Determination of Degradation Rates

Pawel Gazdzicki, DLR

Contents

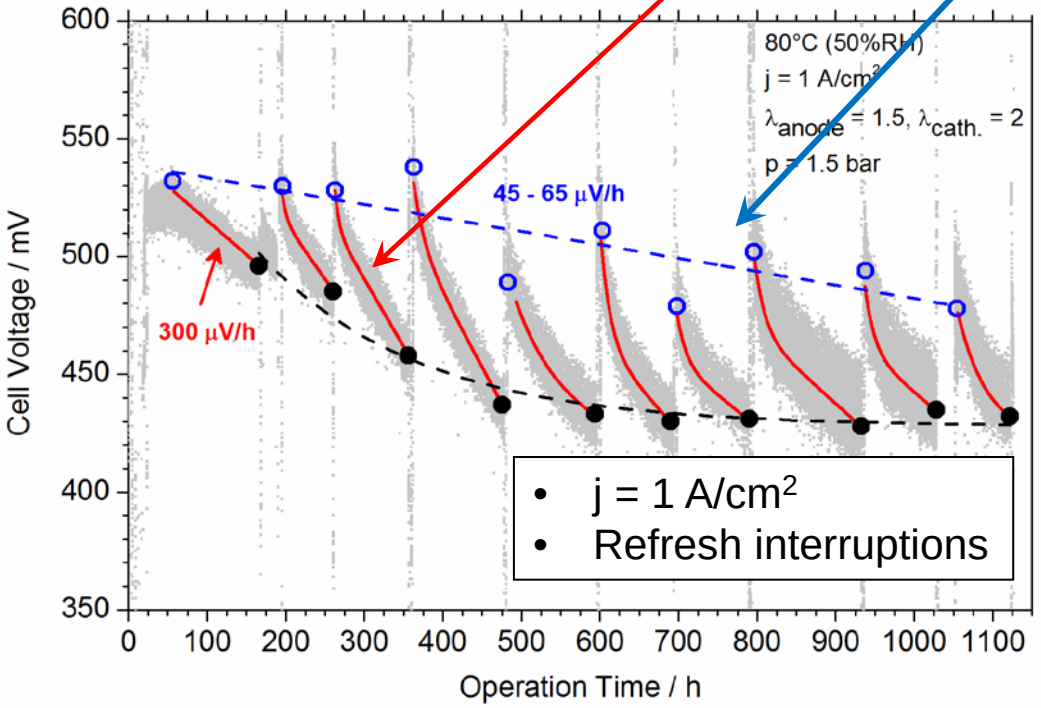
- Motivation
- Evaluation of irreversible degradation
- Evaluation of reversible degradation
- Recovery of reversible degradation
- Degradation vs Pt-loading
- Summary

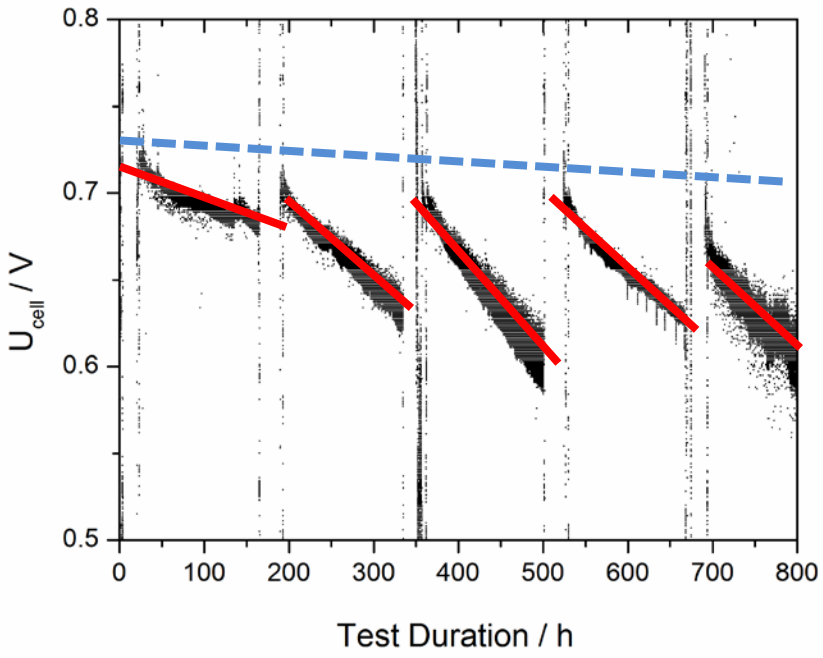
Motivation

Performance targets clearly defined and well verifiable, BUT

determination of **degradation rates** is not well defined.
➔How to determine if **durability goals** are achieved?

Discrimination between **reversible** and **irreversible** degradation needed



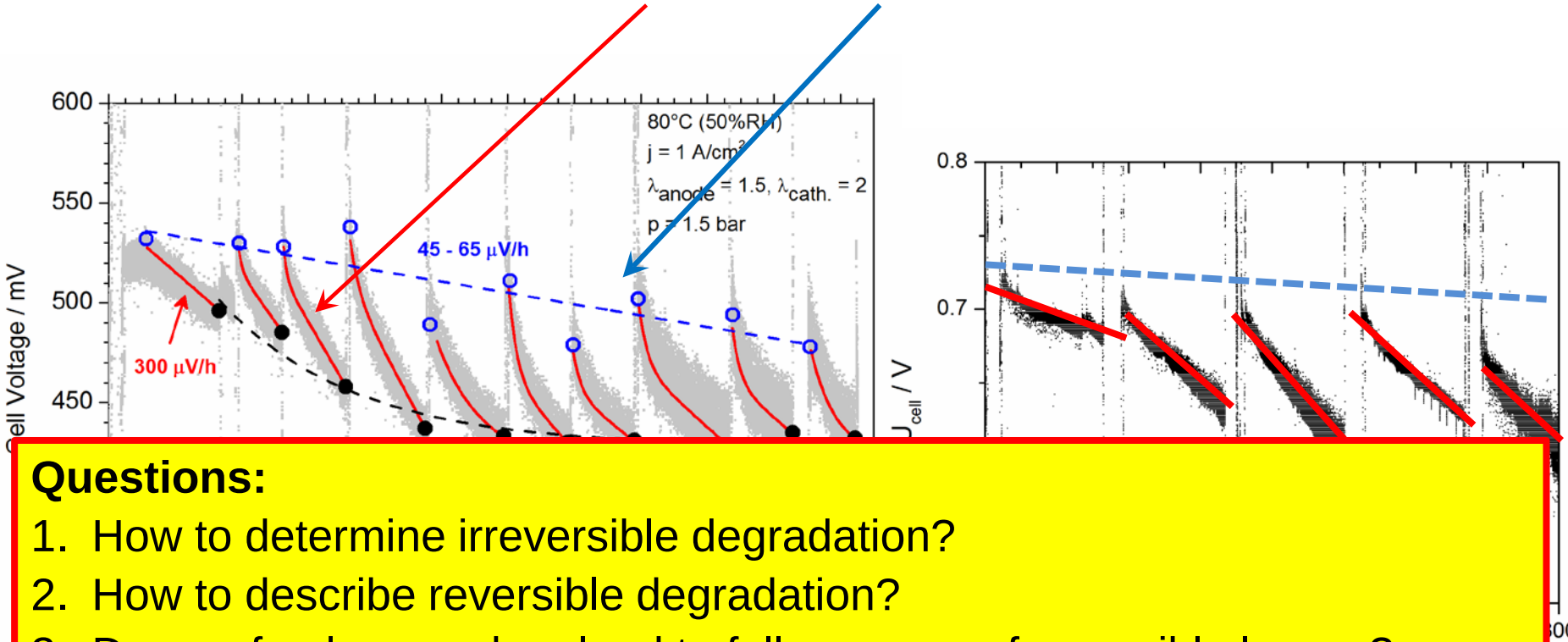


Motivation

Performance targets clearly defined and well verifiable, BUT

determination of **degradation rates** is not well defined.
➔How to determine if **durability goals** are achieved?

Discrimination between **reversible** and **irreversible** degradation needed



Questions:

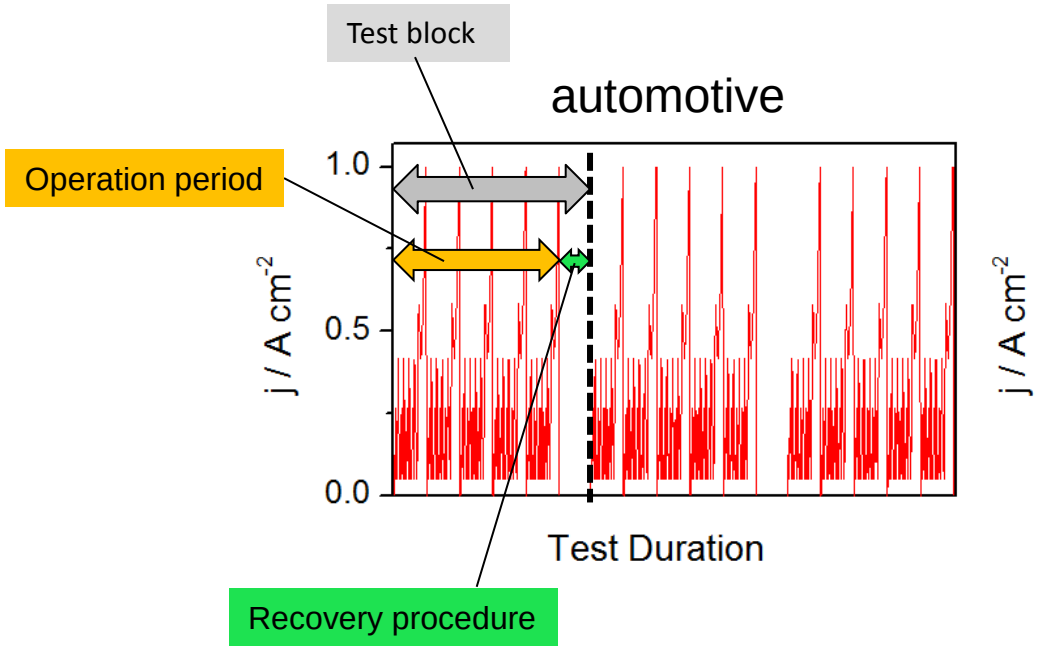
1. How to determine irreversible degradation?
2. How to describe reversible degradation?
3. Does refresh procedure lead to full recovery of reversible losses?

