



POLITECNICO DI MILANO



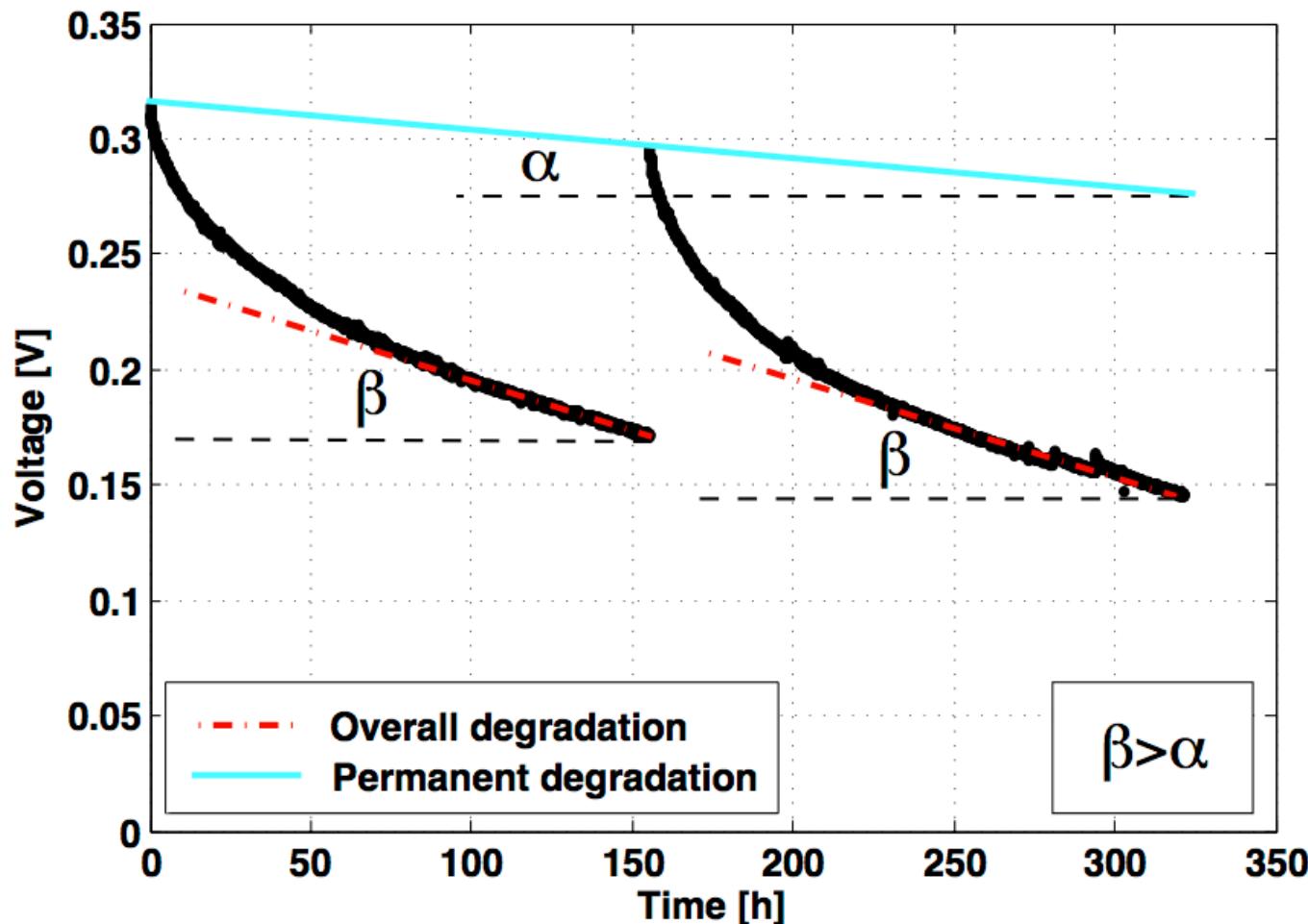
PREMIUM ACT: experimental and modelling analysis of DMFC degradation

A. Casalegno

MRT Fuel Cell Lab – Department of Energy – Politecnico di Milano
www.mrtfuelcell.polimi.it

Workshop on fuel cell degradation 3/4 April 2013 – OSLO

Temporary vs. Permanent Degradation



*Temporary Degradation is due to anode and/or cathode?
What is its origin? How can it be reduced?*

1. DMFC anode degradation



interpretation

2. DMFC overall degradation



confirmation

3. Mass transport analysis

4. Modelling analysis

Experimental methodology

2 experimental DMFC setups:

