

Premium Act

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

(256776)

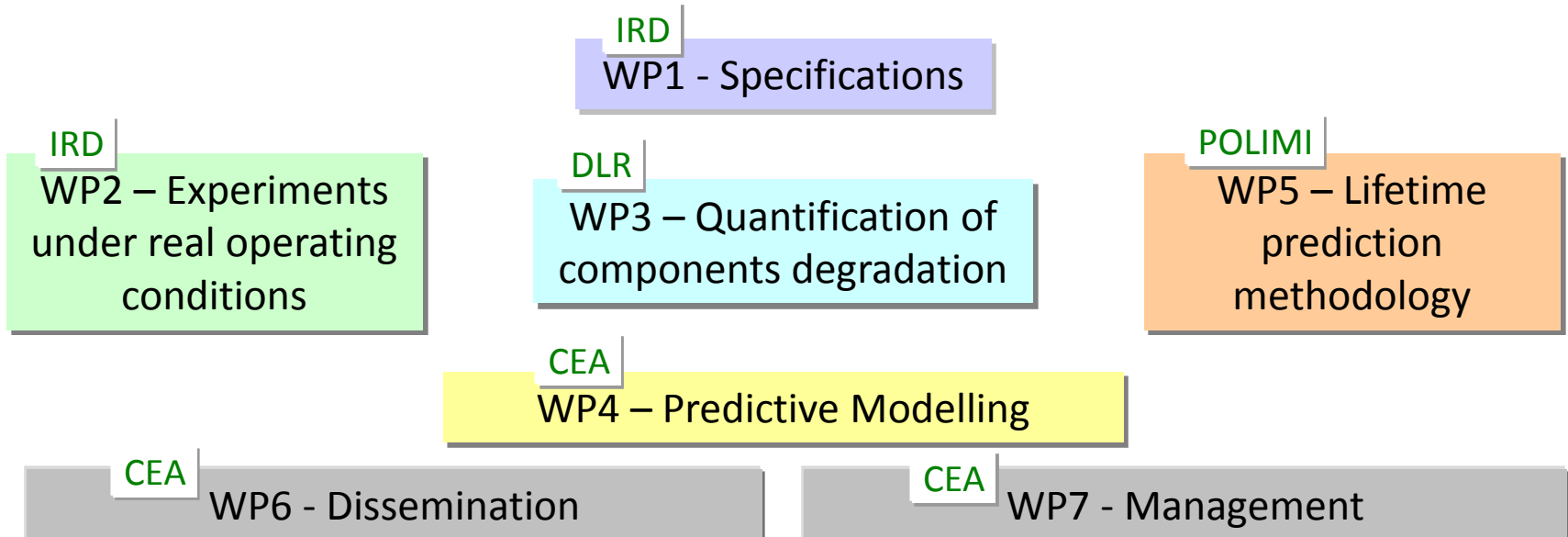
Sylvie Escribano
CEA

- Duration: from 03/2011 to 02/2014
- Total budget: 5 370 190 € - FCH contribution: 2 513 251 €



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

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



- **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:

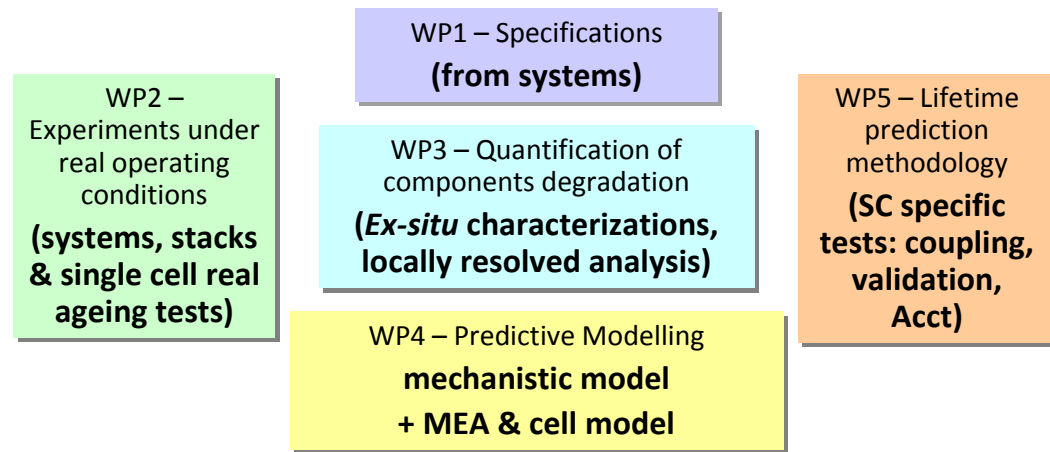
- ➔ DMFC and H₂ reformate PEMFC CHP systems

