

Überblick über die Degradationsmechanismen in PEFC

M. Schulze, K.A. Friedrich, A. Haug





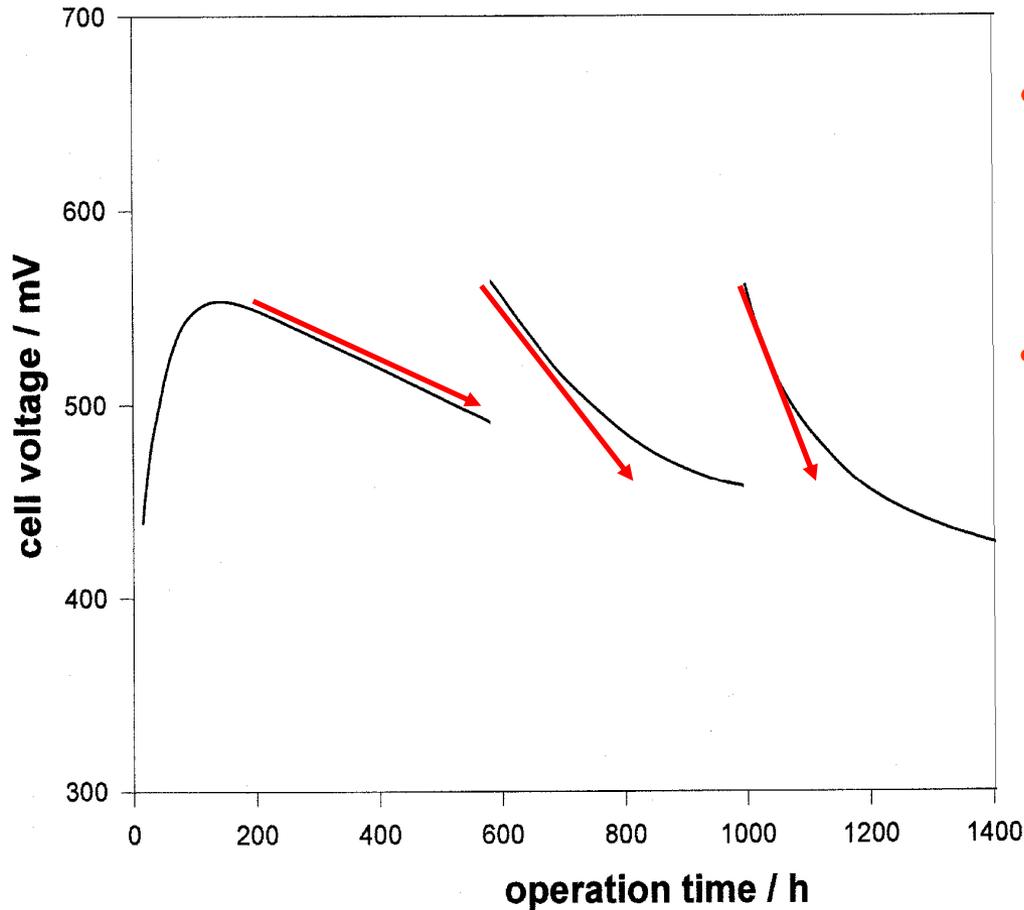
Degradation of PEFC

- Degradation limits the life time of fuel cells
- Understanding of degradation processes insufficient
- Knowledge about the influence of the degradation processes insufficient

Motivation for using diagnostic tools

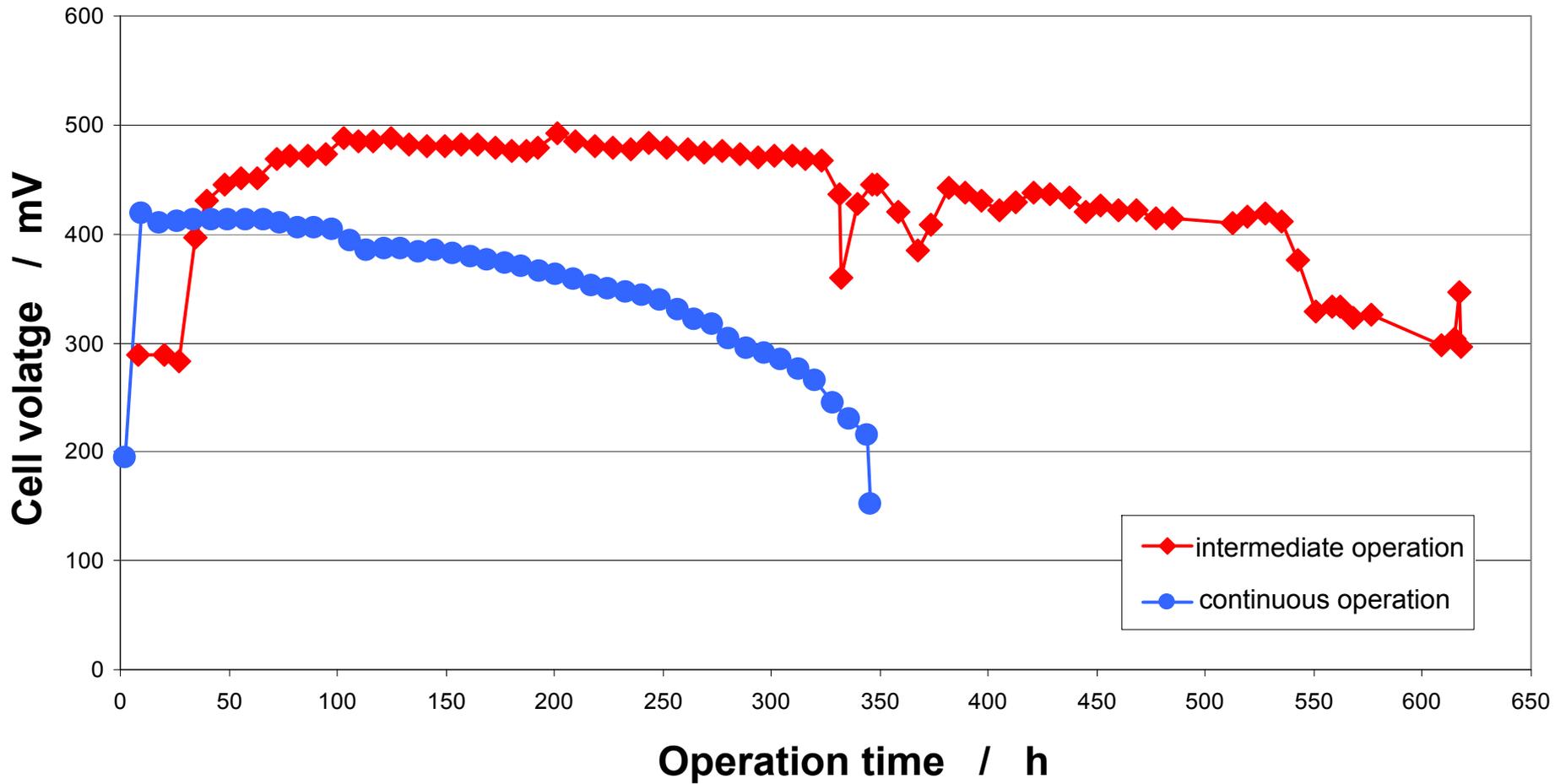
- Understanding of the degradation processes in fuel cells in detail
- Inhibition of degradation processes
- Influence of the operation conditions on the conditions inside the fuel cell

