DECODE

Understanding of Degradation Mechanisms to Improve Components and Design of PEFC
(213295)

Starting Date: 01.01.2008
FP 7 Project

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

Motivation: the project addresses commercialization hurdles for PEFC Technology: Cost, Durability, Reliability, Performance

Goals of DECODE:

- Understanding of the fundamental degradation mechanisms with emphasis on liquid water interaction and water management
- Assess the relevance of the degradation processes of polymer electrolyte fuel cell based on the extensive analysis
- Implement improvements for fuel cell durability based on:
  - Understanding of degradation processes
  - Improved materials
  - Improved operation conditions
- Development of prediction tool for degradation based on modeling (different modeling approaches)

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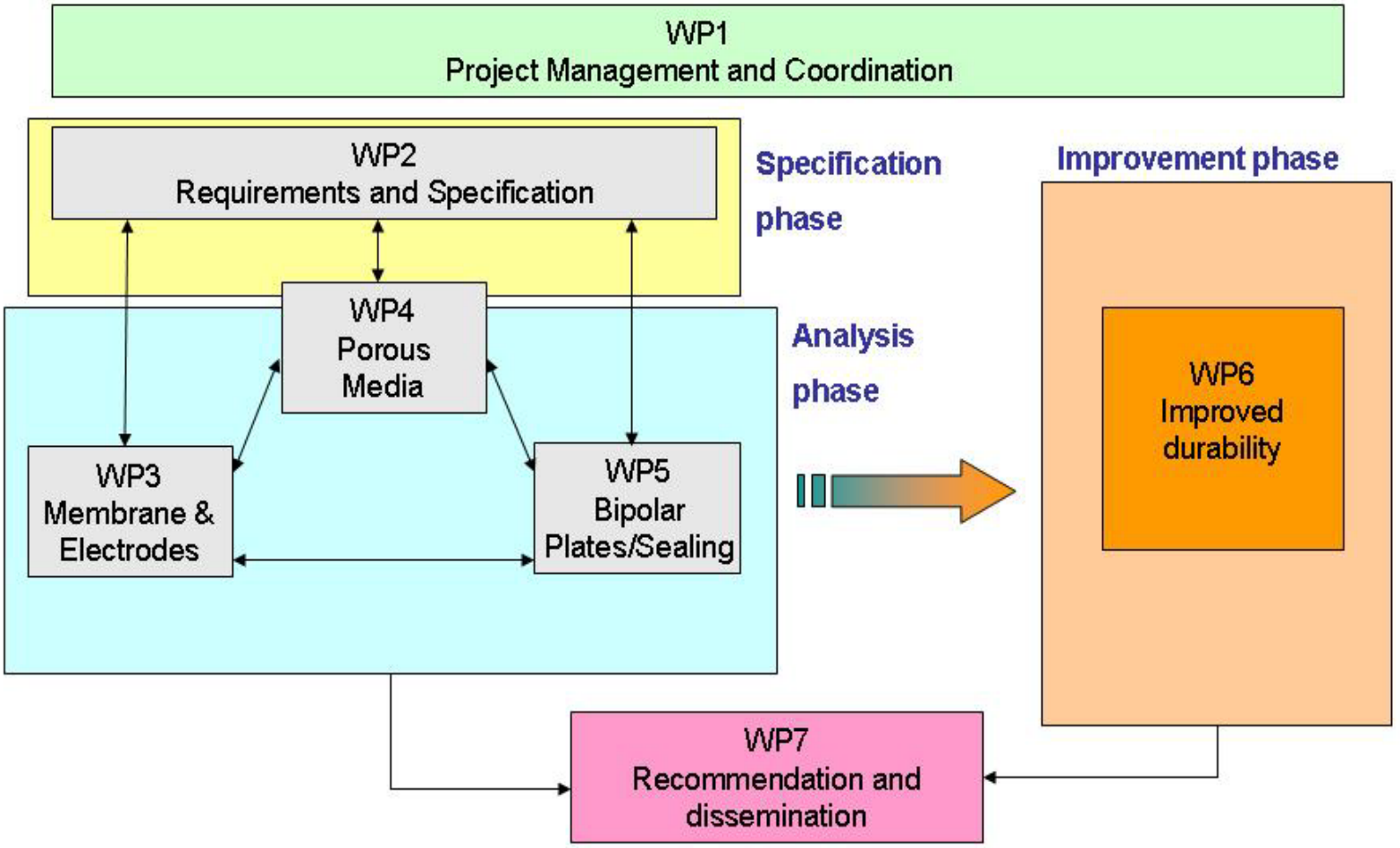
General Approach



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2. Results: Membrane & Electrodes

Activities:

- Development of membranes with chemical stabilization, higher cristallinity, mechanical reinforcement
- Four different generations of membrane electrode assemblies (CCM, CCB and with improved gasket designs)
- Detailed analysis of degradation mechanisms
- Multiscale modelling with life-time prediction

Mechanisms:	Importance & Ranking
• Structural degradation	
– Mechanical degradation of the membrane	++++
– Loss of electrochemical activity at the cathode	+++
– Loss of “electrochemical activity” at the anode	o
• Chemical degradation	?