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





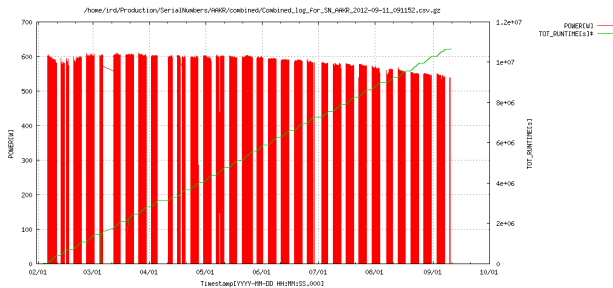
• Ageing studies

DMFC systems



Field tests: IRD
1/2-1 KW_{DC}

IRD



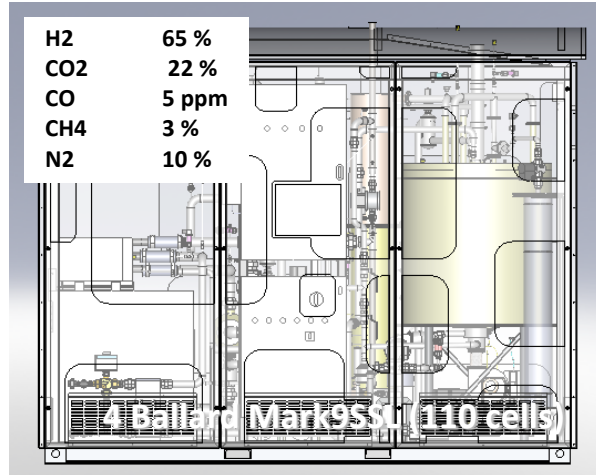
→ Average cell degradation rate ~ 10µV/h @ 40A

→ conditions for DMFC SC tests

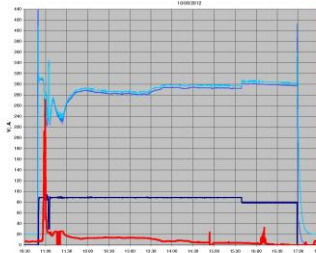
→ Aged DMFC MEAs for analyses

ICI

H2	65 %
CO2	22 %
CO	5 ppm
CH4	3 %
N2	10 %



4 Ballard Mark950 110 cells

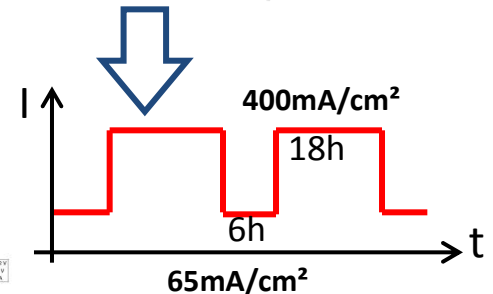
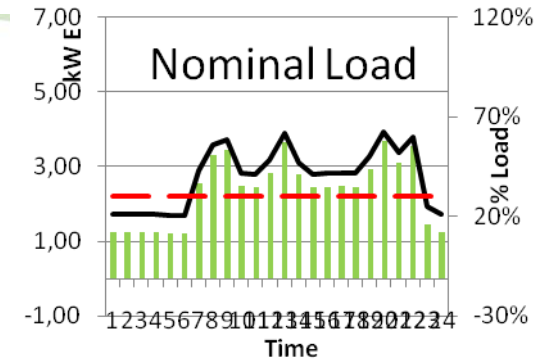


→ fuel composition effect (CO, CO₂, Air bleed)

→ Conditions and protocols for PEMFC single cells and stack tests (→ aged PEMFC MEAs for analyses)

PEMFC systems

Soprano



→ Operating condition tests according to CHP power profiles

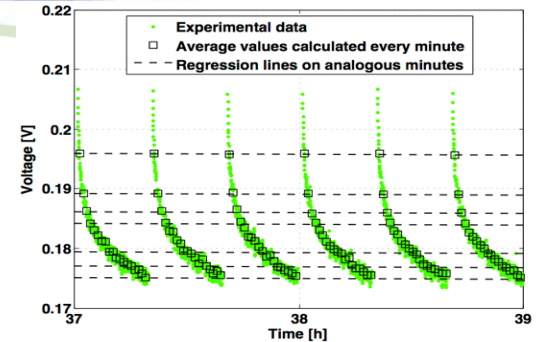
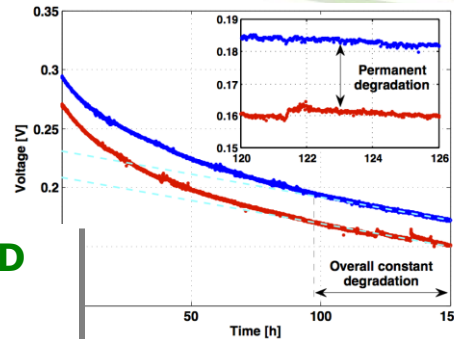


• **Ageing studies**

DMFC stack and single cells

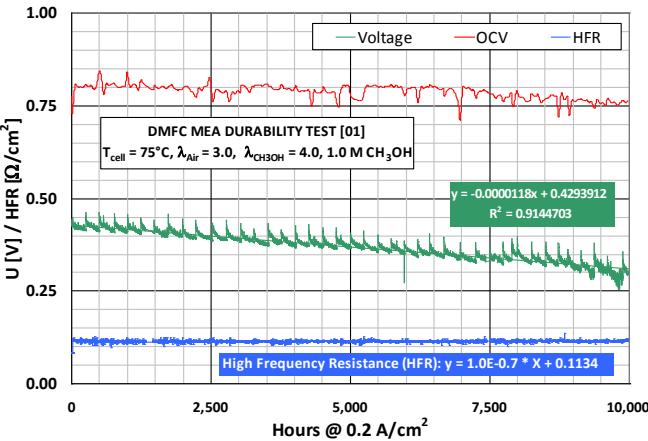
DMFC 5-layer Reference MEAs

Description	Product ID	Catalyst loading
Anode GDL	Sigracet 35DC	
Anode Catalyst	Cabot Dynalyst 62RKR4	1.8 mg PtRu/cm ²
Membrane	Nafion® N115CS	
Cathode Catalyst	Cabot Dynalyst 65KR2	1.2 mg Pt/cm ²
Cathode GDL	Sigracet 35DC	