PEFC long term experiment



- The electrochemical performance decreases at constant load
- After shut-down and drying the initial performance can be achieved but decrease of performance is accelerated

Cell voltage at 500 mA/cm²





Diagnostic tools at DLR, examples:

Physical methods (ex-situ diagnostics)

- Scanning Electron Microscopy (SEM/EDX)
- X-Ray Photoelectron Spectroscopy (XPS)
- X-Ray Diffraction (XRD)
- Porosimetry with mercury intrusion & nitrogen adsorption
- Temperature Programmed Desorption / Reduction / Oxidation (TPD / TPR / TPO)

Electrochemical methods (in-situ diagnostics)

- V-i characteristics
- Electrochemical Impedance Spectroscopy (EIS)
- Locally-resolved measurements (e.g. current density distribution)



Diagnostic tools at DLR

Problems with various diagnostic methods

Ex-situ methods:

- Destructive methods
- Measurements can only be performed after operation
- Correlation of electrochemical behavior and analytical data is often unclear

In-situ methods

- Interpretation of the data needs models, which cannot be derived from the measurement data
- The influence of various parameters cannot be distinguished in each case

⇒ Combination of ex-situ and in-situ methods

Failure modes, degradation processes and stressors Catalysts / Reactive Layers

Degradation process	Qualitative effect on the fuel cell	Assumed mechanisms	Stressor
Structure change of catalyst: Agglomeration of catalyst particles	Loss of the dispersive distribution / loss of specific surface catalyst area → loss of electrochemical performance	Ostwald ripening, dissolution and re-deposition	Potential and liquid water
Oxidation of the carbon support of the catalysts	Thinning of electrodes / influence on performance not clear	Local electrochemical elements with corrosion potential	critical states: open potential, fuel starvation
Alteration of the composition of platinum alloy catalysts	Change of the reaction mechanism → loss of electrochemical performance	Potential depending dissolution of alloy materials	Potential depending dissolution of alloy materials

Failure modes, degradation processes and stressors Catalysts / Reactive Layers

Degradation process	Qualitative effect on the fuel cell	Assumed mechanisms	Stressor
Poisoning of catalysts by dissolved species from other components	Loss of catalytic activity → loss of electrochemical performance	Change of the surface properties and composition	Potential, liquid water phase
Poisoning of the catalyst by fuel/air components	Loss of catalytic activity → loss of electrochemical performance (irreversible/reversible depending on the poisoning component)	Change of the surface properties and composition → blocking of active sites	Impurities
Movement of the catalyst material in the electrical field/loss of electrochemical performance	→ loss of electrochemical performance	Dissolution and re-deposition of the catalyst and diffusion of ions	Potential, liquid water, electrical field
Thinning of the reactive layer	Deterioration of mass transport properties	Carbon corrosion by local undersupply	

Failure modes, degradation processes and stressors Catalysts / Reactive Layers

Degradation process	Qualitative effect on the fuel cell	Assumed mechanisms	Stressor
Loss of particles in reaction layer	Not clear, maybe loss of active surface area/decrease of the Pt utilization / loss of electrochemical performance	Mechanical Erosion	High flow rates High content of water (water droplets)
Partially decomposition of the PTFE in the reactive layer	Loss of hydrophobicity / altered water balance		Liquid water, Electrochemical reaction
Delamination from the membrane	Increase of contact resistance / loss of electrochemical performance	Changes of membrane dimension	wet/dry cycles mechanical stress
Delamination from the GDL	Increase of the contact resistance / loss of electro-chemical performance	Mechanical stress	Maybe induced by formation of liquid water at the interface