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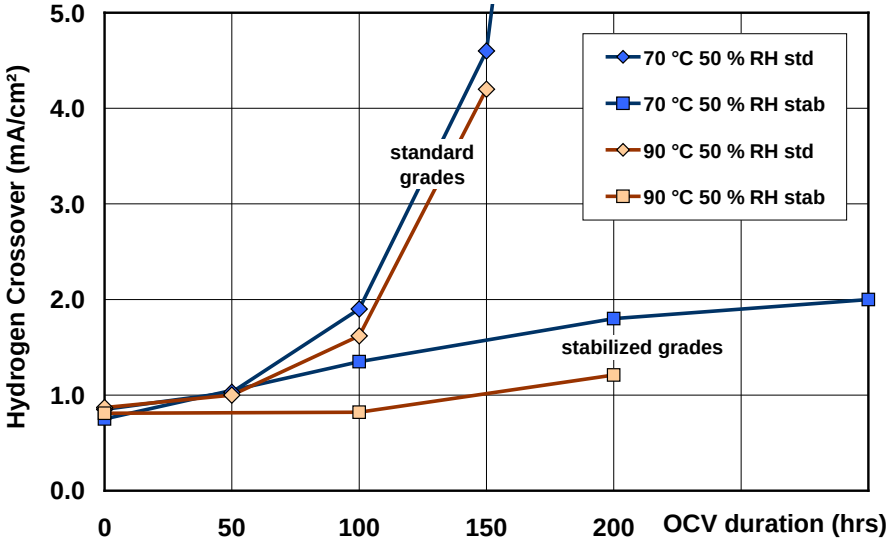
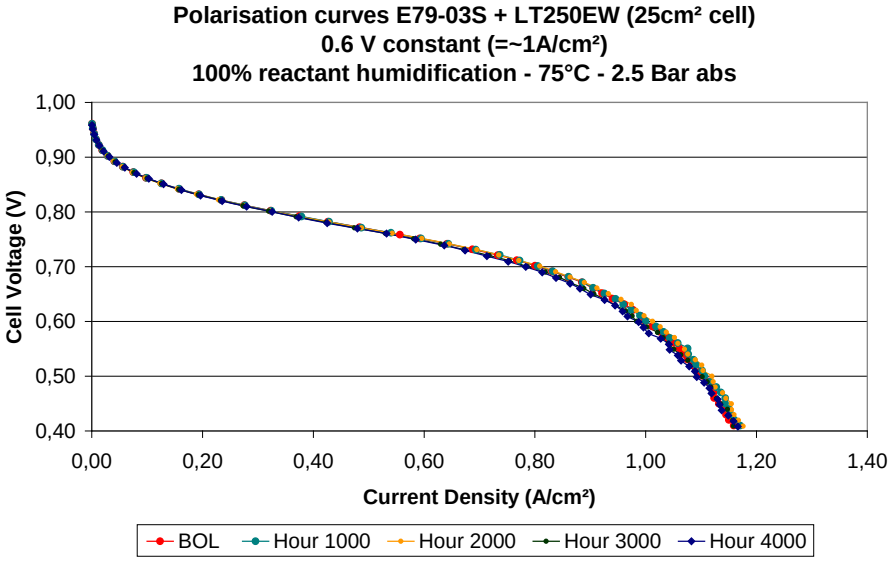
2. Result: Stabilized Aquivion™ Membrane