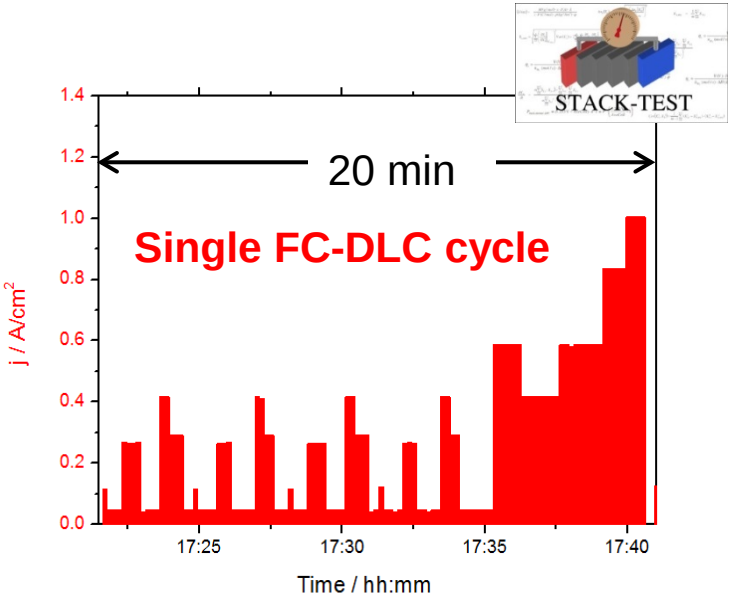
Evaluation of irreversible degradation

Evaluation of irreversible degradation

- **Durability tests: several test blocks of operation period followed by a recovery procedure**
- **FC dynamic load cycle (FC-DLC) according to FCH-JU StackTest project**

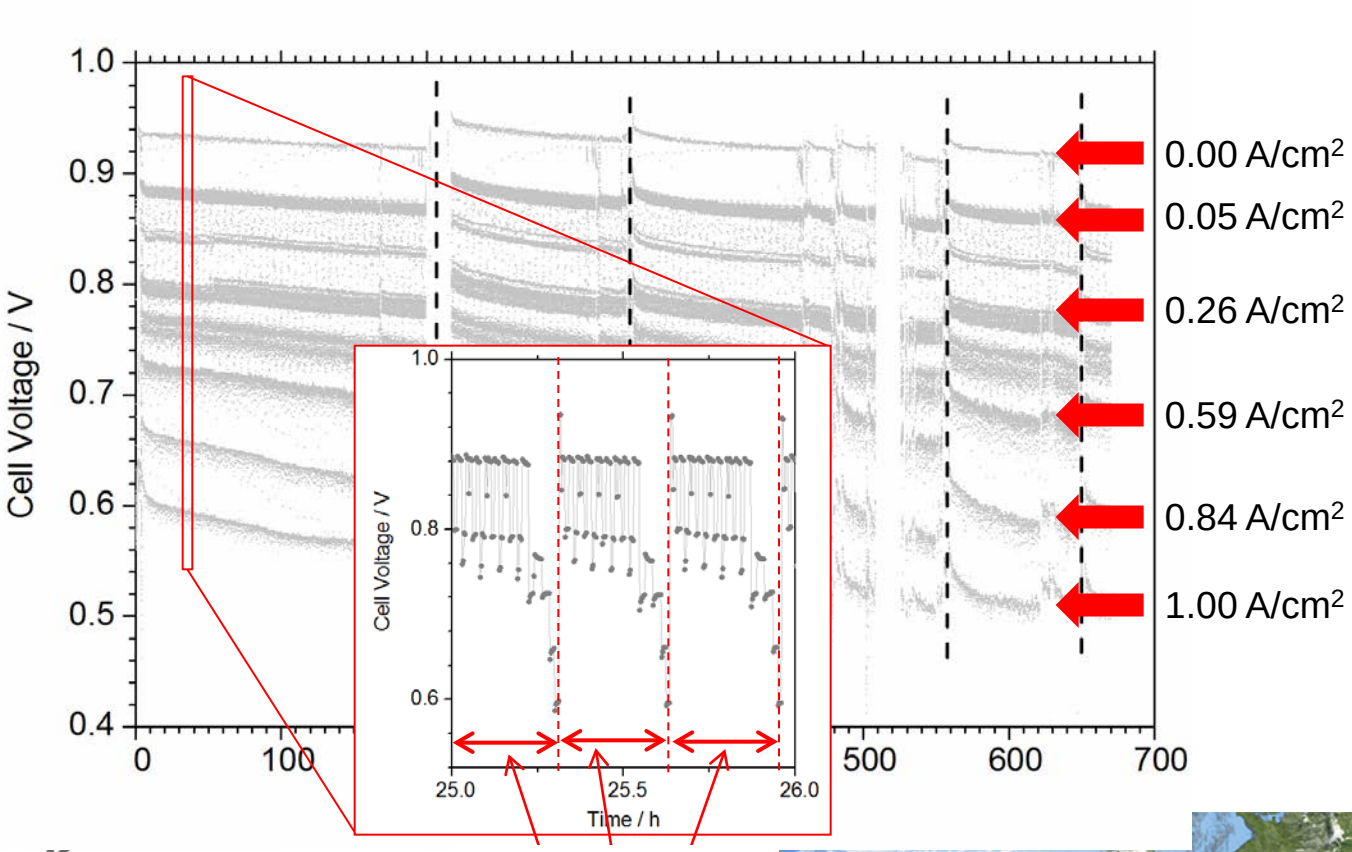
➔ **Automotive conditions**





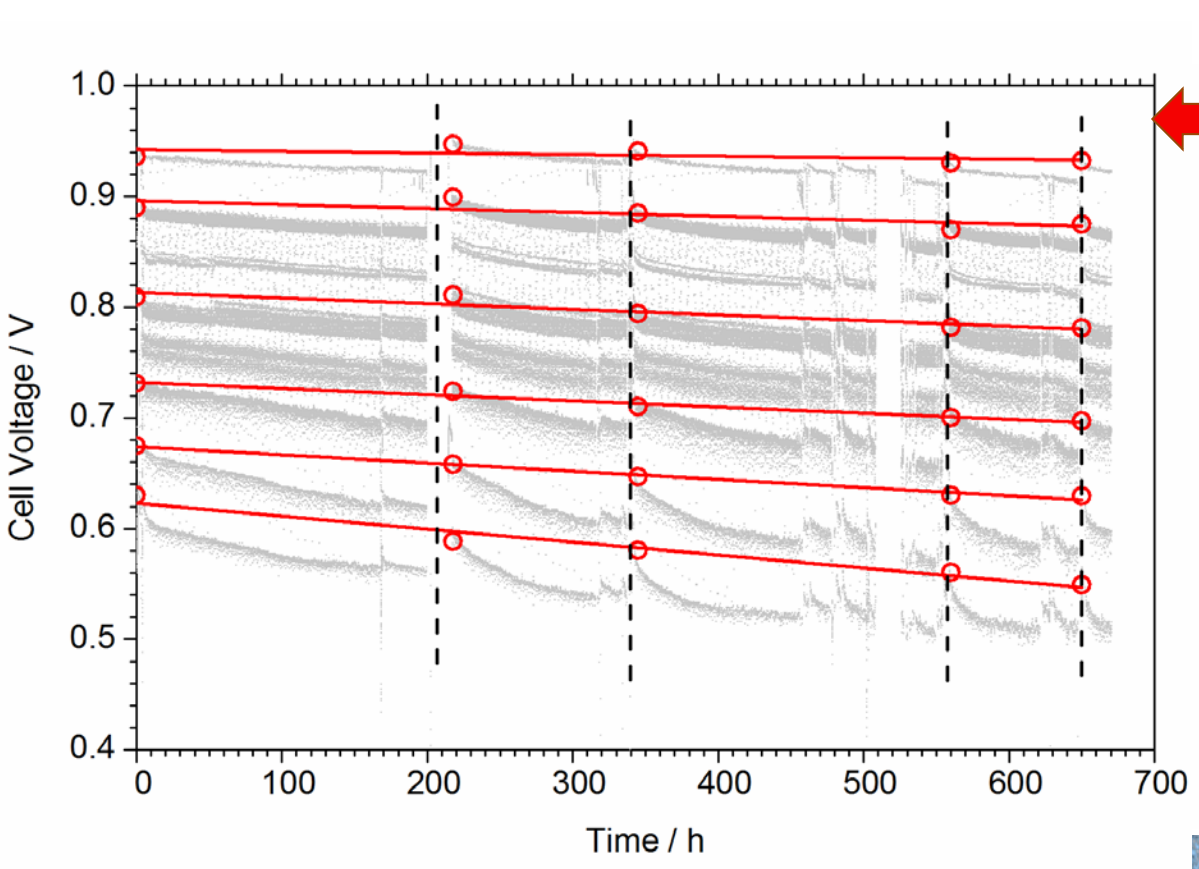
Evaluation of irreversible degradation

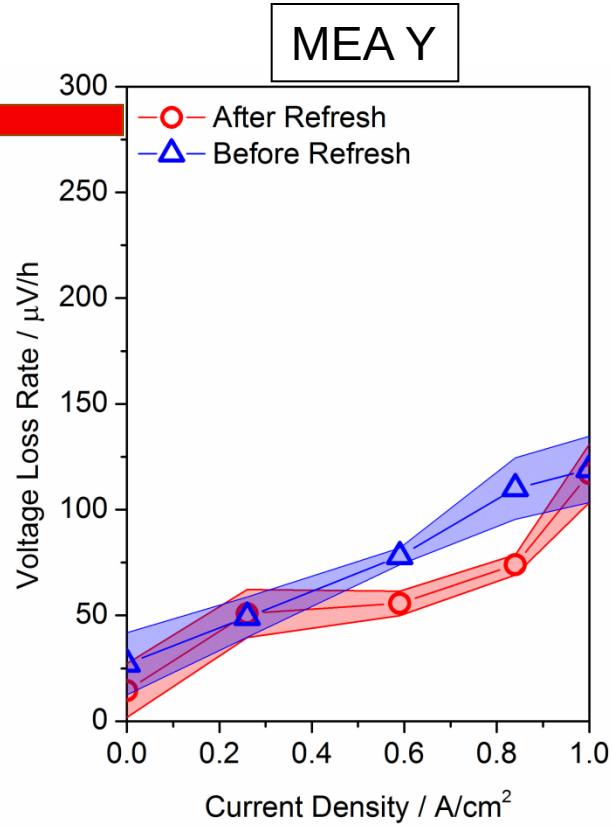
FC dynamic load cycle (FC-DLC) according to FCH-JU StackTest project
➔ Pseudo I-V curve obtained from each cycle



Evaluation of irreversible degradation

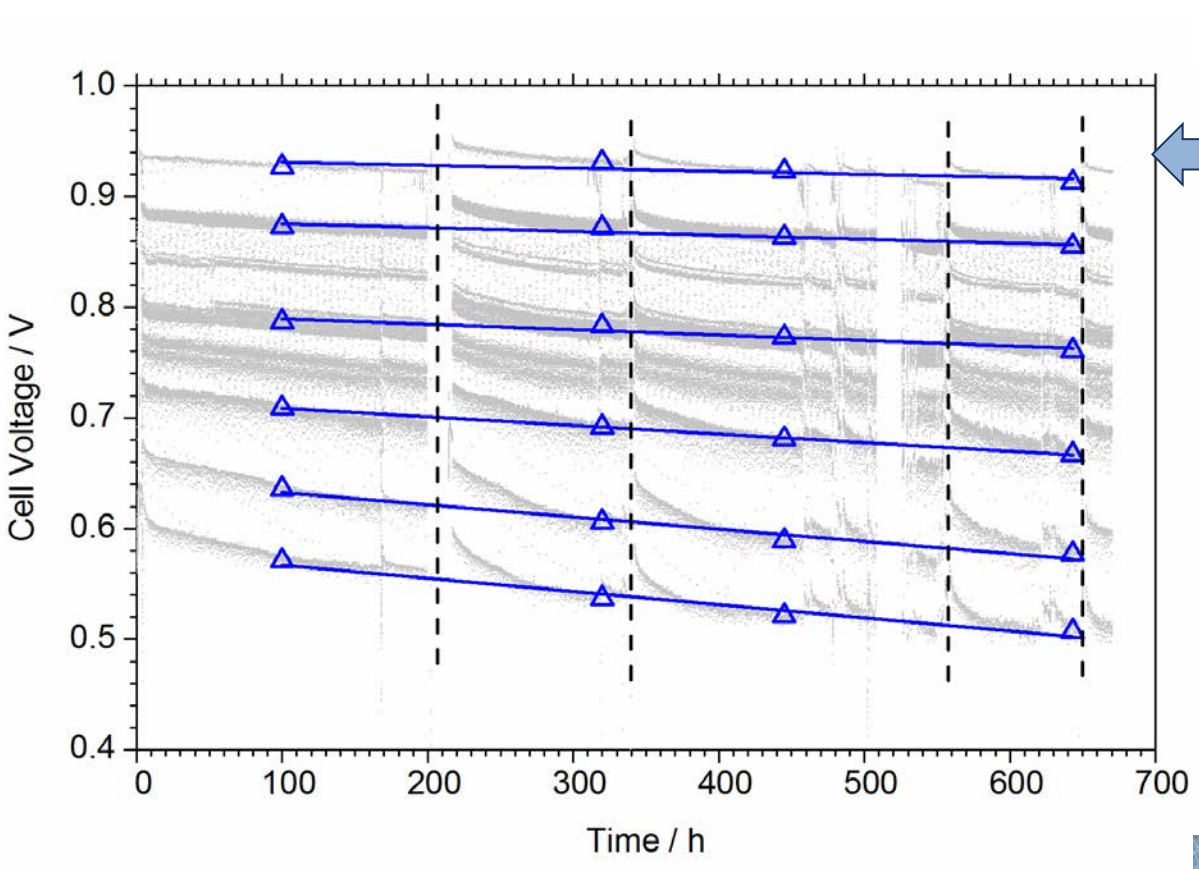
Use voltage values at start of each test block, i.e. after refresh