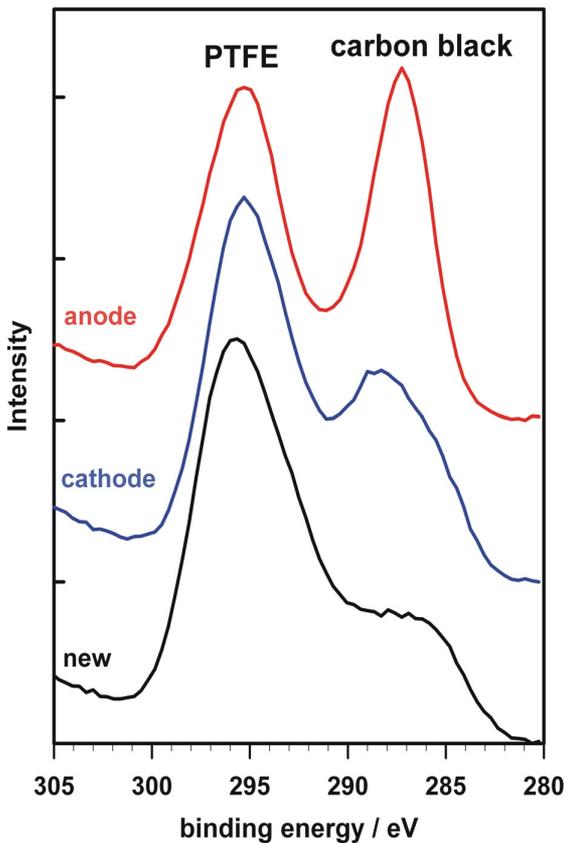
Failure modes, degradation processes and stressors

Gas diffusion layer

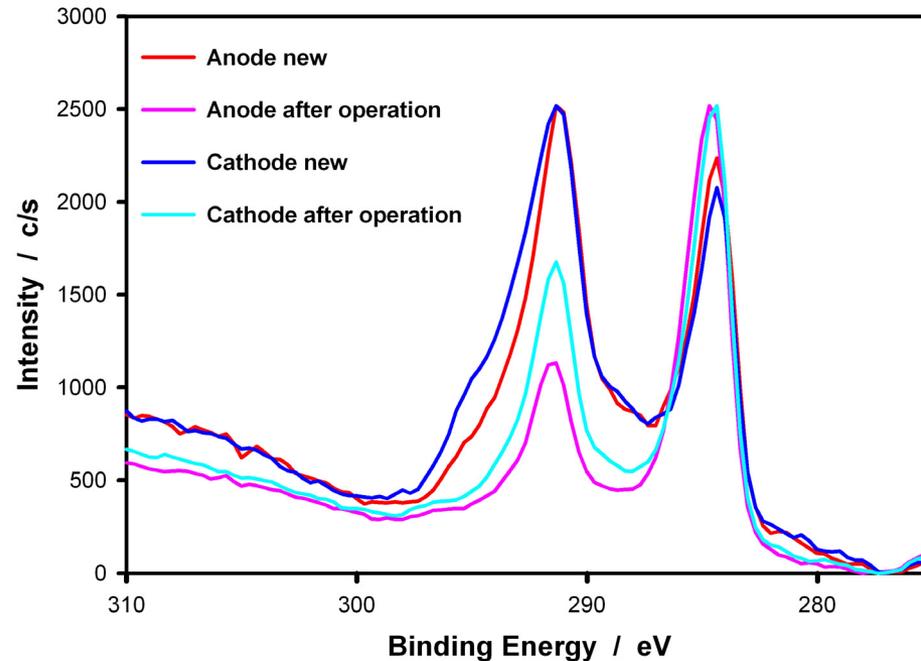
Degradation process	Qualitative effect on the fuel cell	Assumed mechanisms	Stressor
Loss of particles from the micro porous layers	Change of the structure → alteration of the transport properties in the GDL	Mechanical erosion	Mechanical stress
Partially decomposition of the PTFE	Loss of hydrophobicity / alternated water balance	Decomposition of PTFE	Liquid water

Degradation in PEFC

X-ray photoelectron spectroscopy



E-Tek electrodes

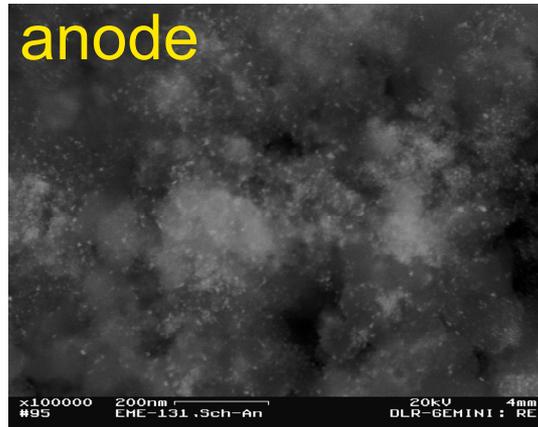


Ionpower CCM

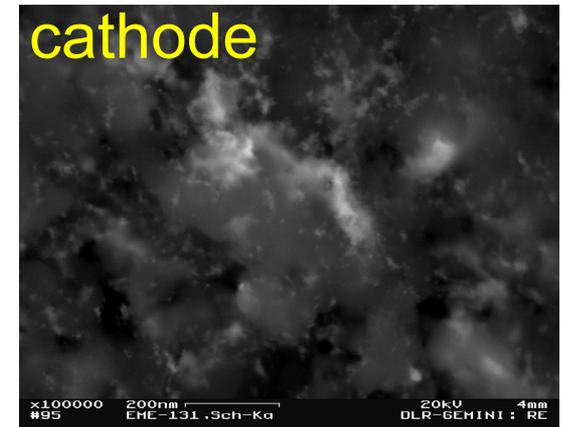
- Partial decomposition of PTFE identified by XPS
- PTFE decomposition mainly on the anode
 - ➔ Decrease of hydrophobicity
 - ➔ Changed water balance
 - ➔ Reversible loss of performance