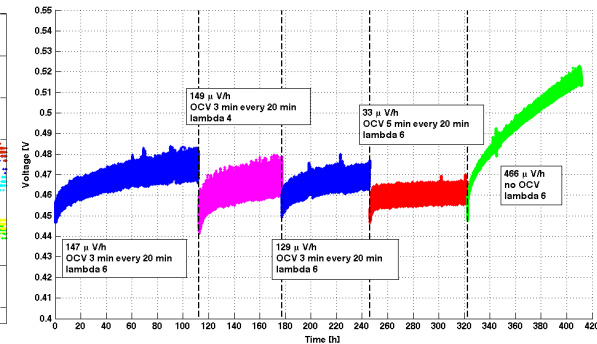
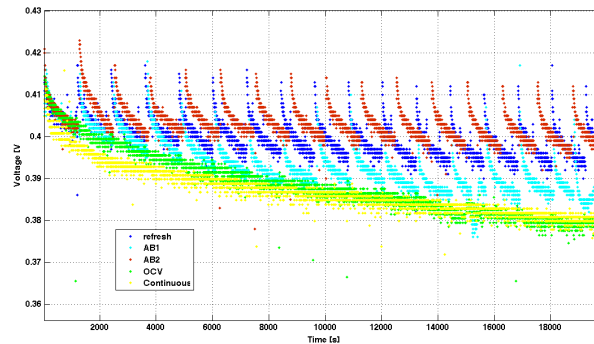


**IRD
&
POLIMI**

Methodologies to analyse temporary and permanent degradation for stationary or cycling operation



Cell voltage degradation for DMFC stack long term operation (< 12 μV/h)



Testing of refresh procedures → Operating strategies to reduce temporary or overall degradation rate

→ Further interpretation of refresh procedures vs. temporary and permanent degradation
Development and application of other protocols and operating strategies

1. Technical Accomplishments and Progress

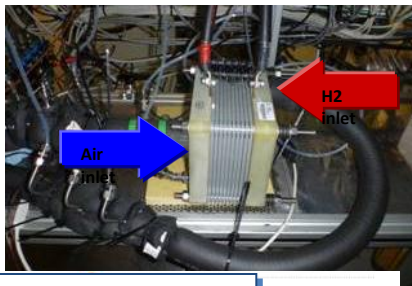


• Ageing studies

LT PEM 5-layer Reference MEAs

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

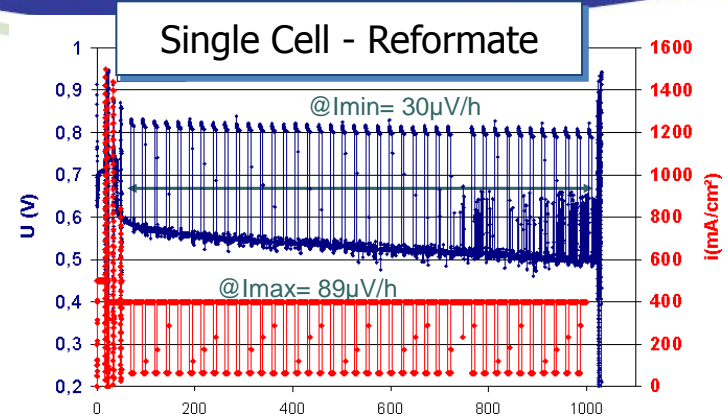
H₂: 79%
CO₂: 20%
CH₄: 1,3%
CO: 26 ppm



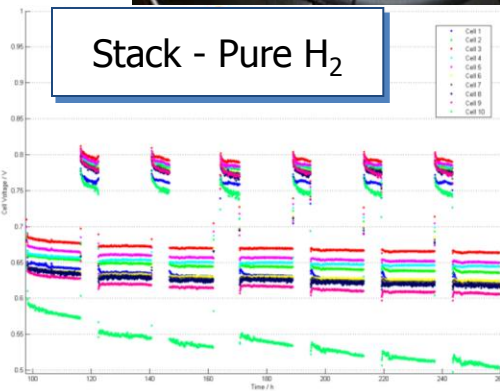
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St_{fuel} 1,2
St_{air} 2
P = 1,2 bar
RH_{fuel} 100%
RH_{air} 50% or 40%
T_{fuelcell} : 75°C