- *Fuel Cell*
- *Half Cell (Anode)*

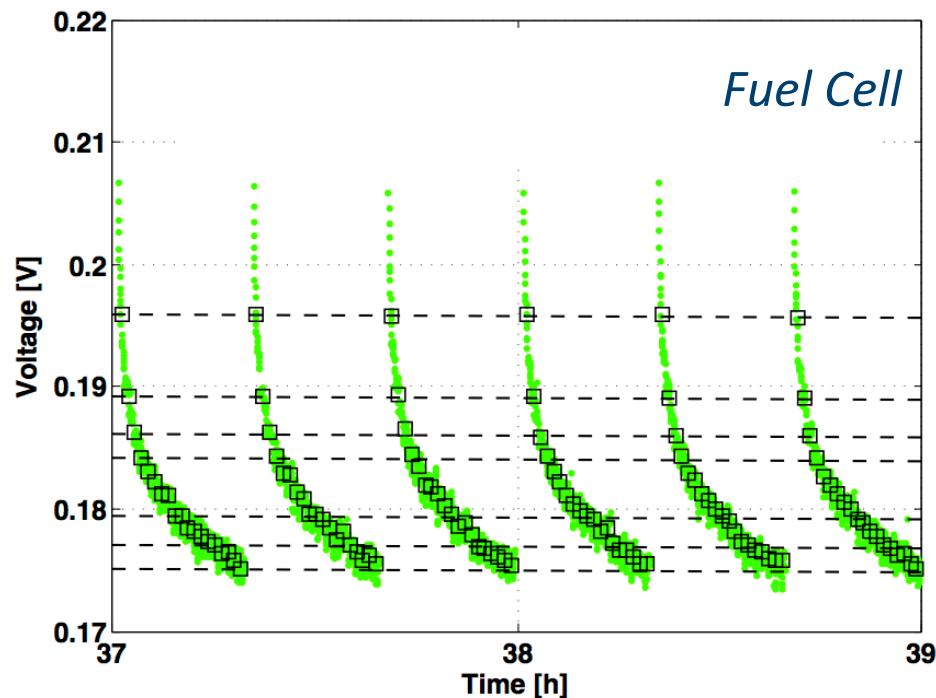
Performance

Mass Transport

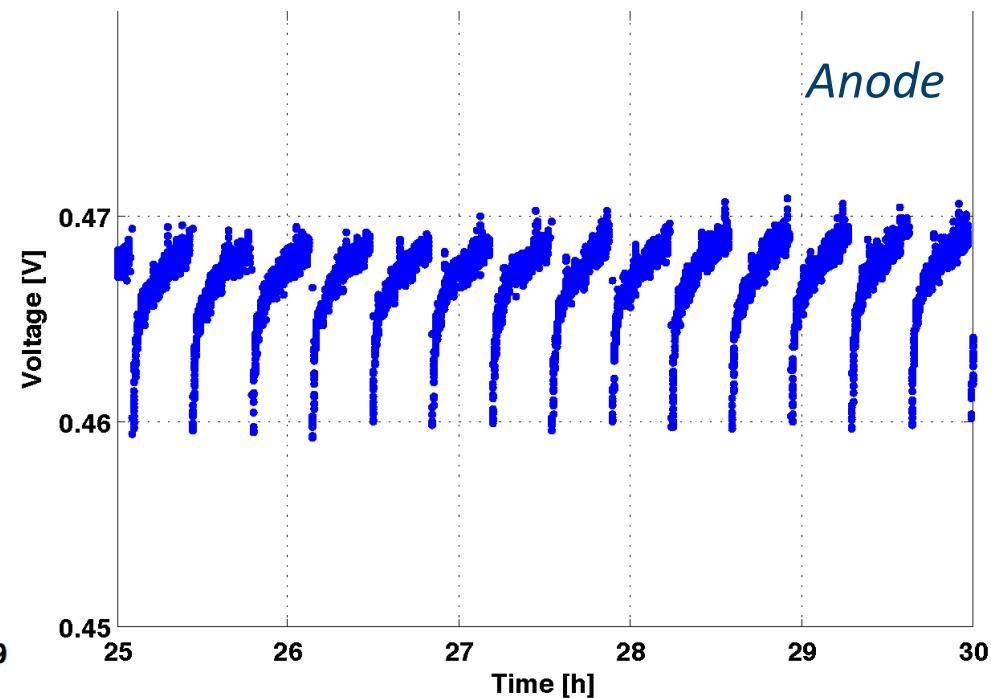
EIS

Operating strategies

Refresh cycle (OCV + Air Break), IRD Fuel Cell



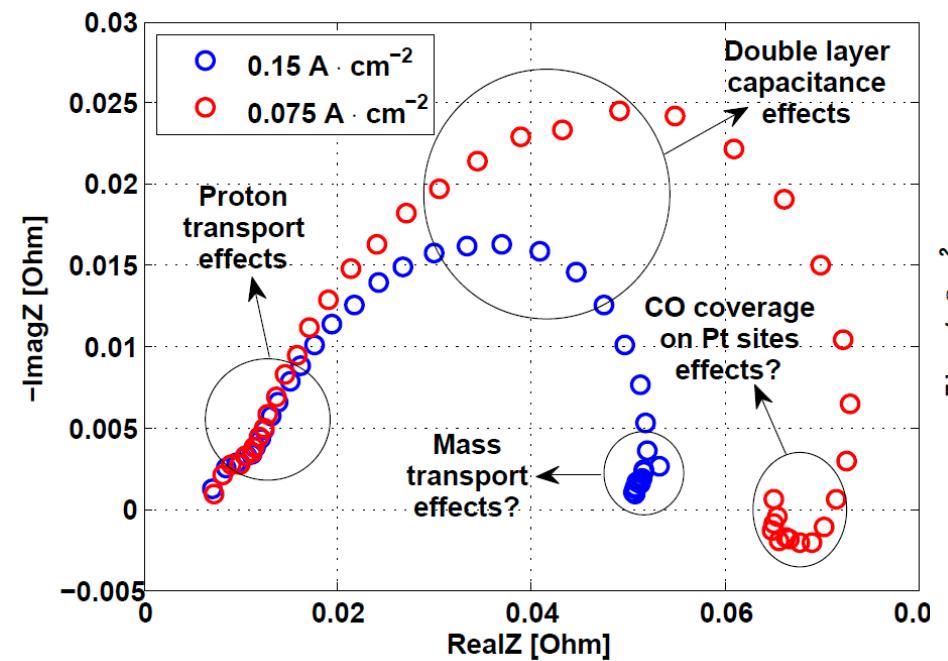
Refresh cycle (OCV - 0 V), Polimi



DMFC anode EIS interpretation

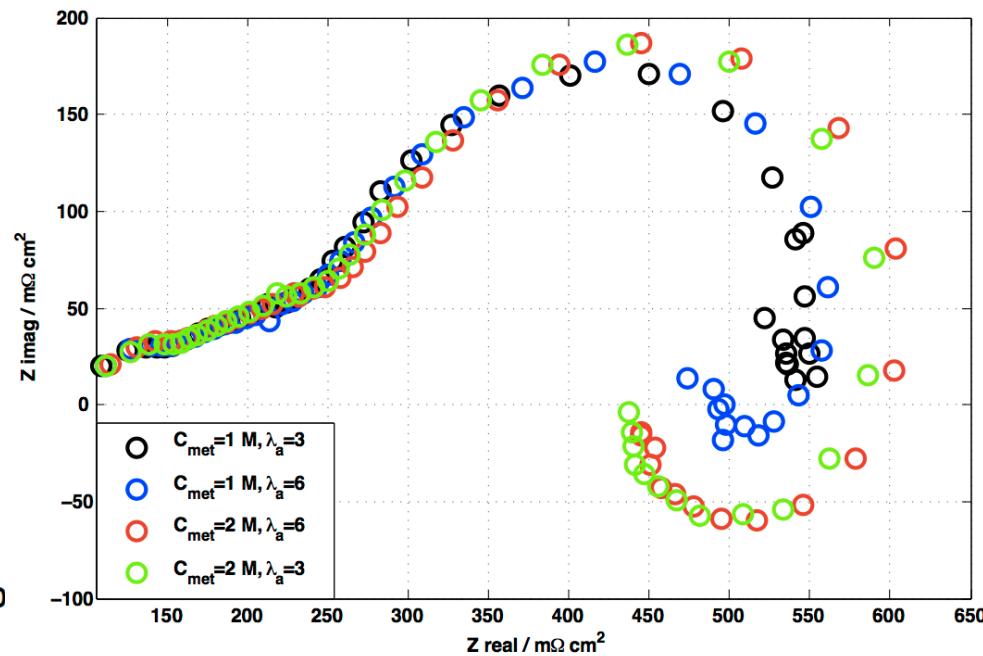