Degradation of the platinum catalyst

reaction layers in MEAs, prepared by the DLR dry spraying technique, normal operated



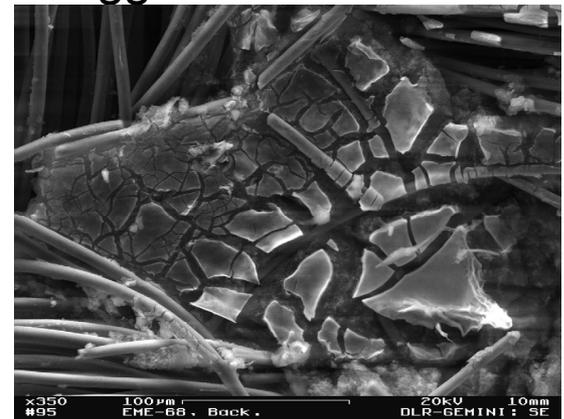
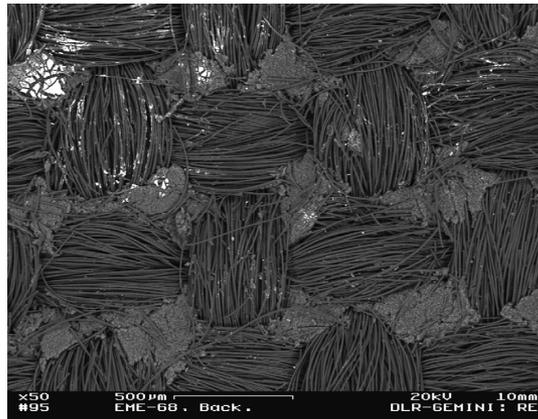
nearly unchanged



agglomeration of Pt

Pt - particle on the back-side of the cathode gas diffusion layer after operation

Gas diffusion layer and flow fields were partially flooded by the reaction water during operation