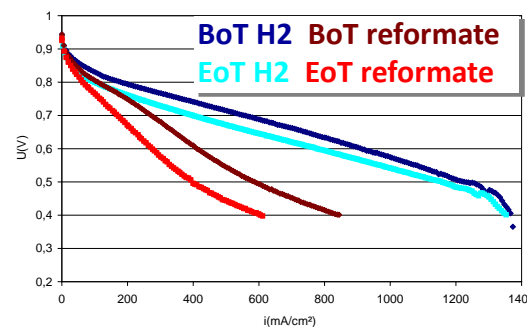
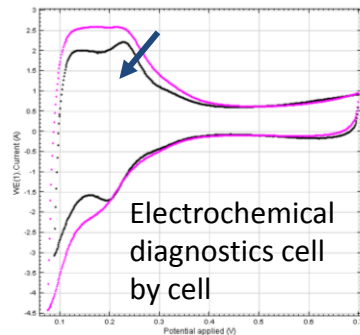
PEMFC stack and single cells



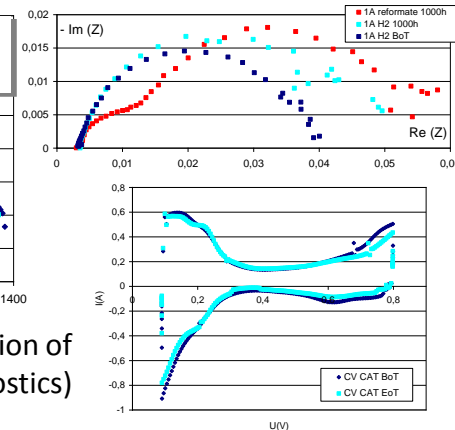
SC voltage / load cycles → high performance degradation rate



10 cells voltages during i_{min}/i_{max} load cycles



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



→ Interpretation to be completed [ex-situ local observations & measurements] - Development and application of other protocols (incl. coupling higher [CO] & cycles) and operating strategies



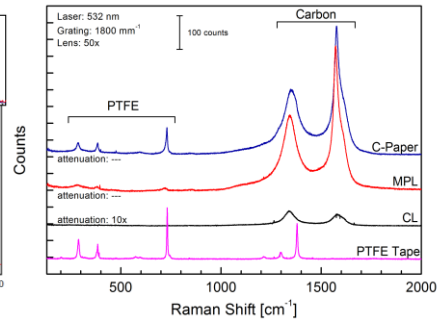
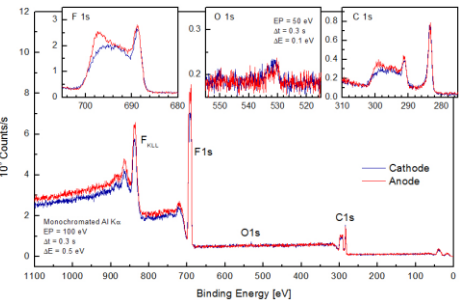
• Characterizations for degradation investigation and quantification

Vertical & lateral Chemical mapping

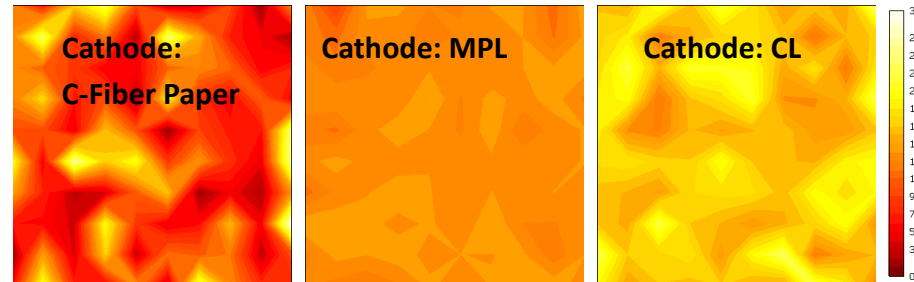
DLR

XPS → atomic concentrations of elements

Raman → microscopic PTFE and C distribution of GDLs



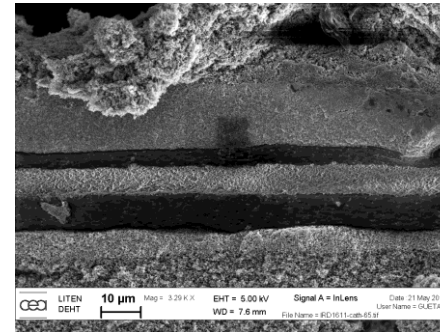
ATR IR (C-F bonds) → macroscopic PTFE & ionomer distribution in the new and aged PEFC and DMFC electrode layers



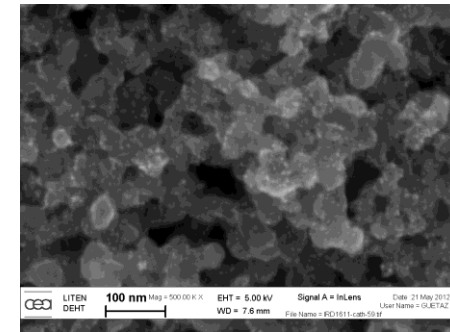
Electron microscopy observations

CEA

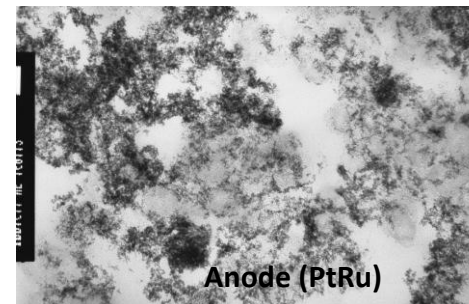
Fresh PEMFC MEA



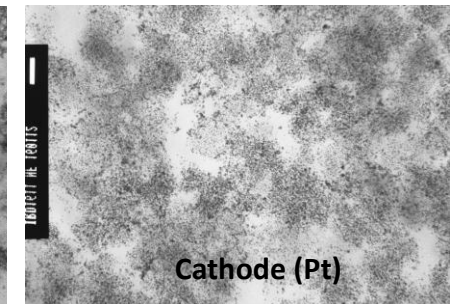
SEM → General aspect of the membrane and MEA



