PREMIUM ACT

PEMFC
Degradation under load cycles with reformate fuel

Sylvie Escribano (CEA)

FCH-JU Projects workshop - PEMFC Degradation
Sintef/OSLO – 3rd April 2013

Premium Act

PREdictive Modelling for Innovative Unit Management and ACcelerated Testing procedures of PEFC

(256776)

Sylvie Escribano
CEA

Premium Act

Premium Act/1

1. project & partnership description

Improvement of stationary PEFC systems durability (40000h required!)

→ A reliable method to predict system lifetime, benchmark components and improve operating strategies

IRD
WP1 - Specifications

IRD
WP2 – Experiments under real operating conditions

DLR
WP3 – Quantification of components degradation

POLIMI
WP5 – Lifetime prediction methodology

CEA
WP4 – Predictive Modelling

CEA
WP6 - Dissemination

CEA
WP7 - Management

Premium Act/2

1. Project objectives & Approach

- **Expected achievements**

→ **Operating strategies,** enhancing lifetime of given MEAs in given stack and system

→ **Design of a lifetime prediction methodology based on coupled modelling and composite accelerated tests experiments** (ranking of selected MEAs in real conditions and then following accelerated tests)

- **Technical aspects**

Two fuel cell stack technologies for stationary power applications:

→ DMFC and H2 reformate PEMFC CHP systems

Experimental investigation

→ Tools to quantify & correlate performance and components degradation to operating conditions

Multi-physics modelling

→ Tools to combine degradation phenomena and analyse their global impact on durability

WP1 – Specifications
(from systems)

WP2 – Experiments under real operating conditions
(systems, stacks & single cell real ageing tests)

WP3 – Quantification of components degradation
(*Ex-situ* characterizations, locally resolved analysis)

WP4 – Predictive Modelling
mechanistic model
+ MEA & cell model

WP5 – Lifetime prediction methodology
(SC specific tests: coupling, validation, Acct)

Outline

- Introduction of objectives and components

- Single cells performance and durability tests
- Stack durability tests
  - **Load cycles**
  - **Voltage losses**
  - **Electrochemical diagnostics**
  - **Focus on fuel composition effect**

- Ex-situ investigations

Performance and ageing tests

- **Premium Act tests objectives (experimental WP tasks)**
  - Tests following applications specifications
  - Specific tests representative of critical operating conditions
  - Sensitivity studies on local & coupling effects
  - Development of specific accelerated tests

- **IRD MEAs**

Description	Product ID	Catalyst loading
Anode GDL	Sigracet 35DC	
Anode Catalyst	Hispec 10000	0.3 mg PtRu/cm^2
Membrane	Nafion® XL100	
Cathode Catalyst	Hispec 9100	0.5 mg Pt/cm^2
Cathode GDL	Sigracet 35DC	

- **Single cells 25cm²**
- **IRD Stack tests at CEA**
  - 10 cells stack – 150 cm²

Performance and ageing tests

- **Performance tests**
  - IRD - 70°C, 100%HR, Patm – pure H2
  - 75°C, 100/50%HR, 1,2 bars – pure H2
  - 75°C, 100/50%HR, 1,2 bars – Reformate

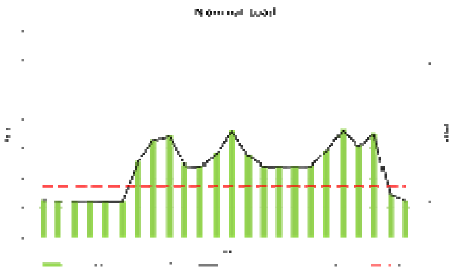
- **Ageing tests – Load cycles**
  - Pure H2 (→ reference test)
  - Reformate: 26ppm then 50ppm CO (extreme case)
  - Various fuel composition : effect of CO content during short term cycling tests

Durability tests in single cells

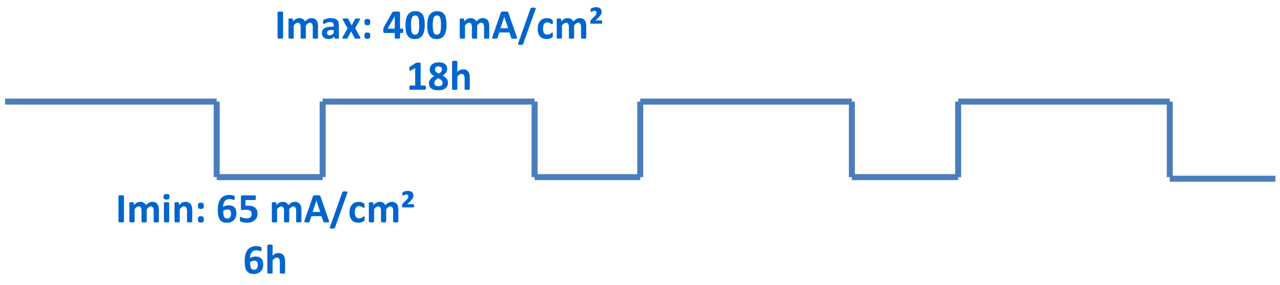
- Durability tests
  - Representative ageing tests in conditions based on systems nominal specifications
  - Then, other conditions & cycling modes

Durability tests in single cells

- Cycling tests



Premium Act reference protocol



St anode : 1, 2 - 1,3 /St cathode: 2
P_{anode}=$P_{cathode}$ 1,2 bar
Anode : RH 90-100%
Cathode : RH 40-50%
T : 65 - 75°C

Reformate: average composition
H_2: 75%
CO_2: 24%
CH_4: 1%
5 < CO < 50 ppm

Objective : identification of accelerating parameters (incl. fuel composition, operating conditions, cycles features)

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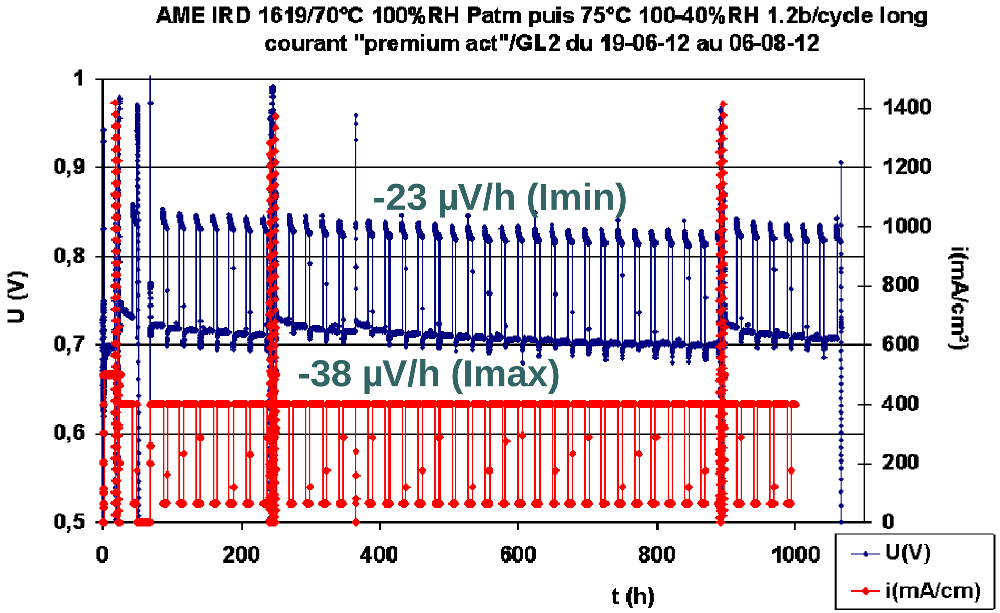
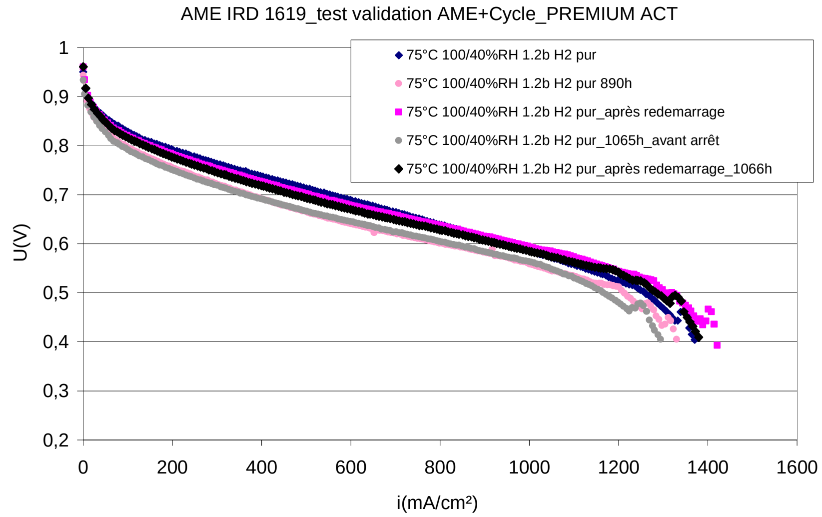
New Energy World JTI

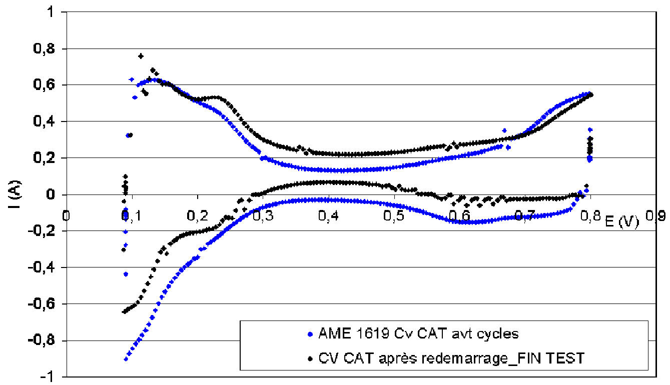
Durability tests in single cells

Cycling test with pure H_2





→ important part of reversible degradation



→ possible cross-over increase

→ catalyst or catalyst layer operation modifications

→ Ex-situ analyses to be conducted (check µstructure and comp. with reformate operation)

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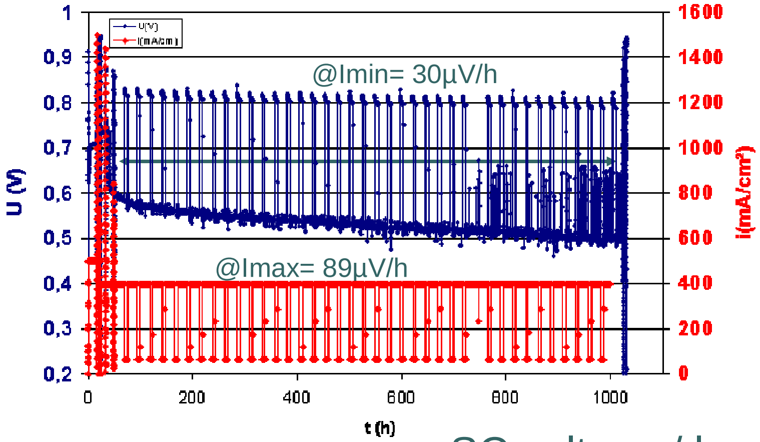
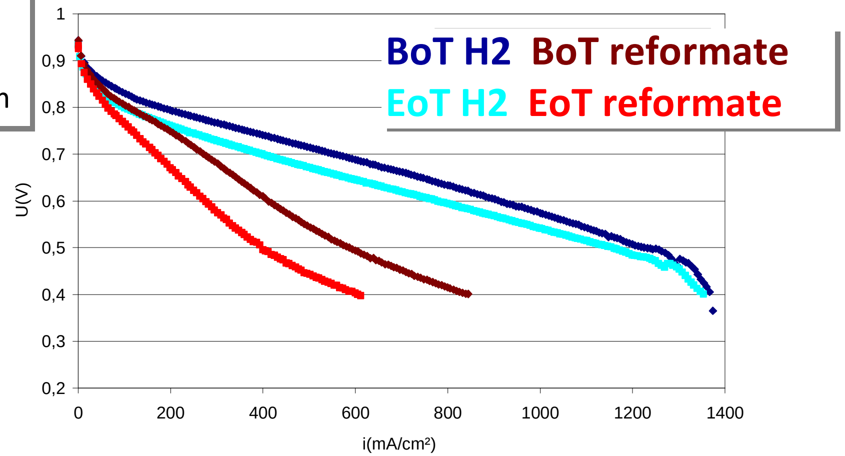
Durability tests in single cells