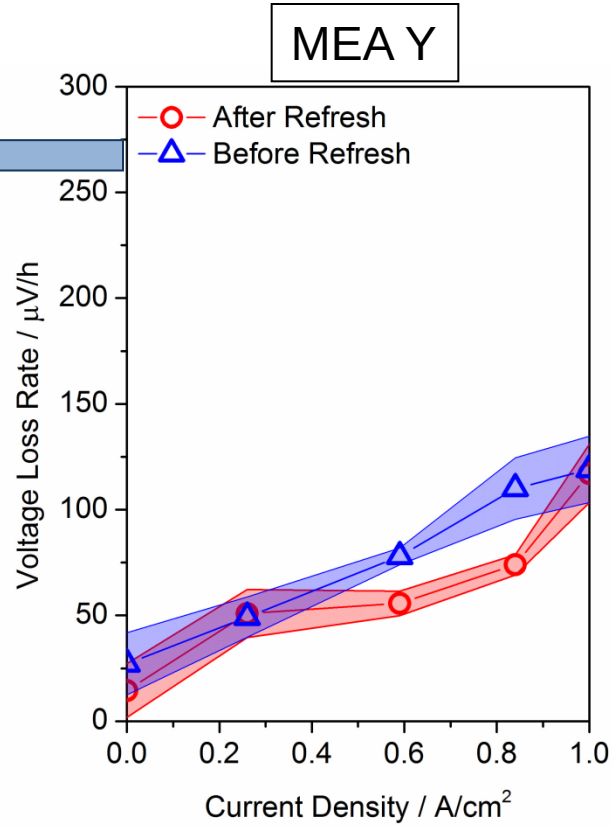




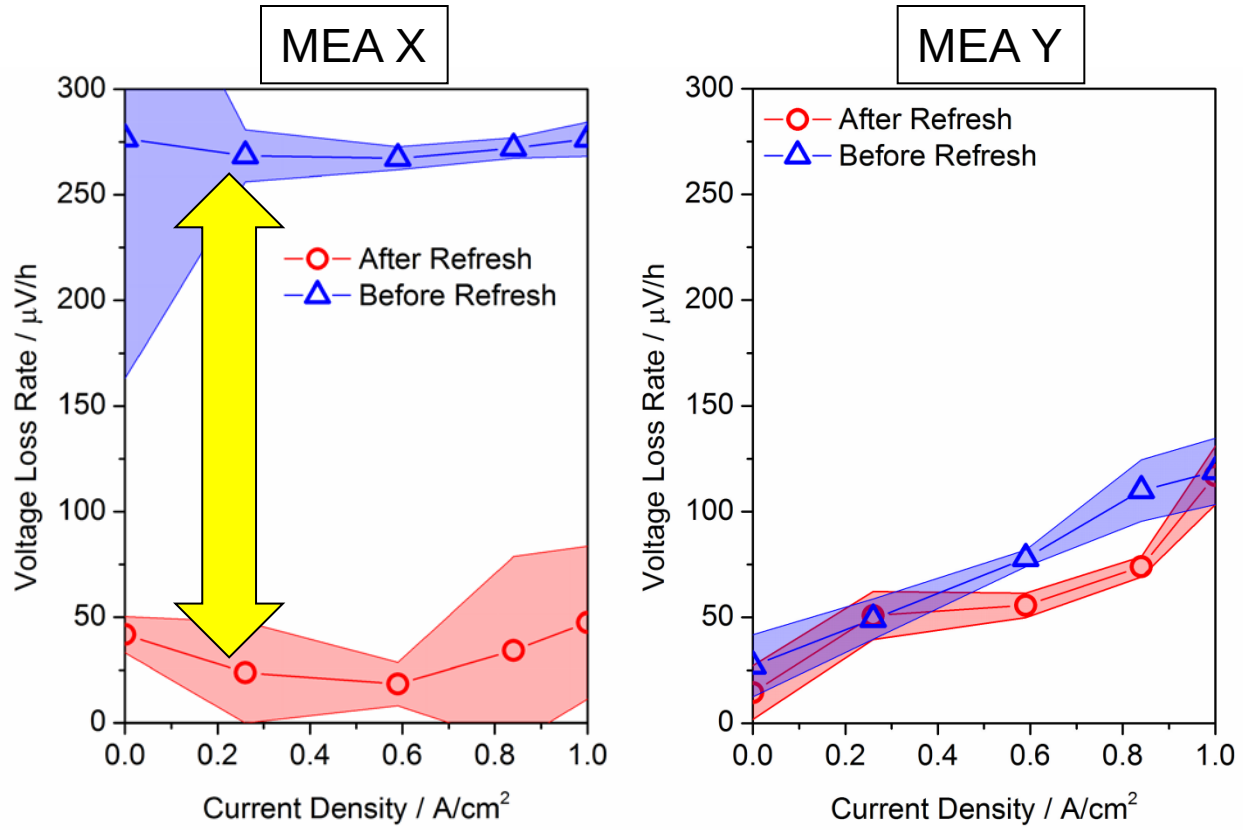
Evaluation of irreversible degradation

Use voltage values at the end of each test block, i.e. before refresh



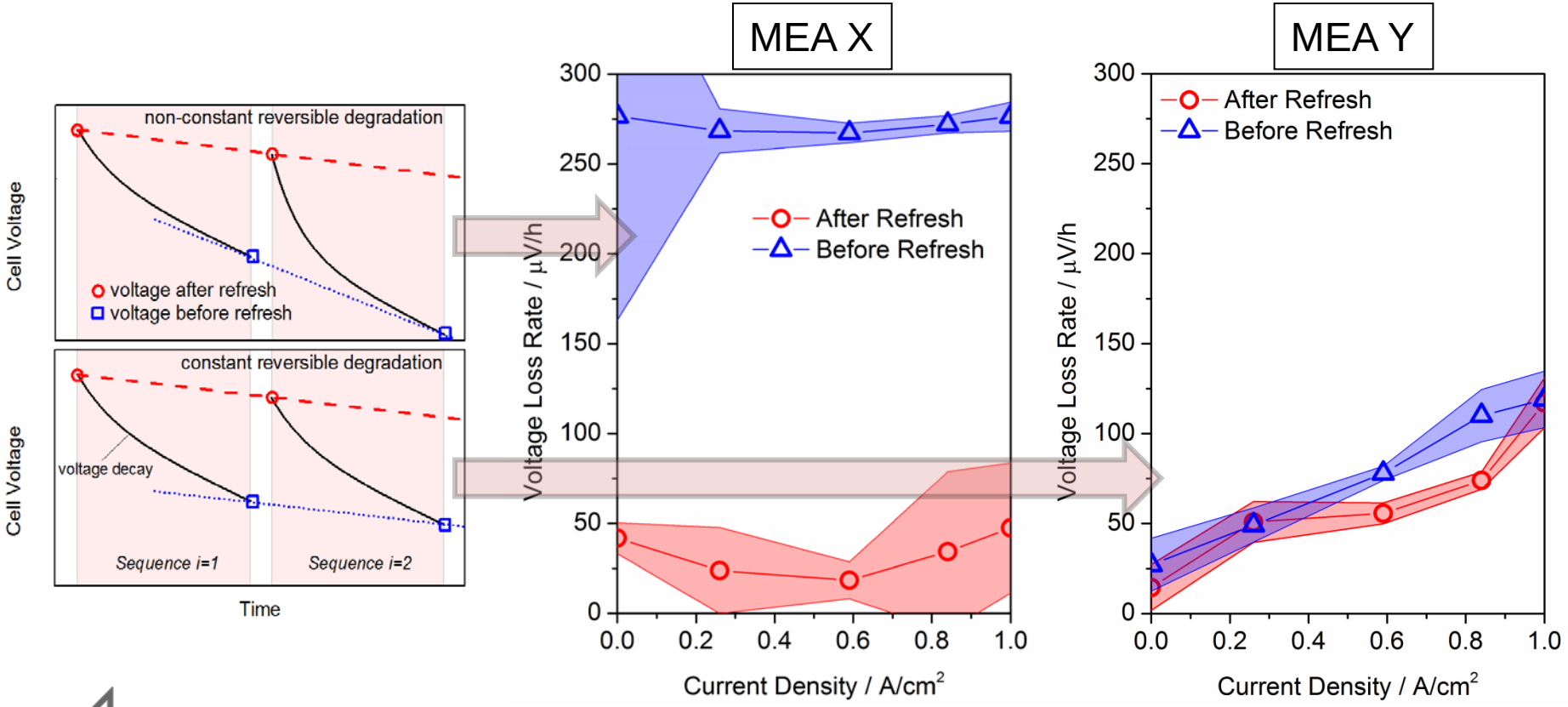


Evaluation of irreversible degradation



Evaluation of irreversible degradation

Constant and non-constant reversible degradation

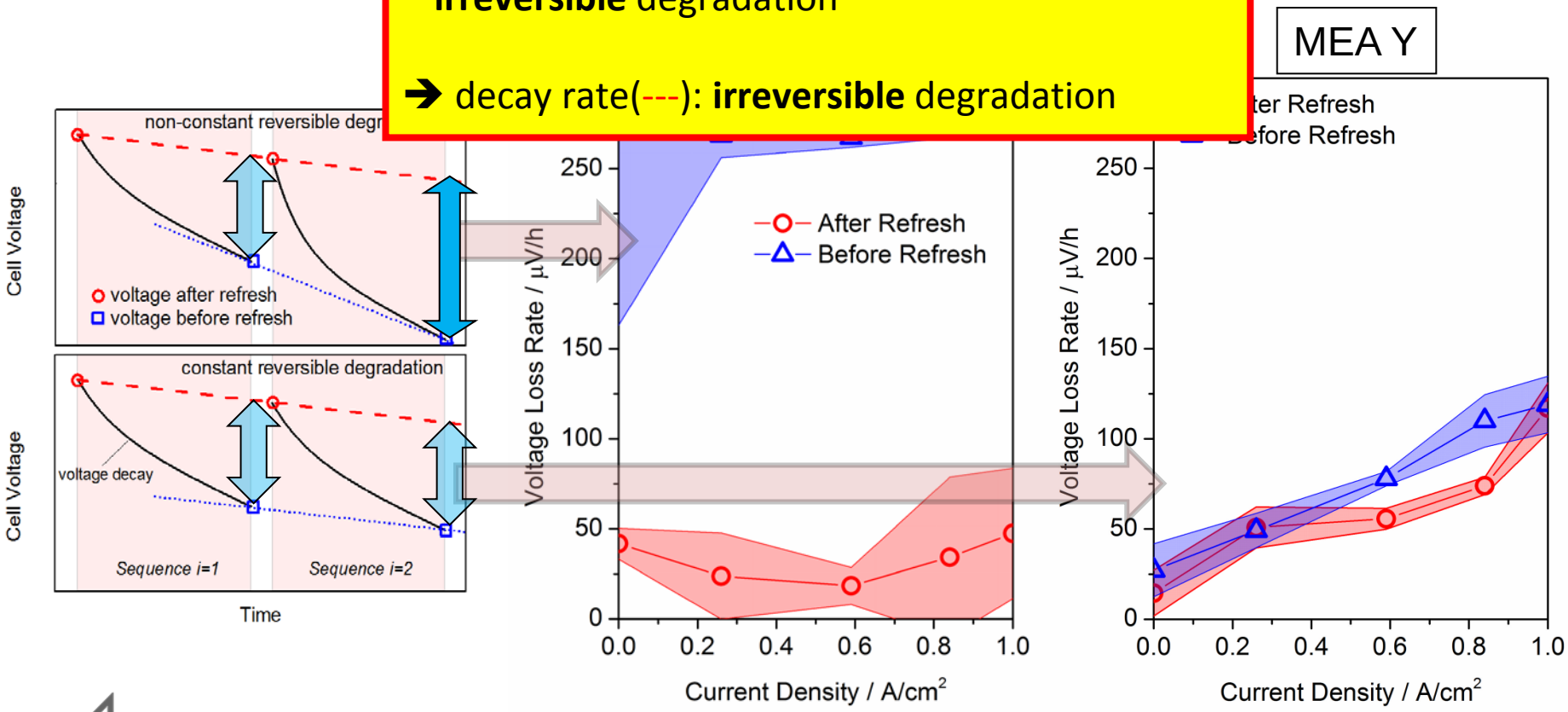


Evaluation of irreversible degradation

Constant and non-constant reversible degradation

➔ decay rate(…): combination or **reversible** an **irreversible** degradation

➔ decay rate(---): **irreversible** degradation



