Overview of the FP7 Project DECODE Results and Recommendations

K. Andreas Friedrich

DECODE

2nd International Workshop on Degradation Issues of Fuel Cells

Thessaloniki, Greece

21 - 23 September 2011

Project General Information

Project full title:	Understanding of Degradation Mechanisms to Improve Components and Design of PEFC
Coordinator:	K. A. Friedrich, DLR
Project major partners:	Opel, Volvo, SGL, Solexis, DANA, CEA, ZSW, JRC, Uni. Erlangen, Chalmers Uni.
Starting Date:	01.01.2008
Ending Date:	31.03.2011
Budget Total/Funding:	5.5 MEUR / 3.7 MEUR
Type of project:	CP

Motivation and Goals

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First main goal of DECODE is to assess the relevance of the degradation processes of polymer electrolyte fuel cell based on the extensive analysis performed in DECODE

Second goal is to identify and implement improvements for fuel cell durability based on:

- Understanding of degradation processes
- Improved materials
- Improved operation conditions

Third goal is the development of prediction tool for degradation based on modelling (different modelling approaches)

Interactions of Work Packages

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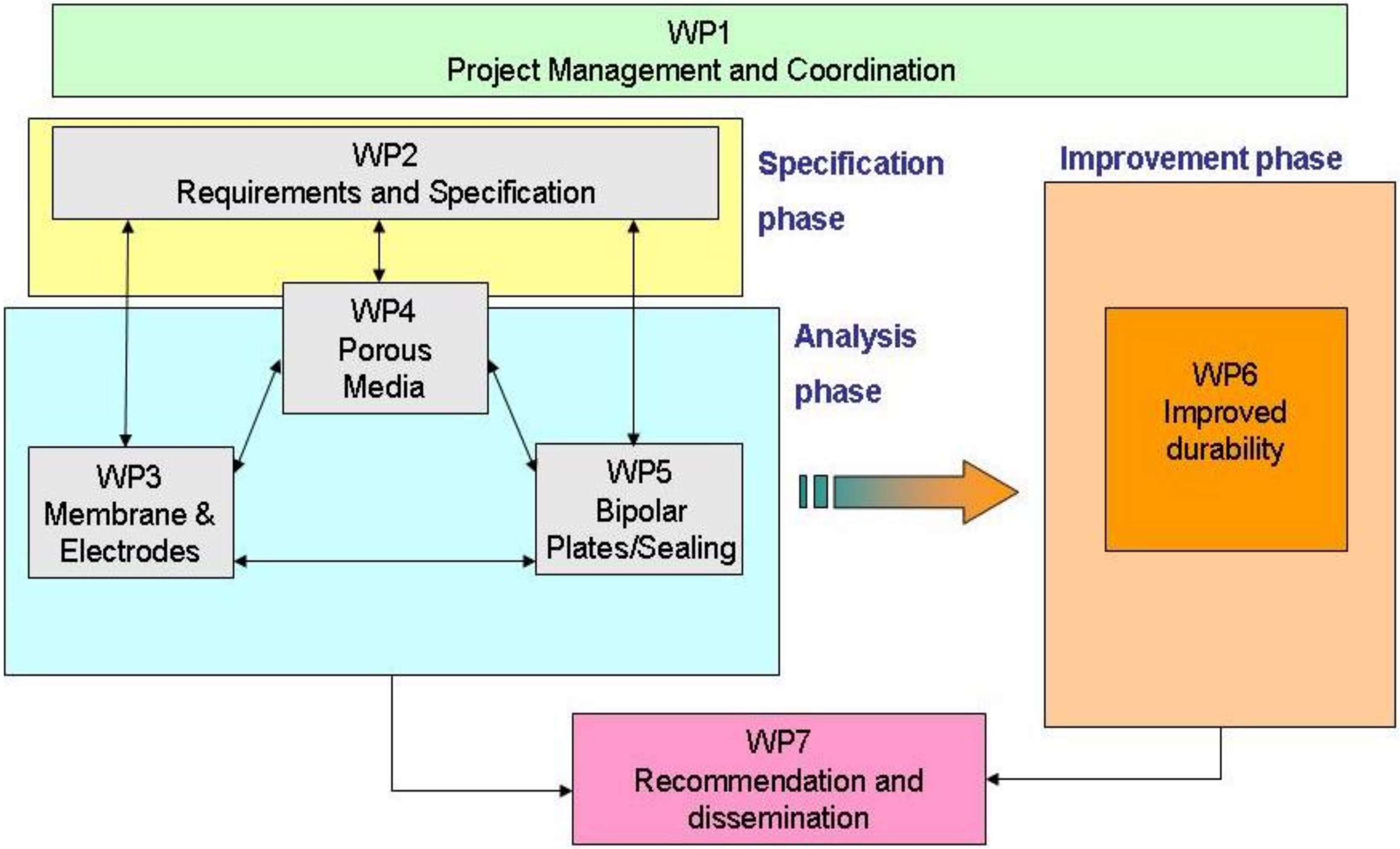

Identification and Ranking of CCM Degradation Mechanisms

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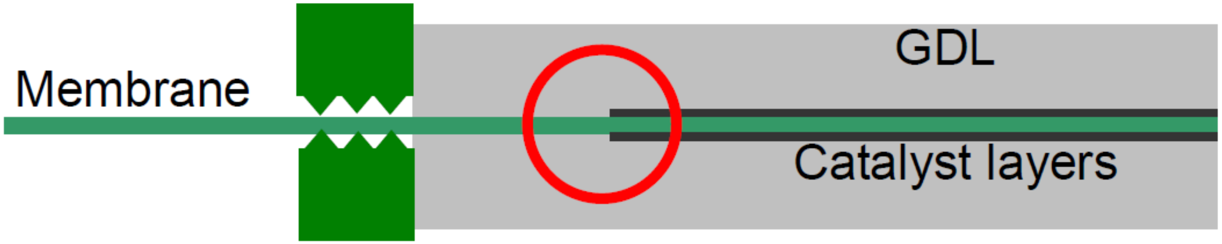
Mechanism	Importance
• Structural degradation	
‣ Mechanical degradation of the membrane	++++
‣ Loss of electrochemical activity at the cathode	+++
‣ Loss of “electrochemical activity” at the anode	o
• Chemical degradation	?

Mechanical + Chemical Stress: Edge Failure

Simple gasket design:



Degradation issues:

- **Gas X-over on the edges leads to chemical degradation**
- **Mechanical shear stress during dynamic operation (membrane expansion/shrinkage)**
- **Membrane exposed to GDL fiber puncture**

Suitable edge/gasket designs will avoid these failure modes

Stabilized Aquivion™ Membrane

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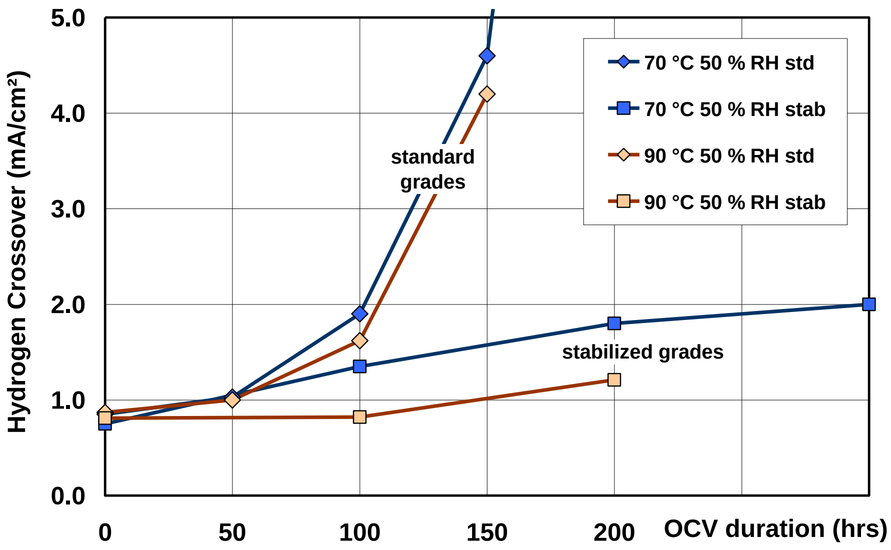
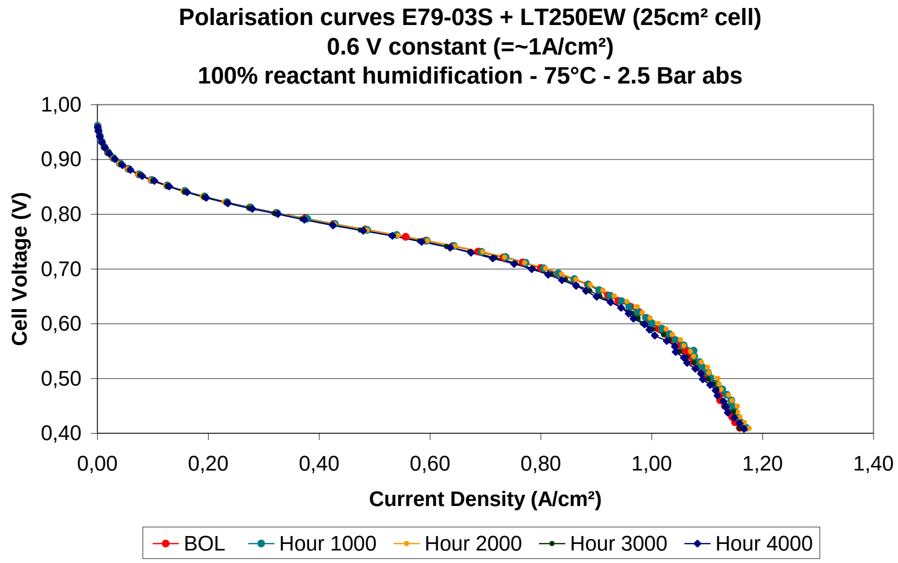
Open Circuit Voltalge at 75 °C
Accelerated aging test for membranes