reminder

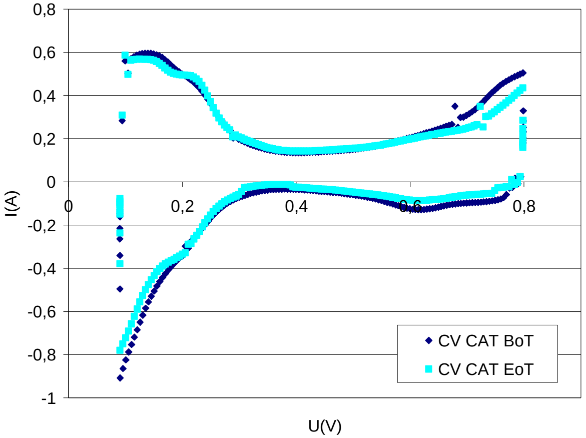
Cycling test with reformate

H2: 79%
CO_2: 20%
CH_4: 1,3%
CO: 26 ppm

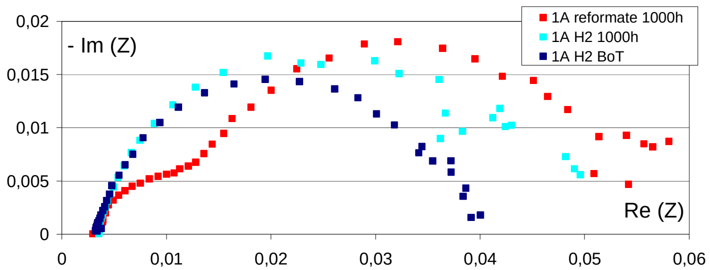




SC voltage / load cycles ➔ high performance degradation rate



➔ but low permanent degradation of components properties (EoT diagnostics)



Maybe some active layer modification
(to be identified)

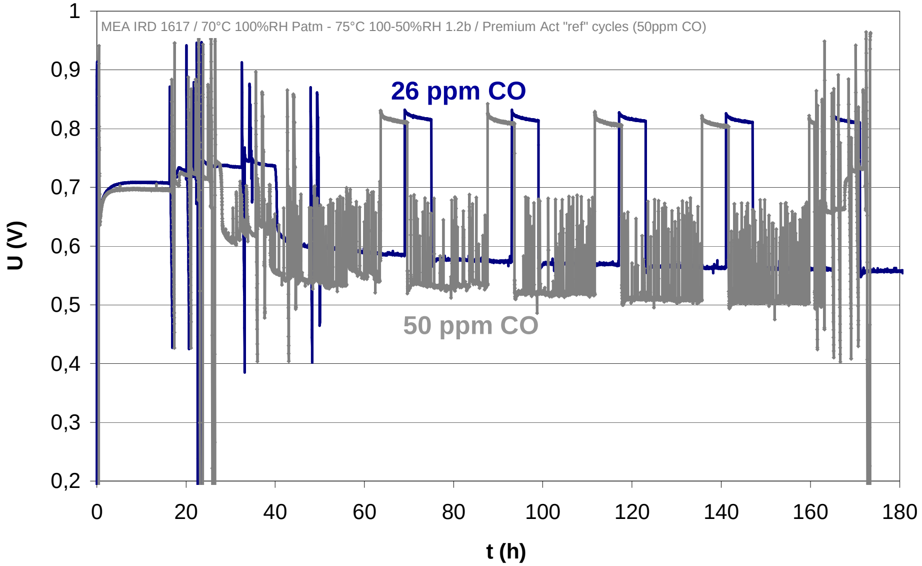
Cross Over: not enough membrane damage to explain voltage instabilities

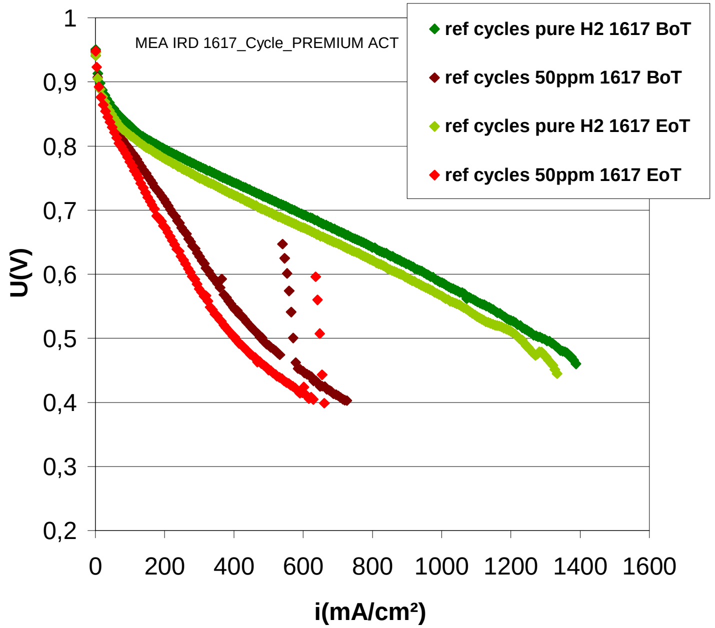
Ex-situ analyses conducted → To be completed for comp. with pure H2 and more CO

Sensitivity analysis of PEMFC degradation

Effect of high [CO]

H_2	78.99 %
CO_2	19.7 %
CH_4	1.3 %
CO	50 ppm





Performance loss but no dramatic increment of degradation (~ slope)

Self-cleaning oscillations related to full CO coverage

➔ Study of [CO] on performance degradation & as accelerating factor

Effect of [CO]: current tests on SC and stack

- Test on single cell:
  - reference load cycles
  - [CO] = 0, 10, 20, 50ppm

  → Effect on the cell voltage value, decrease, and slope over ~200 hours

  → Study of 50 ppm as accelerating factor

- Test on IRD stack:
  - reference load cycles
  - [CO] = 0, 10, 10+Air bleed, 5, *(planned 20+Air bleed, 20ppm)*

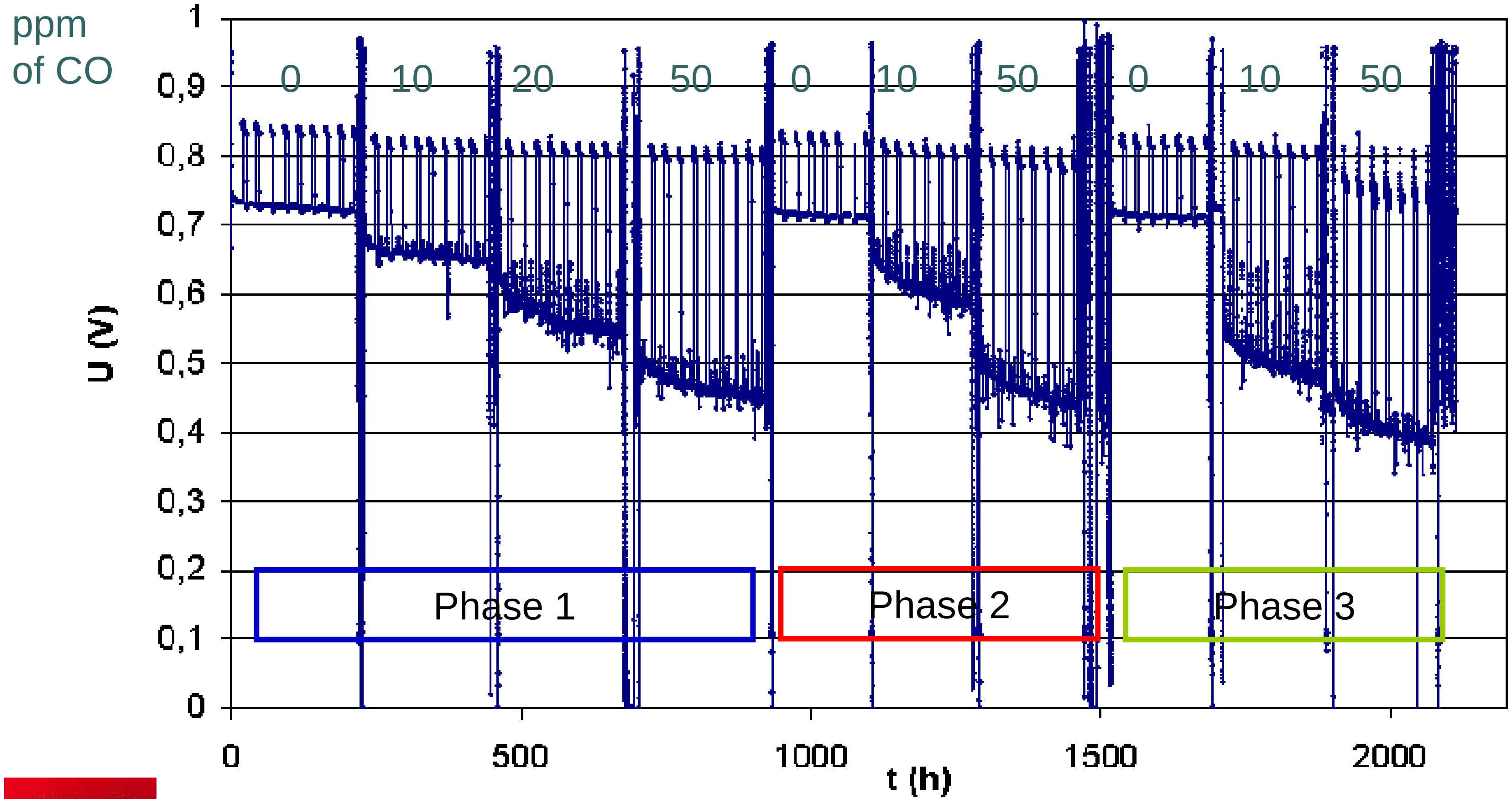
  → Effect on the 10 cells voltage values, decrease, and slope over ~200 hours

  → *Study of 20 ppm or study of T as accelerating factor*

SC test - CO concentration effect

Cycling test → Accelerating effect of high CO concentrations?

Compared effect for pure H2 and 10ppm CO case



SC test - CO concentration effect

Cycling test → Accelerating effect of high CO concentrations?