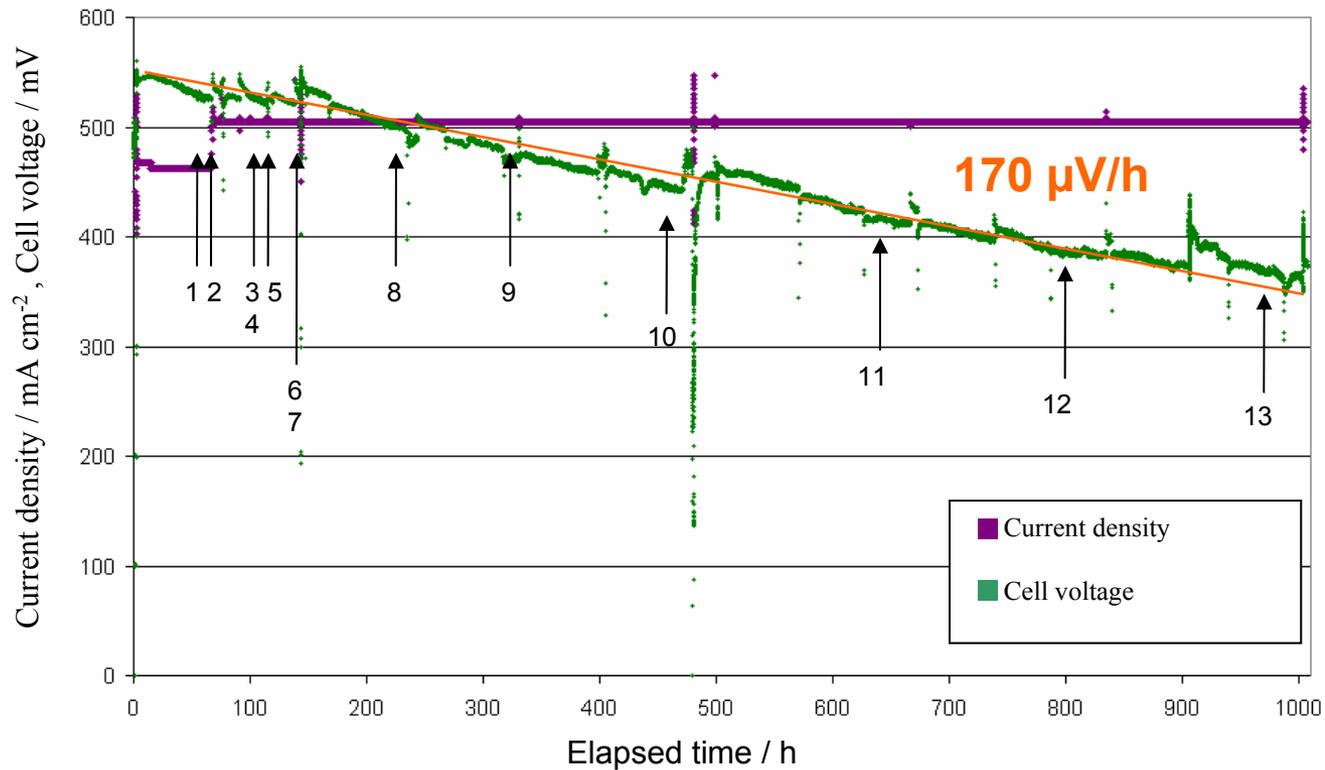




Using of electrochemical impedance spectroscopy

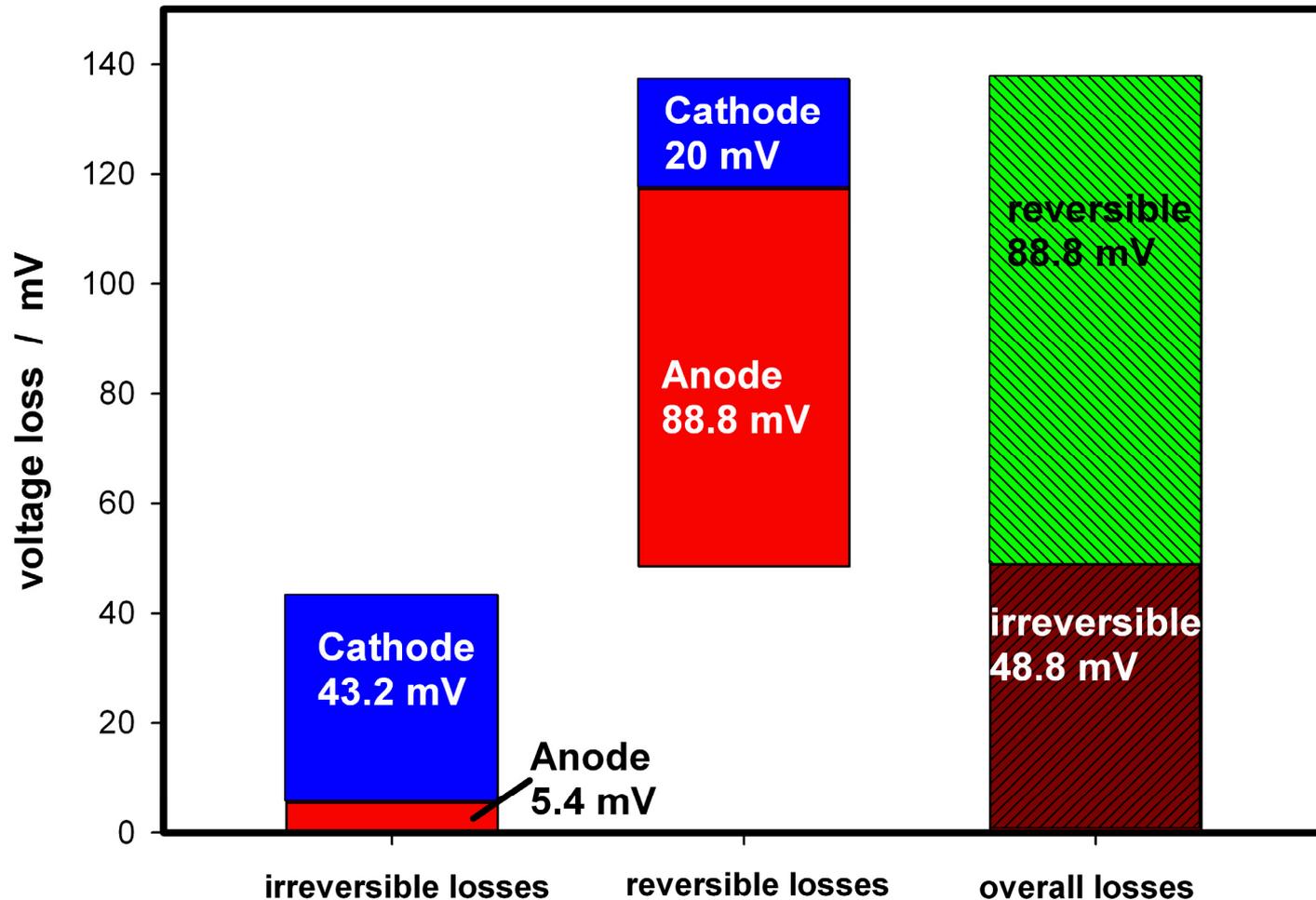
- **Determination of the individual polarisations for the**
 - anode reaction
 - cathode reaction,
 - membrane resistance
- **More detailed information about the time dependence and quantification of the individual contributions to the total polarization**

Change of cell voltage during constant load at 500 mA cm⁻²



Degradation in PEFC

Quantification of voltage losses during degradation by EIS



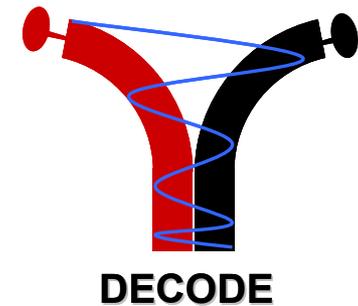


Degradation processes

- **The main irreversible loss of electrochemical performance is on the cathode, e.g. induced by the alteration of the catalyst**
- **Both electrodes have a reversible loss of the electrochemical performance, more significant on the anode**
- **The reversible loss is the consequence of changed transport processes, e.g. induced by the alteration of PTFE**
- **The degradation processes influence not only the performance but also the fuel cell behavior**
- **The influence of the operating conditions must be determined and understood**