FEG-SEM → Active layer structure



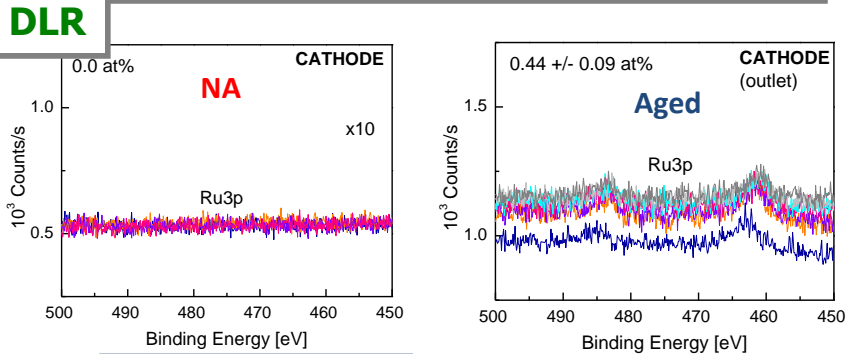
TEM + ultramicrotomy → catalyst layer and particles





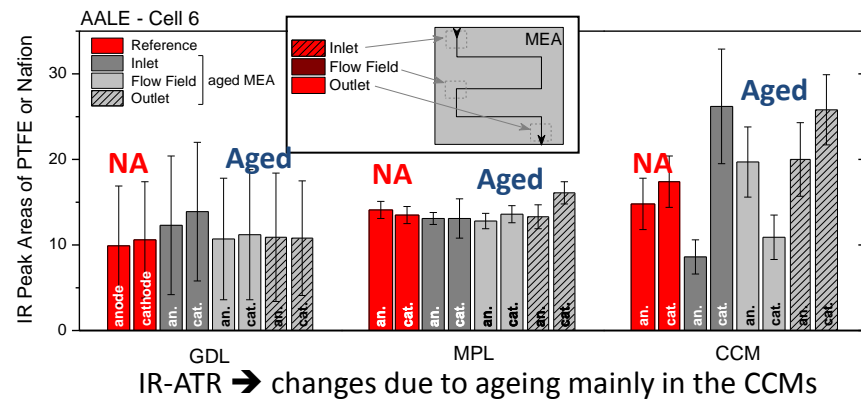
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Vertical & lateral Chemical mapping

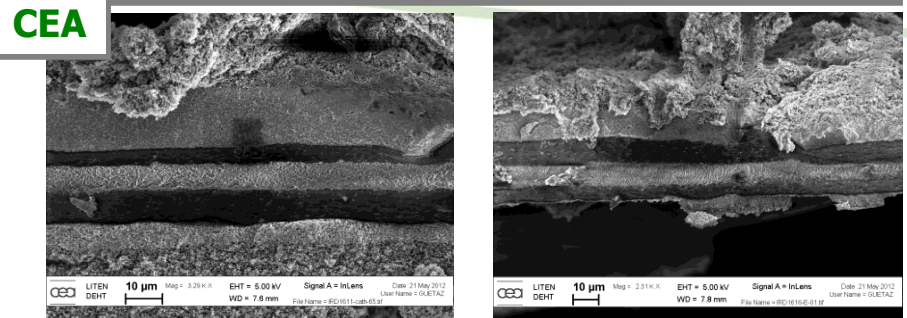


Aged DMFC stack (fuel starvation)

XPS → detection of Ru cathode side

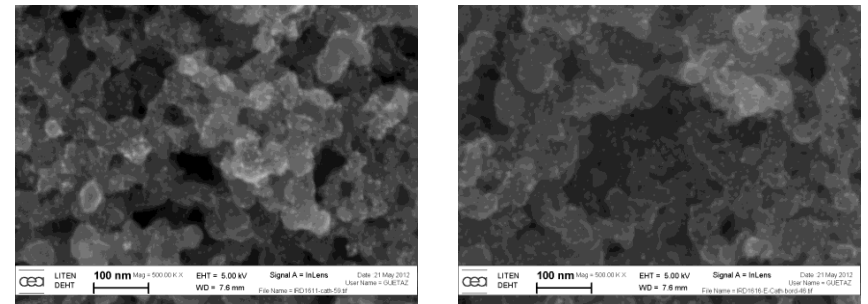


Electron microscopy observations



Fresh PEMFC MEA

Cycled PEMFC MEA



→ No main modifications : membrane not damaged, active layer structure similar to non aged