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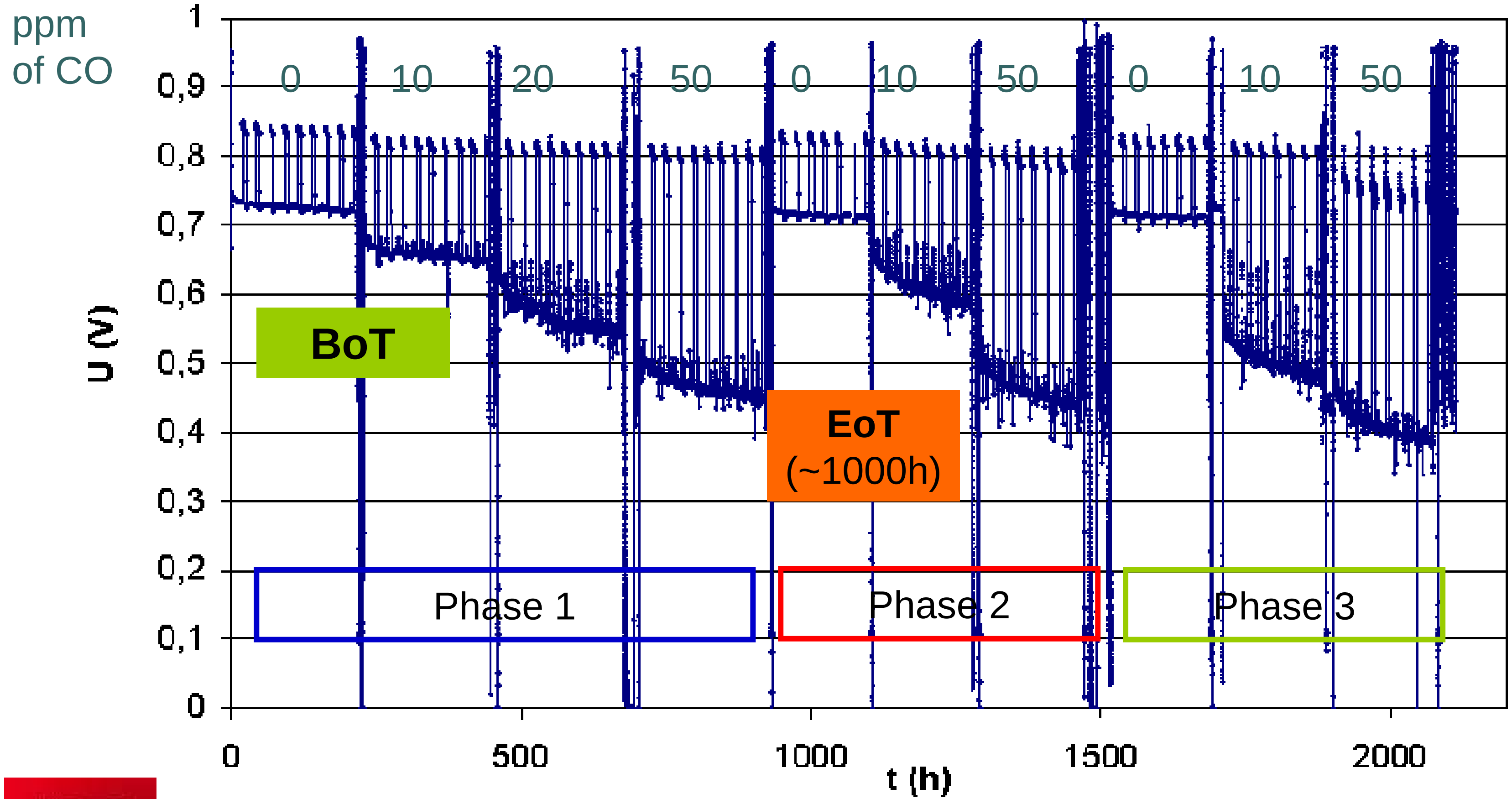
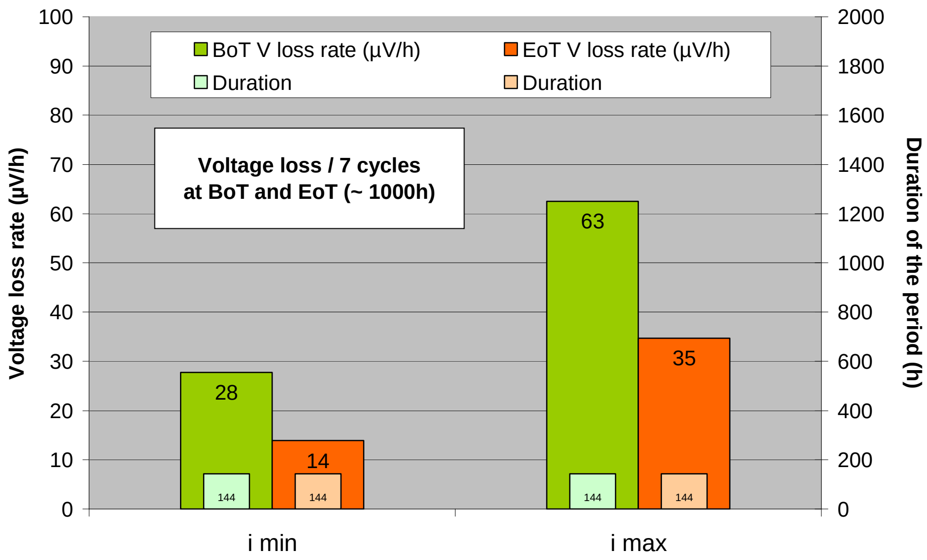
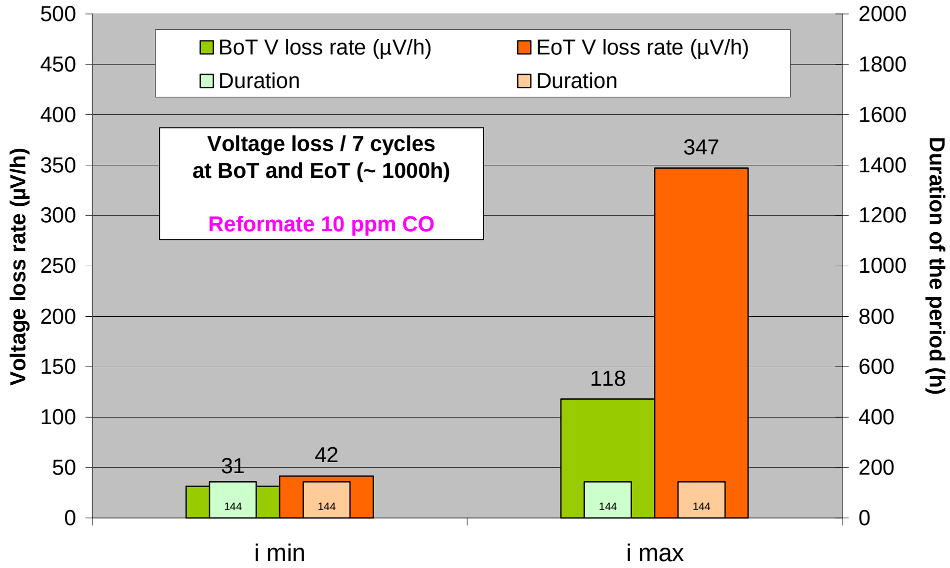


SC test - CO concentration effect

Pure H2



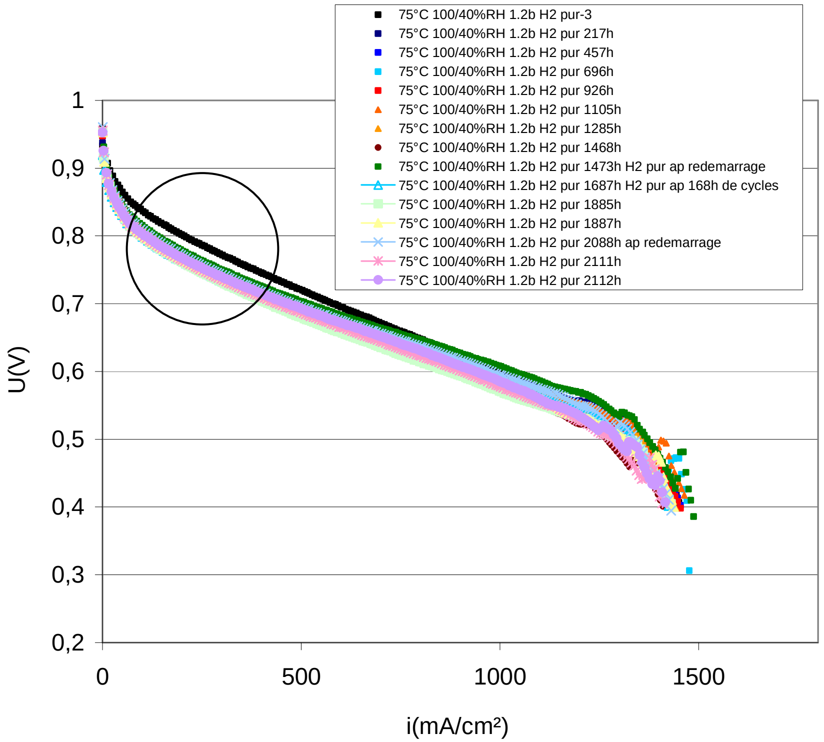
Reformate with 10 ppm CO



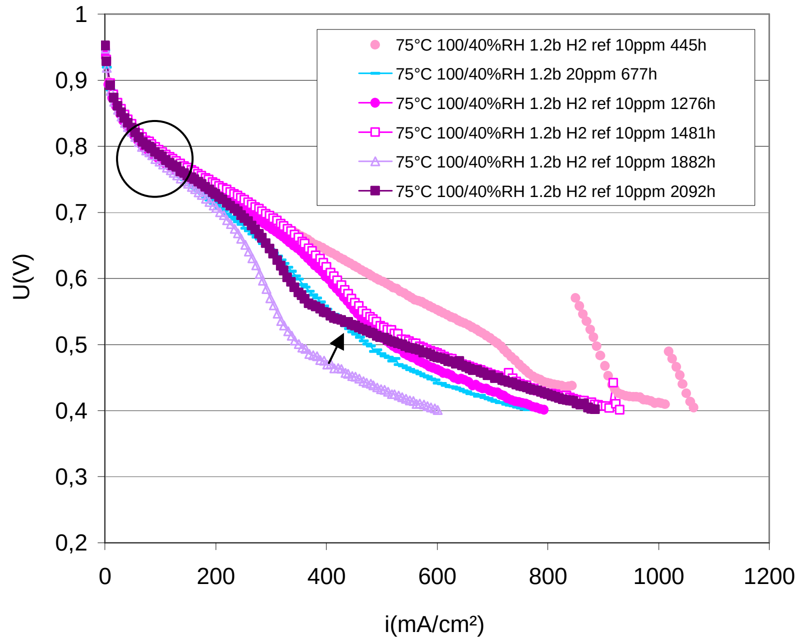
BoT

EoT (~1000h)