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





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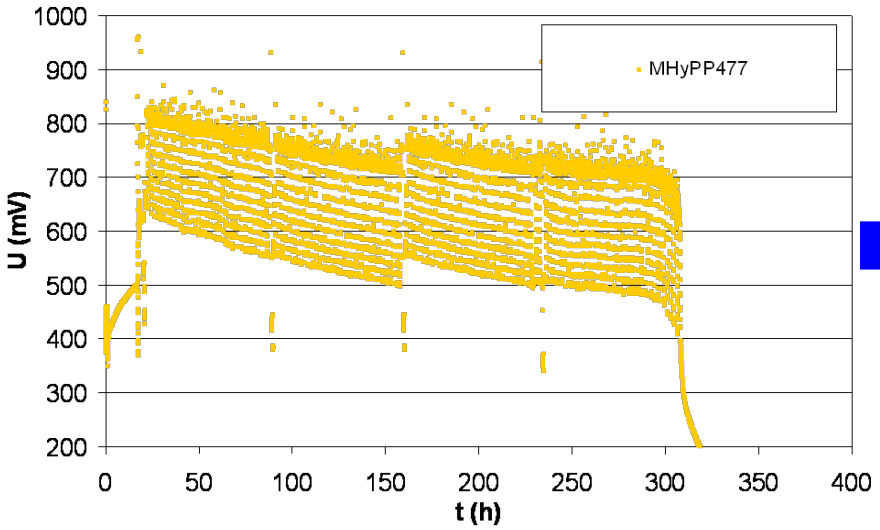
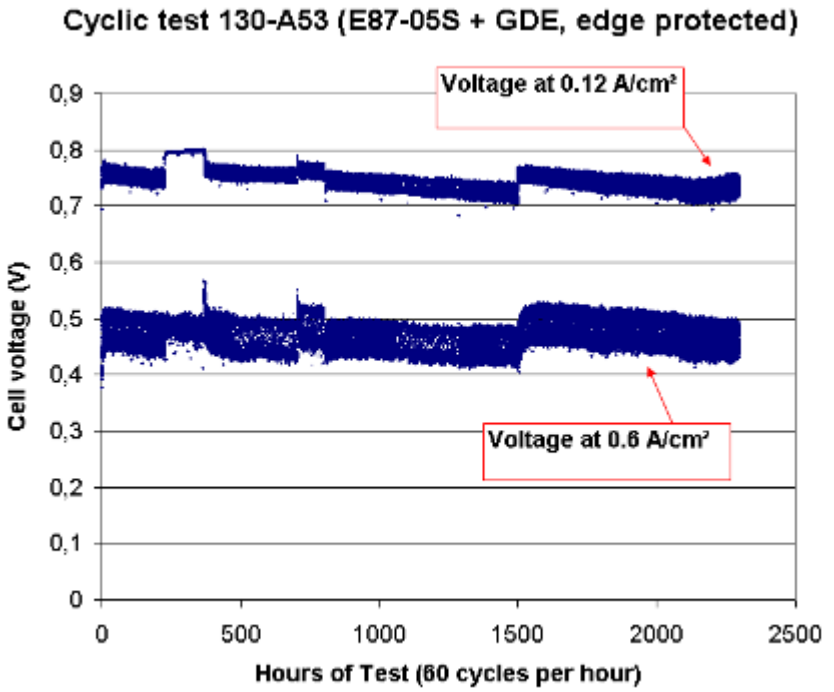
Dynamic testing of MEAs

unstabilized AQUIVION membrane without edge protection (2009)





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

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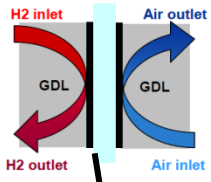
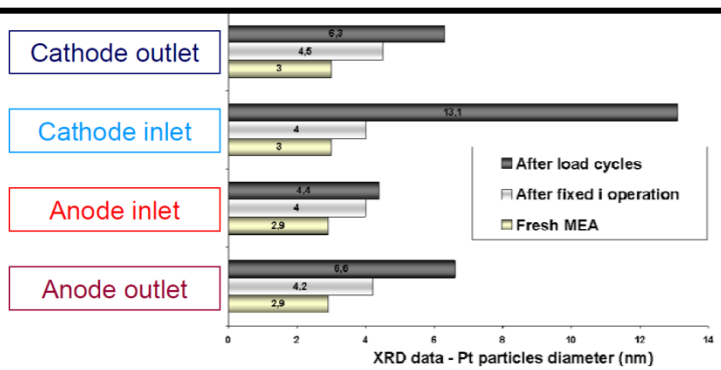
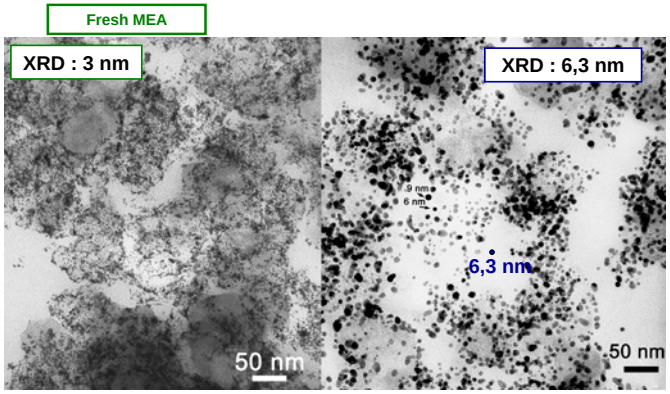
Analysis