Stabilized Aquivion^{TM} Membrane

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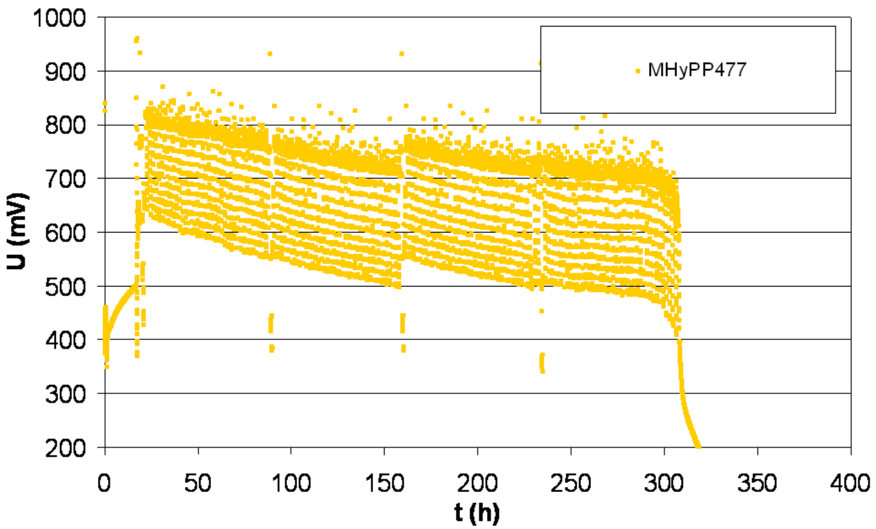
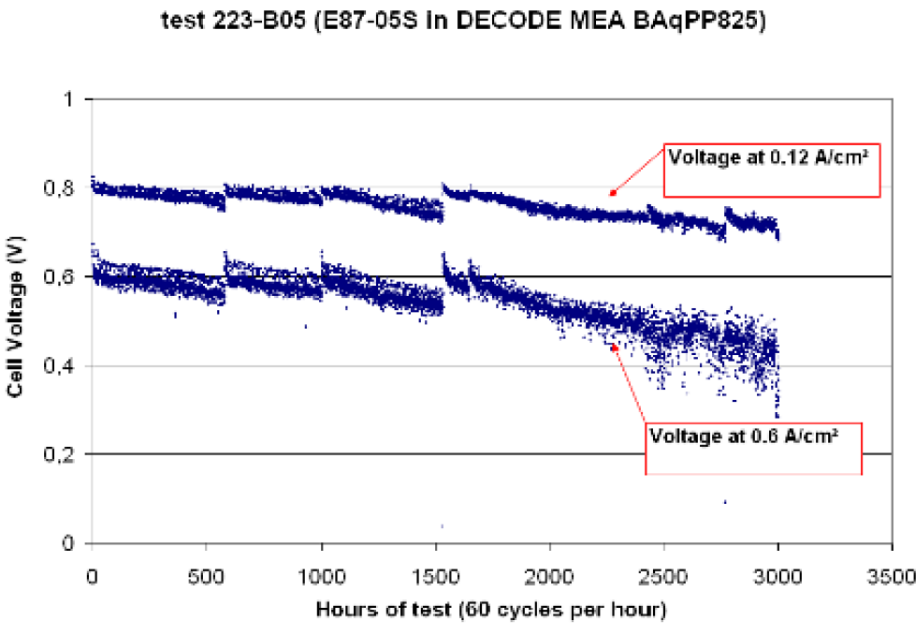
Experimental MEA made by CEA using unstabilized AQUIVION membrane without edge protection (2009)



Experimental MEA made by CEA using reinforced AQUIVION membrane with edge protection (2010)



Ageing of MEAs in single cell

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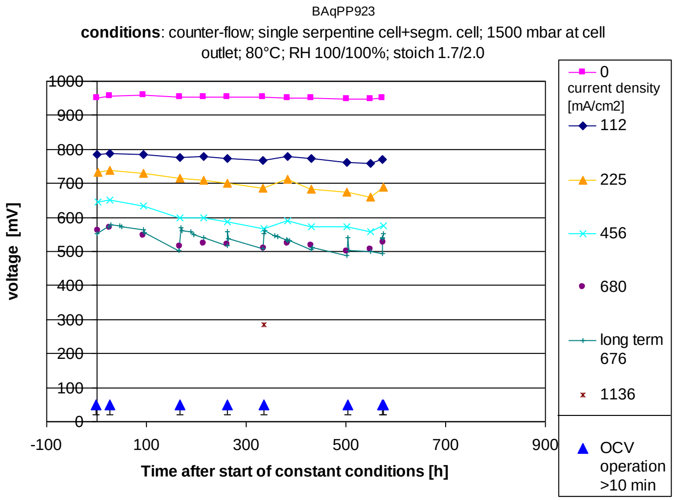
- **Ageing test of DECODE CCB MEA** (E87-05S + sub-gaskets) **+ Segmented-cell (DLR)**
  - Constant load i = 676 mA.cm^{-2}

Counter-flow – 100/100%RH

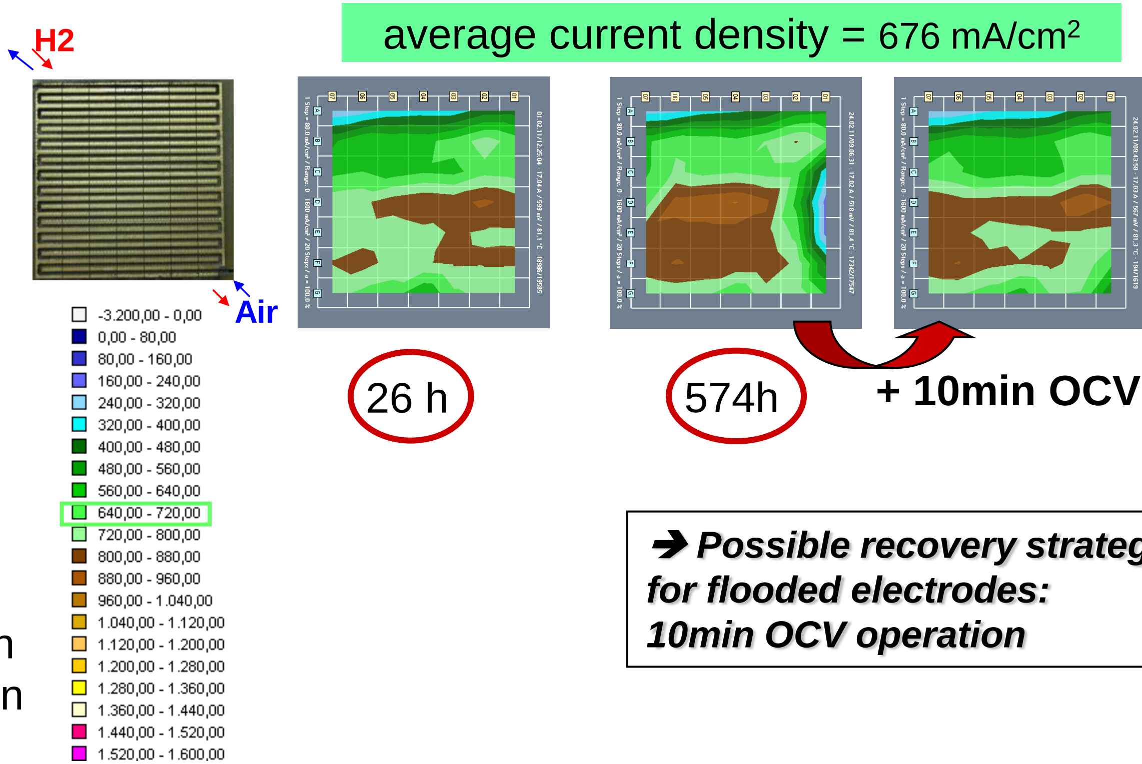
Cell voltage at OCV, low and high current densities



→ No OCV degradation
→ Faster reversible degradation
→ Small irreversible degradation

Current density distribution:

average current density = 676 mA/cm^2



➔ Possible recovery strategy for flooded electrodes: 10min OCV operation

Dynamic Test of Membrane and Electrodes

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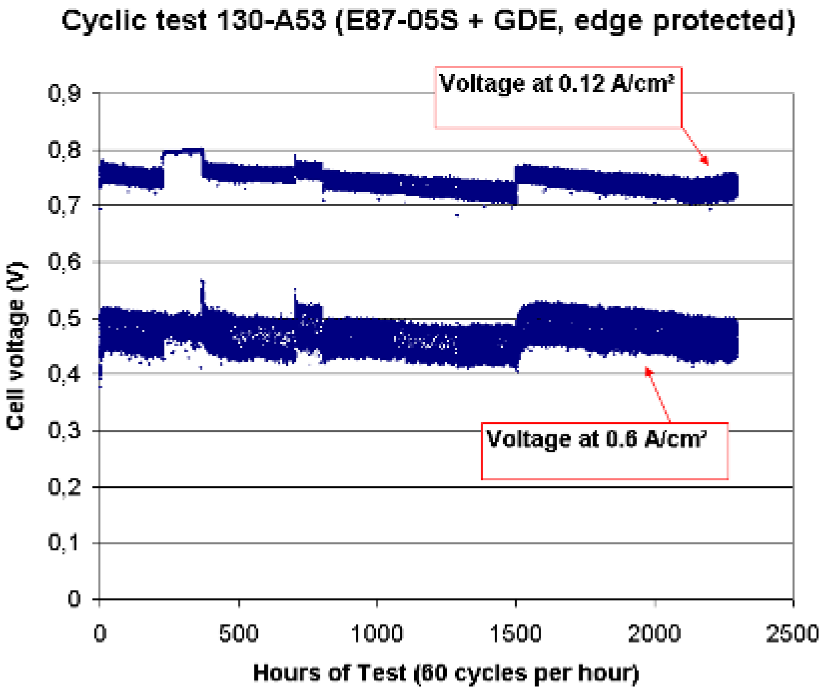
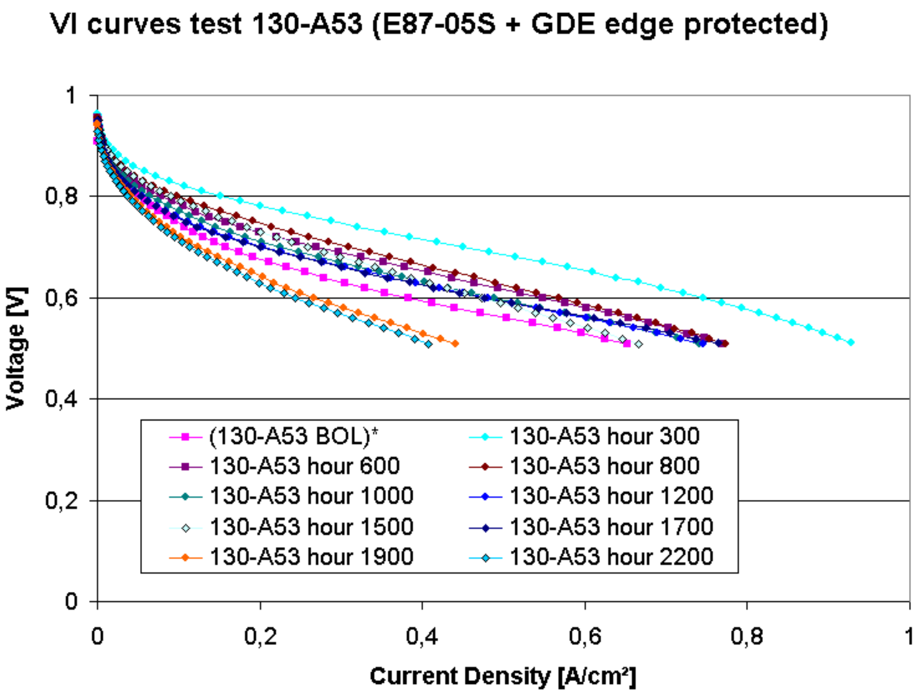
Results with ELAT electrodes (SLX) – <u>E87-05S</u> edge protected