SC test - CO concentration effect



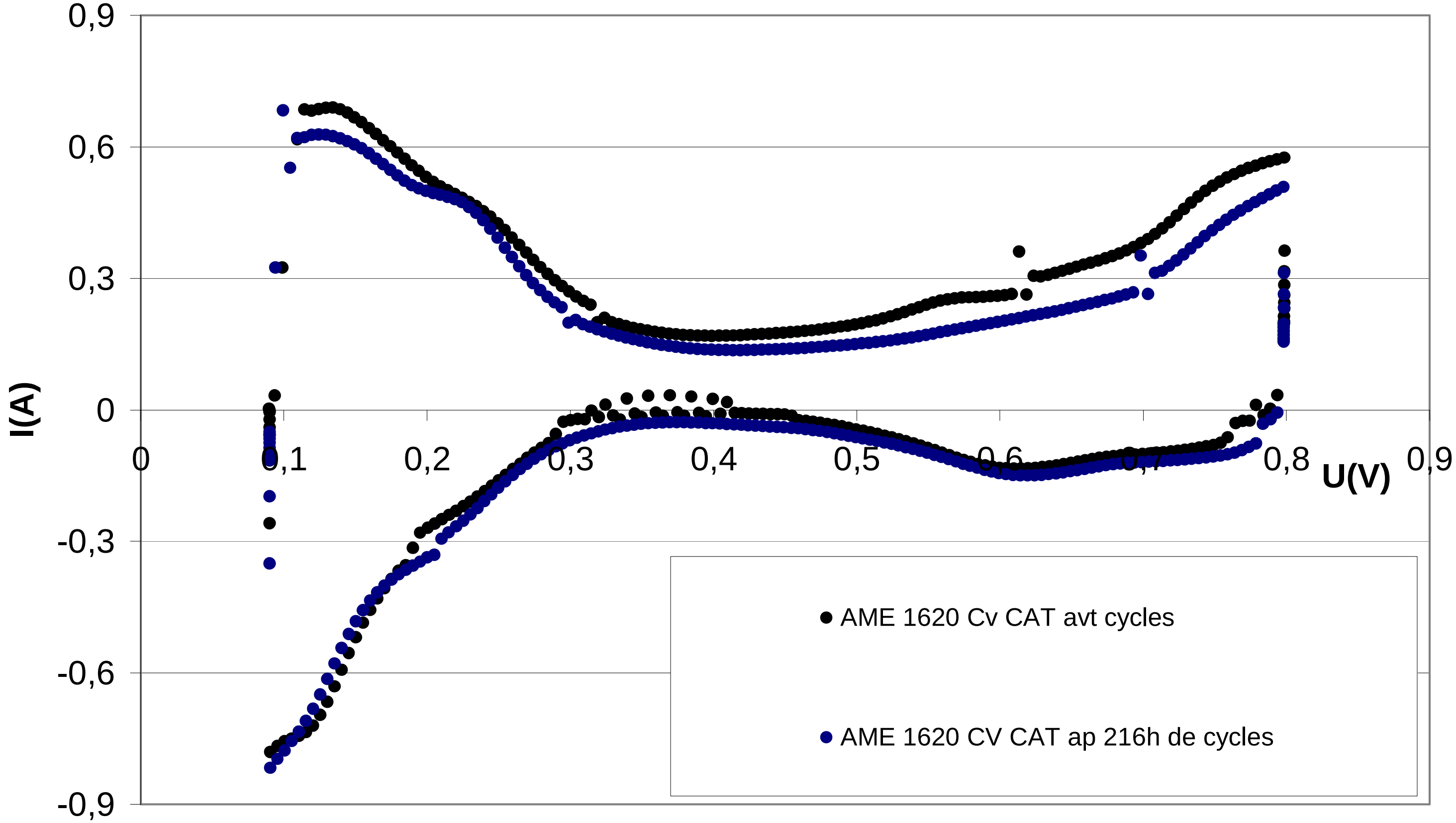
Losses after cycles under pure H2



Additional losses after cycles under 50ppm

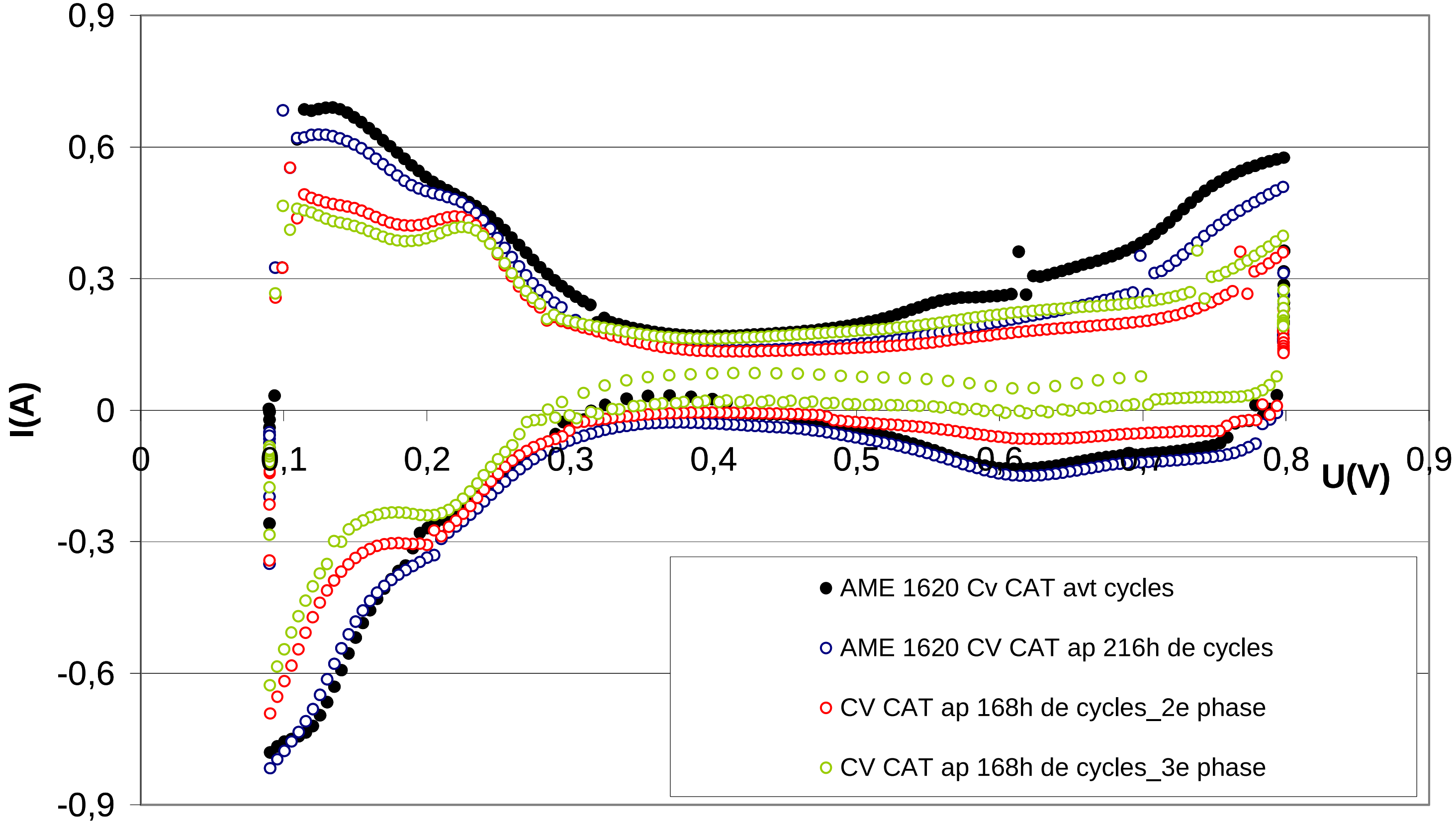
SC test - CO concentration effect

- CV at BoT & after 1st cycles under pure H2



SC test - CO concentration effect

- CV after pure H2



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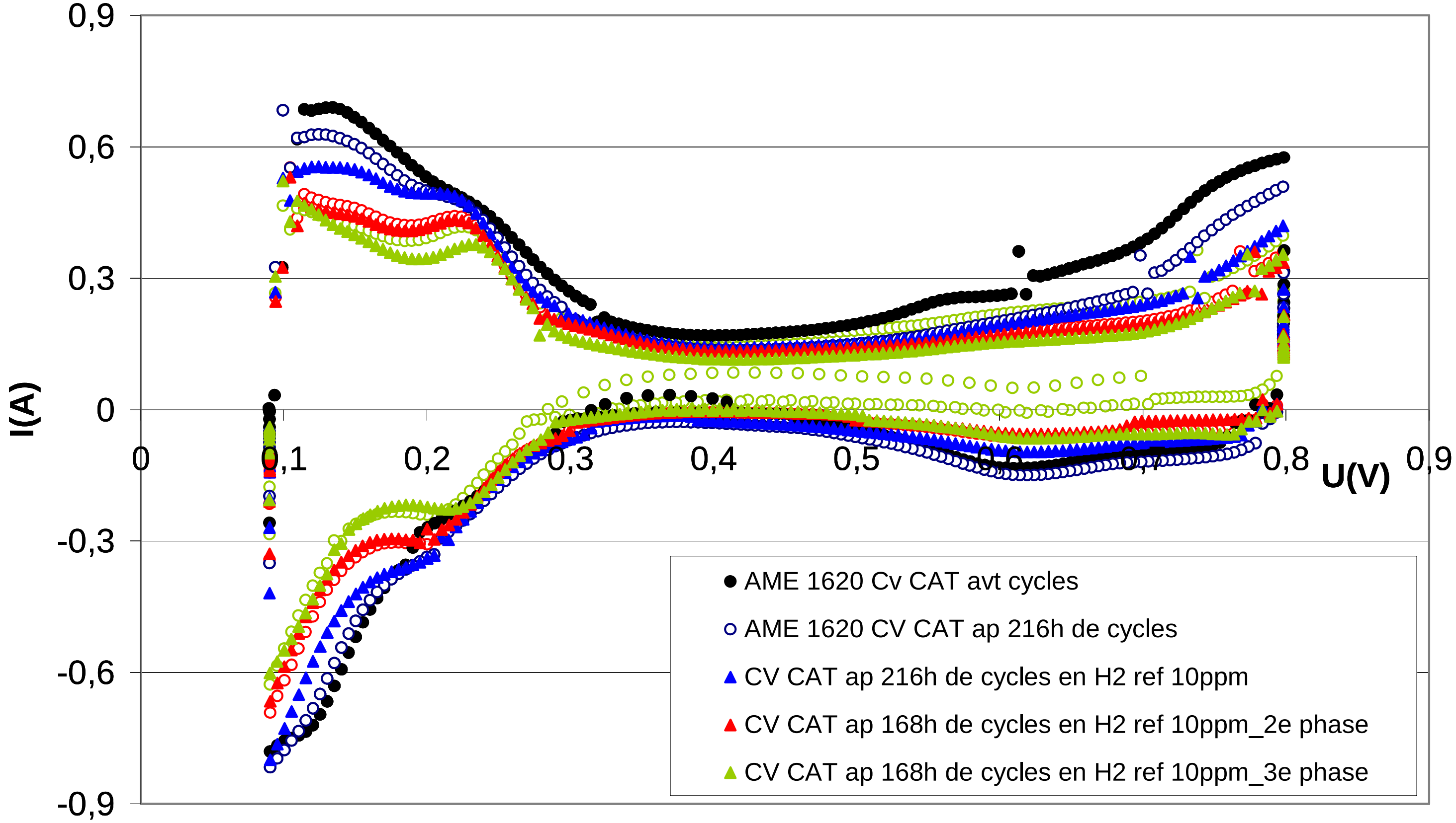
New Energy World JTI