Active layers degradation: after cycling and membrane damaged



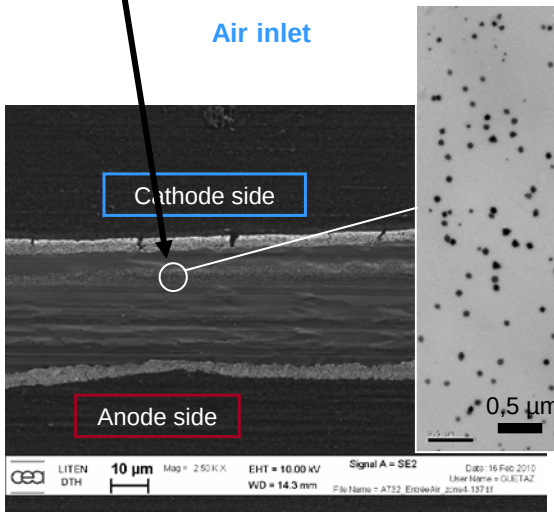


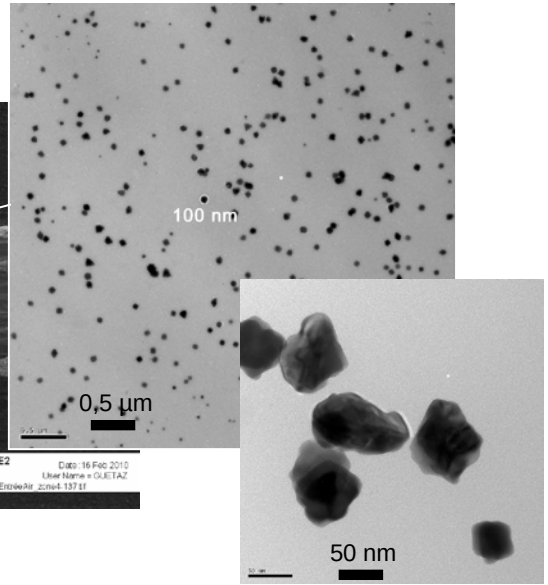
→ Pt particles growth by Ostwald ripening at air outlet



H2 outlet

Air inlet





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

Activities:

- Methodology development
  - Accelerated ageing methods
  - Characterization (porosimetry, wetting, permeation, XPS, IR, bubble point, surface energy etc.)
  - Testing in short stacks
- Ageing
  - Naturally ageing
  - Artificial ageing
- Modelling and thinking tools
- **Modification of hydrophobicity**

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

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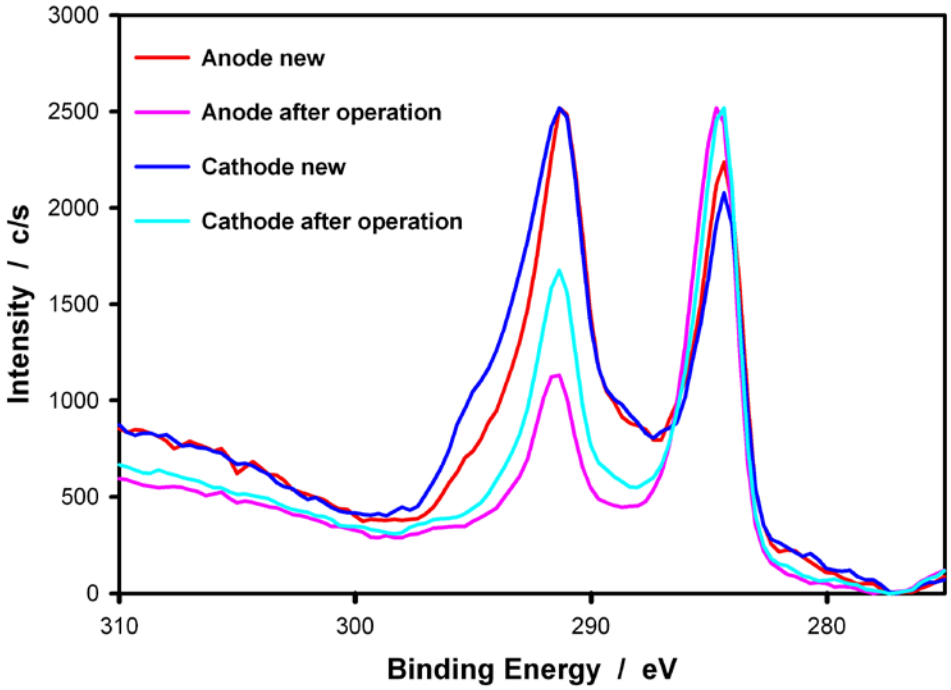
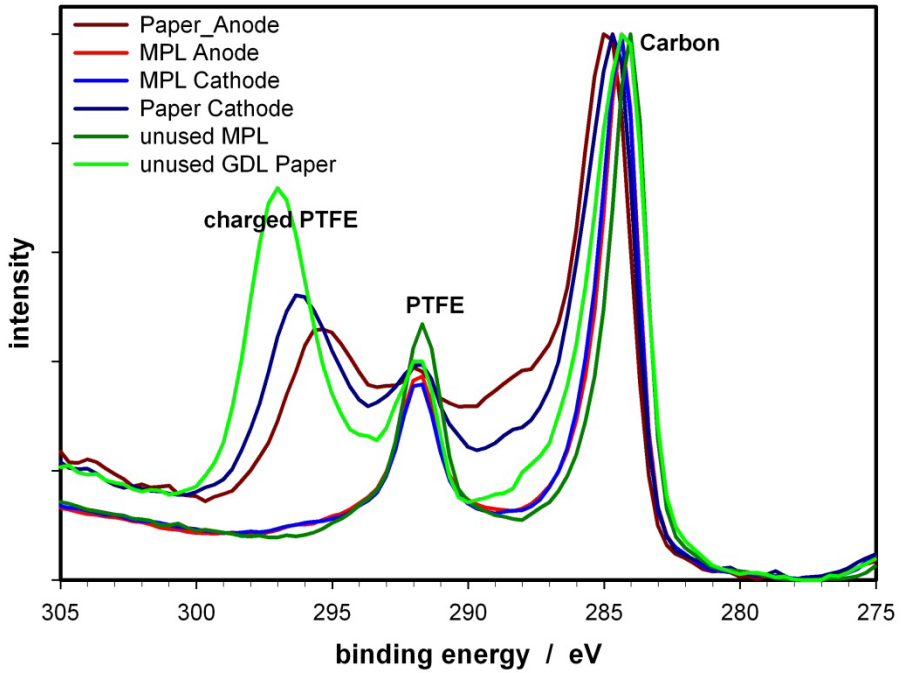
Analysis