- **Dry DECODE conditions**





➔ Evidence of better mechanical stability with increased membrane crystallinity & edge protection

Electrode Characterization

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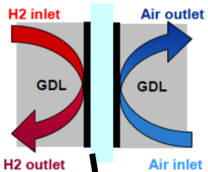
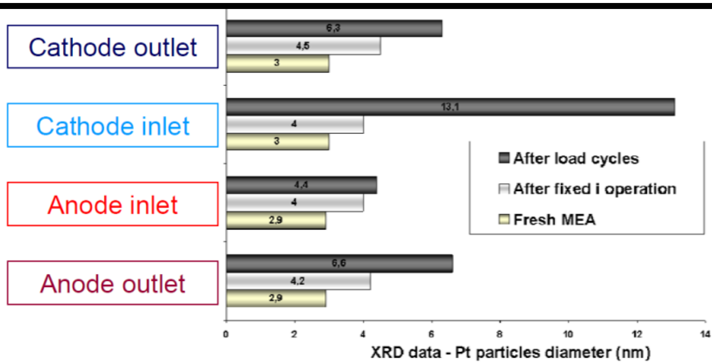
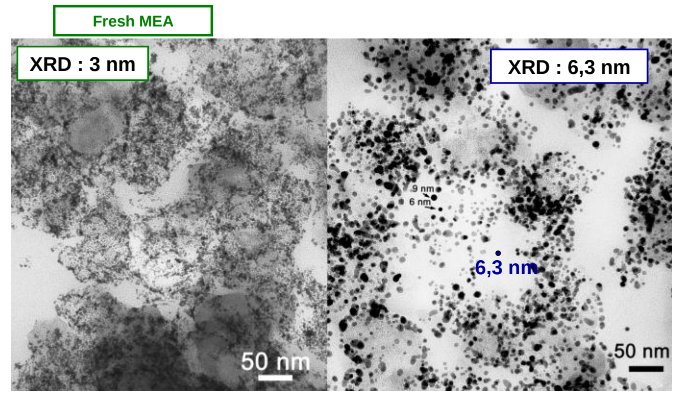
- **TEM observations (CEA)**
  - Active layers degradation: after cycling and membrane damaged



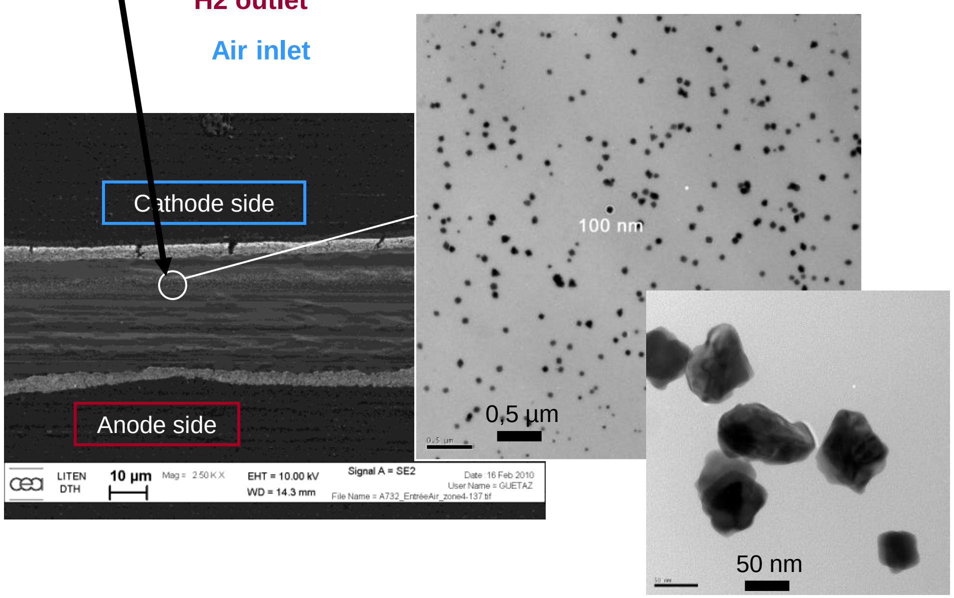


→ Pt particles growth by Ostwald ripening at air outlet



H2 outlet

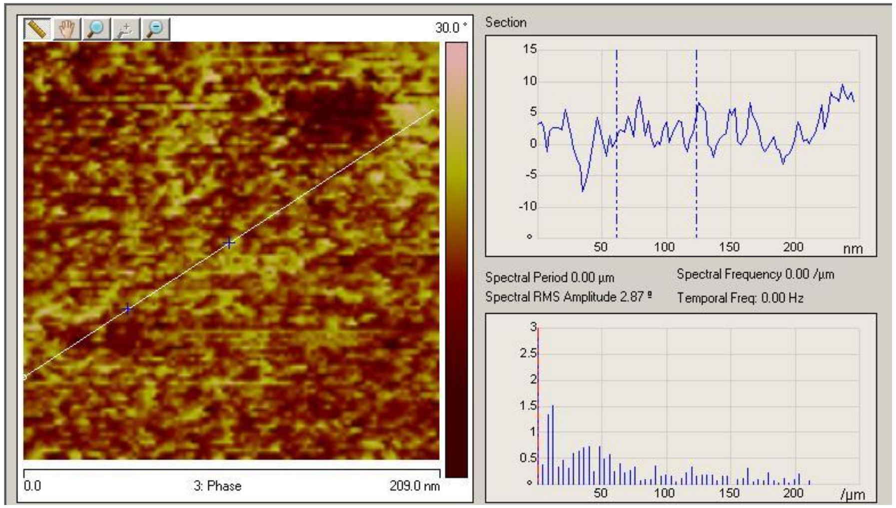
Air inlet

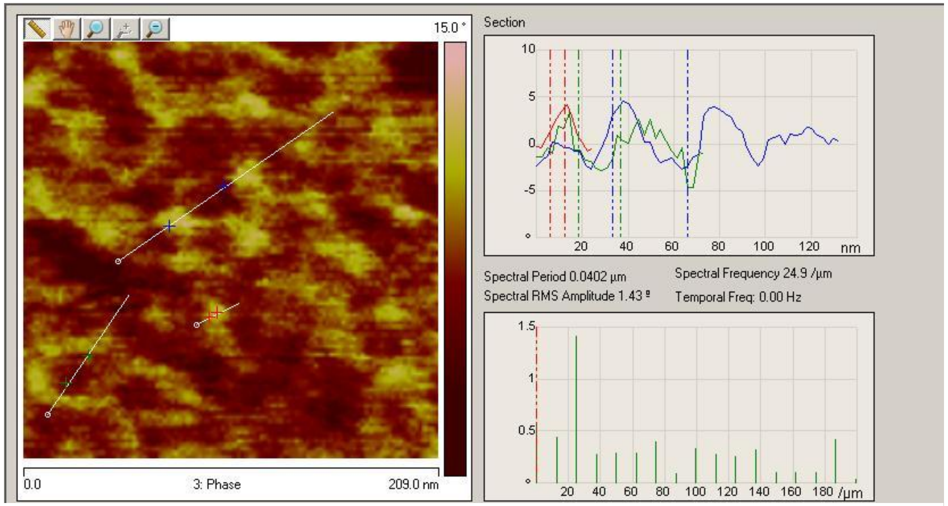


→ C corrosion and massive Pt dissolution + reduction in AL or membrane at air inlet

Characterization: Conductive AFM

Solexis E87-05S
Comparison baseline after 24 h and after 20000 h stationary Operation



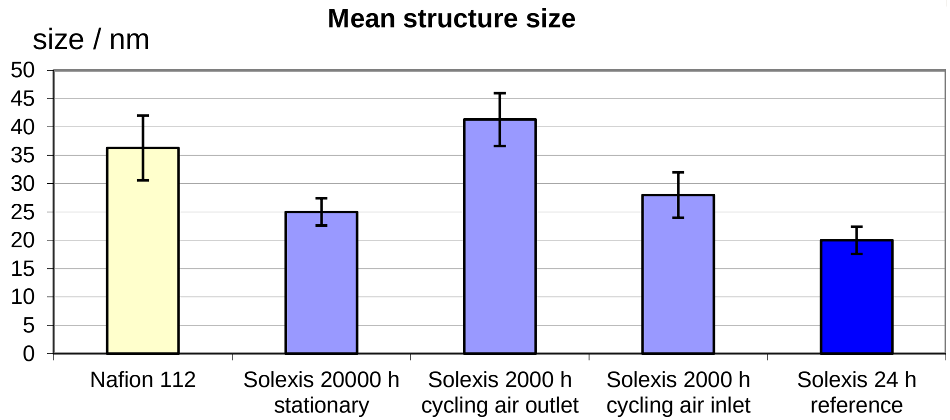


left:
reference outlet baseline, 24 h

right:
20000 h stationary operation

Other Methods in DECODE:

- EIS, CV, LSV
- Raman spectroscopy
- XPS



Identification and Ranking of GDL Degradation Mechanisms

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Mechanism	Importance
• Chemical degradation	++++
‣ Loss of hydrophobicity	++++
‣ Carbon / structure corrosion	+++
• Structural degradation	
‣ Change in (gas phase) transport parameters	Observed, but influence on performance limited
‣ Change in wetting behaviour	

