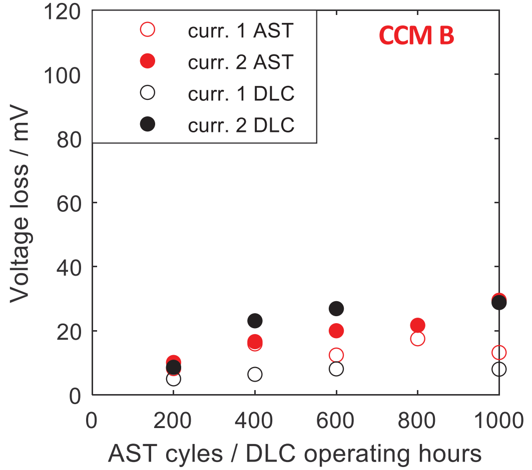


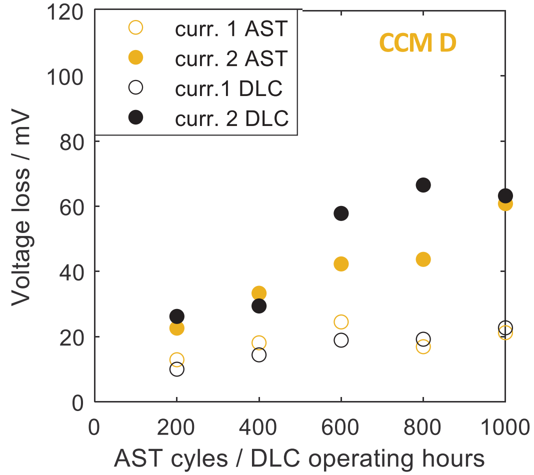
Validation of Combined AST

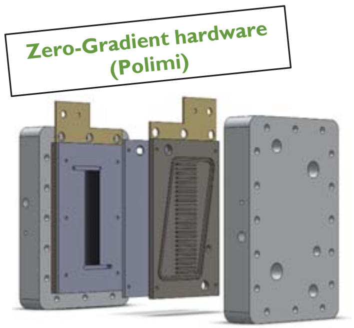
1’000 Combined AST cycles *(alternating 200/200 Low/High)* **=** **1’000 ID-FAST Driving cycles** *(1 hour each)*

x 7 acceleration in operating time
x 10 acceleration in total testing time *(stops included)*









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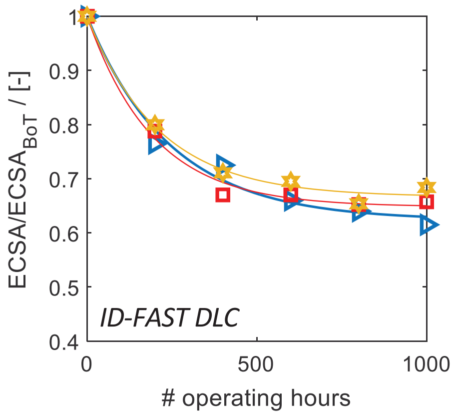
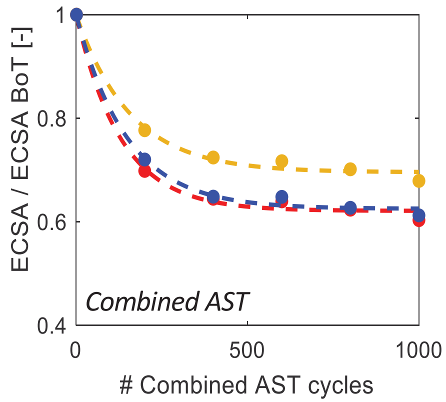
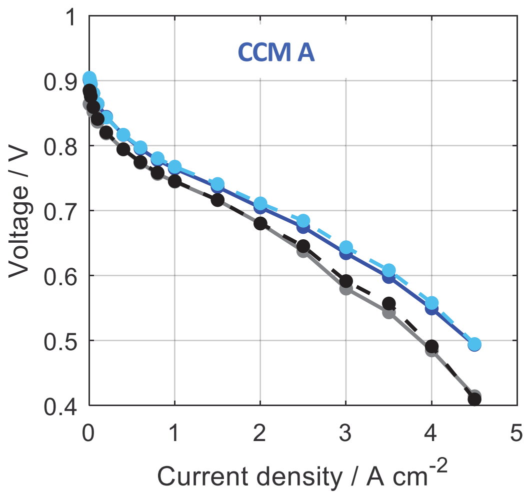


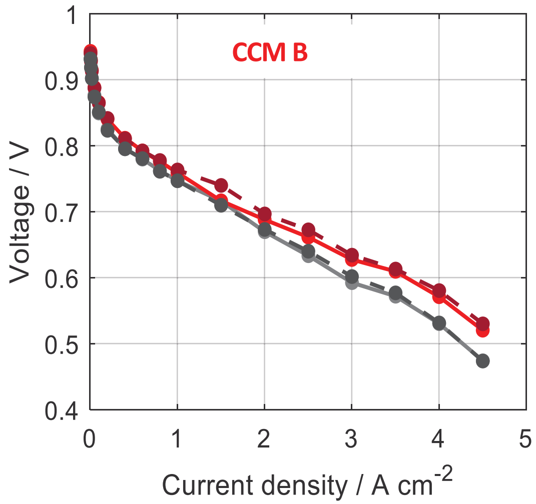


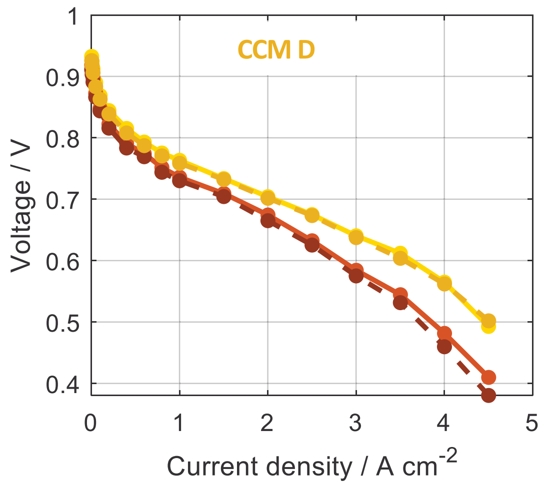
Lower Current at 0.78 V, BoT	curr. 1
Higher Current at 0.65 V, BoT	curr. 2

AST results repeatability

1'000 Combined AST cycles vs BoT







Dotted curves: **Combined AST, test 1**
Solid curves: **Combined AST, test 2**

Repeatability is verified

Conclusions

ID-FAST DRIVING CYCLE: TEST IN SEGMENTED SINGLE CELL

- **Considerable reversible degradation is observed**
- **Permanent degradation**
  - *higher at inlet and outlet regions*
  - *middle region is representative of the whole cell*
  - *degradation is mainly caused by CCL ageing*
  - *ECSA and performance decrease tends to stabilize around 600 h*

COMBINED AST: TEST IN ZERO GRADIENT CELL

- **Representativeness**
  - *mimics ΔV profile and stops of driving cycle*
  - *keeps the representative conditions of middle region*
  - *reproduces HFR cycling*
- **Acceleration: testing time reduced by a x 10 factor**
- **Validation**
  - *obtained for 1'000 h on 3 CCMs*
  - *ECSA and performance loss are reproduced*

Acknowledgements

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THANK YOU FOR YOUR ATTENTION