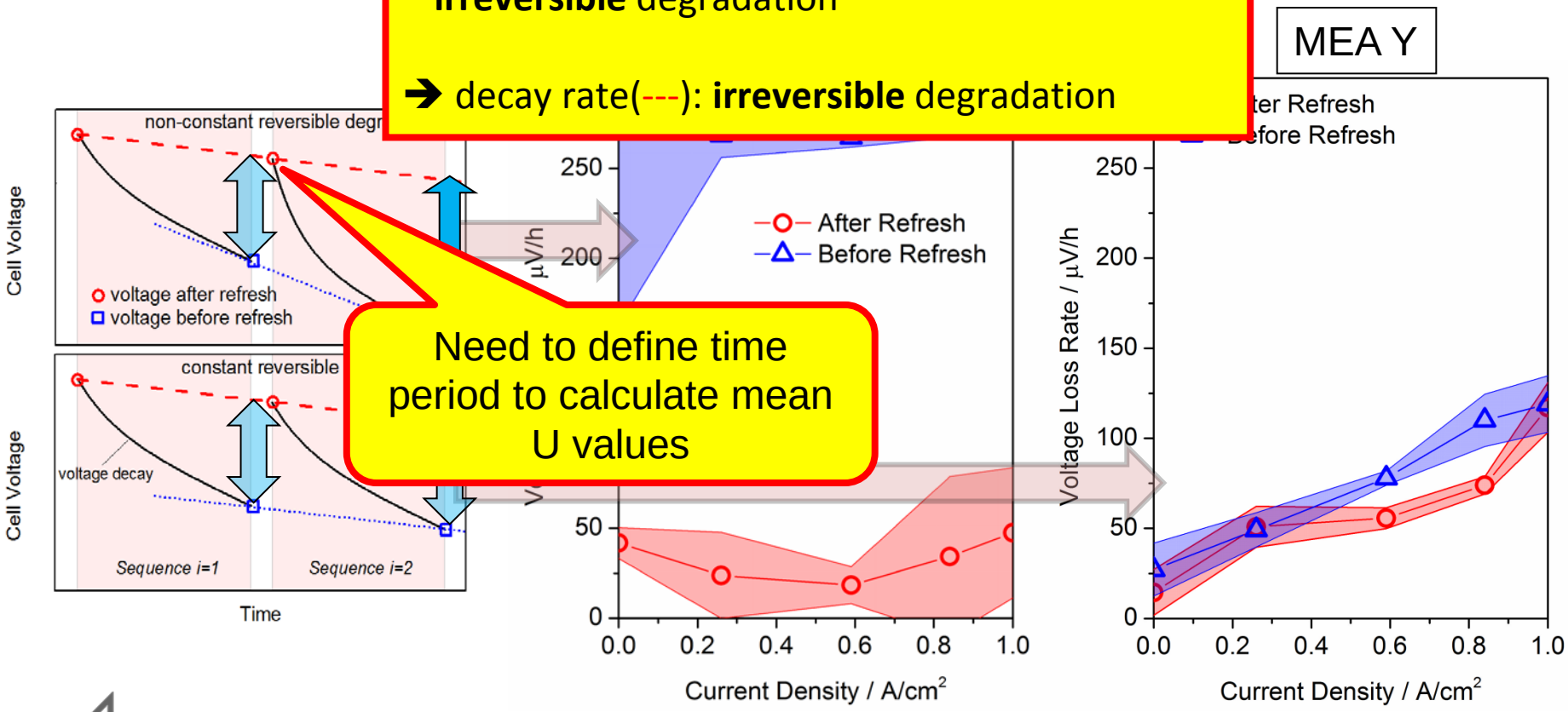
Evaluation of irreversible degradation

Constant and non-constant reversible degradation

➔ decay rate(…): combination or **reversible** an **irreversible** degradation

➔ decay rate(---): **irreversible** degradation

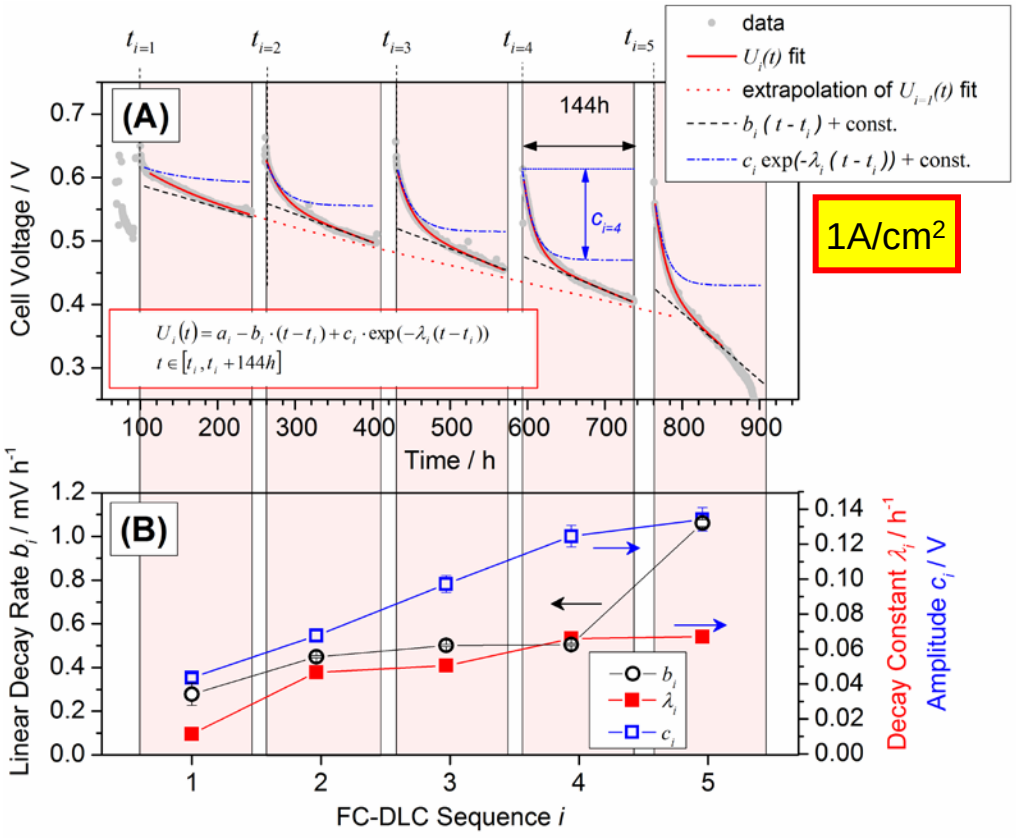
Need to define time period to calculate mean U values



Evaluation of reversible degradation

Evaluation of reversible degradation

Systematic FC-DLC test for accurate determination of reversible degradation

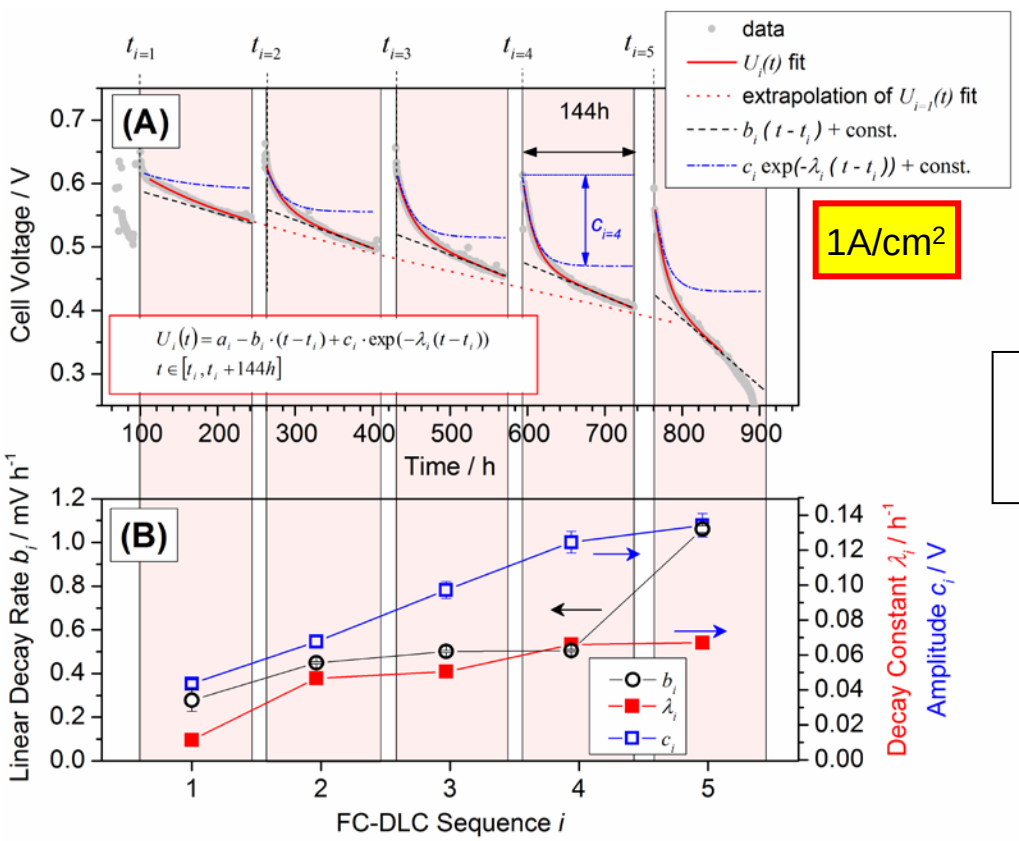


1A/cm²

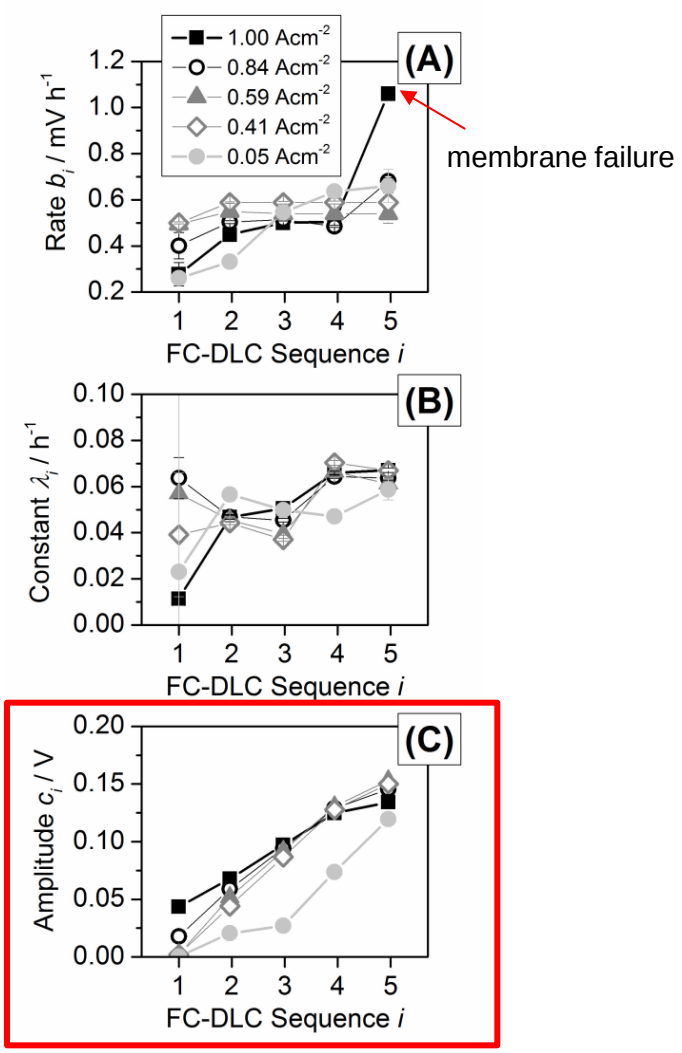
Reversible degradation can be described by a linear-exponential function