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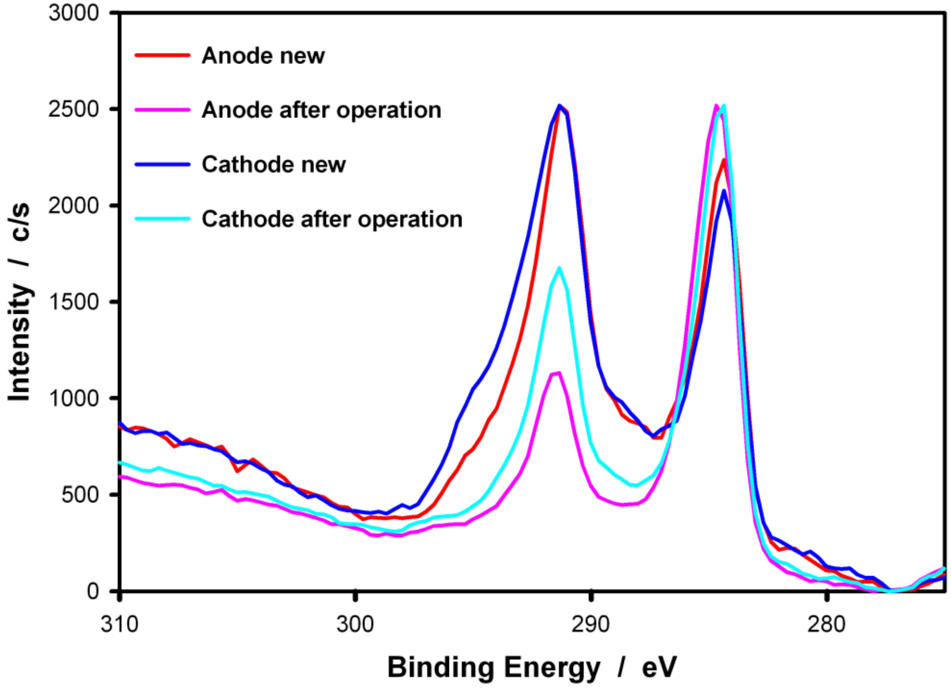
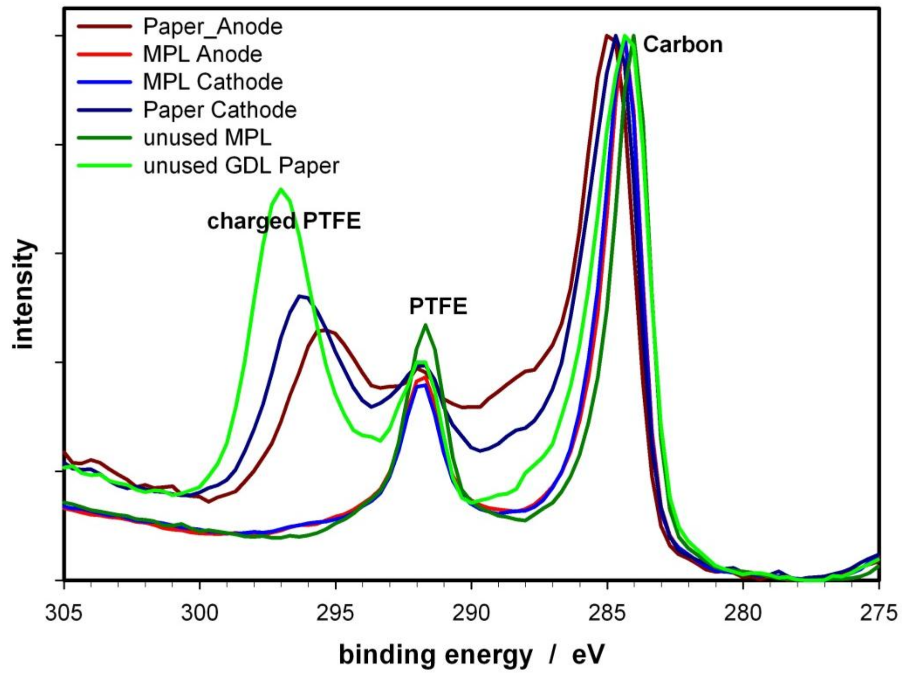
Loss of hydrophobicity





- **Partial decomposition of PTFE identified by XPS**
- **PTFE decomposition mainly on the anode**

→ Decrease of hydrophobicity

→ Changed water balance

→ Reversible loss of performance

Chemical Degradation - Carbon Corrosion

- **Carbon corrosion** could be detected
- No fluoride was found -> **No PTFE *decomposition*** for this chemical degradation experiment
- Mass loss study for quantification

Chemical reactions:

$$C + 2H_2O_2 \rightarrow CO_2 + 2H_2O$$

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

$$CaCO_3 + H_2CO_3 \rightarrow Ca(HCO_3)_2$$

In DECODE:
Comparison of naturally aged and artifically aged GDLs!

(a) The washing flask before carbon corrosion experiment for GDL 25BC Std.

(b) The washing flask after carbon corrosion experiment for GDL 25BC Std.

Table 4.8: Mass losses of GDL samples after ageing processes.

GDL sample	Mass loss after ageing (% of new sample)	Mass loss after ageing (mg/mg)
25BC Std samples from original artificial ageing process	6.46–7.45	92/1425–108/1450
25BC Mod samples from original artificial ageing process	4.05–7.42	59/1457–108/1455
25BA samples from carbon corrosion experiments	4.36–6.67	24/550–46/688
25BC Std samples from carbon corrosion experiments	3.39–3.91	18/531–11/281

Hydrohead Measurements for Testing Hydrophobicity

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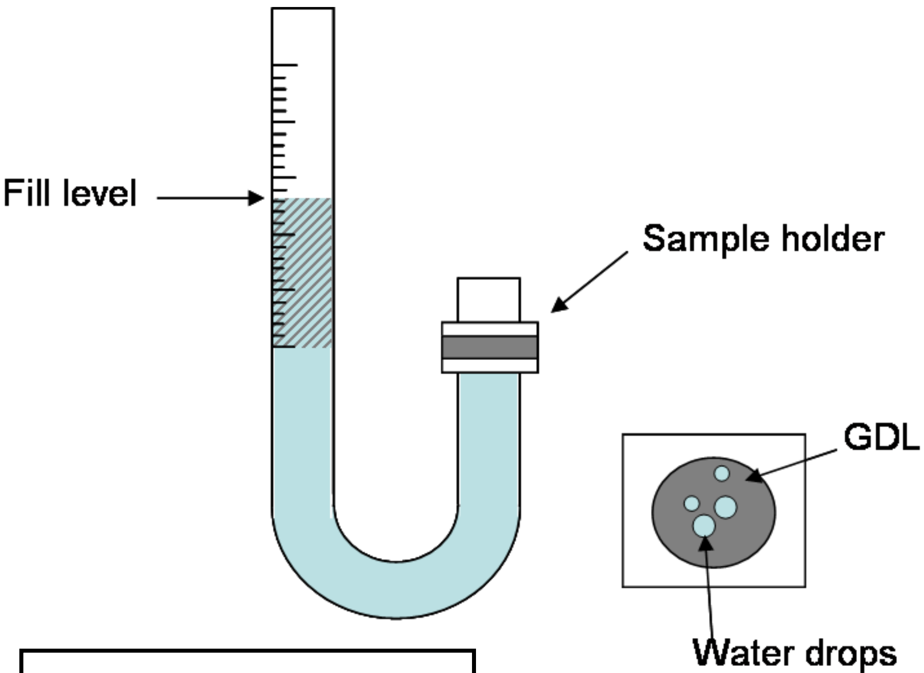

$$\Delta p = \rho_{fluid} \cdot g \cdot h$$

Other Characterization methods:

- Mercury porosimetry
- Capillary flow porosimetry
- EDX mappings
- Contact angle

GDL type	Δp (mbar)
New GDL 25BC	86.3 ± 3.0
Naturally aged GDL 25BC for 1000h	70.1 ± 6.2
Artificially aged GDL 25BC for 24h in $H_2 0_2$	76.2 ± 4.8
Modified new GDL 25BC	78.9 ± 5.3
Modified artificially aged GDL 25BC for 24h in $H_2 0_2$	79.4 ± 2.1
New GDL 25BA	15.7 ± 1.2

IR Spectroscopy
Inhomogenity in the Intensity of the C-F Vibration

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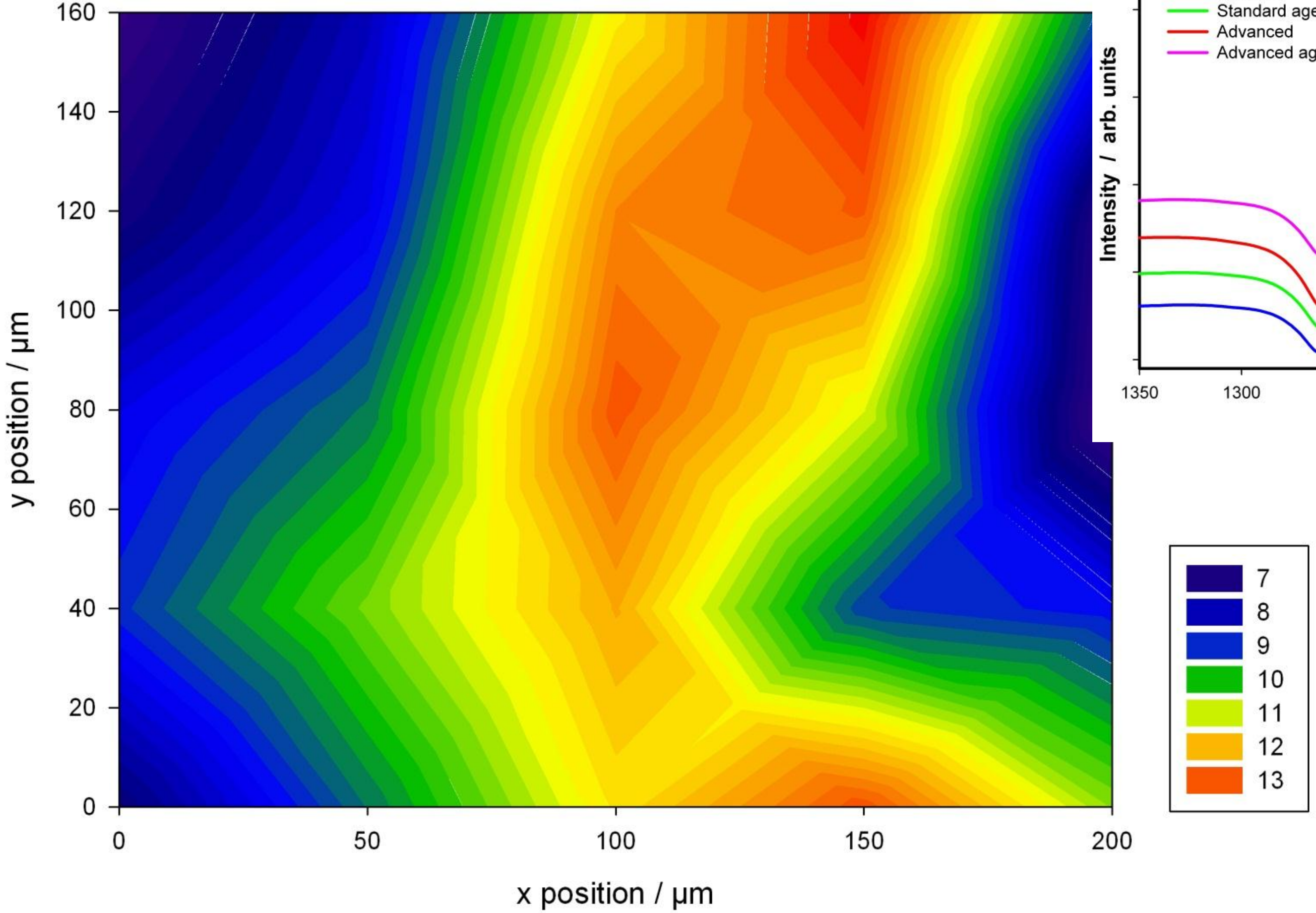