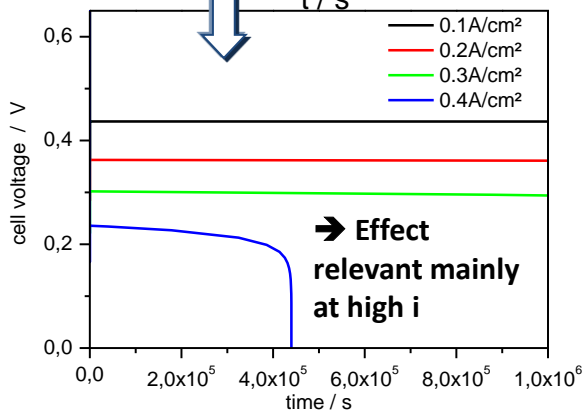
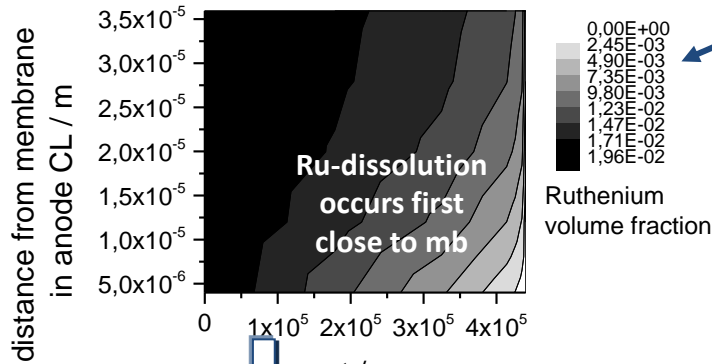
→ **Analysis of other aged samples from stack and single cell DMFC & PEMFC**
Impact of the testing conditions on the components degradation



• Degradation models

DLR

- Detailed basic model developed → *basis for degradation studies (transient behaviour, EIS)*
- Degradation mechanism implemented

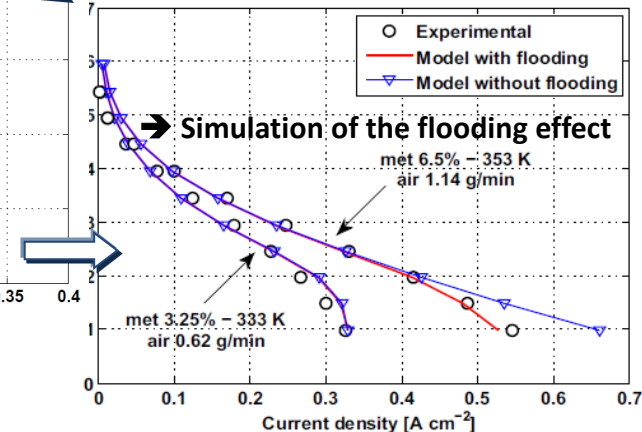
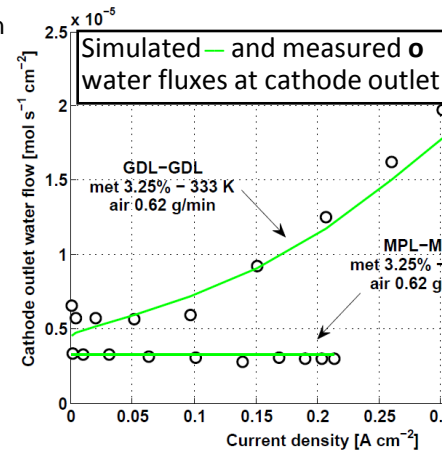
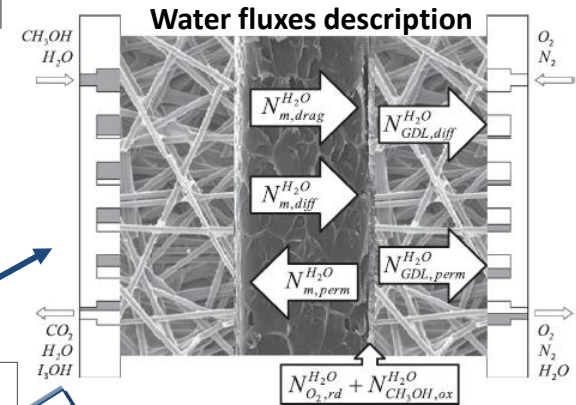


→ To be validated

DMFC cell modeling

POLIMI

- Dev of electrochemical impedance model → *coupling phenomena interpretation*
- Single cell model (incl. water transport)



→ Evolution of physical parameters to be integrated for DMFC degradation modelling