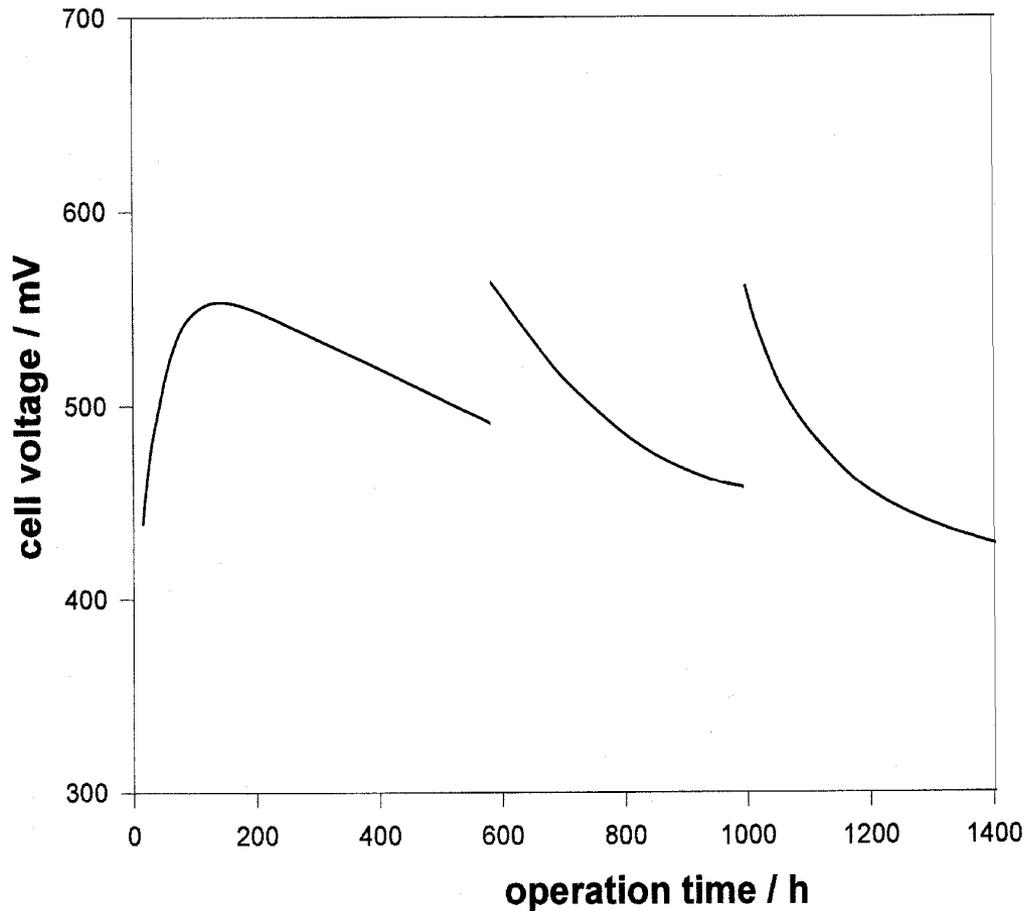


Acknowledgement of the Financial Support by EU Project DECODE



Thank you for your Attention

PEFC long term experiment



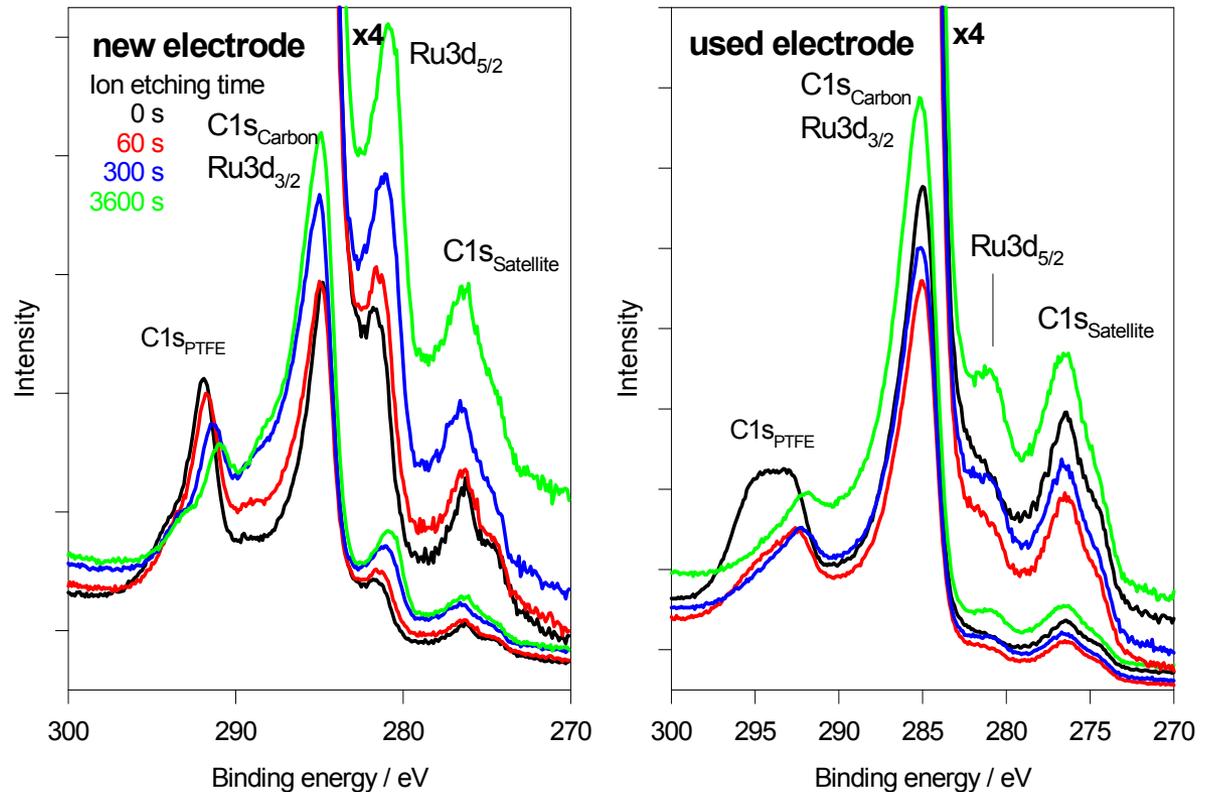
Nafion 1135
Pt 0.2 mg/cm² each electrode
T = 70 °C
 $p_{\text{H}_2} = 2$ bar, dead end
 $p_{\text{air}} = 2$ bar, $\lambda_{\text{air}} = 2$
 $i = 300$ mA/cm²