SC test - CO concentration effect

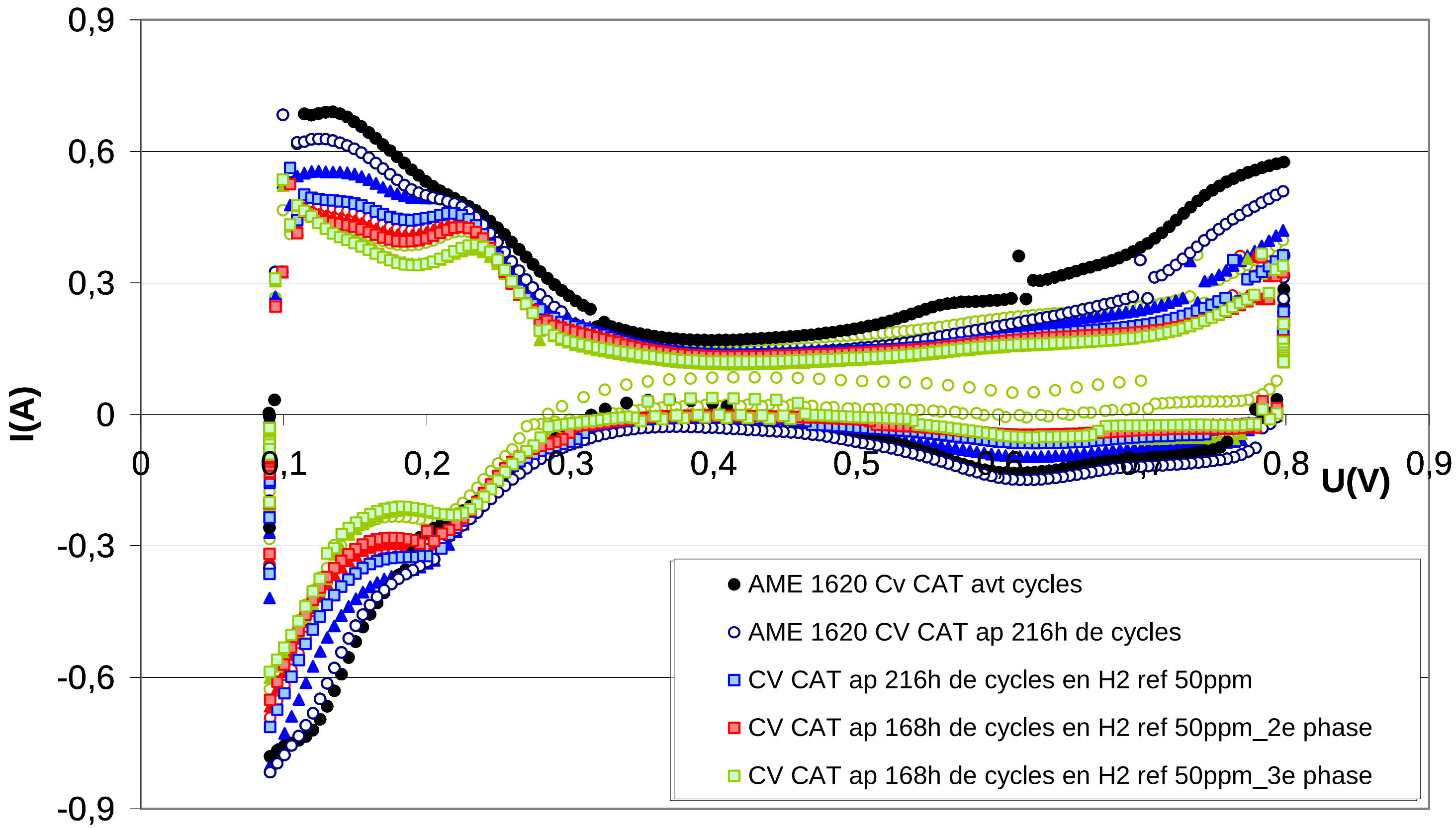
- CV after pure H2 & 10 ppm



cea

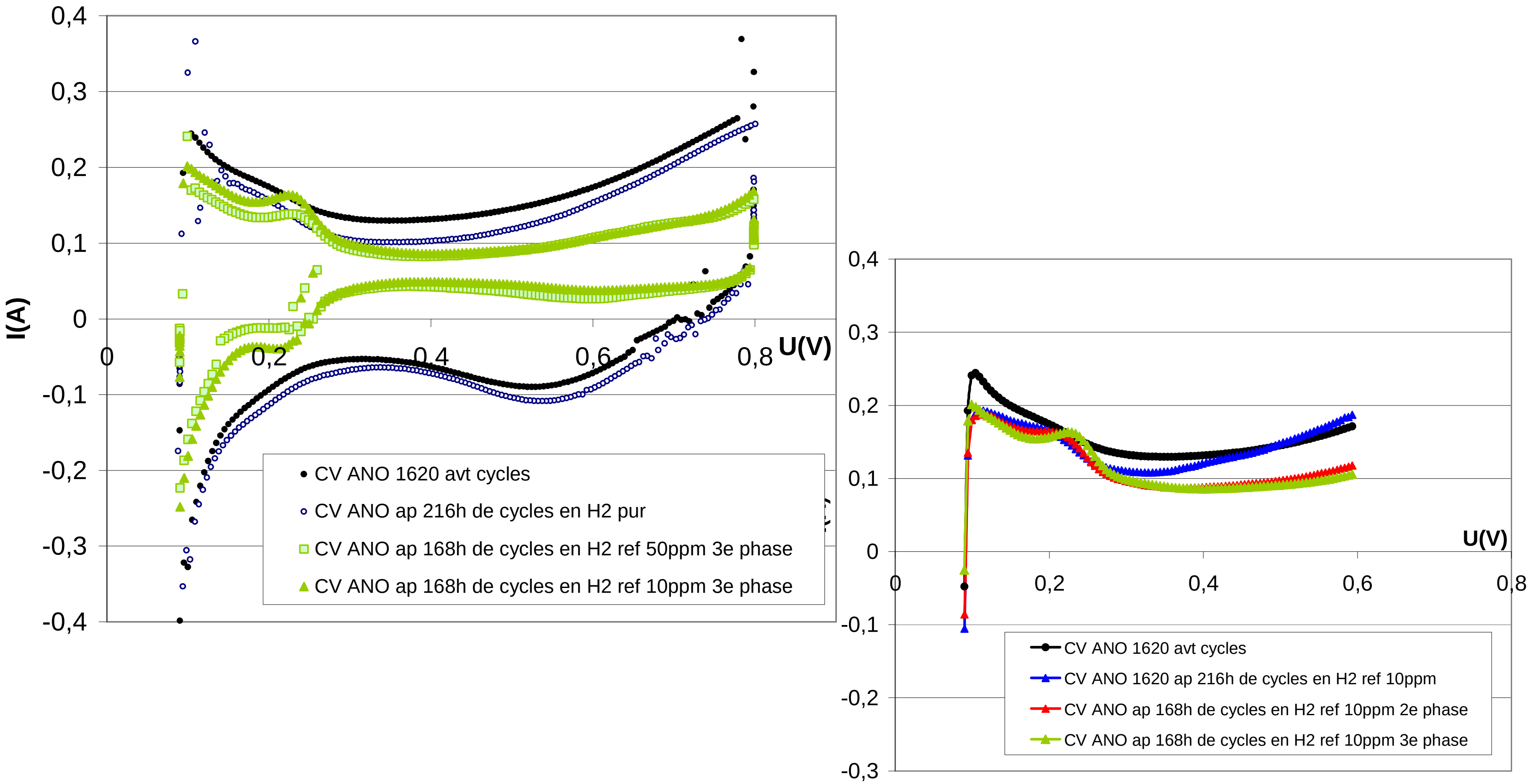
SC test - CO concentration effect

- CV after pure H2 & 10 ppm & 50 ppm



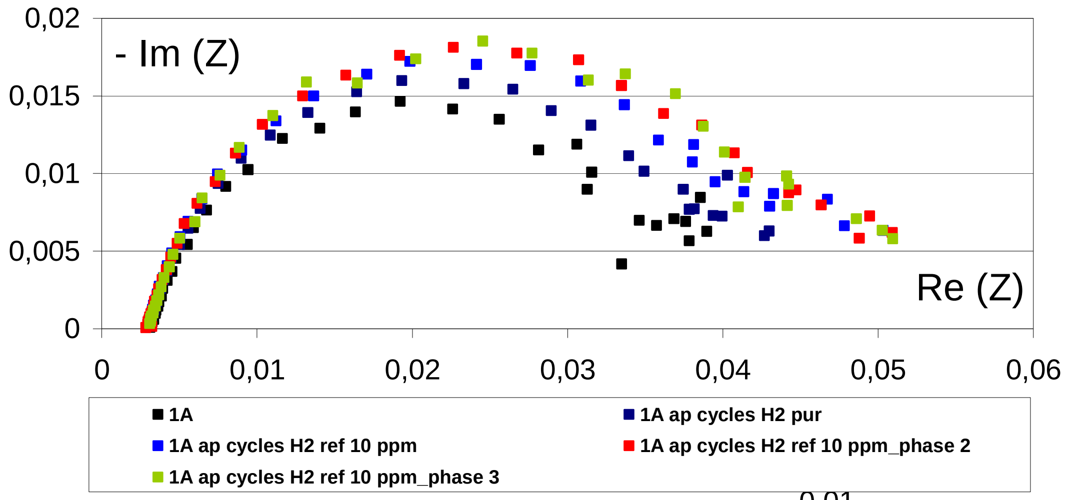
SC test - CO concentration effect

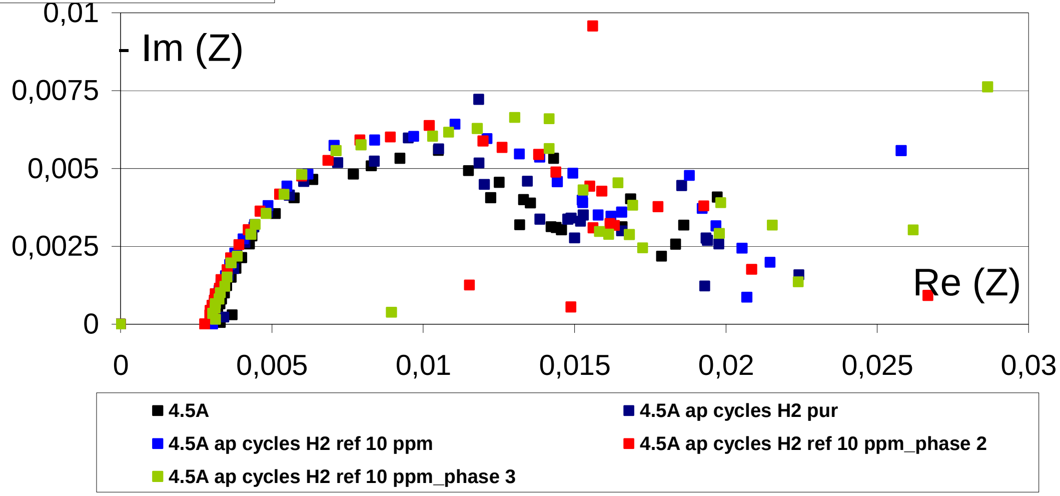
- CV after pure H2 & 10 ppm & 50 ppm



SC test - CO concentration effect

- EIS pure H2

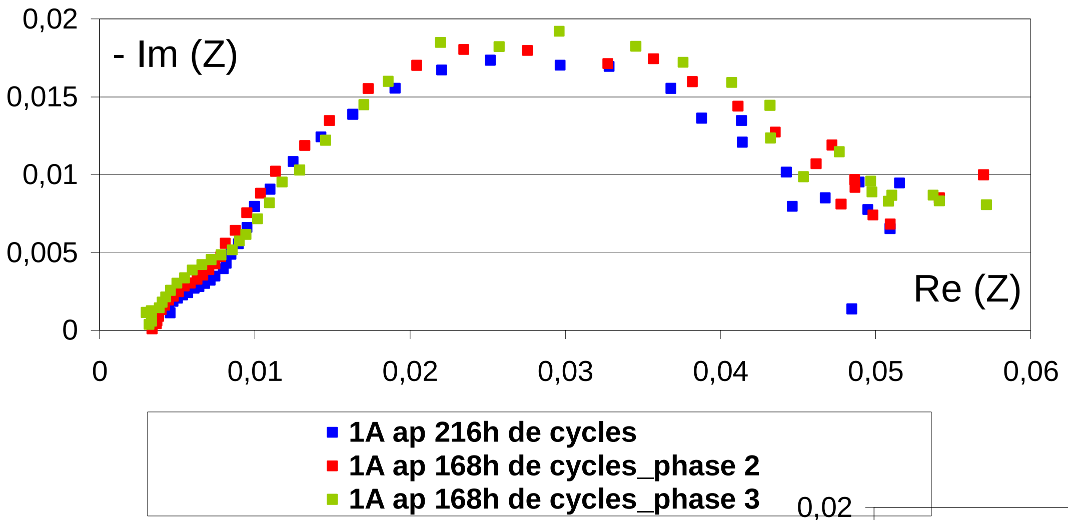




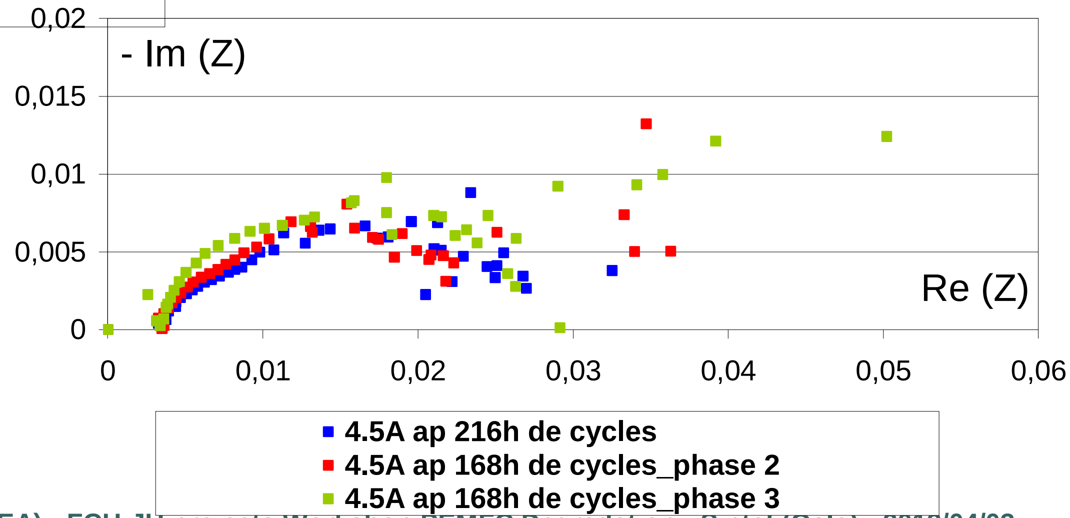
Consistent with i-V curves

SC test - CO concentration effect

- EIS 10 ppm

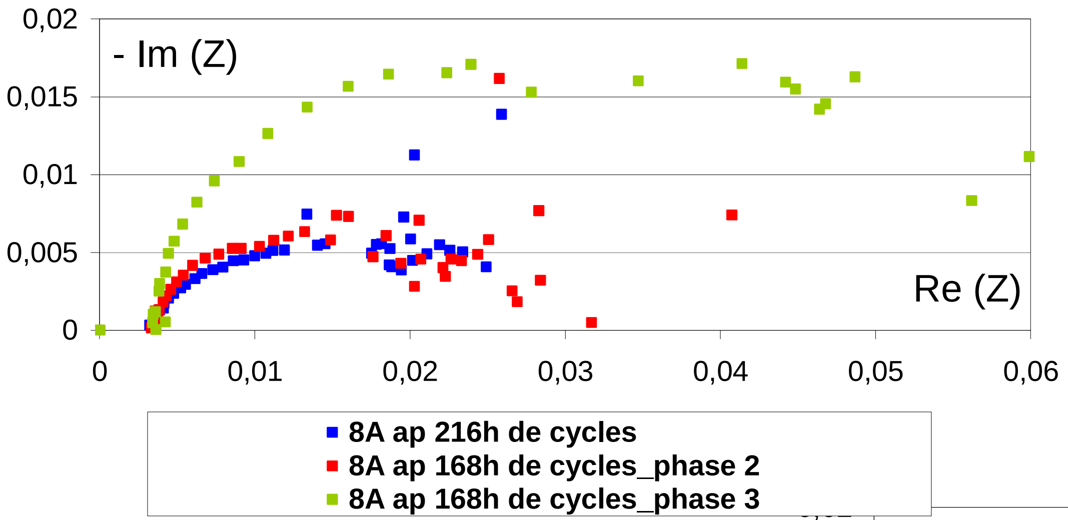


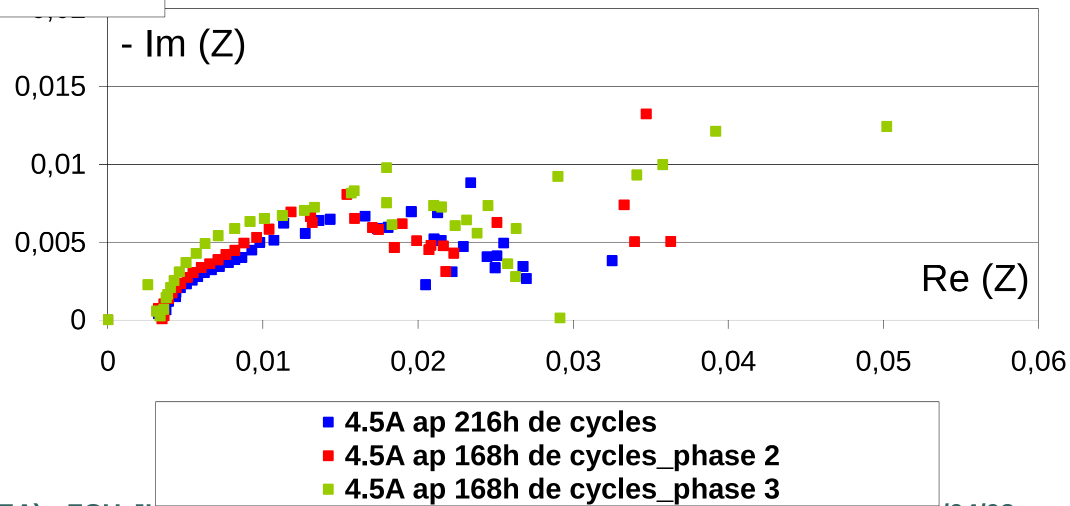
Anode activity degradation



SC test - CO concentration effect

- EIS 10 ppm





SC test - CO concentration effect

• Main causes for performance degradation

Active layers & Catalyst

Size increase cathode side

In addition surface structure modifications anode side

→ *to be checked with local post-test analyses*

Fuel composition effect – PEMFC stack

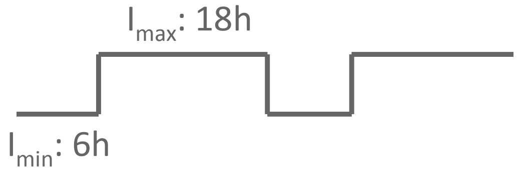