Evaluation of reversible degradation

Systematic FC-DLC test for accurate determination of reversible degradation



1A/cm²

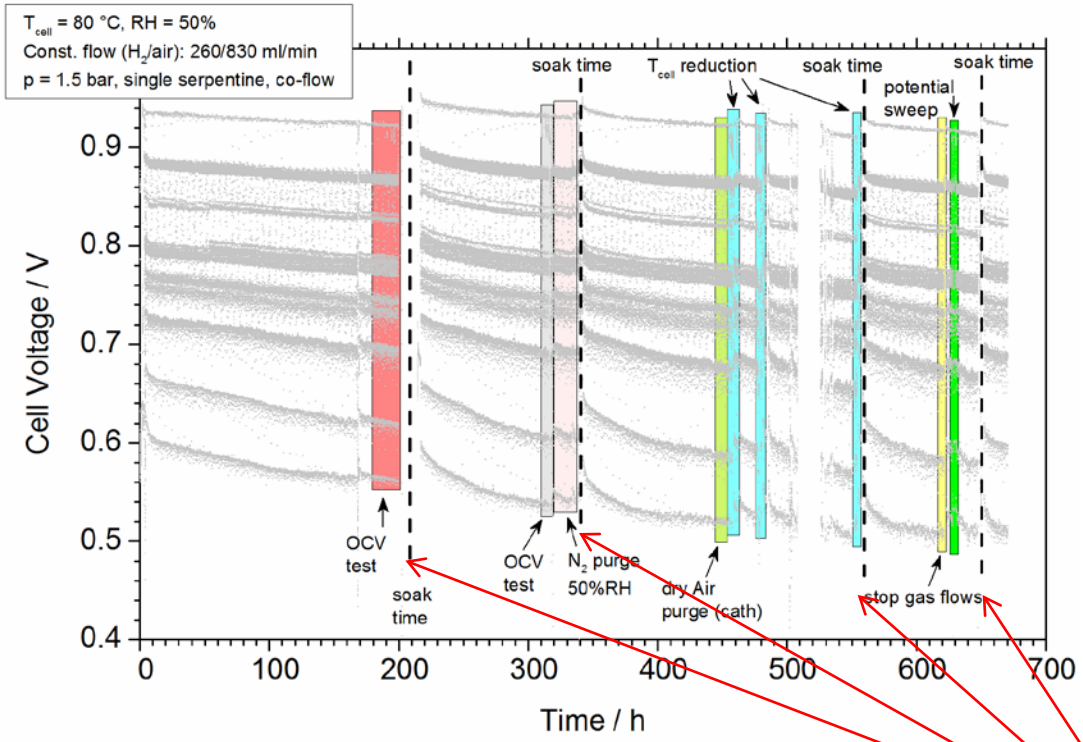


Amplitude of exp. part responsible for increase of reversible degradation with operation time

Recovery of reversible degradation

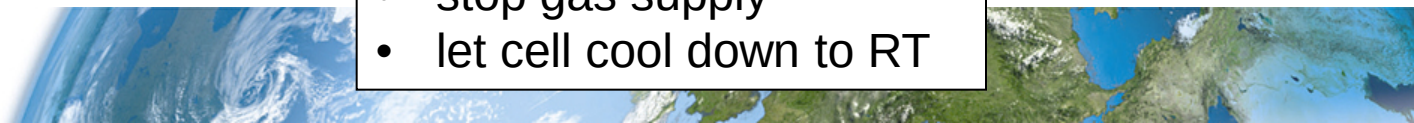
Recovery of reversible degradation

Test of conditions that occur during **shutdown recovery procedure** and could be the reason for recovery

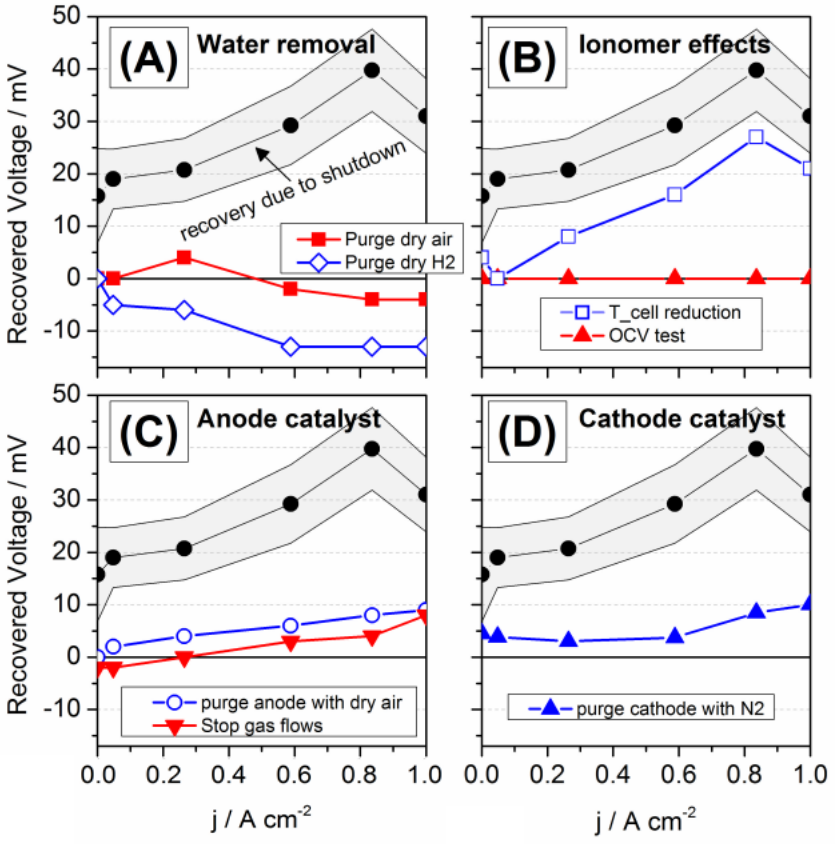


- Stop gas supply
- Drying
- reduction of T_{cell}
- OCV period
- purging anode with air
- potential sweep
- low potential, N_2 purge

- Switch off load
- stop gas supply
- let cell cool down to RT



Recovery of reversible degradation

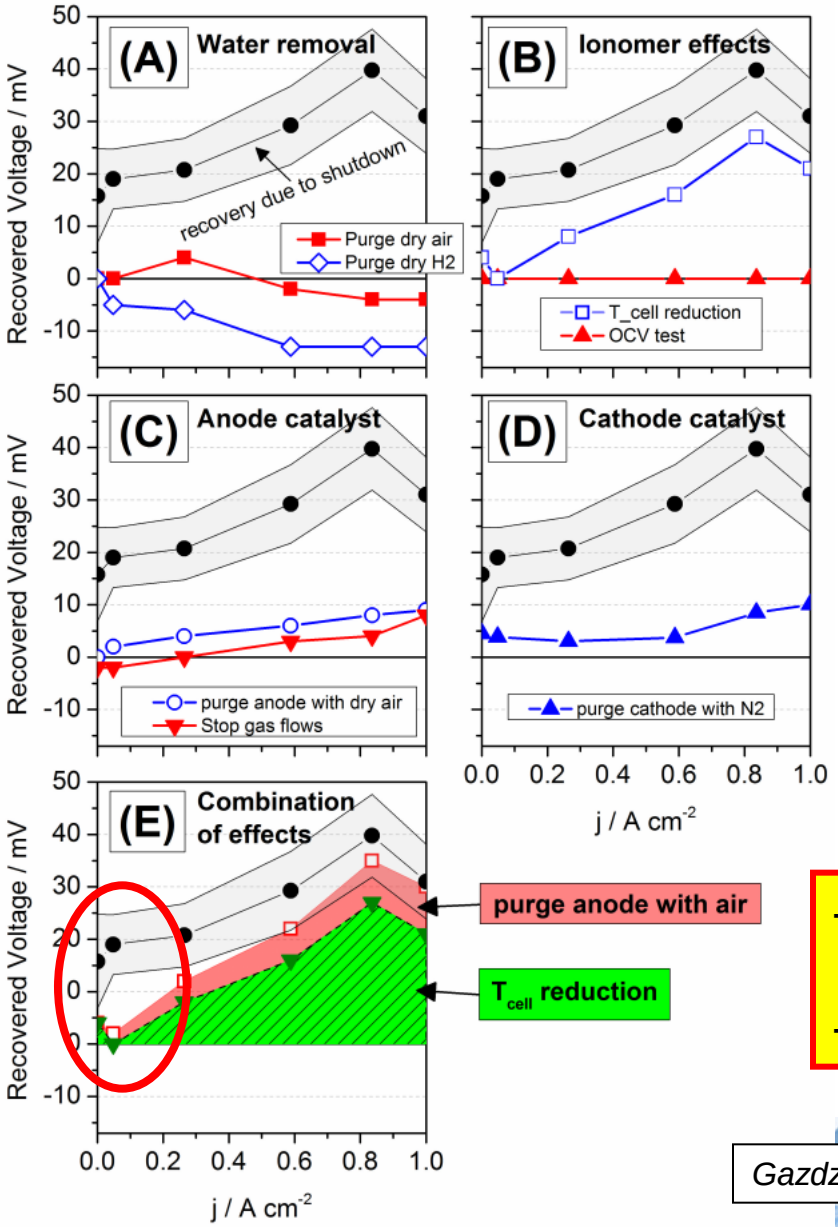


Recovery test	Intention	Recovered voltage @ 0.2 A cm^{-2}	Recovered voltage @ 0.8 A cm^{-2}
Purging anode with dry H_2	Remove water from anode	-28 %	-20 %
Purging cathode with dry air	Remove water from cathode	19 %	-10 %
Reduction of cell temperature	Increase humidity and decrease mechanical membrane stress	38 %	68 %
OCV-Test	Drying of MEA and increase of cathode potential	0 %	0 %
Purging anode with air	Increase anode potential to remove contaminants	19 %	20 %
Stopping gas flow	Increase anode potential to remove contaminants	0 %	10 %
Purging cathode with N_2	Decrease cathode potential to reduce platinum oxide	14 %	21 %

Recovery by shutdown could not be exceeded by any other procedure
➔ It is assumed that shutdown leads to **full recovery** of reversible losses