Systematic analysis to interpret degradation

MEA anode spectra varying current: anode GDL without MPL, cathode GDL with MPL



Strong influence of current density

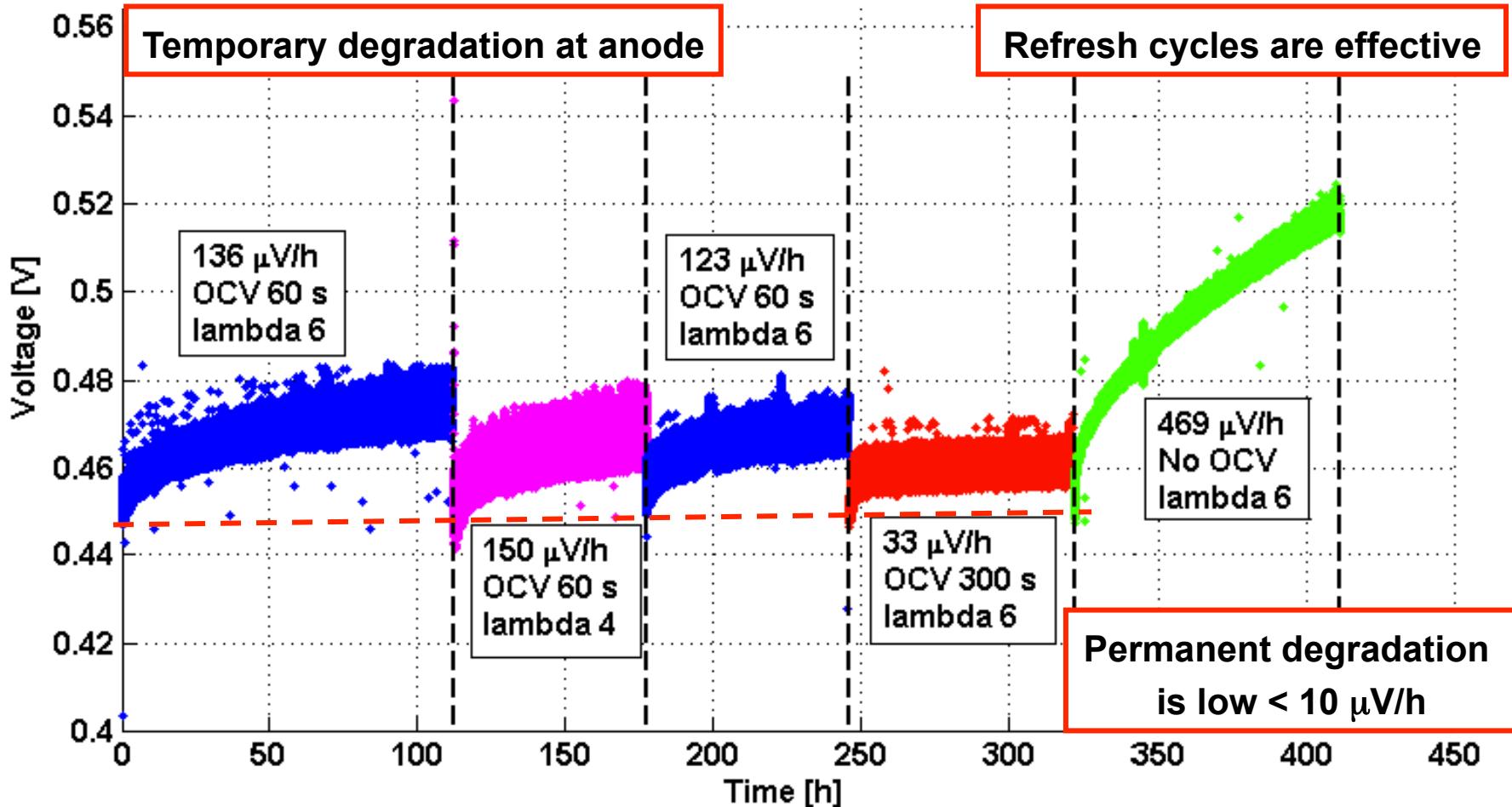
Reference MEA anode spectra varying some operating conditions ($i=0.25 \text{ A} \cdot \text{cm}^{-2}$ $T=75^\circ\text{C}$).