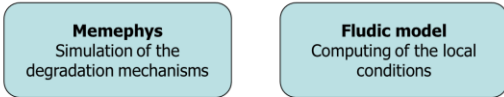


PEMFC cell modeling

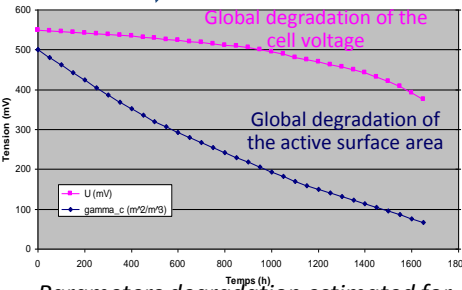
• Degradation models

CEA

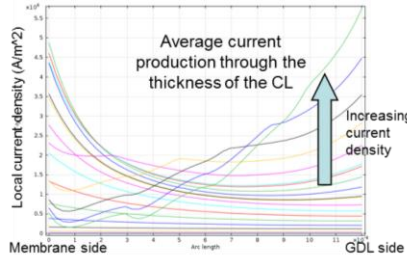
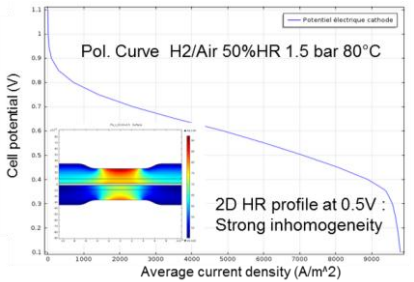
Specific surface, reactions kinetics, electrolyte status



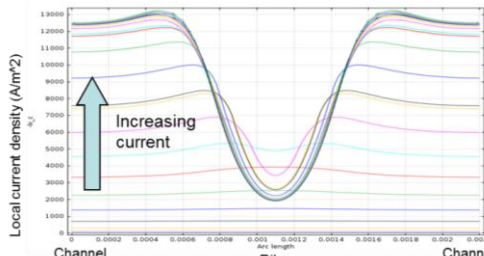
Current densities, species concentrations, water distributions



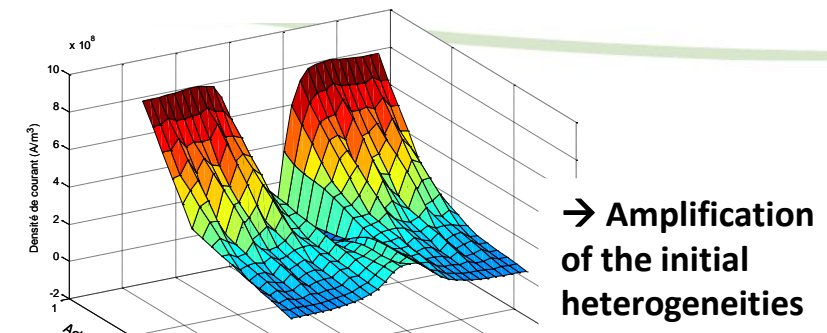
Parameters degradation estimated for each local conditions



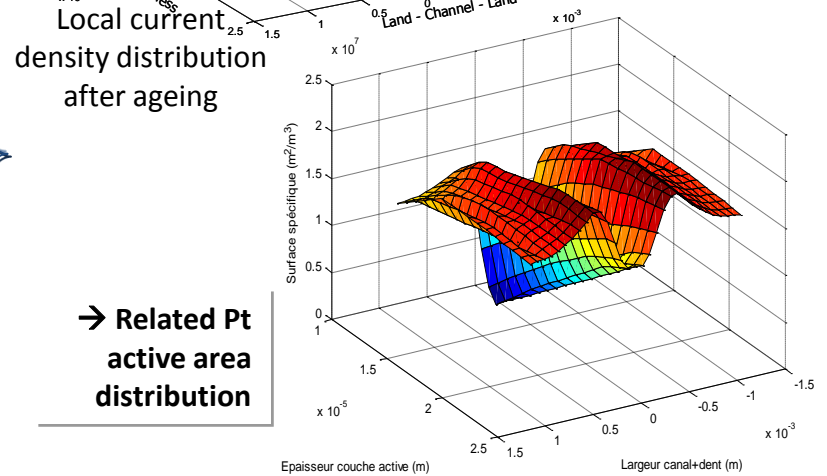
The current production distribution through the thickness of the CL depends on the average current density



Strong heterogeneities, especially at high current density



→ Amplification of the initial heterogeneities



→ Related Pt active area distribution

→ To be correlated with experimental degradation of components and performance regarding the different conditions and protocols

- **Correlation of the project with the corresponding Application Area** (as mentioned in MAIP/AIP documents)
 - **Application area: Stationary Power Generation**
 - “emphasis on long-term basic research to better understand degradation/failure mechanisms and the lifetime requirements of all fuel cell stack types (SOFC, MCFC, PEMFC), for different fuels and levels of power.”
 - “For lifetime predictions, research is necessary to establish methodologies as well as tools for modelling, operational controls and diagnostics.”

Topic: “Fundamentals of fuel cell degradation for stationary power application”

→ **“Research on critical parameters and operating conditions that impact degradation and life time of cells and stacks, for all power ranges and fuel cell technologies”**

- Detailed project activities & results versus MAIP/AIP document targets
 - ✓ Direct link between previously described activities & targets (Cf. approach slides)
 - **Application**
 - μ -CHP systems with different requirements
 - 2 Fuel Cell types / fuels : DMFC (Methanol) & PEMFC (reformate)
 - Power ranges: from 500W stack to 30kWe PEM CHP syst.
 - **Technical activities**
 - FC tests (system, stack and cell levels): nominal and critical conditions
 - Studies of the microstructure & properties before/after ageing
 - Modelling of the degradation mechanisms
 - **Identification of main parameters enhancing degradation**
 - **Development of accelerated tests**
 - **Proposal & validation of lifetime prediction methodology**