IRD 10 cells stack

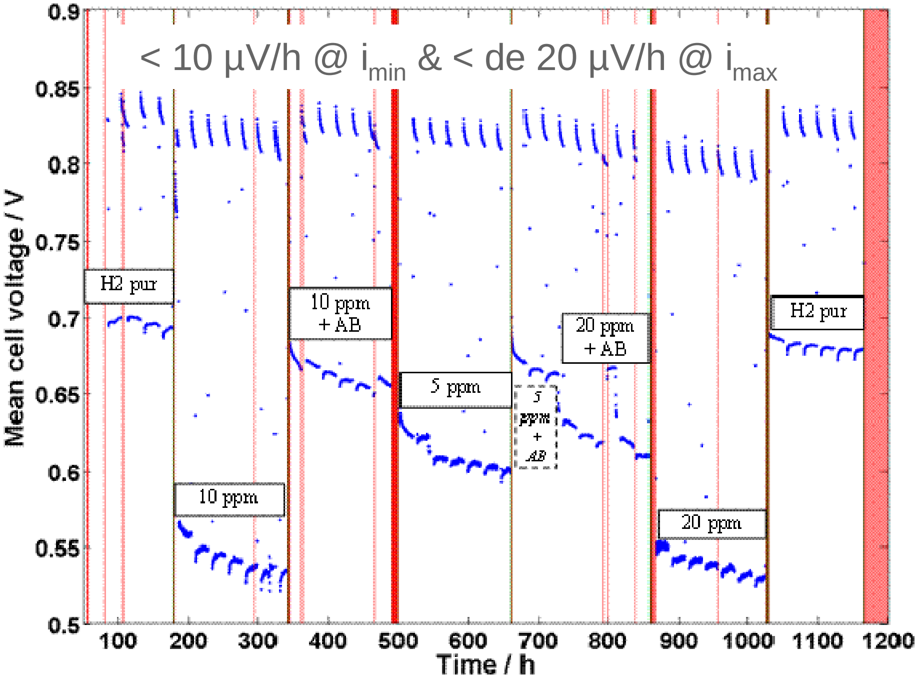
- **CEA test bench for synthetic reformate H_2**
  - **1kW electrical power**
  - **Stack temperature : up to 90°C**
  - **Gas mixture available at the anode side:**
    - **Pure H_2**
    - **Pure CO_2**
    - **H_4 + CO** (2000 ppm)
    - **Air + CO** (2500 ppm) **for air bleeding tests**
  - **Air: 0-100%RH by vapor injection**
  - **Temperature, Pressure and RH measured at the stack inlet/outlet**
  - **Open-end configuration**

Fuel composition effect – PEMFC stack

- **Stack tests with different fuel compositions**
  - **Durability tests**

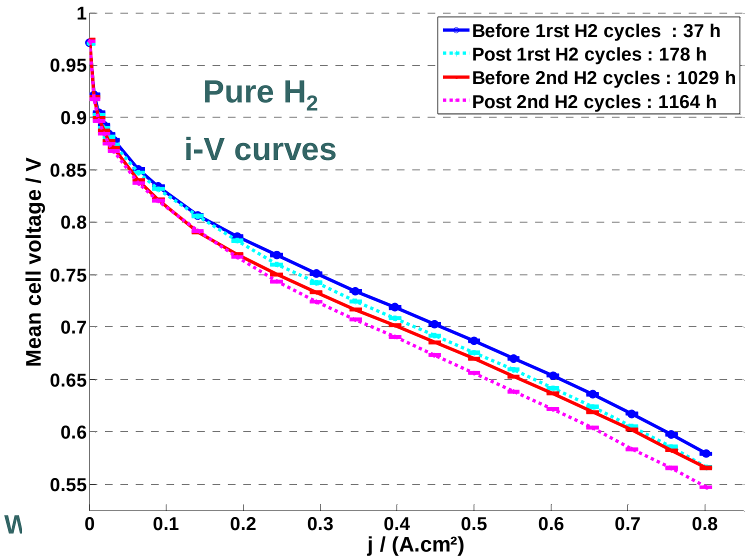
Current cycles with reformate (10 cells)





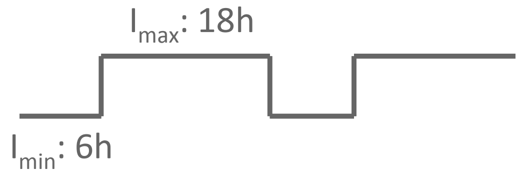
T = 65°C - RH90%/50% (fuel/air)
P = 1,2 bar, St1,5/2
75%H_2 + 24% CO_2 + [CO + (CH4 or Air)]

BoT and EoT



Fuel composition effect – PEMFC stack

- **Stack tests with different fuel compositions**



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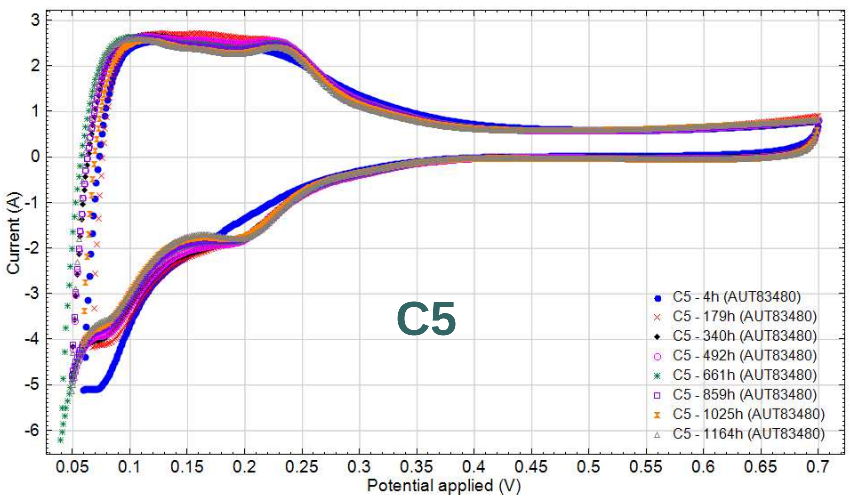
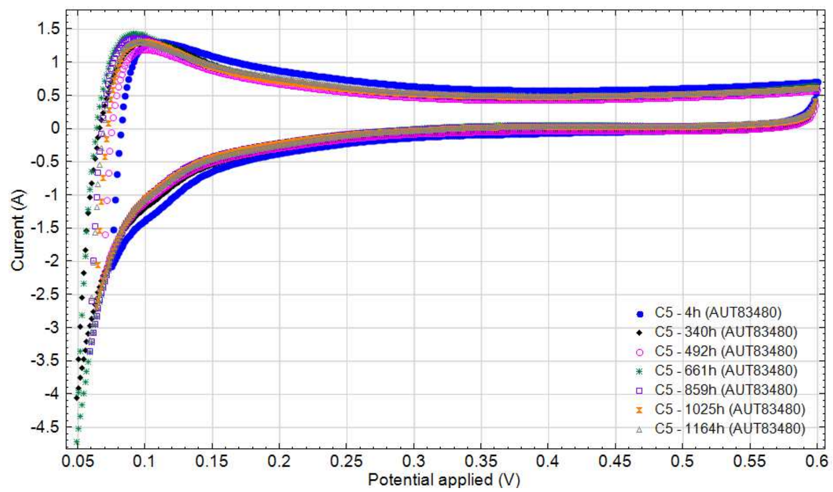
CV - Cathodes