Gazdzicki et al. (2016) J. Power Sources, doi: 10.1016/j.jpowsour.2016.07.049

Recovery of reversible degradation



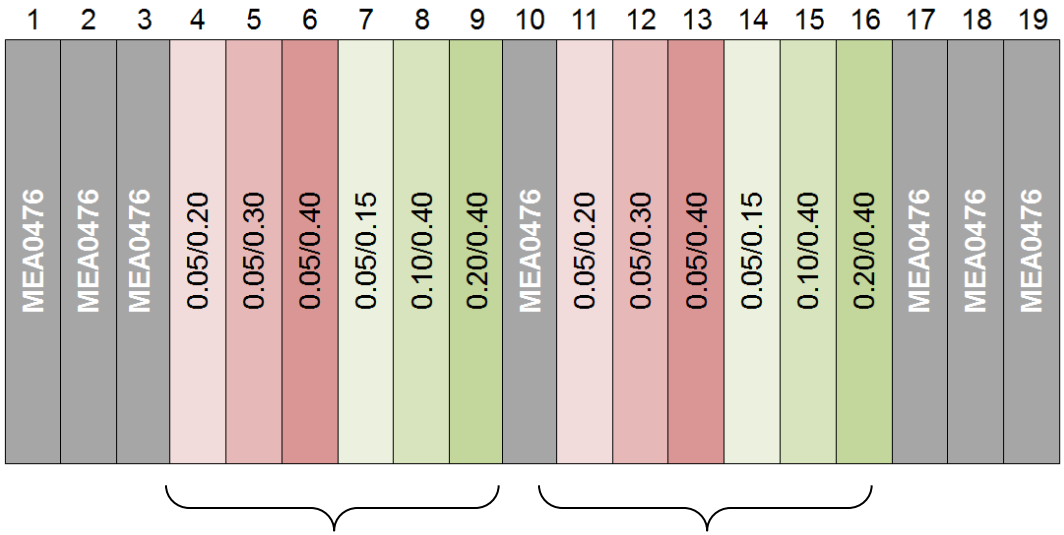
Recovery test	Intention	Recovered voltage @ 0.2 A cm^{-2}	Recovered voltage @ 0.8 A cm^{-2}
Purging anode with dry H_2	Remove water from anode	-28 %	-20 %
Purging cathode with dry air	Remove water from cathode	19 %	-10 %
Reduction of cell temperature	Increase humidity and decrease mechanical membrane stress	38 %	68 %
OCV-Test	Drying of MEA and increase of cathode potential	0 %	0 %
Purging anode with air	Increase anode potential to remove contaminants	19 %	20 %
Stopping gas flow	Increase anode potential to remove contaminants	0 %	10 %
Purging cathode with N_2	Decrease cathode potential to reduce platinum oxide	14 %	21 %

- Water management plays major role in recovery
- Reason for recovery at low loads unclear

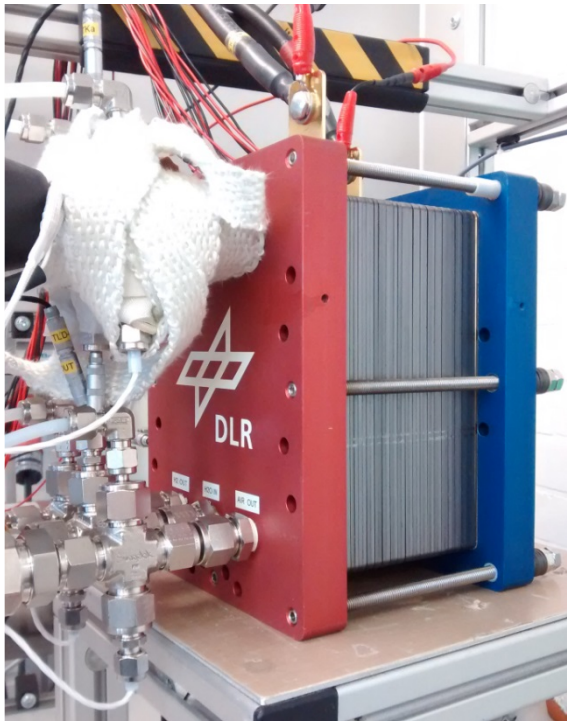
Gazdzicki et al. (2016) J. Power Sources, doi: 10.1016/j.jpowsour.2016.07.049

Degradation Vs Pt-loading

Pt-loadings at anode/cathode in mg_{Pt}/cm^2

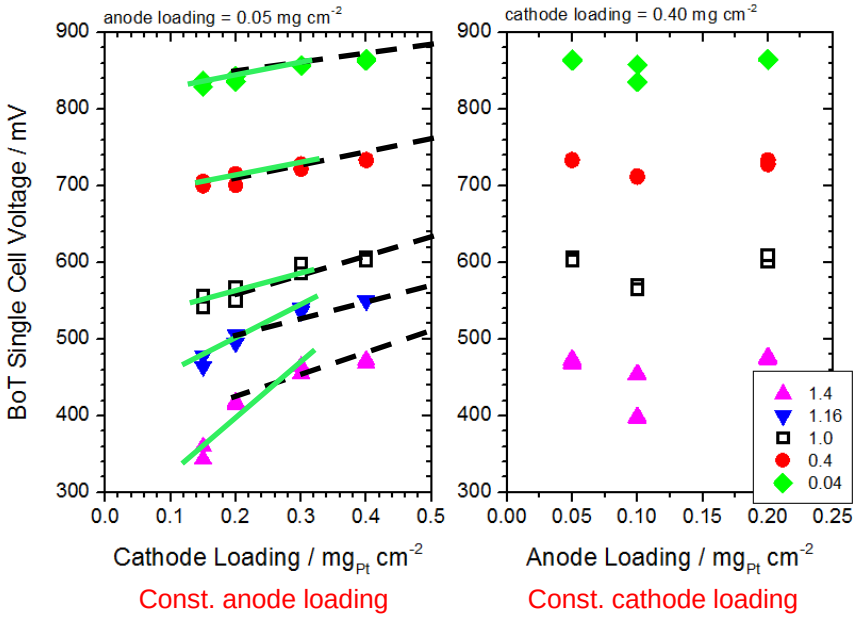


DLR Rainbow-Stack



Degradation Vs Pt-loading

BoT Voltages versus Loading



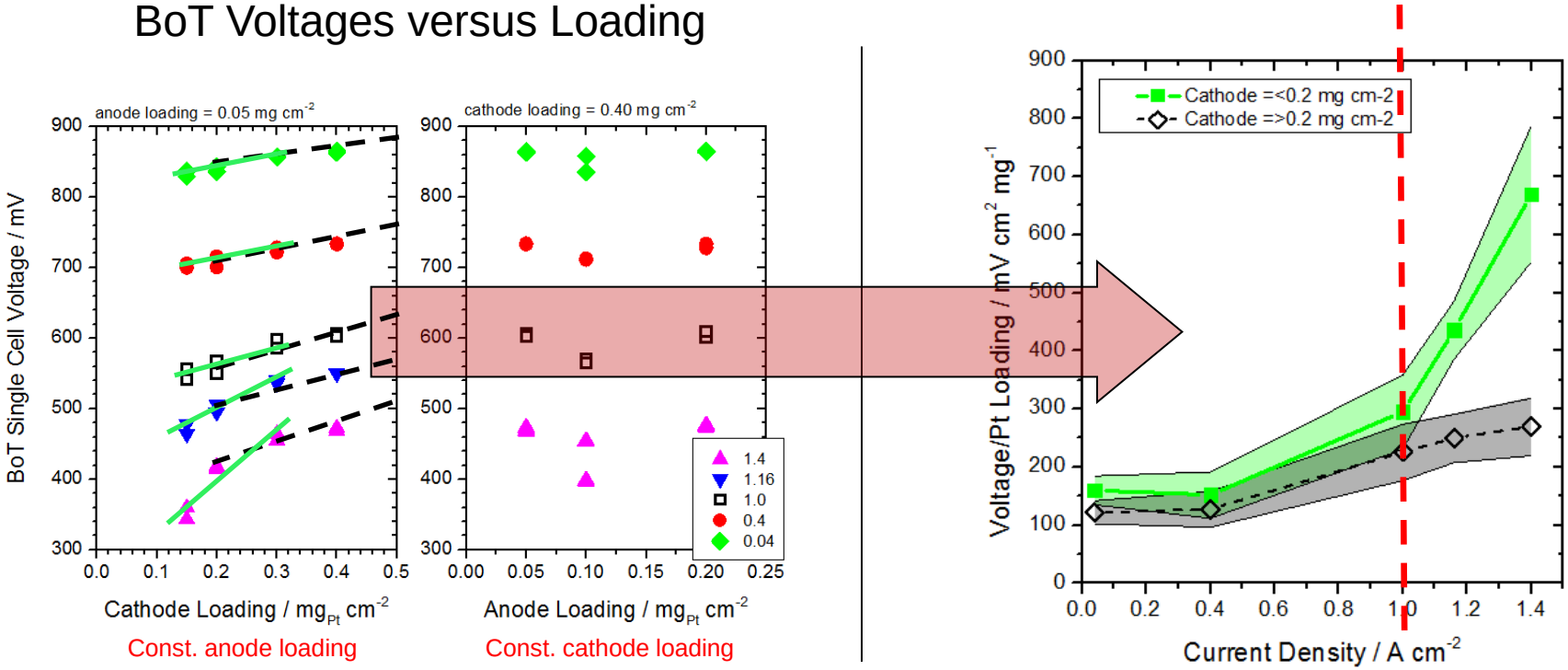
Const. anode loading

Const. cathode loading

- Clear dependence of Cell Voltage on cathode Pt loading
- No dependence of Cell Voltage on anode Pt loading

Degradation Vs Pt-loading

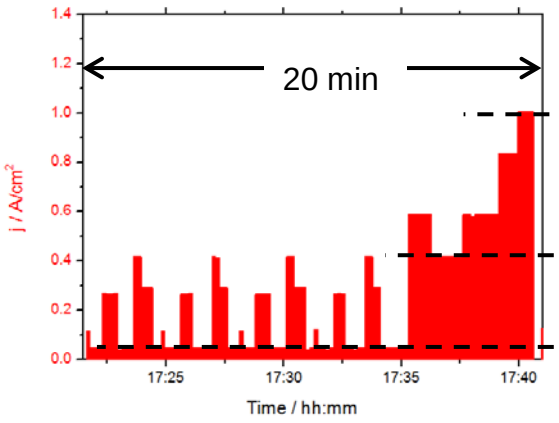
BoT Voltages versus Loading

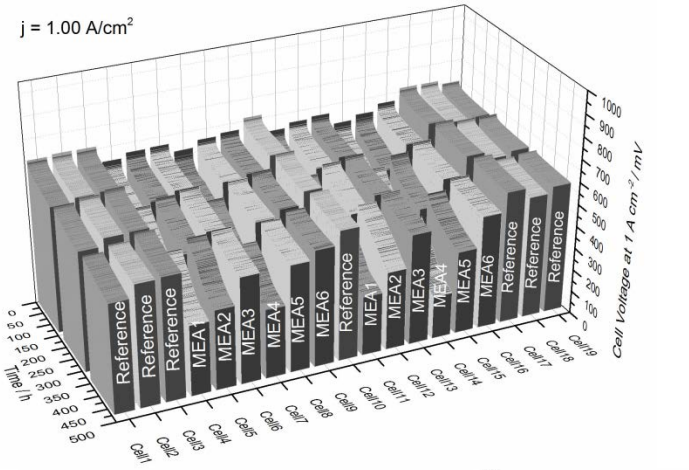


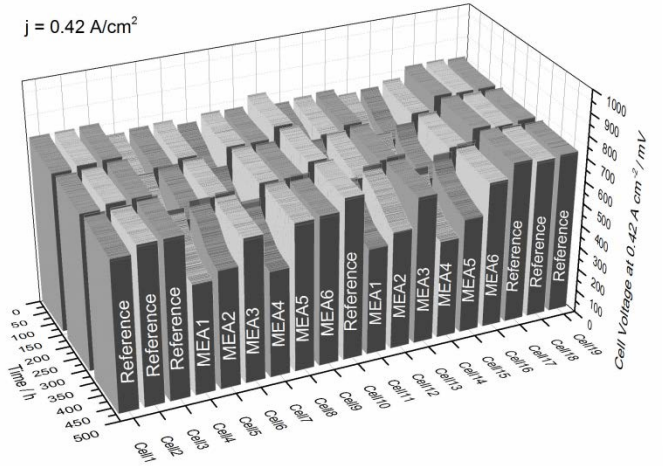
- Clear dependence of Cell Voltage on cathode Pt loading
- No dependence of Cell Voltage on anode Pt loading
- Onset of mass transport issues observed at cathode loading <=0.2 mg/cm2 and j>1 A/cm2