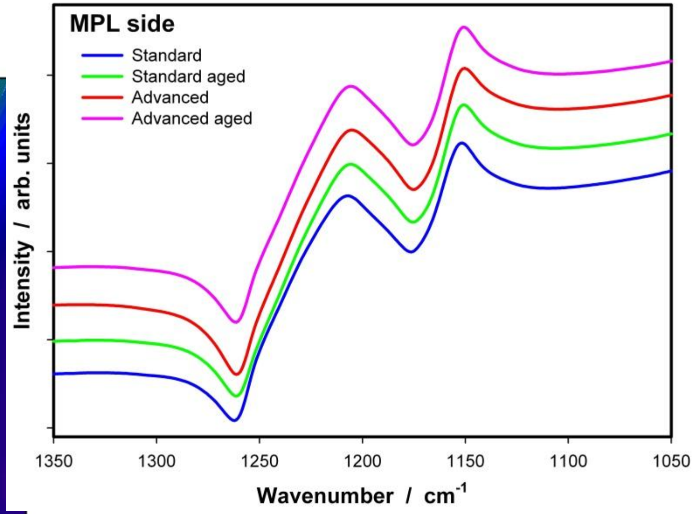

Recommendation: Improve homogeneity of hydrophobic agent distribution

In Situ Single Cell Tests (SGL)

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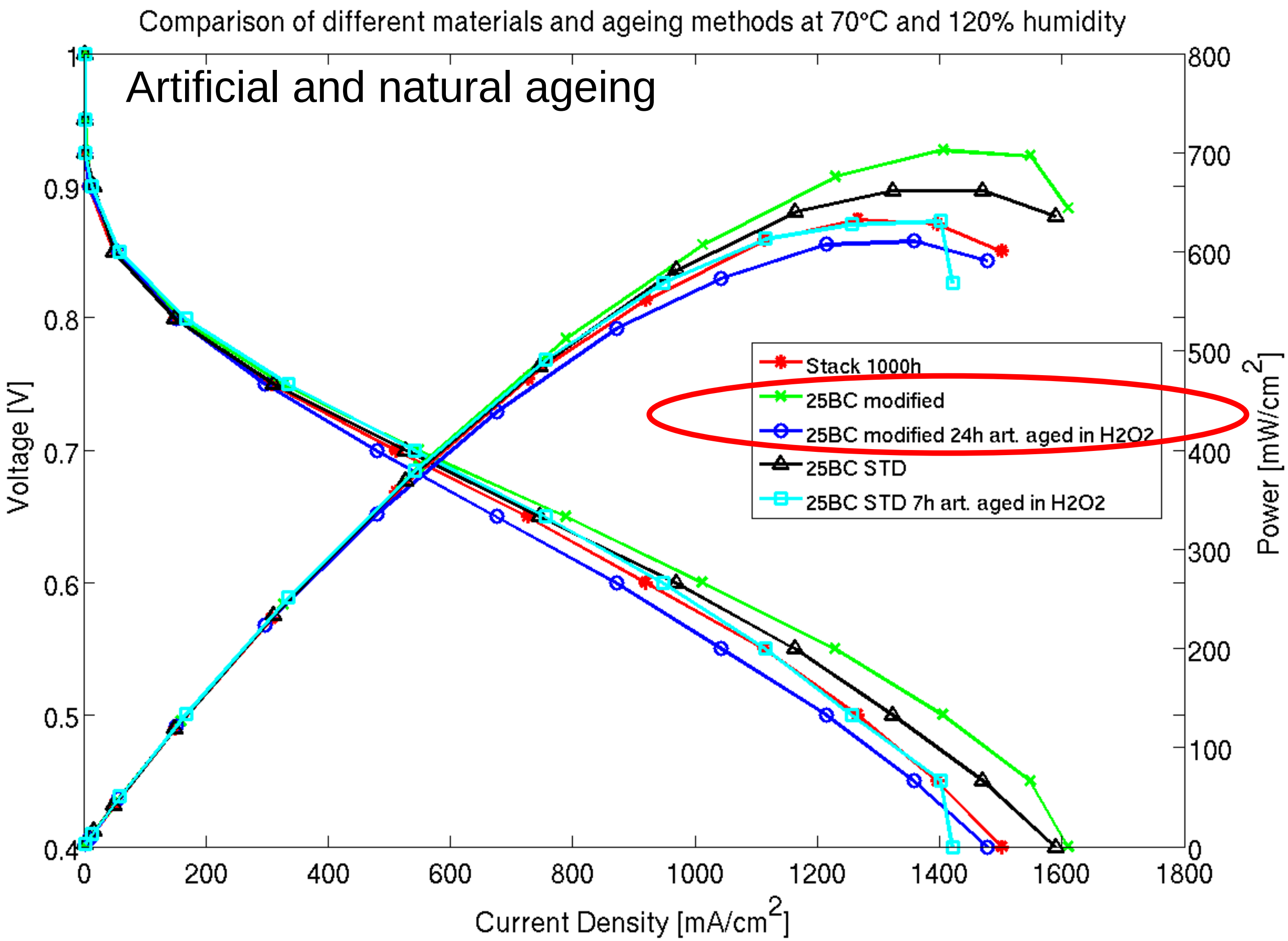

Short Stack Long Term Test – Temperature Cycling Test

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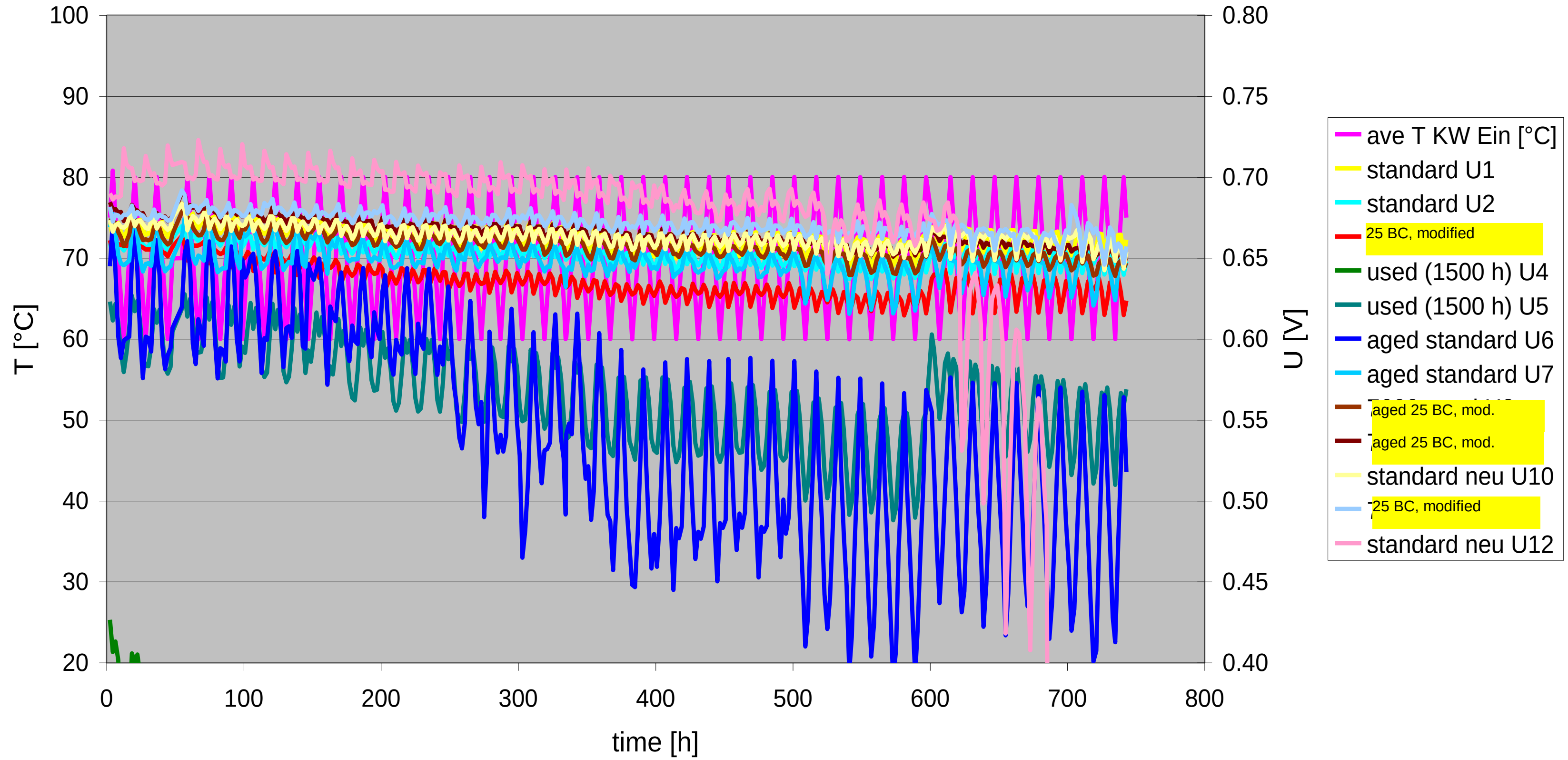
DECODE 25– Voltage time chart over 700 h



- Very low degradation of cells with modified GDLs compared to cells with standard GDLs

Identification and Ranking of Bipolar Plate Degradation Mechanisms

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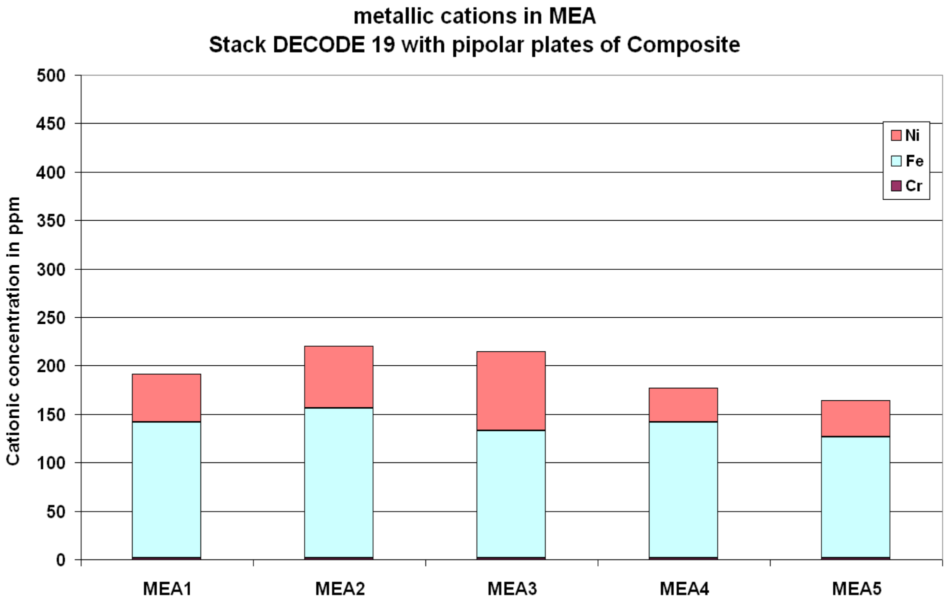
Mechanism	Importance
• Contamination of the Ionomer from external sources via port region	++++
• Change of contact resistance	++++
• Water accumulation in areas of low flow and low pressure difference	++
• Potential MEA contamination from the plates	+
• Release of silicon from the seal material	?