Methanol feeding affects the inductive loop

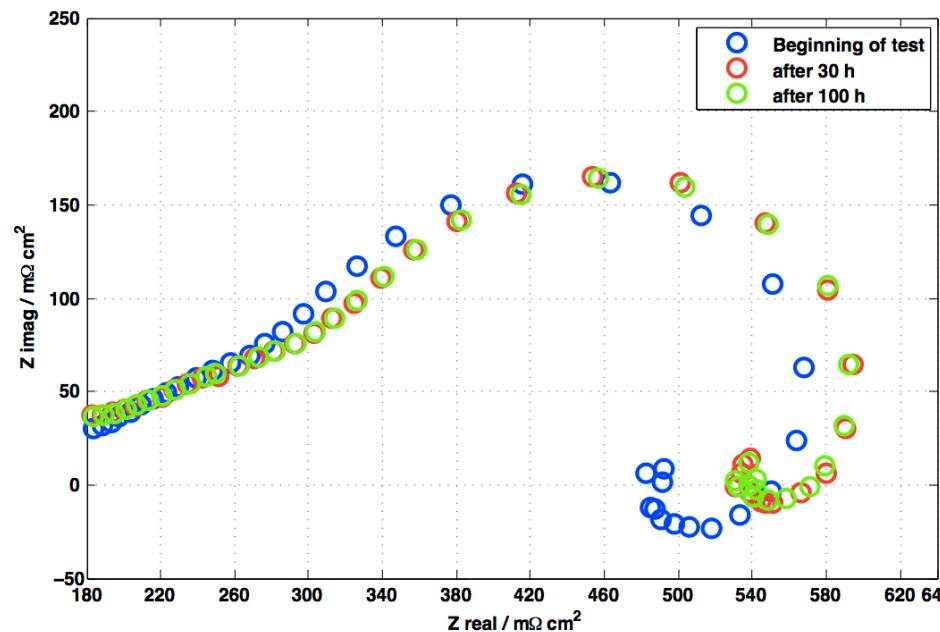
Analysis of DMFC anode degradation

Cycling operation: Cycles of 20 minutes + n minutes of OCV

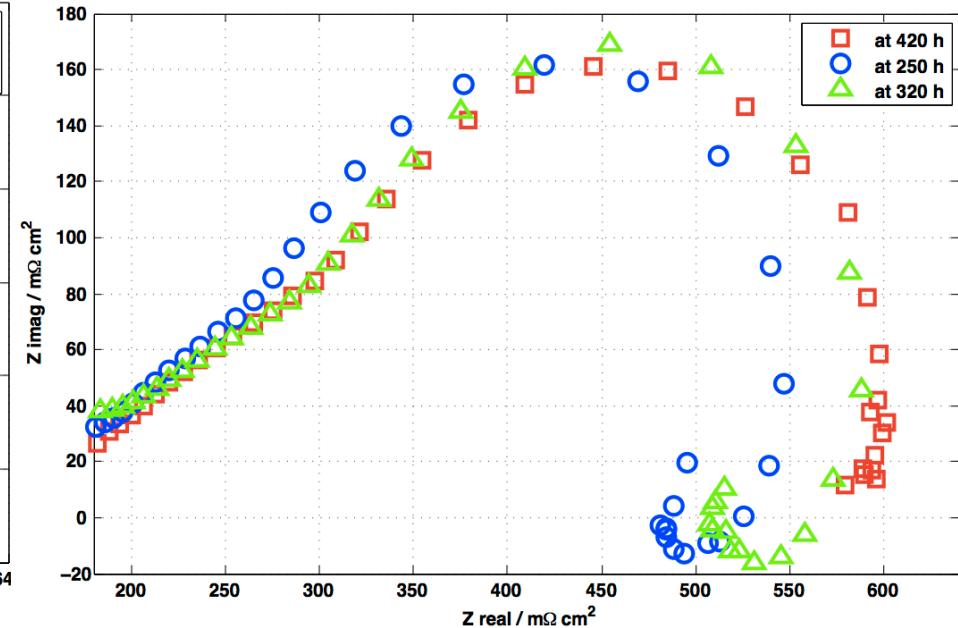


Operating conditions ($i=0.25 \text{ A} \cdot \text{cm}^{-2}$ $T=75^\circ\text{C}$).

Analysis of DMFC anode degradation



Reference MEA anode spectra in time ($i=0.25 \text{ A} \cdot \text{cm}^{-2}$ $T=75^\circ\text{C}$)



Linear branch extension +
mass transport effect

Anode Temporary Degradation suspected origin:

Consumption of CH_3OH and H_2O accumulated in GDL

other possibilities: hydrogen crossover, catalyst poisoning, oxides formation...