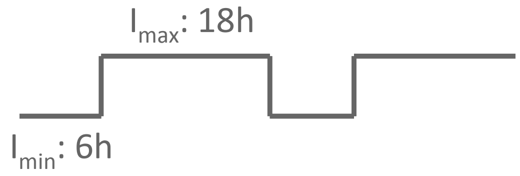


CV - Anodes



Fuel composition effect – PEMFC stack

- **Stack tests with different fuel compositions**



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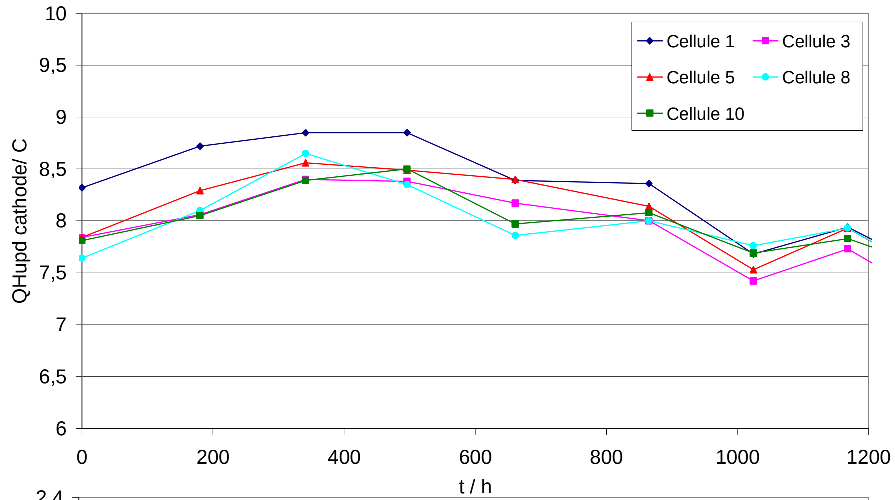
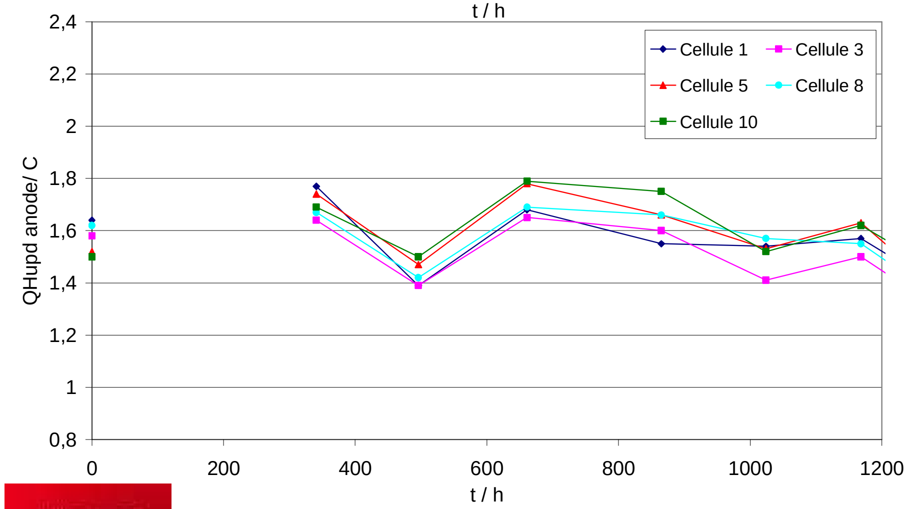
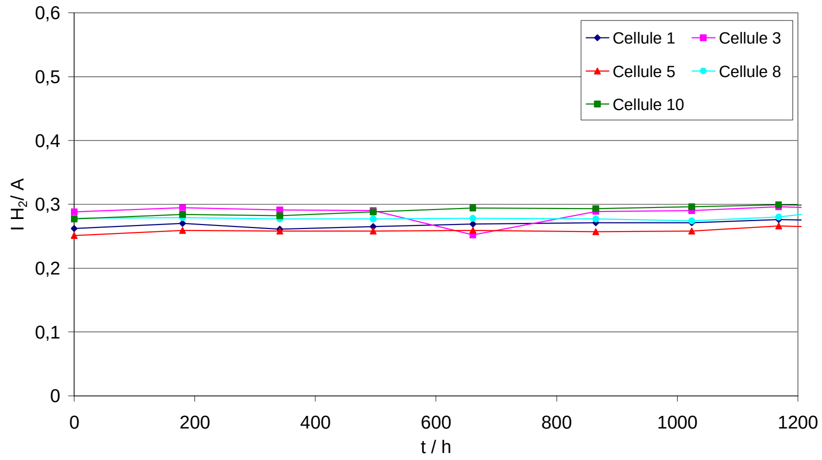




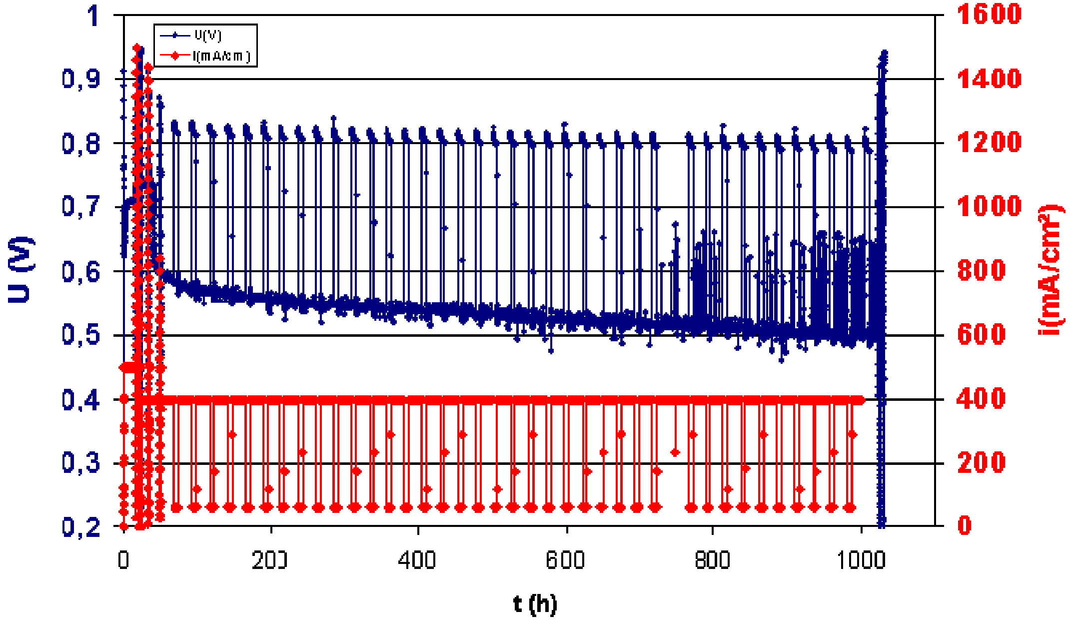


➔ **Conclusions about causes similar to SC**

Ex-situ characterisation by electron microscopy

•New MEA

•MEA aged following reference cycles with reformate 26ppm of CO

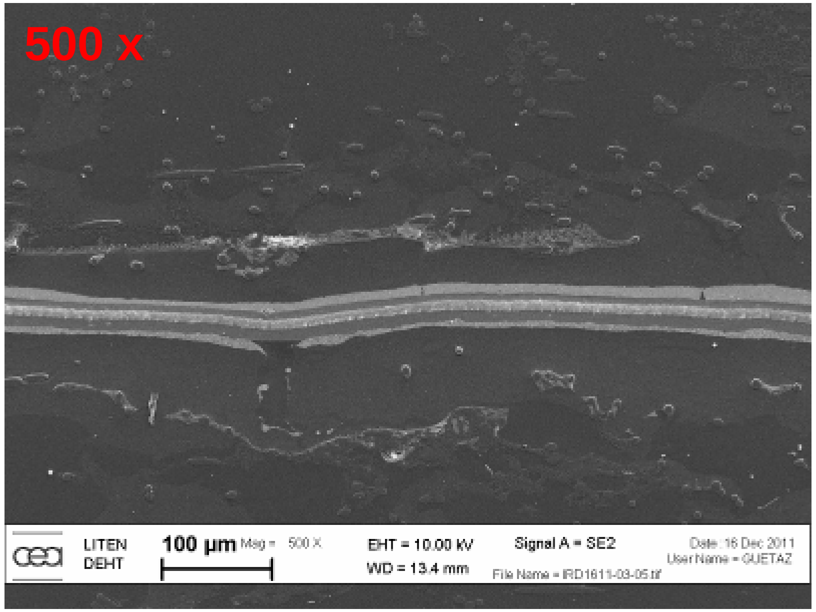


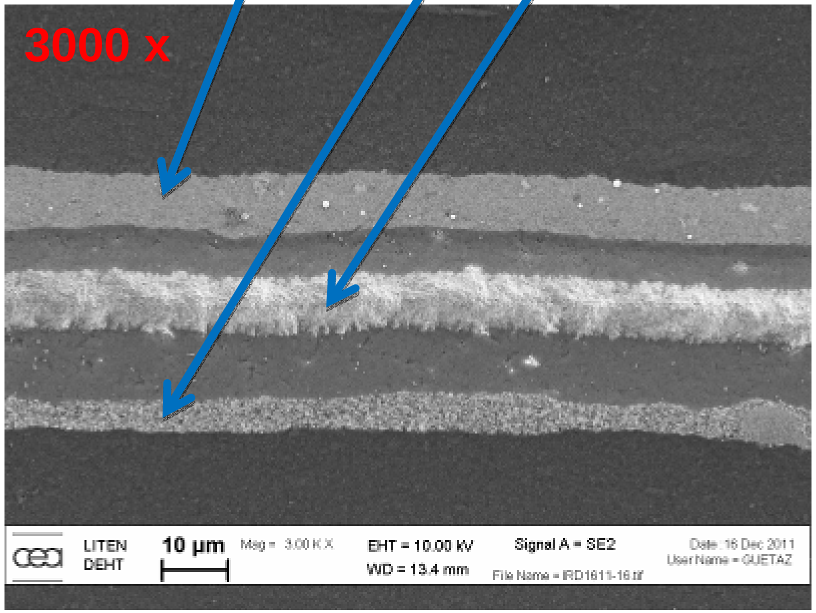
SEM: PEMFC MEAs (CEA)