Corrosion products

<u>Corrosion products:</u> nickel, iron, chromium

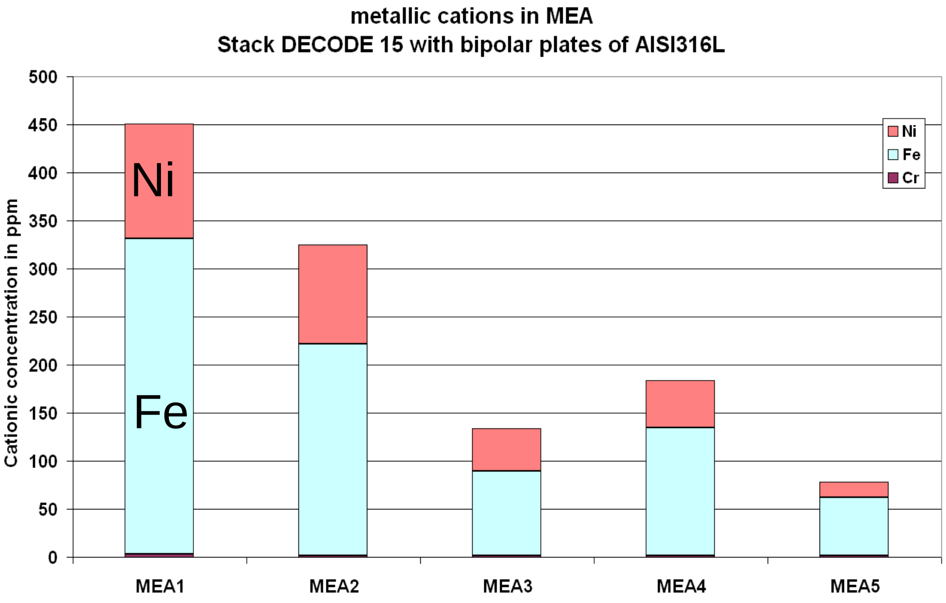
degradation products (composite)



Total sum of metallic cations in the stack

968 ppm

degradation products (AISI316L)



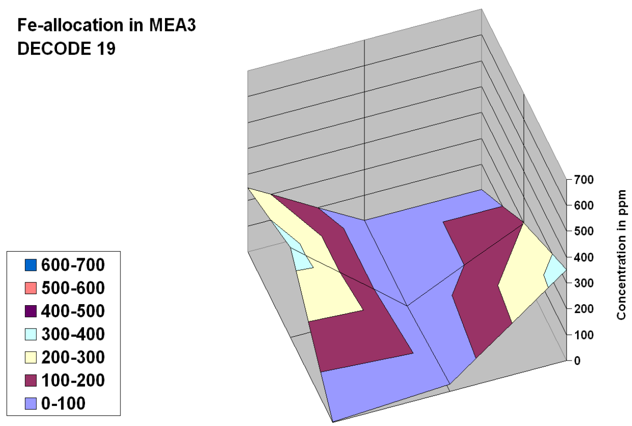
Total sum of metallic cations in the stack

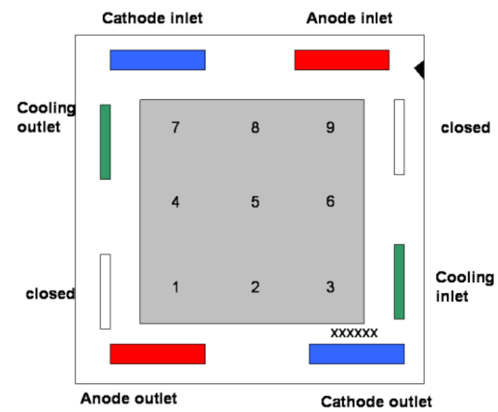
1172 ppm

comparable metallic contamination of both materials – **can this be possible?**

Distribution of contaminants

peaks are allocated to the coolant inlet and coolant outlet region





direct contact of the ionomer to the medias trough the port cut-outs

design proposal elaborated to avoid this contamination

DECODE - Stack Contaminations

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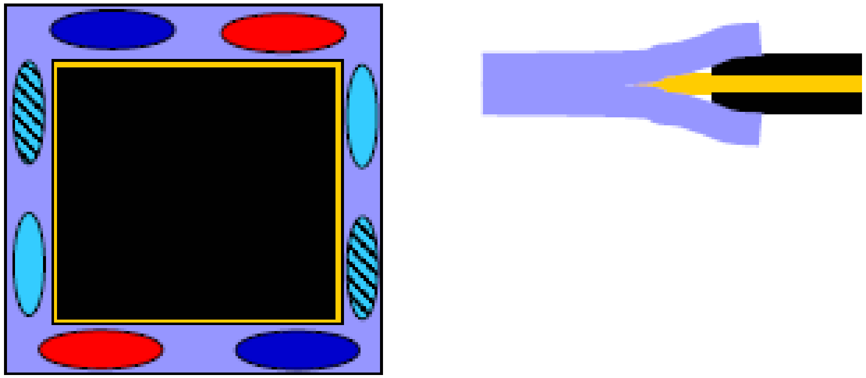
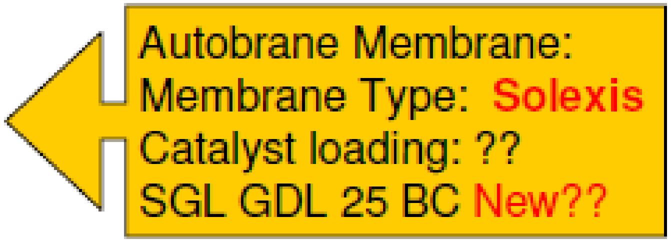
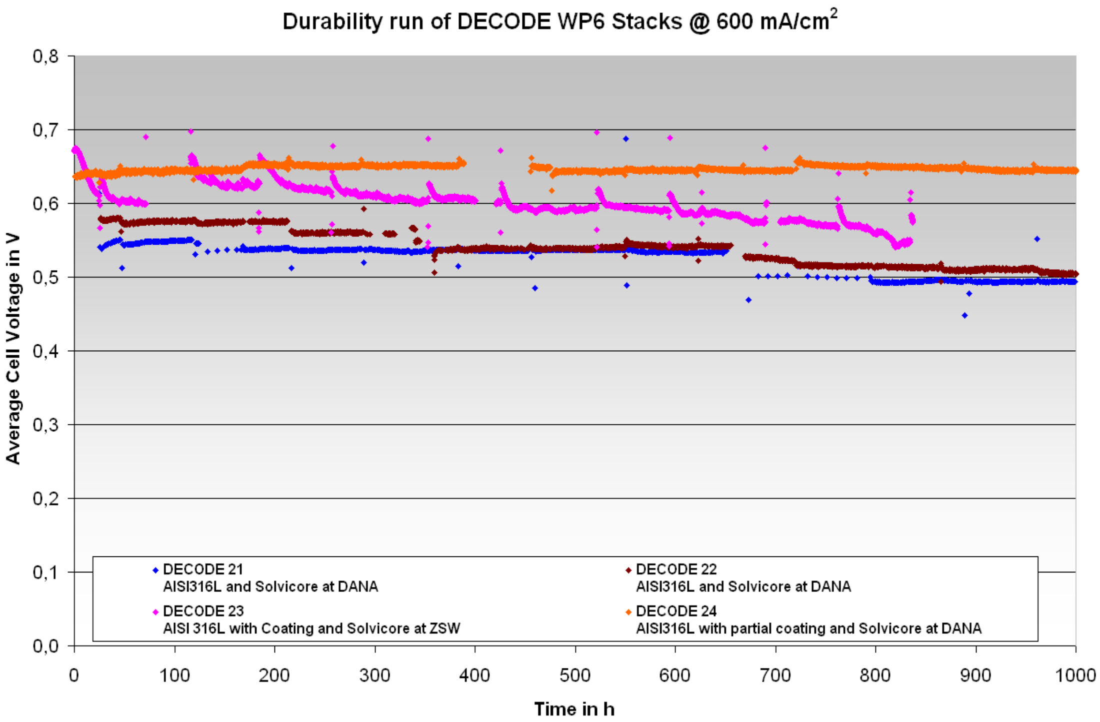
Contamination of the ionomer from external sources via port region

- Step one introduce Solvicore 5 Layer MEA (Membrane Solexis, Catalyst, Sub gasket, Membrane extended to the edge of the bipolar plate
- Step two change of MEA design to Ionomer free Sub gasket, Port area





Stack Tests with Improved Stack Design



- Durability run with AISI316L blank and **new MEA** with old configuration – at DANA
- Durability run with AISI316L blank and **new MEA** with new configuration – at DANA
- Durability run with conductive coating and new MEA configuration
- Durability run with modified conductive coating, new MEA design and further developed conditions