Proposed interpretation

Existence of a anode temporary degradation



Consumption of CH_3OH and H_2O accumulated in GDL

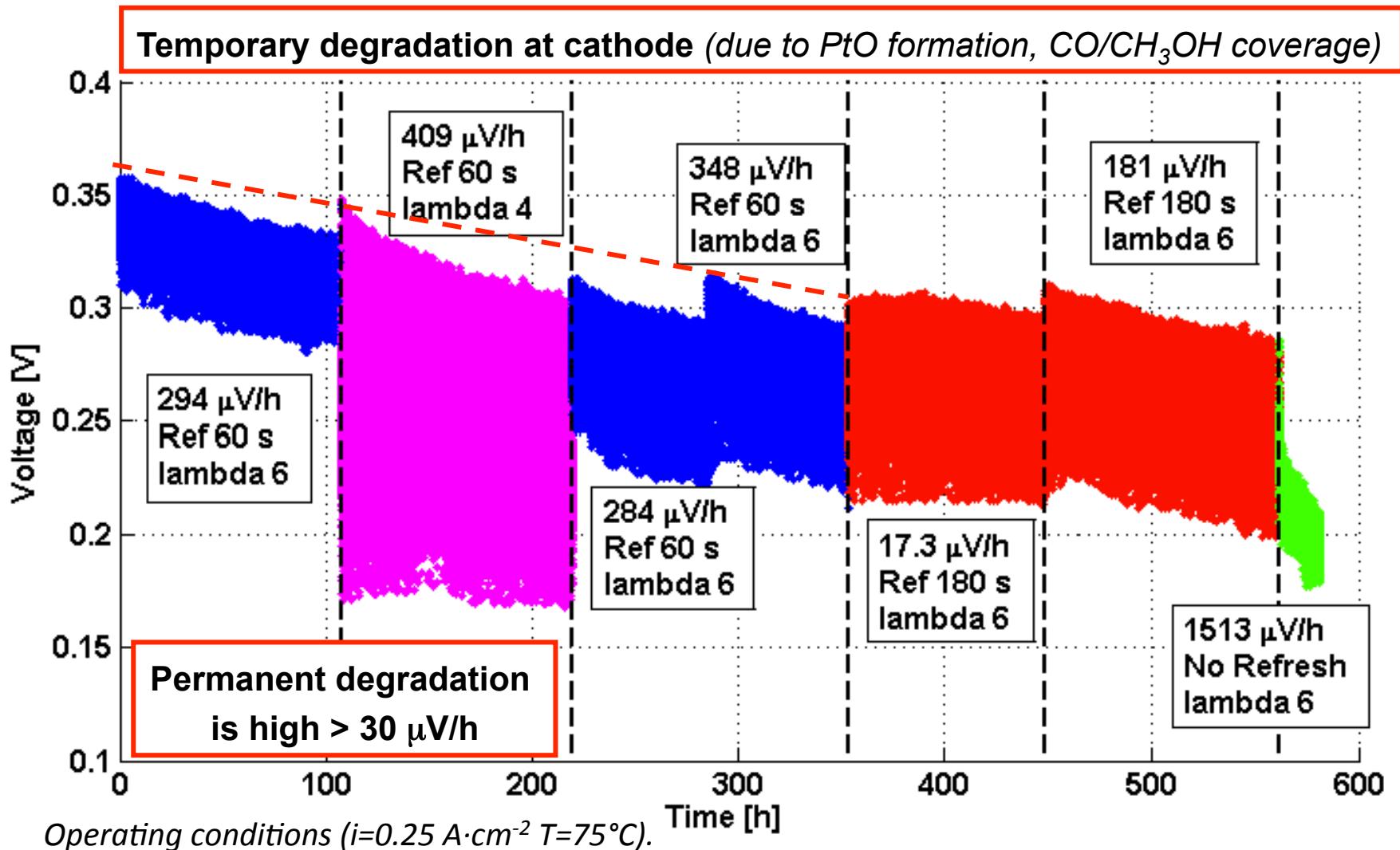


Effect on methanol crossover

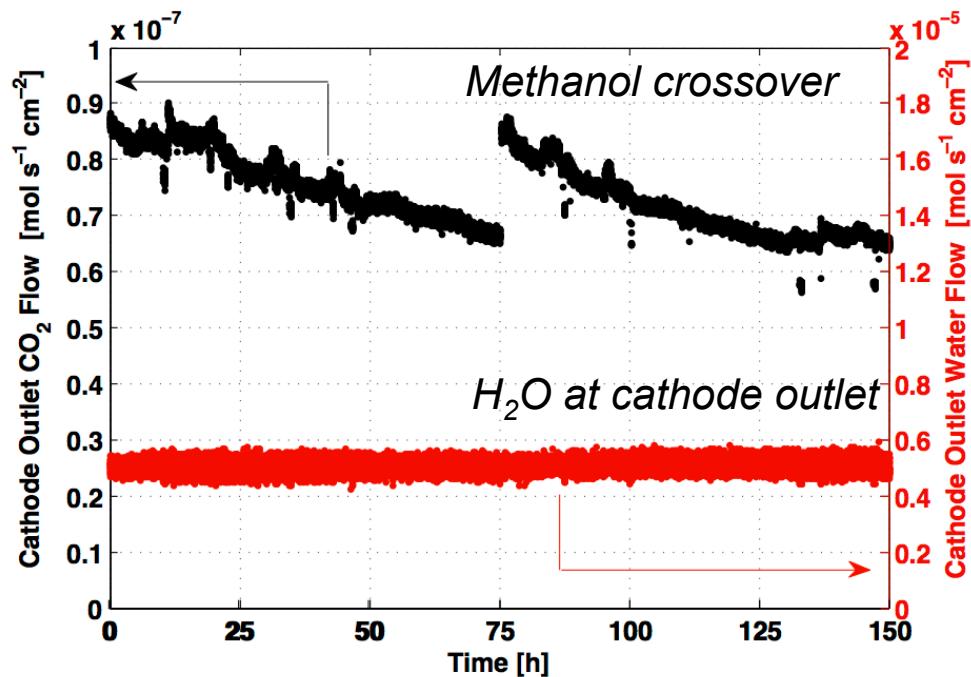
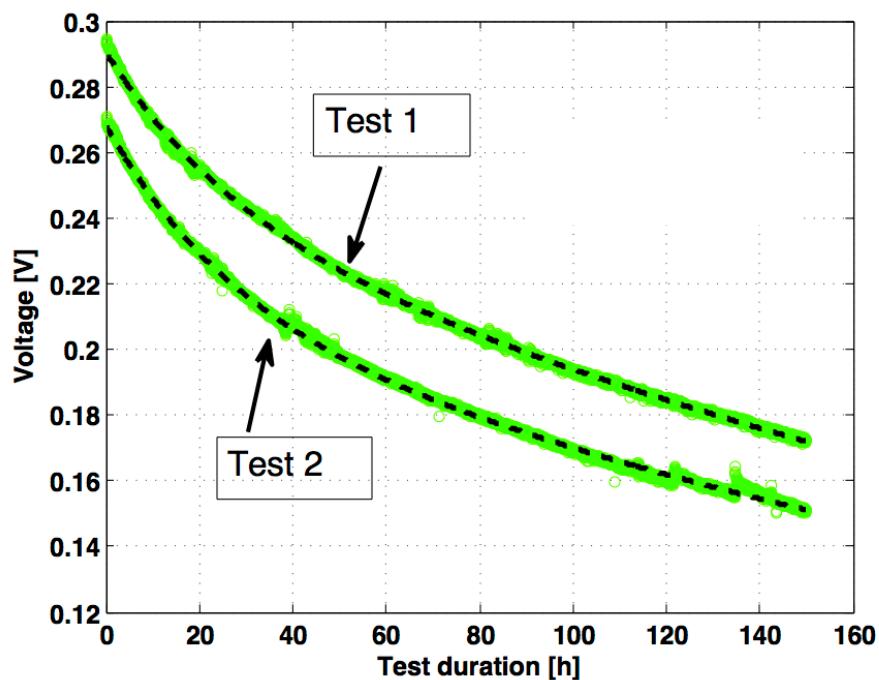
(due to diffusion, depends on CH_3OH concentration)