Fresh MEA - IRD 1611

Cathode Anode

Membrane





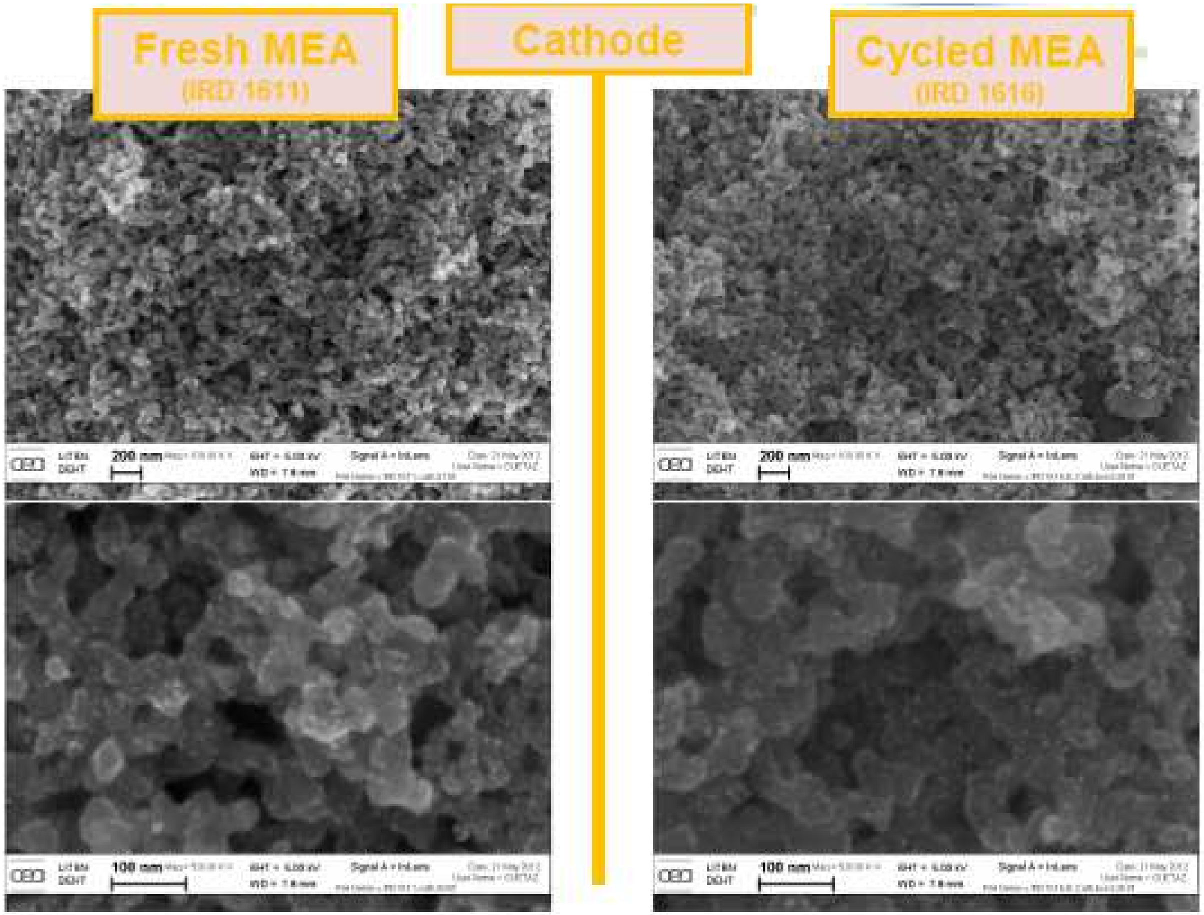
Cathode : Pt

Anode : Pt-Ru ($Pt_{L\ 50\%}$ $Ru_{L\ 50\%}$)

Membrane : reinforced

SEM: PEFC MEA (CEA)

Cathode Air inlet

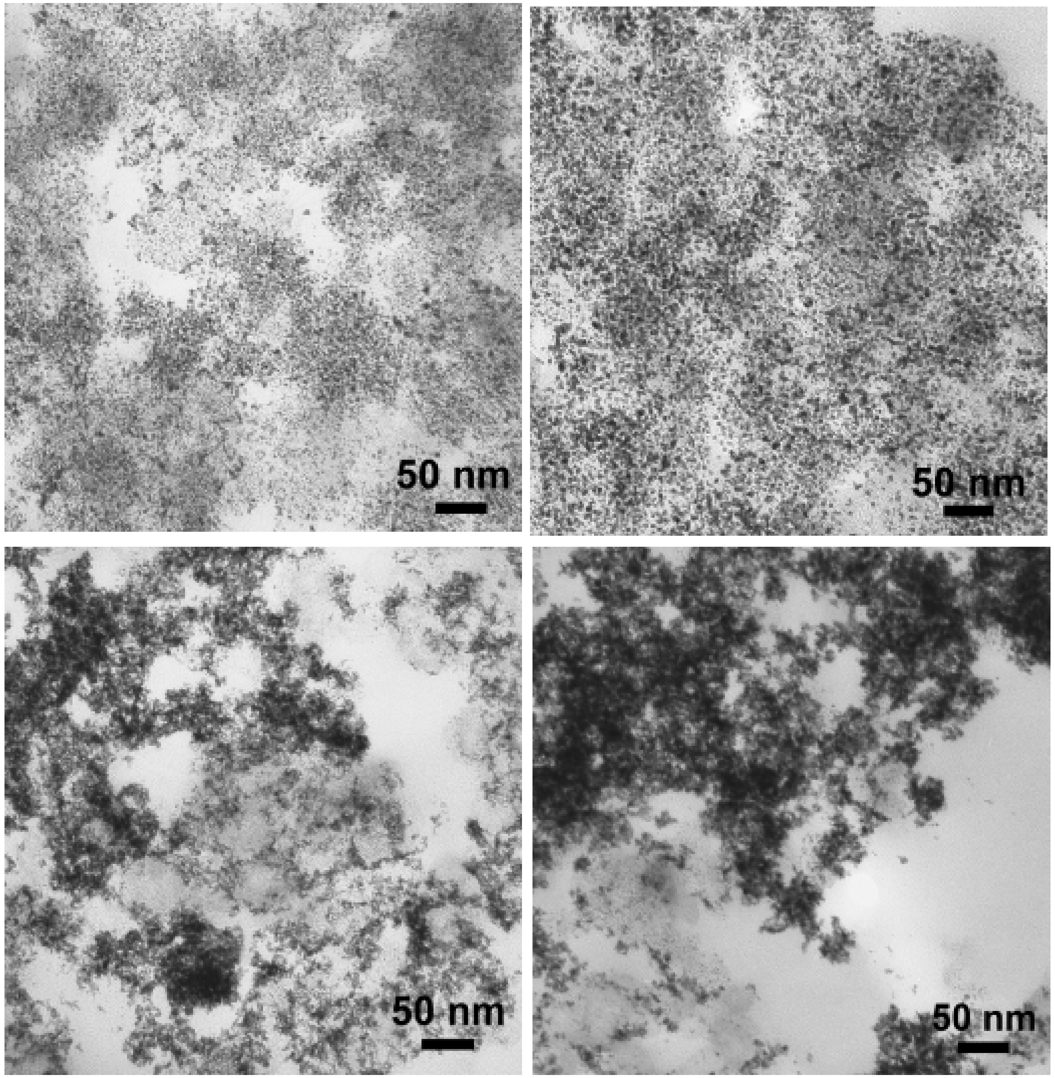


Task 3.1 – TEM: PEFC MEA (CEA)

fresh | aged

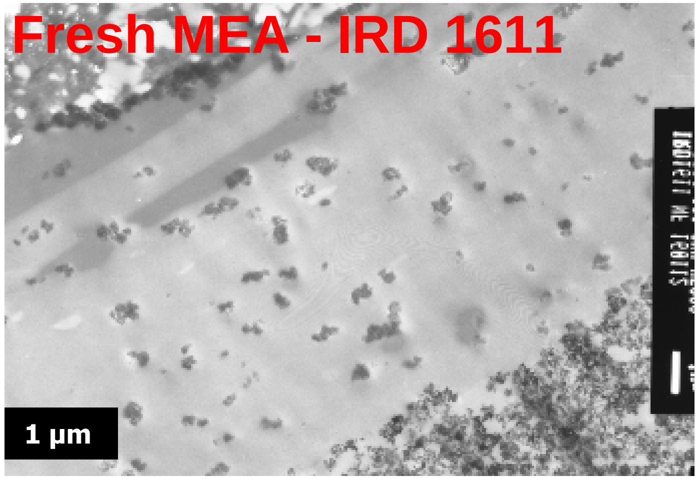
Cathode

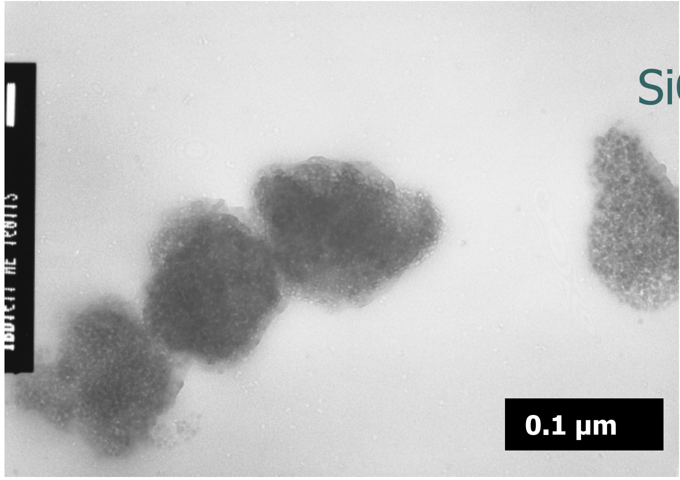
Anode



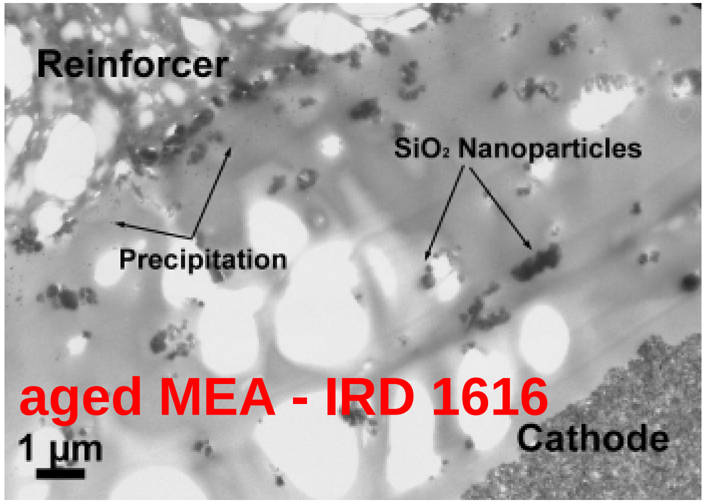
Increase of catalyst size on cathode

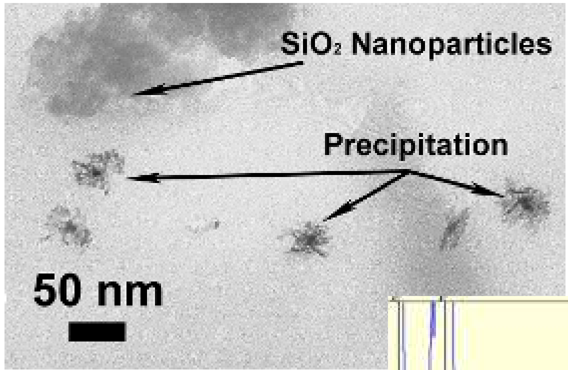
TEM: PEFC Membrane (CEA)

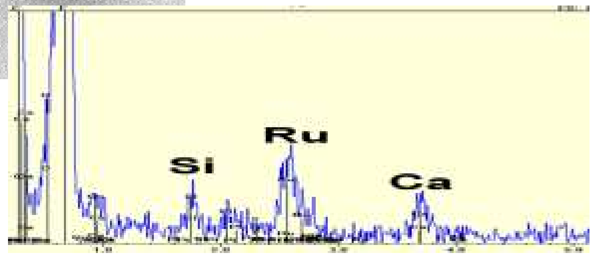




SiO_2 particles







Observed degradation

- No membrane mechanical degradation
- Different alteration of the properties at inlet and outlet zone
- Alteration in the catalysts
- Increase of the catalyst particle size on the cathode
- Ru from anode to membrane (?)

Thank you

for your attention

Work supported by the European's Union's seventh programme
(grant agreement 256776)