<u>Conclusions of WP6 durability runs:</u>

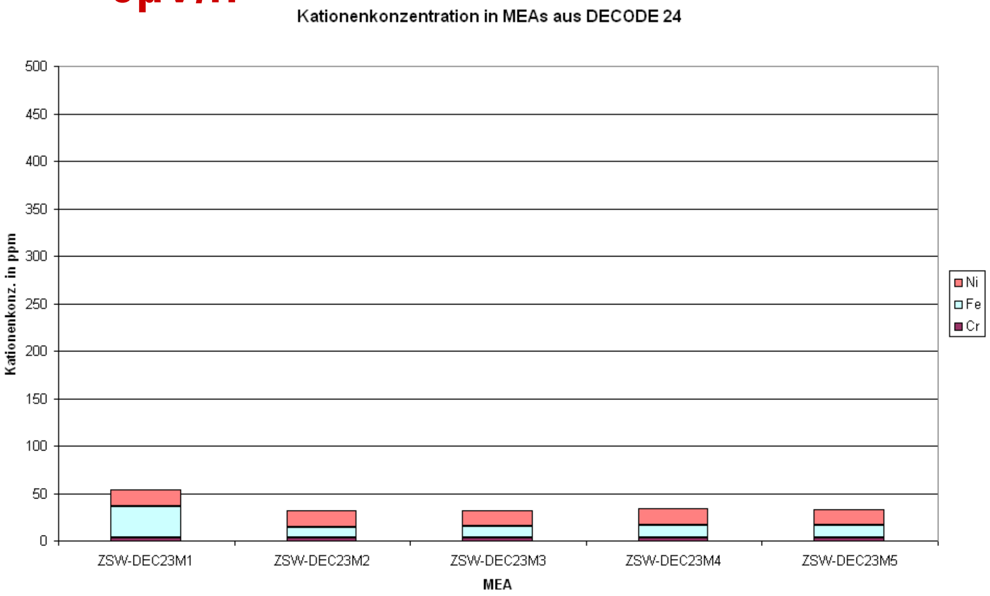
- Comparable behavior between new and old MEA configuration
- Higher cell voltage with conductive coating, irregular cell behavior
- Modified coating and further developed conditions with excellent performance results

Contaminations in MEA

Corrosion products: nickel, iron, chromium

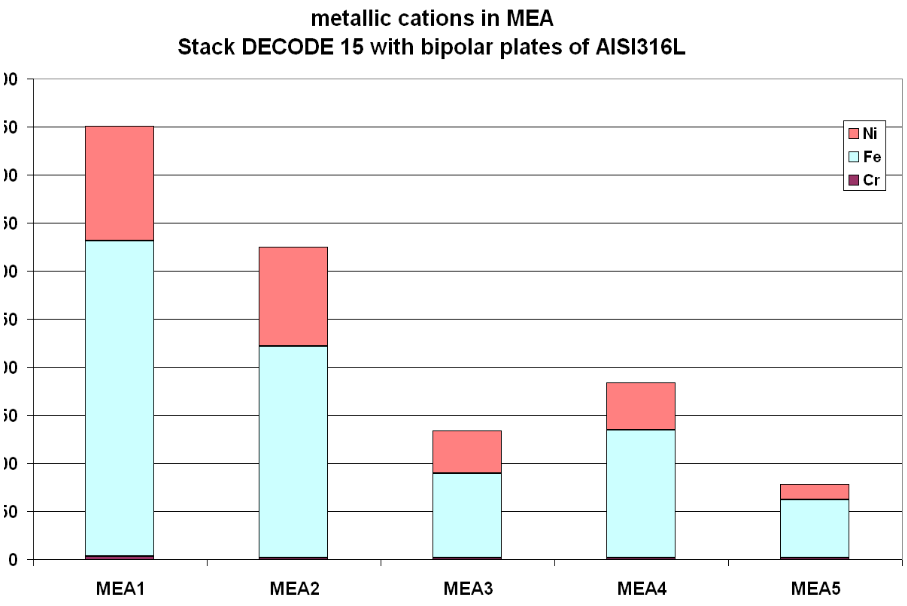
DECODE 24 (AISI316L bipolar plates with organic coating, new MEA Design and new operating conditions)

0µV/h



DECODE 15 (AISI316L bipolar plates)

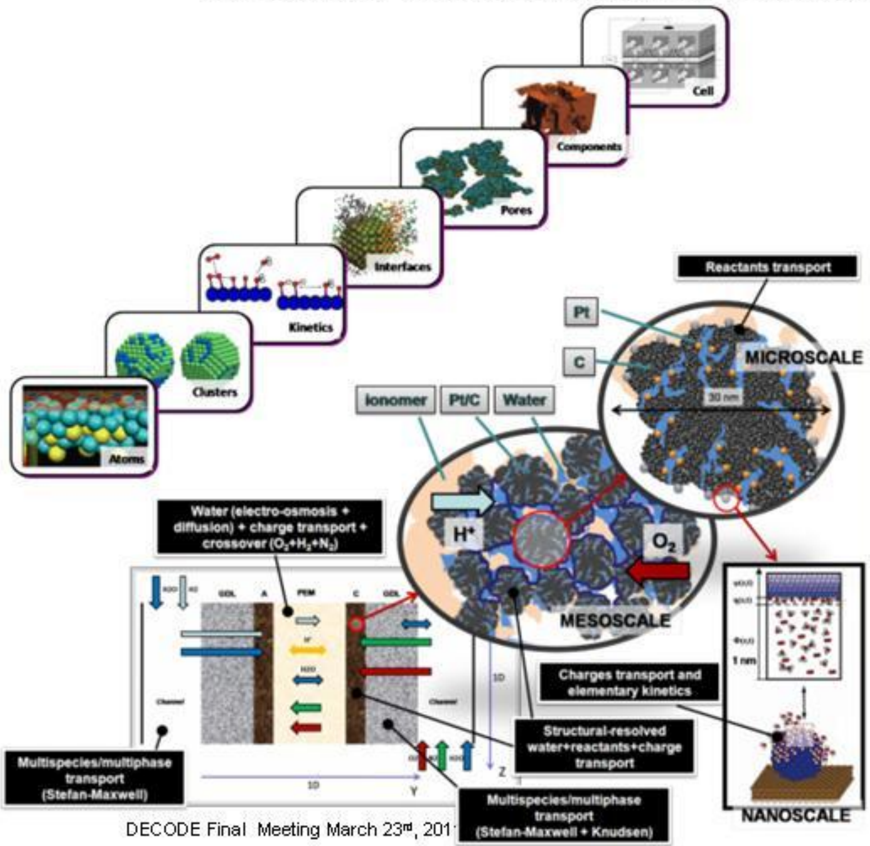
60µV/h



Modelling and Lifetime Prediction

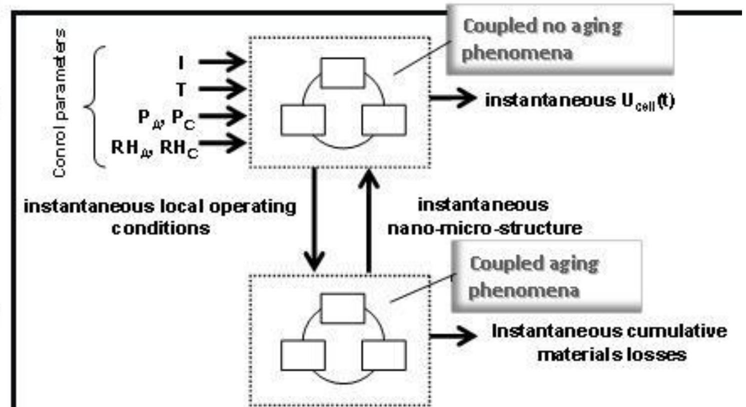
Using MEMEPhys® simulation package to optimize PEMFC components

- **MEMEPhys®** (developed at CEA since 2002): **bottom-up** multiscale simulation platform of the electrochemical generators, scaling up *ab initio* data into an irreversible thermodynamics framework, accounting, within a *continuum* approach, for:
  - the mechanisms in the components (e.g. electrodes) at spatial nano, micro, meso and macroscale (elementary kinetics, transport)
  - the intrinsic materials aging and couplings between aging mechanisms



DECODE Final Meeting March 23rd, 2011

Description of the feedback between performance and aging: DURABILITY PREDICTION (unique in literature)



- A.A. Franco, "Degradation modeling and analysis", **book chapter** in: *Fundamental Science and Engineering of PEMFC and DMFC*, C. Hartnig & C. Roth Eds., Woodhead Publisher, Cambridge (UK), in press (2011).
- A.A. Franco et al., *J. Electrochem. Soc.* **153** (6) A1053 (2006).
- A.A. Franco et al., *Fuel Cells*, **7** (2) 99 (2007).
- A.A. Franco et al., *J. Electrochem. Soc.*, **155** (4) B367 (2008).

Modelling and Lifetime Prediction

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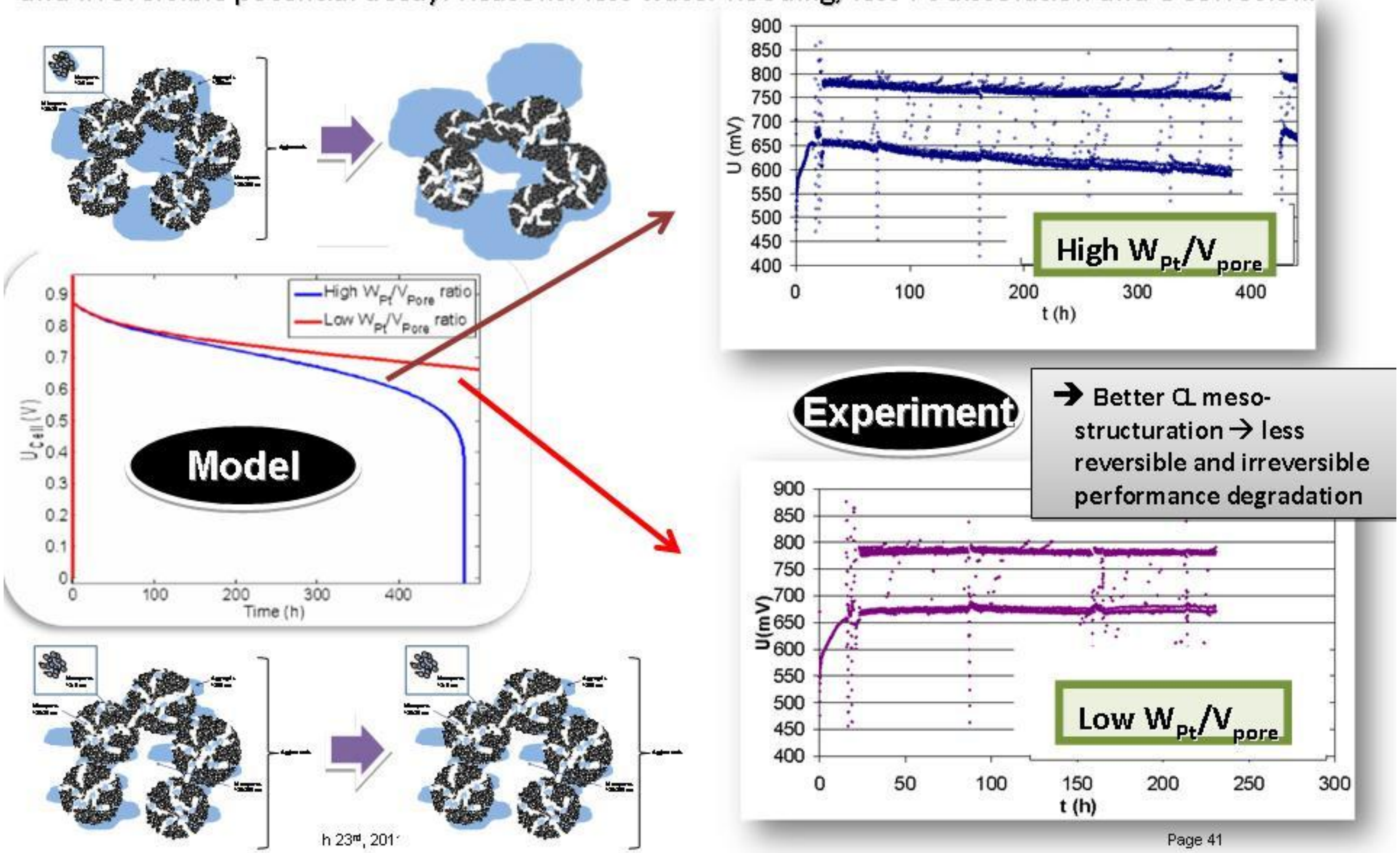
Simulation example: decreasing w_{Pt}/V_{pore} to reduce reversible and irreversible performance degradation

➔ The model suggests that a decrease of Pt loading per unit of pore volume mitigates both reversible and irreversible potential decay. Reasons: less water flooding, less Pt dissolution and C corrosion.