Analysis of overall DMFC degradation

Cycling operation: Cycles of 20 minutes + n minutes of REFRESH



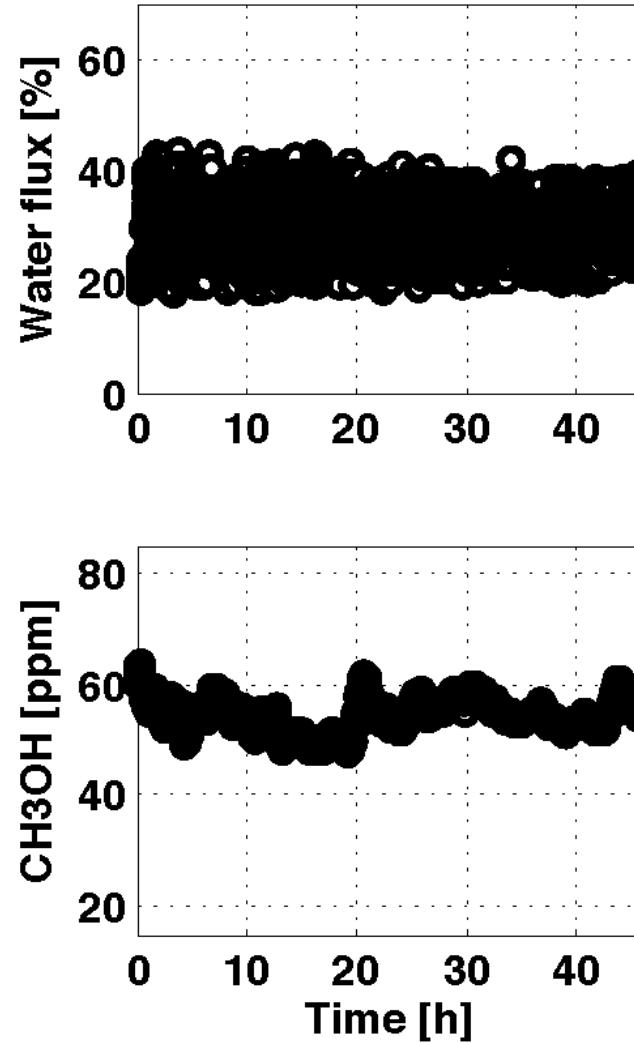
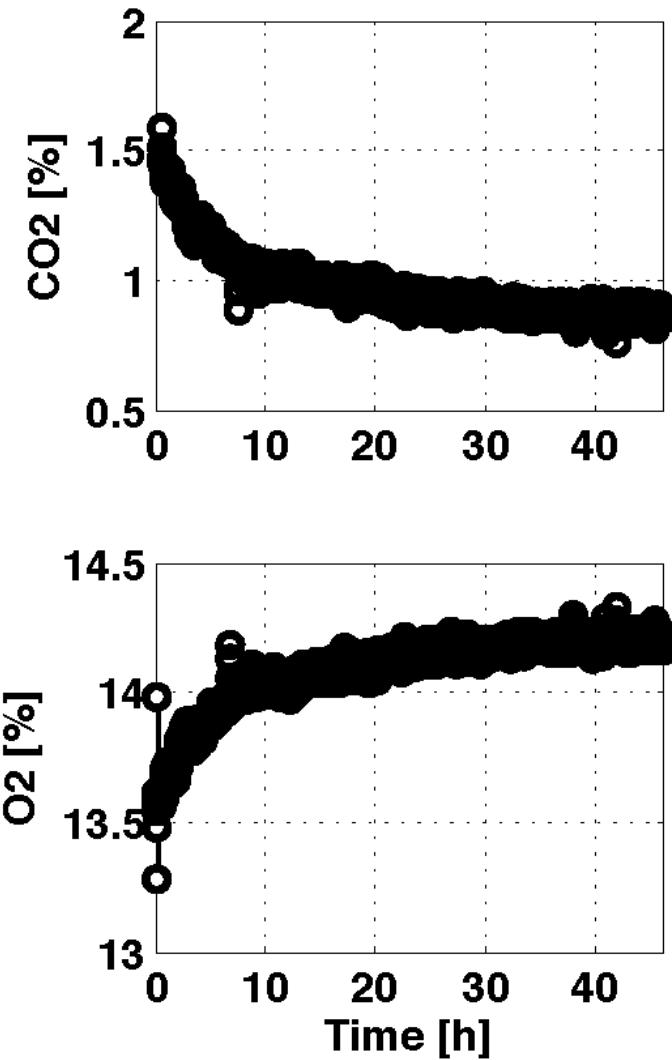
Methanol crossover analysis



Two possible explanations...