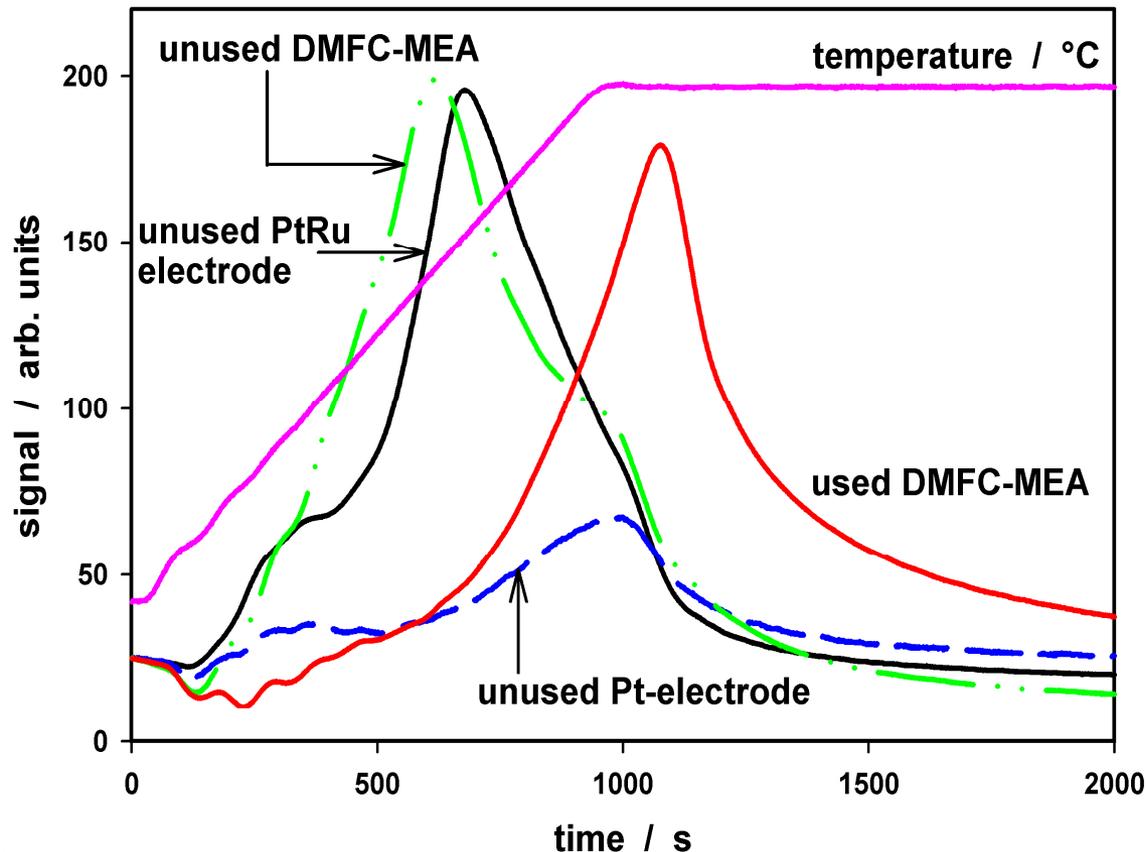
- **Feuchte hat sehr signifikanten Einfluss auf die Degradation**
 - höhere Feuchte beschleunigte Degradation
 - PTFE – Degradation beschleunigt
 - Katalysator Agglomeration beschleunigt
- **Bei intermetrierenden Betrieb ist die Degradationsrate geringer**
- **Veränderung der Hydrophobizität auch im Intermetierenden Betrieb → Veränderung der Kennlinie (Hysterese)**