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

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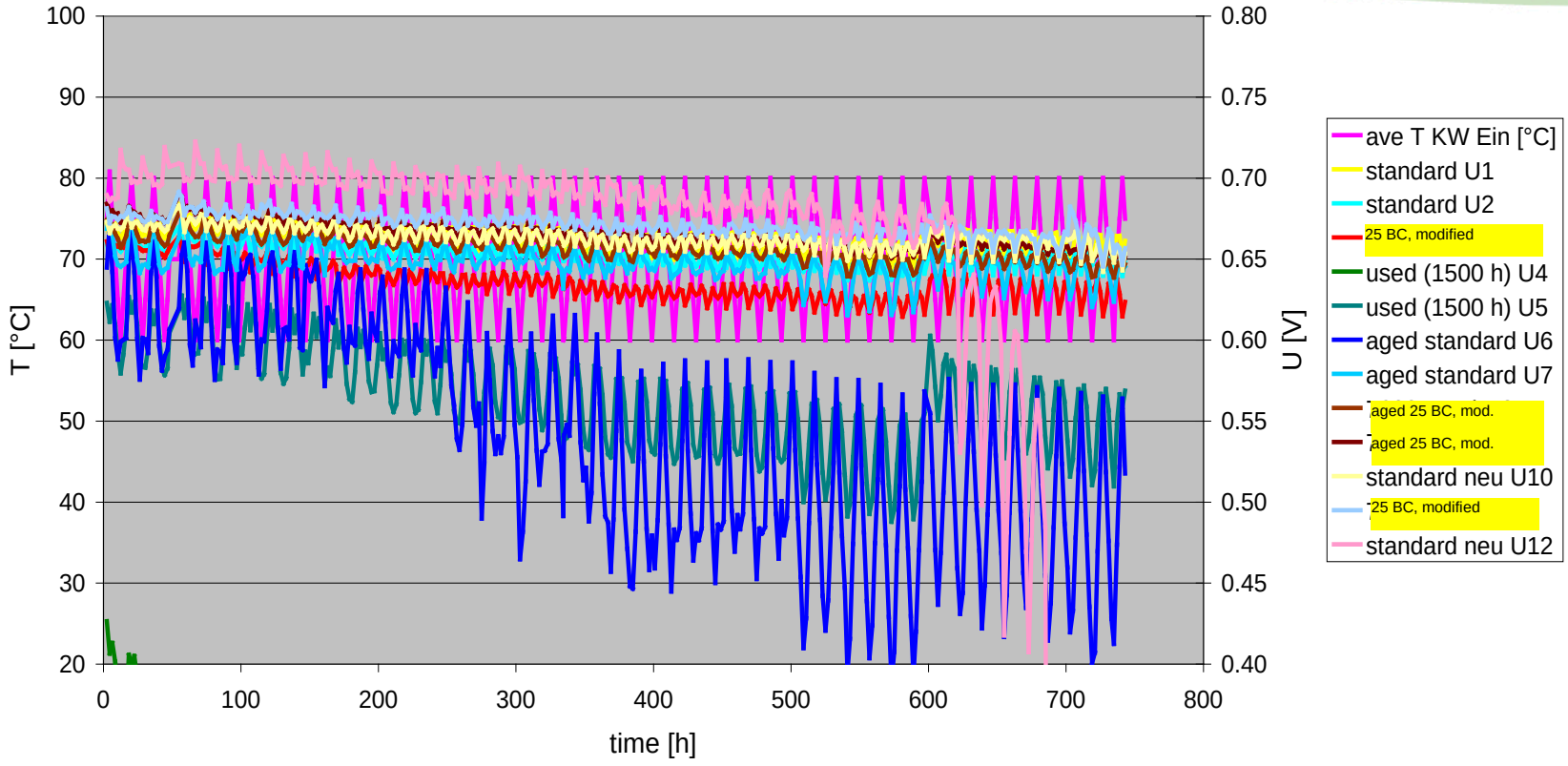
Porous media improvement

DECODE 25– Voltage time chart over 700 h



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

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2. Results: Membrane & Electrodes

Activities:

- Long term testing in short stacks with different bipolar plates (composite, uncoated stainless steel, coated etc.)
- Methology for experimental determination of ageing BPP and seals
- Development of models and thinking tools
- Design and material improvements

Mechanisms:	**Importance & Ranking**
• 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	?