- During operation: reduction of CH_3OH concentration at the anode electrode
 - During refresh: gas-phase CO_2 removal, accumulation of CH_3OH and H_2O in the anode GDL
-
- During operation: reduction of cathode catalyst effectiveness versus methanol oxidation due to PtO formation, $\text{CO}/\text{CH}_3\text{OH}$ coverage, poisoning
 - During refresh: de-poisoning of cathode catalyst

Mass transport analysis



CO₂ reduction
O₂ increase
CH₃OH is constant



CH₃OH crossover is reduced



CH₃OH concentration at anode is reduced

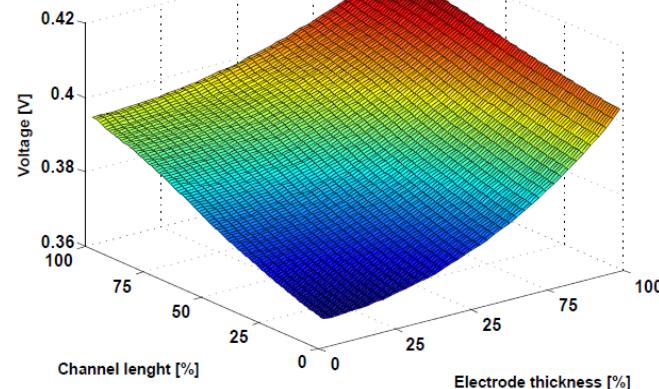
Modelling analysis: physical model of anode EIS

$$\frac{\partial i}{\partial x} = i_{*1} \cdot \left(\frac{C_{met}}{C_{ref}} \right)^\alpha \cdot (1 - \gamma_{CO}) \cdot e^{\left(\frac{\eta}{b_1} \right)} + i_{*2} \cdot C_{H_2O} \cdot \gamma_{CO} \cdot e^{\left(\frac{\eta}{b_2} \right)} + C_{dl} \cdot \frac{\partial \eta}{\partial t}$$

$$\frac{\partial \eta}{\partial x} = \frac{i}{\sigma_t}$$

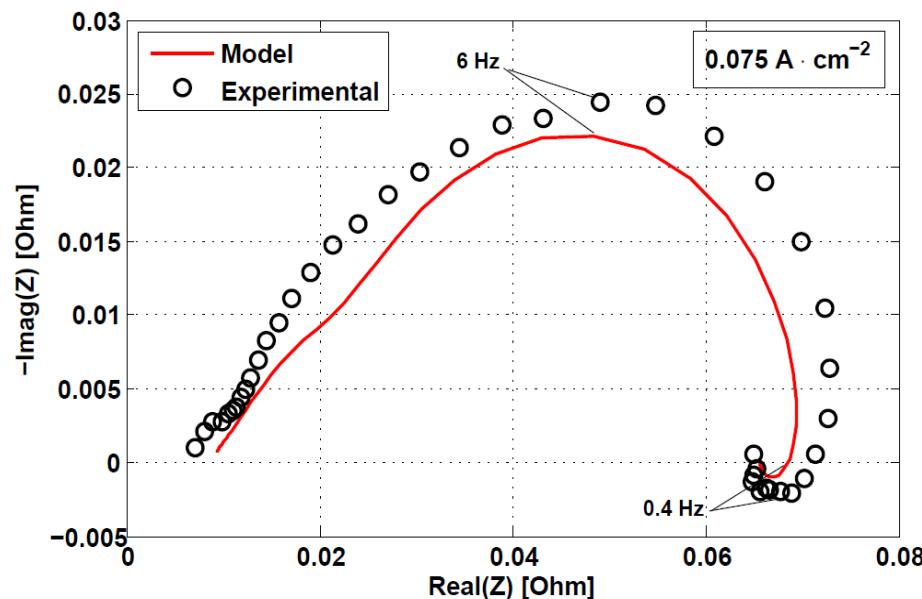
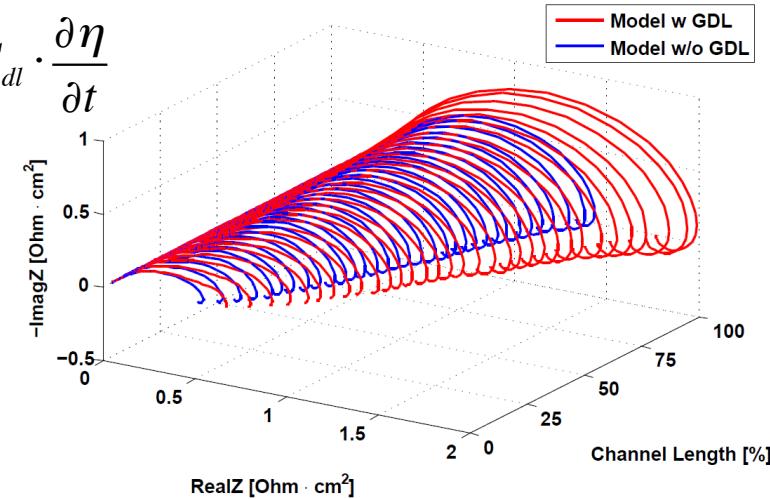
$$D \frac{\partial^2 C}{\partial x^2} = \varepsilon \cdot \frac{\partial C}{\partial t}$$

$$\Gamma \frac{\partial \gamma_{CO}}{\partial t} = \frac{i_{x1}}{4 \cdot F} - \frac{i_{x2}}{2 \cdot F}$$