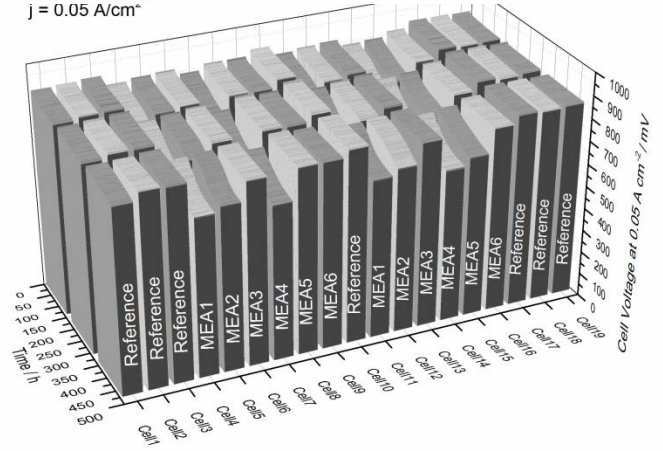
Degradation Vs Pt-loading

~500 h FC-DLC degradation test



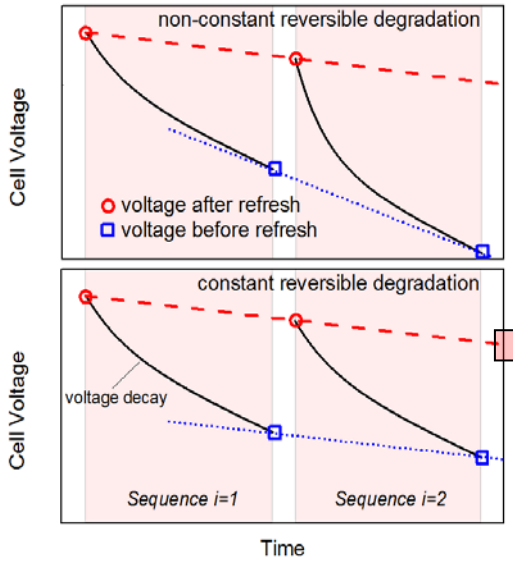




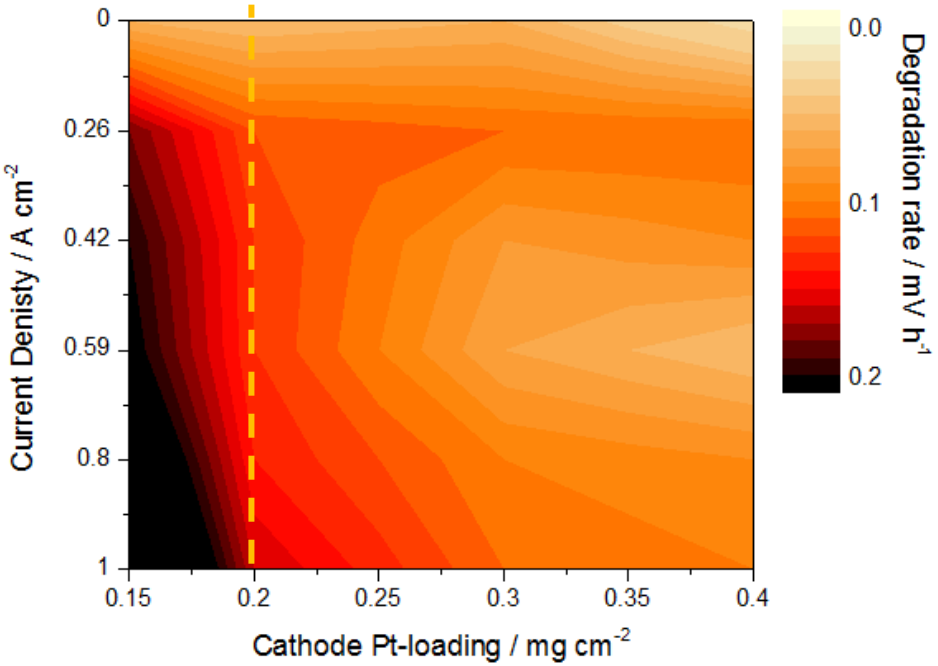


Degradation Vs Pt-loading: evaluation of irrev. degradation

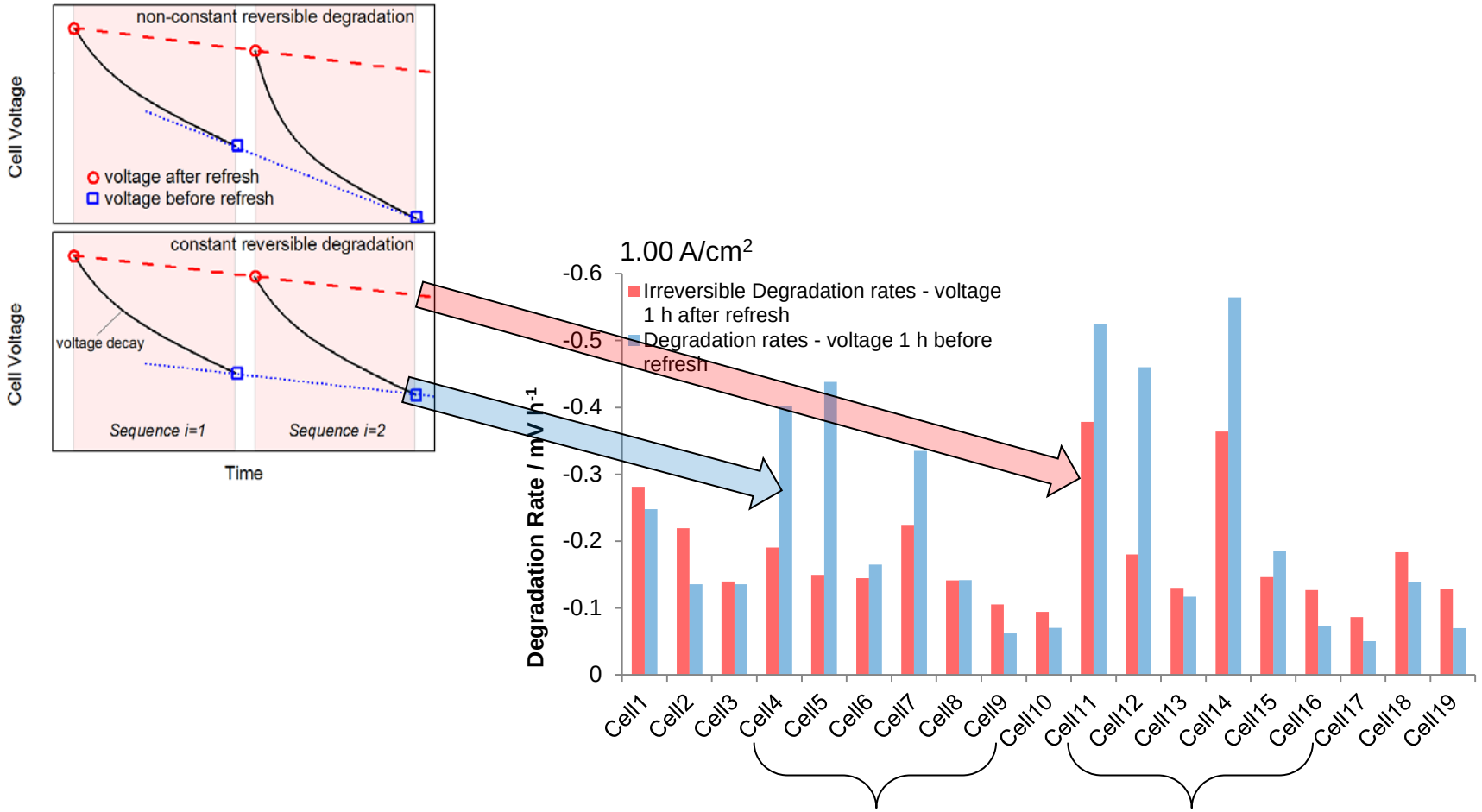
Significant increase of irrev. degradation for cathode loading <0.2 mg/cm^2 and high loads



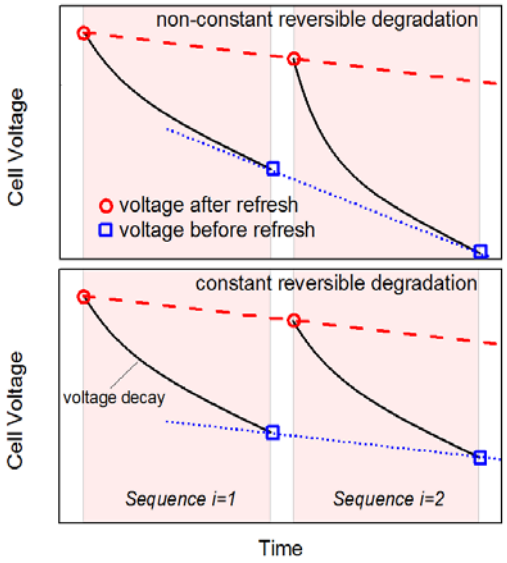
Determination of irrev. degradation (cells 4..9)

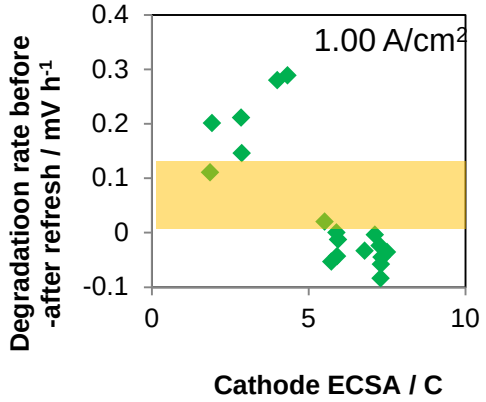


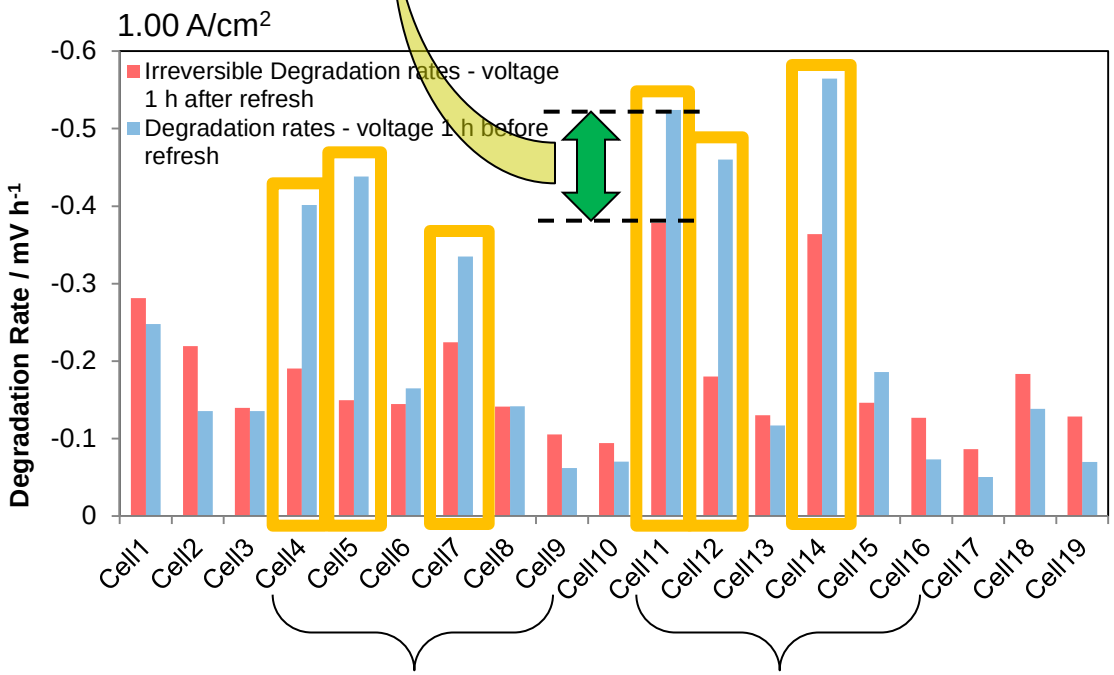
Degradation Vs Pt-loading: evaluation of rev. degradation