Specific degradation mechanisms for PEFC operating with methanol and reformate

- Identify and comment on gaps/bottlenecks in RTD&D proposed by MAIP/AIP documents
 - *Most topics of Premium Act are considered in the MAIP/AIP*
 - ✓ **DMFC technology is not directly included in the implementation plan whereas currently subjected to a significant commercial interest**
- Comments on priorities and topics possibly under/over-estimated in the AIPs in terms of technical challenge
 - *For stationary applications, degradation understanding and durability improvement are the right priorities*
 - ✓ **Durability of 40000 hours: too wide requirement**
 - ➔ **more focused targets to be proposed / specific application**
 - ➔ **technical challenges to be more related to components or operating conditions constraints**

Premium Act

• Training and Education

- Post-doctoral researchers, PhD and MSc students involved in activities at CEA, DLR & POLIMI
- Polimi personal exchange:
 - M. Zago → DLR from 6/12 to 8/12
 - F. Bresciani → IRD Fuel Cell 8/12 to 10/12

• Safety, Regulations, Codes and Standards

- Possibility to contribute to future standards definition thanks to project outcomes on traditional and accelerated testing & on degradation models

• Dissemination & public awareness

- Journal publication: Zago, M., Casalegno, A., Santoro, C., Marchesi, R. "Water transport and flooding in DMFC: Experimental and modeling analyses", 2012, Journal of Power Sources 217 , pp. 381-391
- Premium Act results to be presented at FC papers & conferences (incl. exhibition for indust.) (All partners) [ex: FDFC 2013]
- **Premium Act workshop**



“Characterization and quantification of MEA degradation processes”

September 26-27, 2012 in Grenoble, France

Invited Speakers:

- **Atsushi Ohma** (Nissan Research Center, Japan):
“Study on Microstructure of Catalyst Layer and its Impact on Performance and Degradation”
- **Karren More** (Oak Ridge National Laboratory, USA):
“Application of Advanced Microscopy Methods to Understand MEA Materials Degradation”
- **Hans Bettermann** (University of Düsseldorf, Germany):
“On-Line Gas Detections from PEM Fuel Cell Flow Fields by Raman Measurements and Electric Arc Emission Spectroscopy”
- **Laetitia Dubau** (LEPMI, Grenoble University, France):
“Durability of Pt/Co/C Cathode Electrocatalyst during Long-term Real PEMFC Operation”
- **Arnaud Morin** (LITEN, CEA-Grenoble, France):
“What about the link between chemical degradation of membrane and PEMFC durability? The example of S-PEEK Membrane”

Visit of the Nano-characterization Platform at Minatec:



- **Technology Transfer / Collaborations**
 - **Interaction with EU projects**
 - Use of knowledge & results from DECODE project [degradation mechanisms, modelling data, investigation methods]
 - Exchanges possible with new projects e.g. IMPACT, IMPALA, PUMAMIND... [degradation, water management, modelling]
 - **Interactions at national level** (French, German, Italian or Danish FC projects)
 - Possible exchanges and use of knowledge & results from national funded or other collaborative projects (all partners)
 - Interaction with the national Real FC project : exchanges regards experimental data and testing methodology (POLIMI - Italy)
 - **Interactions at international level**
 - Possible exchanges about methodologies (for all technical aspects of testing, characterization or modelling) thanks to:
 - close direct relationships with other industrial groups, institutes or universities
 - involvement in international working groups (IEA, standardization bodies...)

- **Project Future Perspectives**

- Proposed future research approach and relevance & Need/opportunities [for increasing cooperation, building alliances & for international collaboration]

- **RTD topics: Emphasis on fuel/methanol purity**

Development of more generic ACCT for DMFC and PEMFC

- **Premium Act: balanced consortium with 3 industries developing FC systems**

→ possible extended collaboration for further optimisation of the FC systems studied

→ possible extension to other industries or institutes interested in the approach

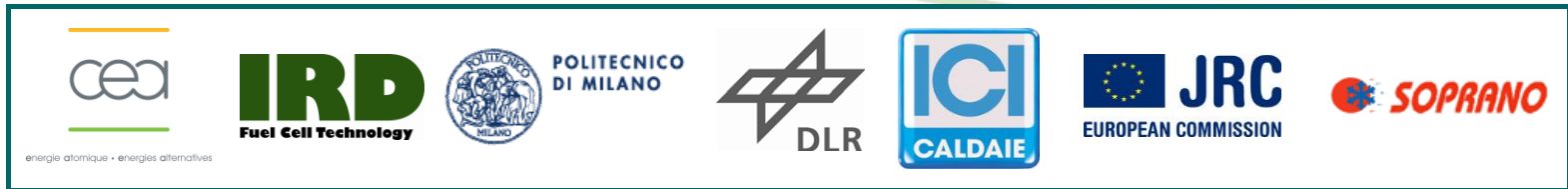
- ***At international level: contribution to future definition of RCS (methanol purity, degradation tests or models)***

- Possible contribution to the future FCH JU Programme

- **Include research and demonstration of methanol/greenfuel based fuel cells e.g. DMFC in the implementation plan.**

- **Recommendations for projects dedicated to specific systems development:**

- Proposition of; exp./model methodology for degradation study; *ex-situ* investigation methods and testing protocols; validated prediction methodology



Thank you for your attention