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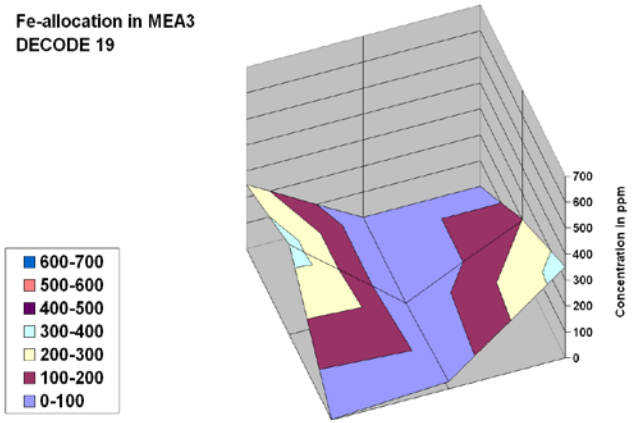
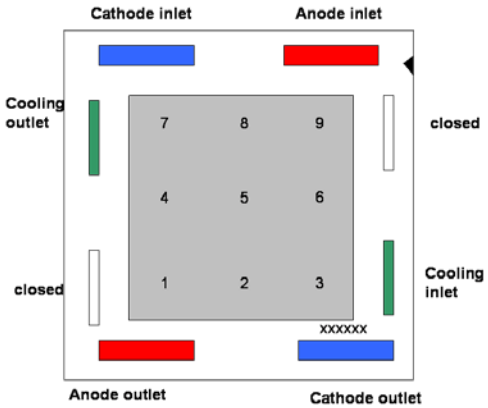
Analysis

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

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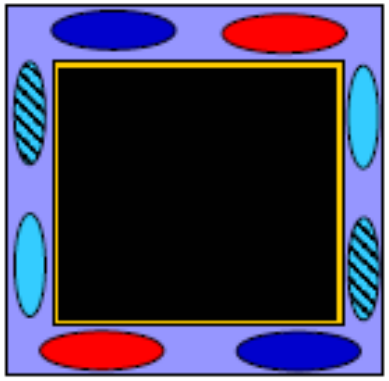
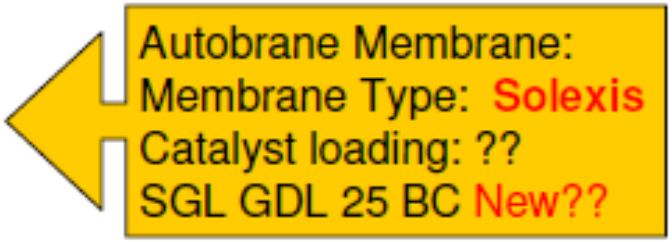
Bipolar plate improvement

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**





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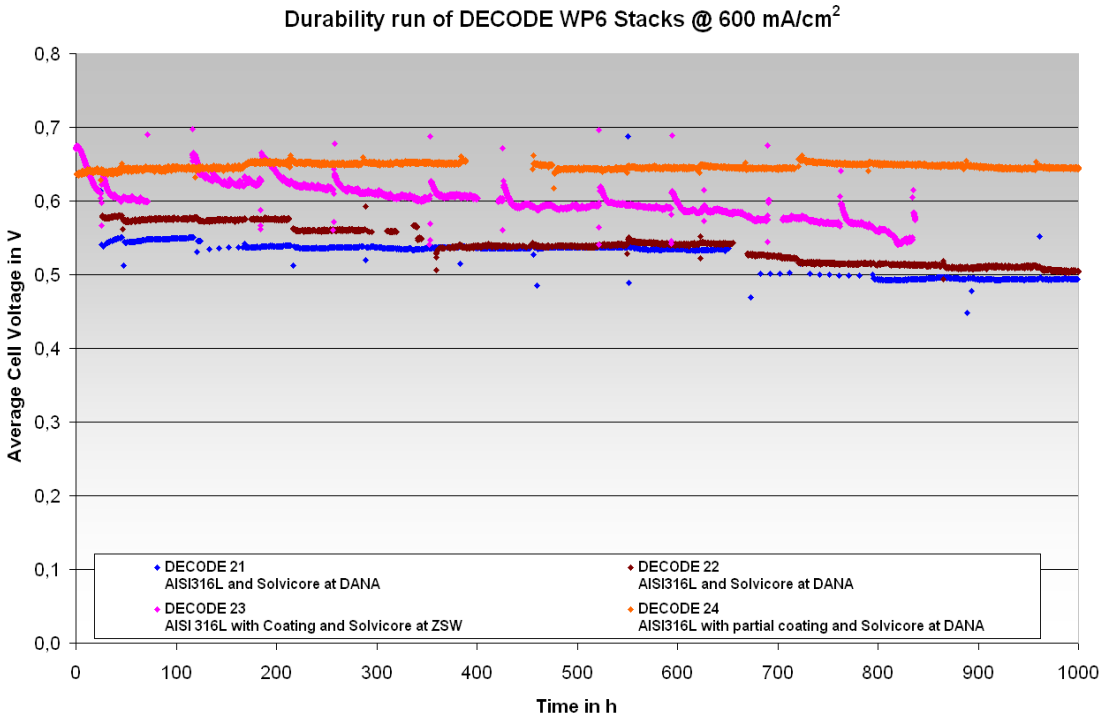
Bipolar plate improvement