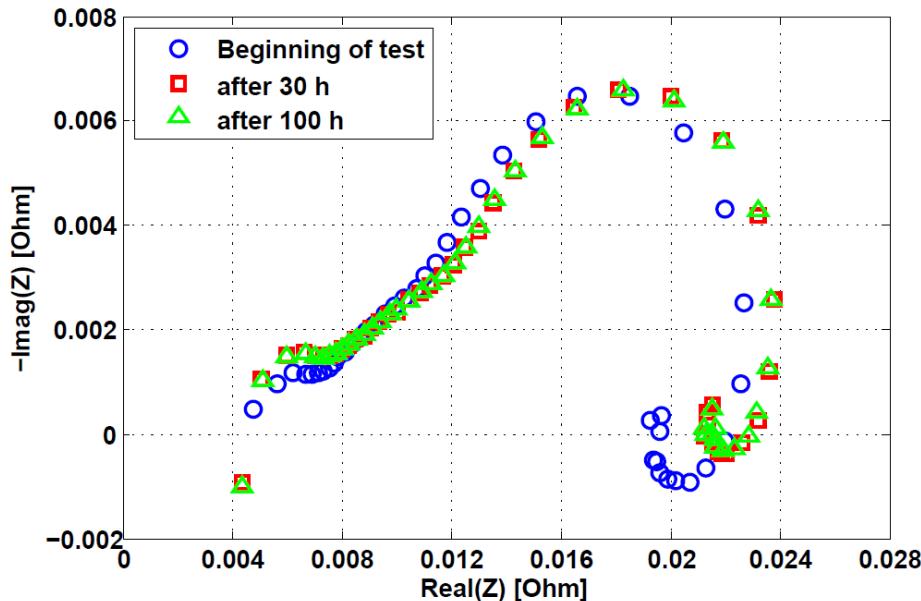
*Electrode model:
2D dynamic*

*GDL model:
2D dynamic two-phase
multi-mechanisms*



Modelling analysis: physical model of anode EIS

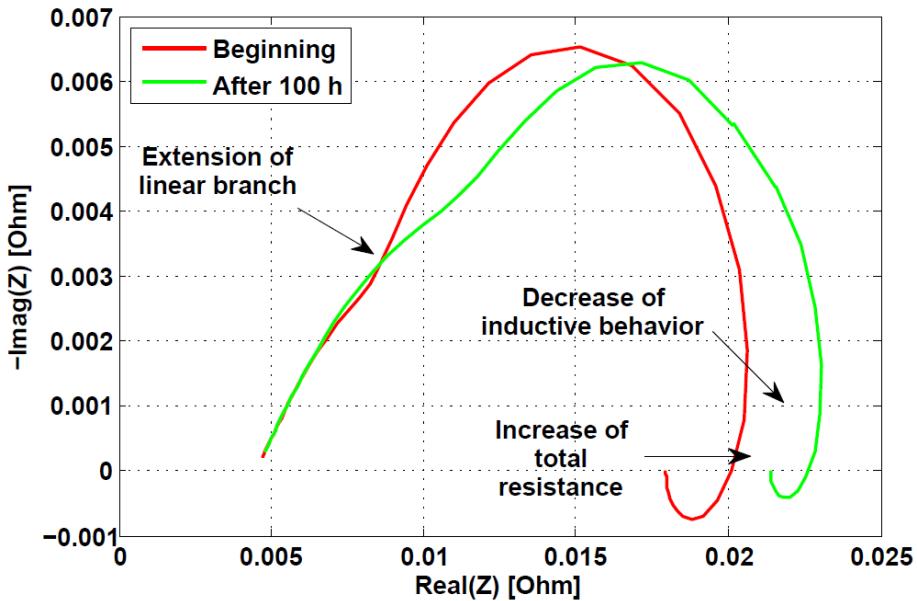
Model application to anode temporary degradation study.



Simulation of the proposed interpretation



Reduction of methanol concentration and proton conductivity in anode CL.



The model reproduces qualitatively the anode temporary degradation.



Model results confirm the proposed origin.

Conclusions

- Existence of a **temporary degradation at the anode**
- Suspected origin: **accumulation of gas-phase CO₂** and consumption of accumulated CH₃OH and H₂O in the GDL
- Confirmed by **mass transport** analysis and **modelling** analysis
- Anode temporary degradation is around **half of overall temporary degradation**
- **Temporary** degradation can be minimized by **refresh cycles**
- Permanent degradation is mainly associated to the **cathode electrode**
(to be confirmed by CV and post mortem analysis)

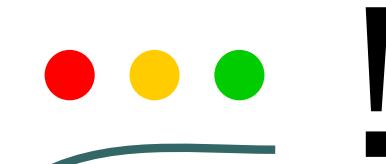
Conclusions

MEA

DMFC IRD

stationary (j / Cell Voltage) 0,15-0,25 A/cm²
 automotive (start/stop, air/N2, cycling Vmin-Vmax) none
 OCV (refresh cycles adopted)
 humidification (dry/humid; RH=0) none
 Temperature (high/low; T=75°C)

Main degradation mechanisms (irreversible/reversible) - rank from 1-6 confirmed/expected contribution to cell voltage decay (Anode/Cathode)		Further details - please specify further if possible
Contamination (A/C)	2 (C/A: reversible)	intermediate/compound at anode, PtO at cathode?
ECSA loss (A/C)	1 (C: high, A: low)	(CV/pol) particle growth/Pt dissolution or carbon corrosion?
increase electronic resistance (A/C)	6	negligible
membrane - increase of proton resistance	3	proton: very low (EIS) ; electron: very low (LSV)
membrane - increase in H ₂ X-over	5	negligible (LSV+methanol crossover)
flooding / loss of hydrophobicity (A/C)	4 (A/C: probable)	evident in stack, no evidence in MEA water/methanol transport



Premium Act

The research leading to these results has received funding from European Union's Seventh Framework Programme (FP7/2007-2013) for the Fuel Cells and Hydrogen Joint Technology Initiative under grant agreement n° 256776.