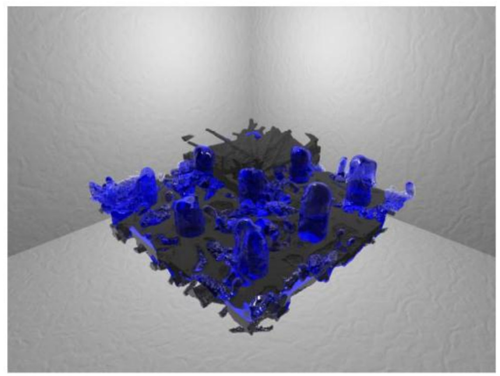
Modelling activities and results

Membrane and Electrodes:

- Multiscale elementary kinetics simulation with coupling to microscopical structure

Porous media:

- Molecular Dynamics
- Lattice Boltzmann
- Monte-Carlo
- Performance modelling



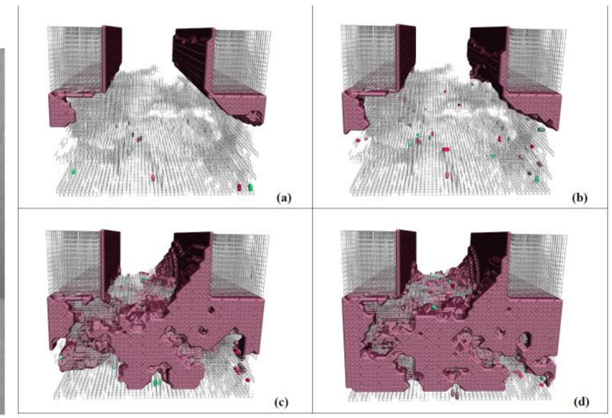
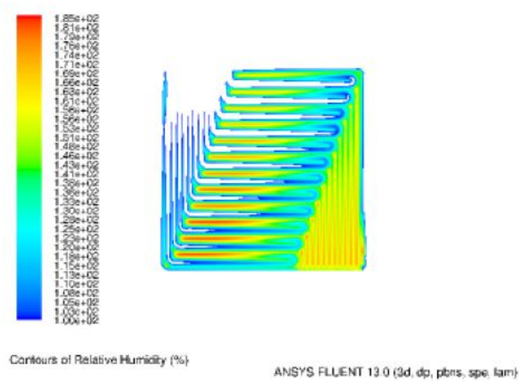
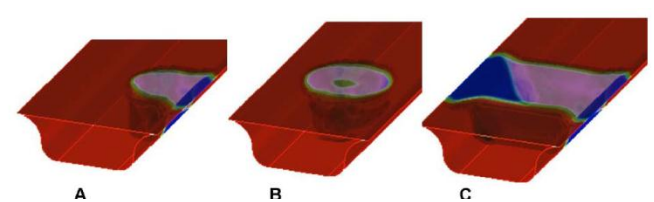


Fig. 19: Mean hydration for different PTFE content values using reconstructed tomography data. (a) 85% PTFE, (b) 75% PTFE, (c) 65% PTFE and (d) 55% PTFE.

Bipolar Plates:

- CFD
- Movement of droplets by VOF (volume of fluid)





Summary

- Improvement achieved by materials:
  - Reinforced membrane with higher crystalinity
  - Modified gas diffusion layer
- Improvement achieved by design:
  - Edge protection of membrane
  - Blocking of external contermination by new sealing concept
  -
- Improvement achieved by operation conditions:
  - Avoiding liquid water phase
  - Excursion to open circuit conditions to recover reversible voltage losses
- Different models with life time prediction capability

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THANK YOU FOR YOUR ATTENTION

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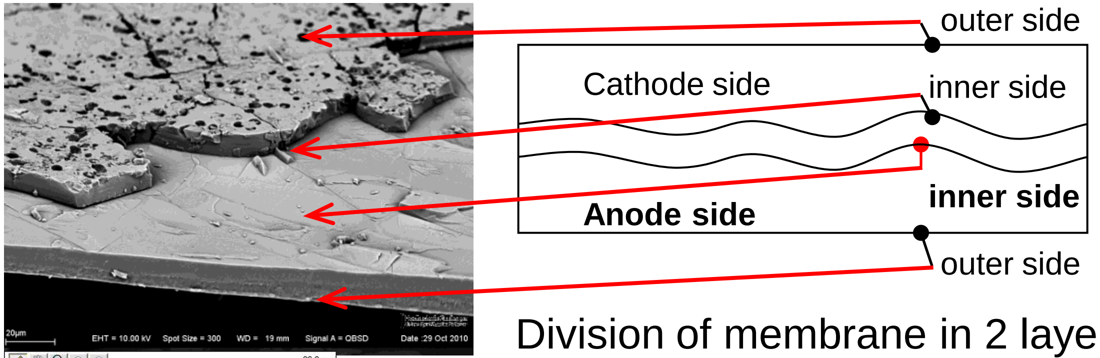
- *M. Schulze, A. Haug, E. Gülzow, K.A. Friedrich,* „Investigation of Local Degradation Effects", ECS Transactions 26 (2010) 237-245
- *K. Seidenberger, F. Wilhelm, J. Scholta,* „Monte-Carlo-Simulation - Wasserhaushalt in der GDL einer PEM-Brennstoffzelle" article (German), HZwei (April 2011), pages 17-19
- *S Pulloor Kuttanikkad, J.Pauchet, M.Prat;* „Pore-network simulations of two-phase flow in a thin porous layer of mixed wettability", Journal of Power Sources 196 (2011) 1145
- *K. Seidenberger, F. Wilhelm, T. Schmitt,W. Lehnert, J. Scholta,* „Estimation of water distribution and degradation mechanisms in polymer electrolyte membrane fuel cell gas diffusion layers using a 3D Monte Carlo model" J. Power Sources 196 (2011) 5317
- *M. Holber, P. Johansson and P. Jacobsson,* "Raman spectroscopy of an aged low temperature polymer electrolyte fuel cell membrane", *Fuel Cells,* 2011, accepted
- J. Pauchet, M. Prat, P. Schott, S. Pulloor Kuttanikkad, „Analysis of the effect of hydrophobicity loss of GDL on performance of PEMFC by coupling pore network and performance modelling", Submitted to the Journal of Power Sources

Acknowledgement to the partners of DECODE:

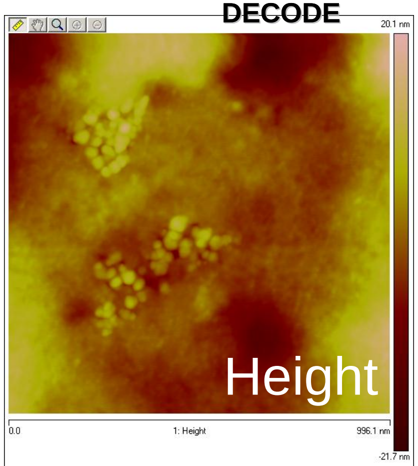
T. Damjanovic[8], S. Donath[7], S. Escribano[3], S. Fell[1], K.A. Friedrich[5], R. Glück[4], A. Haug[5], M. Holber[10], P. Jacobson[2], P. Johansson[2], D. Kehrwald[1], J. Pauchet[3], T. Malkow[6], K. Mecke[7], L. Merlo[9], M. Messerschmitt[11], D. Münter[4], R. Reissner[5], U. Rüde[7], M. Schätzle[11], J. Scholta[11], M. Schulze[5], R. Ströbel[4], D. Veyret[6], G. Tsotridis[6], Ch. Wieser[1], F. Wilhelm[11], P. Wilde[8]

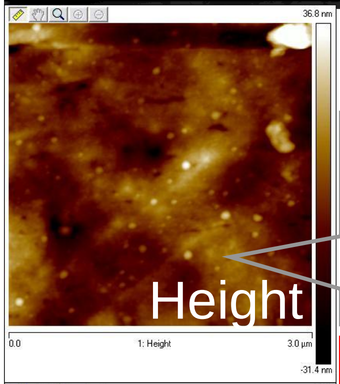
[1]Adam Opel GmbH, Germany, [2]Chalmers University of Technology, Sweden, [3]Commissariat à l'Energie Atomique (CEA), France, [4]DANA SEALING PRODUCTS - VICTOR REINZ, REINZ-Dichtungs-GMBH, Germany, [5]Deutsches Zentrum für Luft- und Raumfahrt (DLR), Germany, [6]European Commission, DG Joint Research Centre, Institute for Energy (JRC-IE), Belgium, [7]Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany, [8]SGL Technologies GmbH, Germany, [9]SOLVAY SOLEXIS S.p.A., Italy, [10]VolvoTechnology AB, Sweden, [11]Zentrum für Sonnenenergie- und Wasserstoff-Forschung Baden-Württemberg (ZSW), Germany

AFM Analysis of Solexis E87-05S, 20000 h

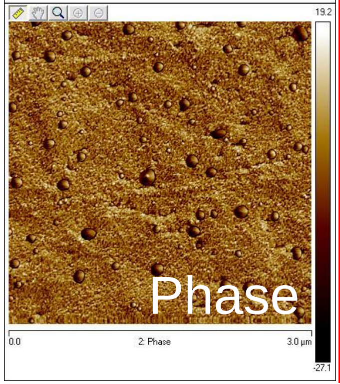


Division of membrane in 2 layers of 15 µm after storage in water





Overall high density of particles with small phase shift: probably no Pt



Platinum particles with high phase shift and high DMT modulus (~elasticity) at inner side of anode with mean diameter of 21 nm (11 nm - 44 nm)