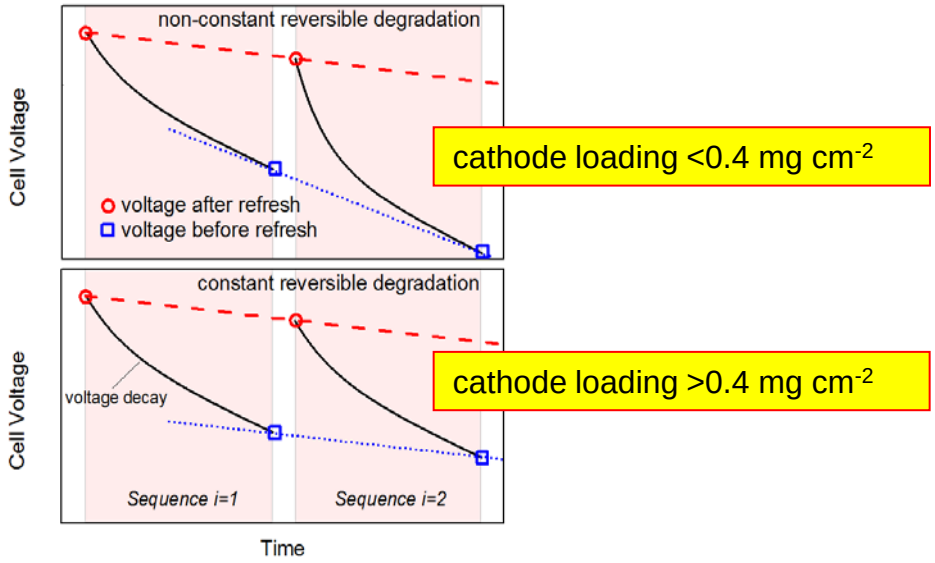
Degradation Vs Pt-loading: evaluation of rev. degradation

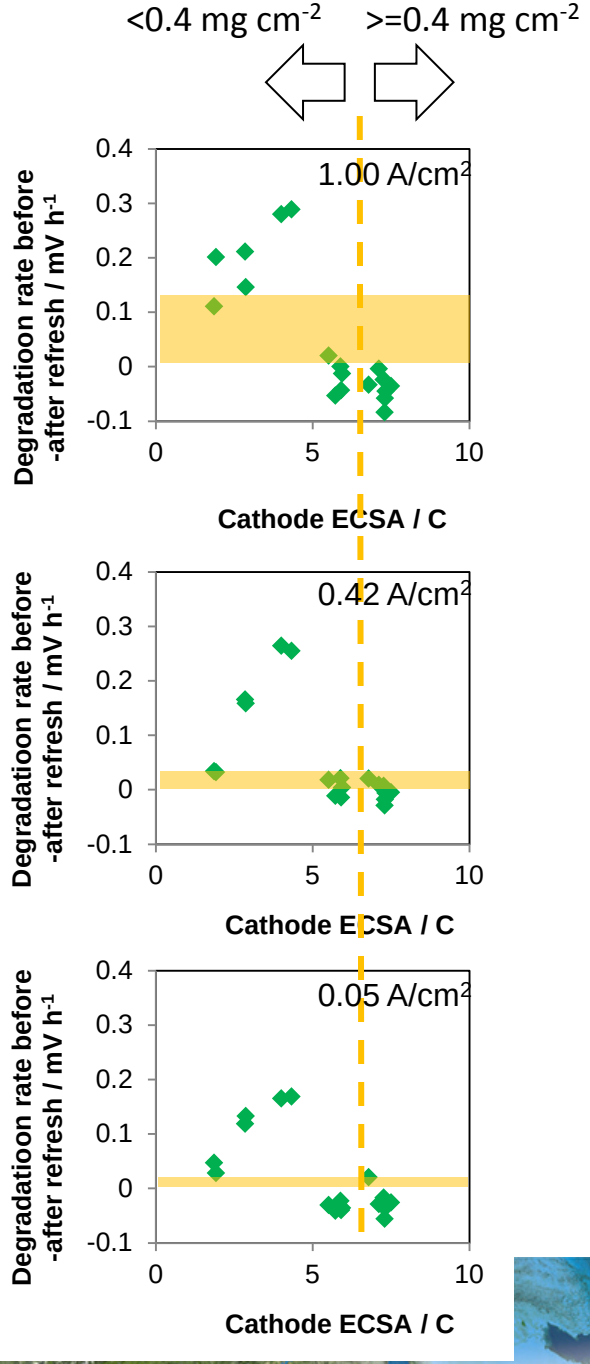






Degradation Vs Pt-loading: evaluation of rev. degradation



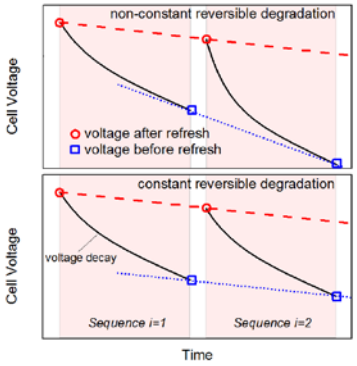


- MEAs with cathode loading <0.4 mg cm^{-2} exhibit non-constant reversible degradation
- Effect strongest at high current density

Summary

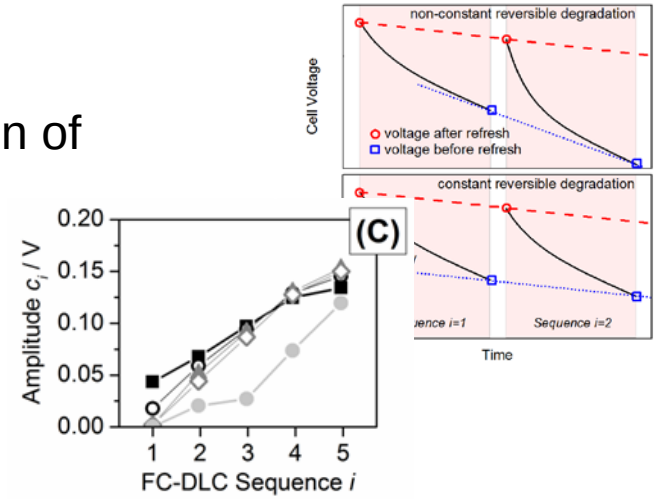
Summary

- Irreversible degradation rate: linear regression of voltage values after refresh



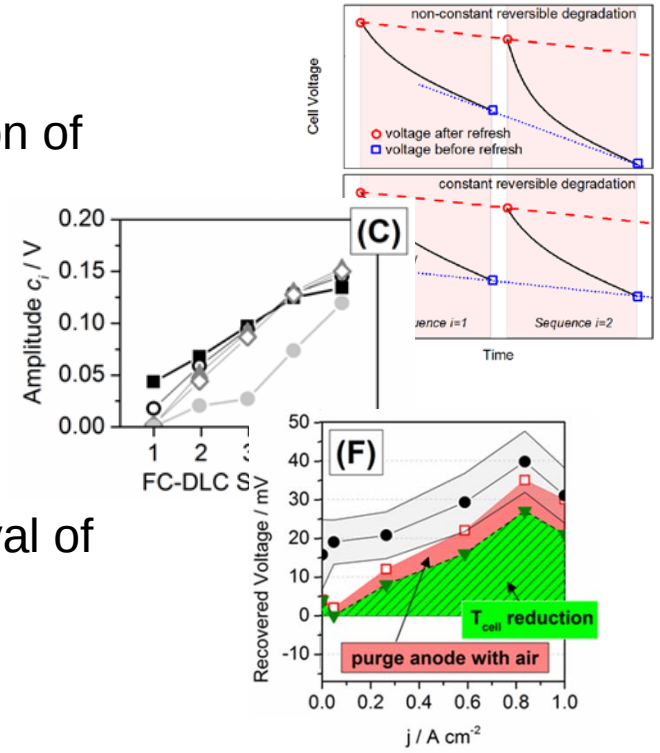
Summary

- Irreversible degradation rate: linear regression of voltage values after refresh
- Reversible degradation described by linear-exponential function with c_i responsible for acceleration of reversible degradation



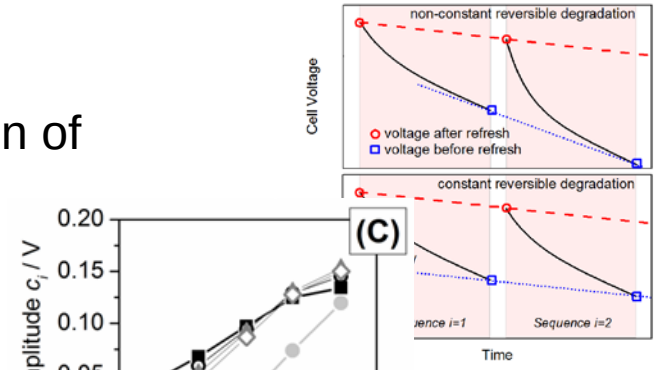
Summary

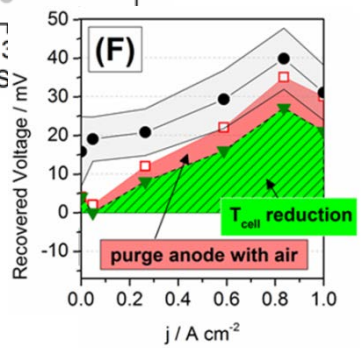
- Irreversible degradation rate: linear regression of voltage values after refresh
- Reversible degradation described by linear-exponential function with c_i responsible for acceleration of reversible degradation
- Voltage recovery: water management, removal of anodic contaminants

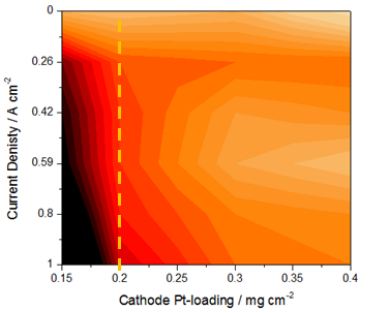


Summary

- Irreversible degradation rate: linear regression of voltage values after refresh
- Reversible degradation described by linear-exponential function with c_i responsible for acceleration of reversible degradation
- Voltage recovery: water management, removal of anodic contaminants
- Degradation Vs Pt-loading:
  - accelerated rev. degradation for cathode loadings <0.4 mg cm^{-2}
  - increased irrev. Degradation for cathode loading <0.2 mg cm^{-2}







Thank you for your attention.

The research leading to these results has received funding from the European Union's Seventh Framework Programme (FP7/2007-2013) for Fuel Cell and Hydrogen Joint Technology Initiative under Grant nº 303452 (**Impact**).