- 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

Conclusions of WP6 durability runs:

- 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

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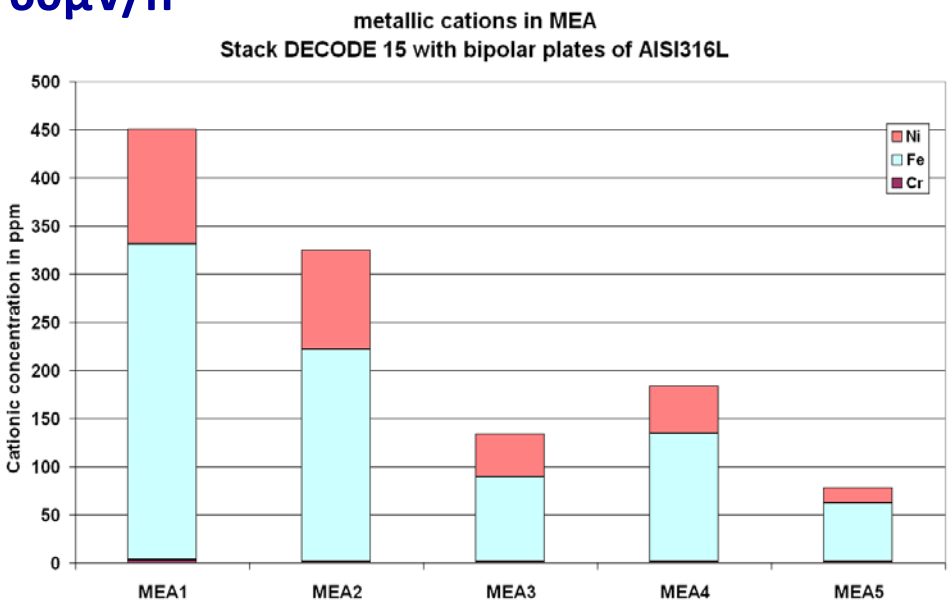
Bipolar plate improvement

Corrosion products: nickel, iron, chromium

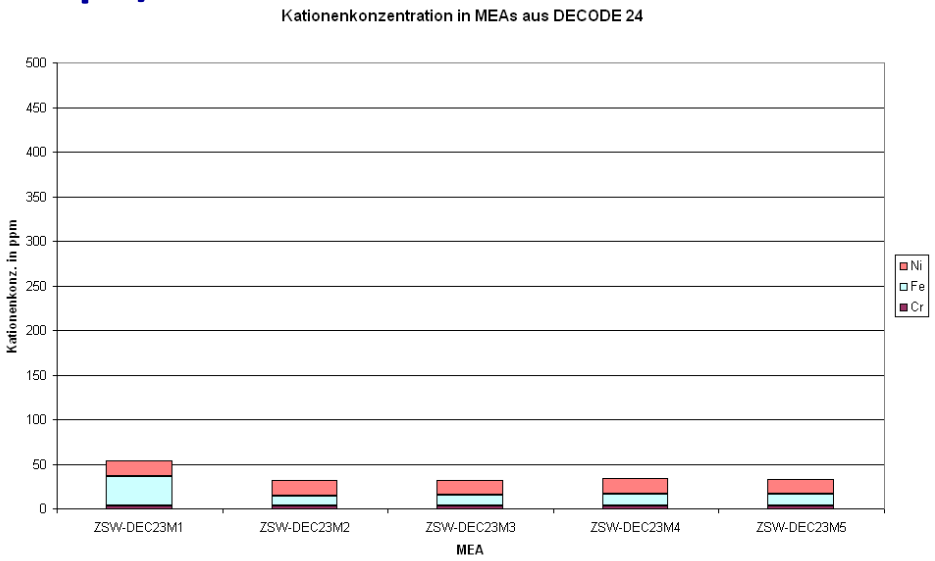
DECODE 15 (AISI316L bipolar plates)

60µV/h



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

0µV/h



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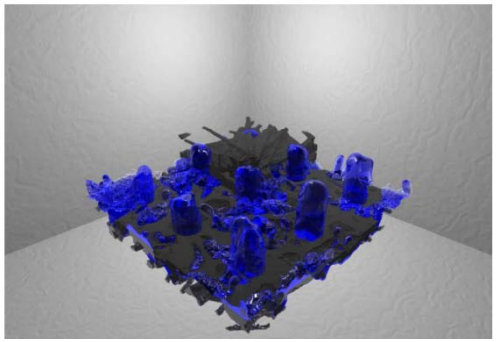
Membrane and Electrodes:

- Multiscale elementary kinetics simulation with coupling to microscopical structure
- Life prediction
- Interaction of individual degradation processes (carbo corrosion, catalyst agglommeration, membrane thinning etc.)

Porous media:

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



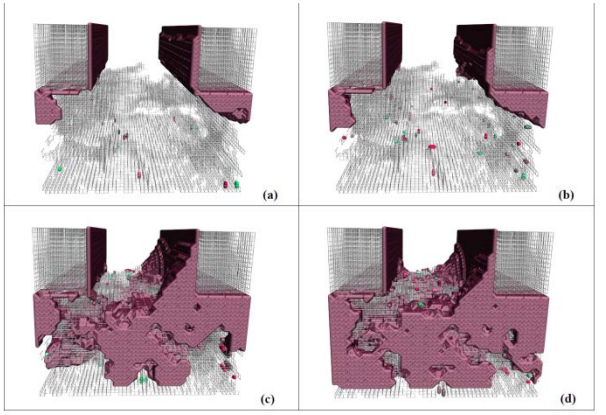
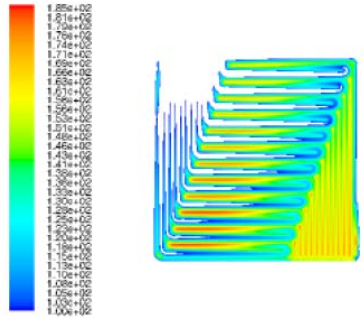


Fig. 19: Mean hydration for different PTFE content values using reconstructed tomography data. (a) 85% PTFE, (b) 75% PTFE, (c) 65% PTFE and (d) 55% PTFE.

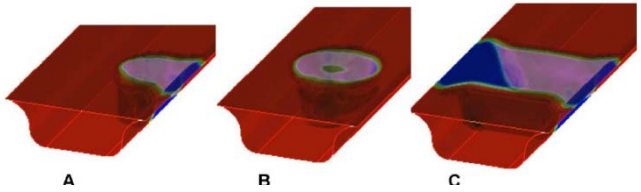
Bipolar Plates:

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



Contours of Relative Humidity (%)

ANSYS FLUENT 13.0 (3d, dp, pbns, spe, lam)



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Achievements

- Improvement achieved by materials:
  - Reinforced membrane with higher crystalinity
  - Modified gas diffusion layer
- Improvement achieved by design:
  - Edge protection of membrane
  - Blocking of external contamination 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

Correlation of the project with the corresponding Application Area (as mentioned in MAIP/AIP documents)

Application area: Transport & Refuelling Infrastructure

"Research and technological development will mainly address specific issues related to PEMFC technology for transport applications. This will include inter alia: **mechanically stable and long-life membranes** allowing for system architectures simplification; **electrochemically stable** and low-cost catalysts for polymer **Membrane and Electrode Assemblies** (MEAs); **corrosion resistant and low-weight, -volume and -cost bipolar plates** to achieve the target power densities; manufacturing and process development; **methodology and tools for reliable life-time assessments** that help improving system and vehicle operating strategies."

- **Topic: "Investigation of degradation phenomena"**

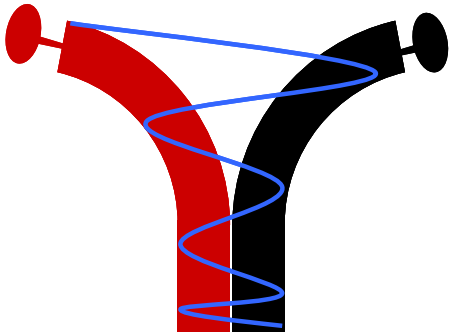
→ "Research and development on critical system operating parameters and conditions to establish a solid methodology and develop tools for safe life-time assessments and help improve system and vehicle operating strategies"

- **Training and Education**
  - Post-doctoral researchers, PhD and MSc students involved in activities at Universities of Chalmers, Erlangen, CEA, DLR & ZSW
- **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**

FC papers & conferences (incl. exhibition for indust.) (All partners)

- about 40 presentations by posters and talks
- 10 papers
- EUCAR-Workshops and “European Fuel Cell and Hydrogen week”
- **Two public workshops: Progress MEA Carisma Conference in La Grande Motte, September 2010 and a public workshop of the DECODE project with approx. 80 participants on 24th of March 2011 at Chalmers University in Gothenburg**

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]

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