XP spectra of a new and an used DMFC anode

- reduction of the Ru concentration on the surface
- decomposition of PTFE



TPR-measurements of DMFC-MEA



➤ TPR-spectrum of the MEA is determined by the PtRu-catalyst

➤ The spectrum is changed after the electrochemical stressing

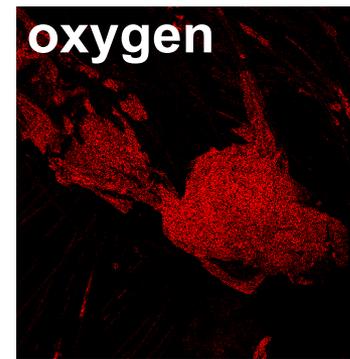
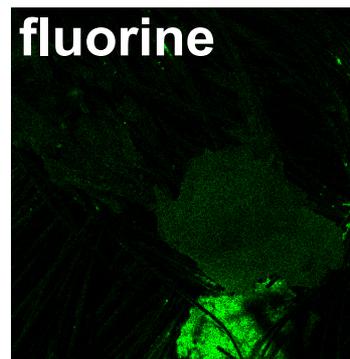
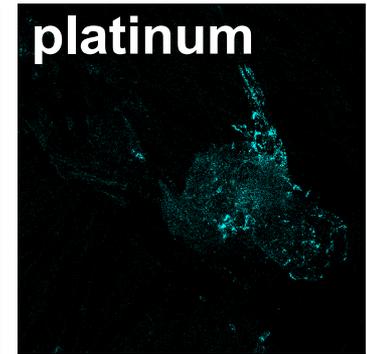
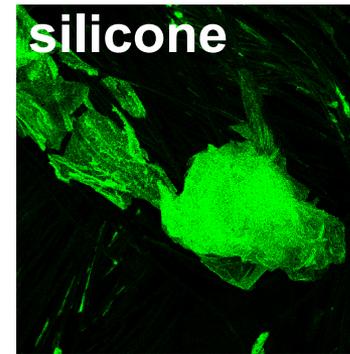
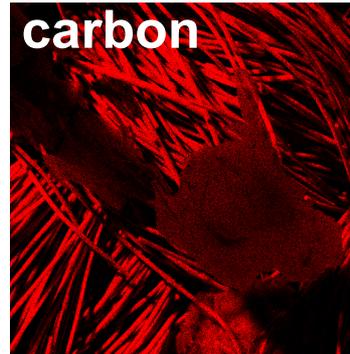
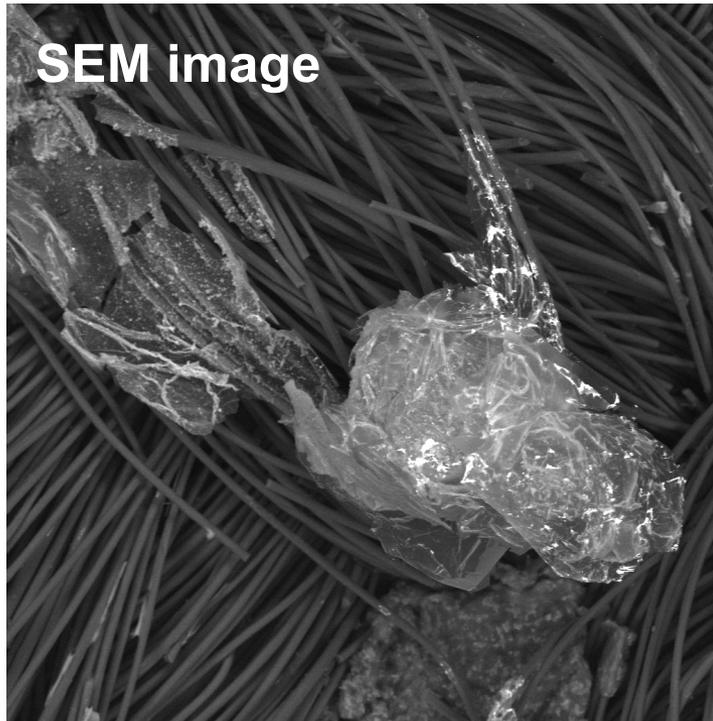
➤ → The TPR-spektrum of the used DMFC-MEA indicates an enrichment of Pt on the surface



Veränderungen von DMFC-Anoden

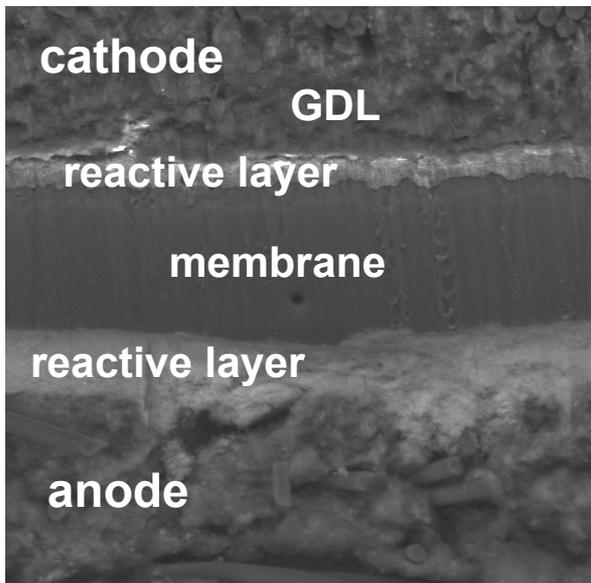
- Veränderung des Katalysators
 - Ruthenium wird aus der Anode gelöst und wandert durch die Membran zur Kathodenoberfläche
 - Die chemischen Eigenschaften des PtRu verändern sich in Richtung derer eines Pt-Katalysators
- PTFE wird auch in den DMFC-Anoden teilweise zersetzt

SEM /EDX investigation of the silicon deposition in the membrane-electrode-assembly

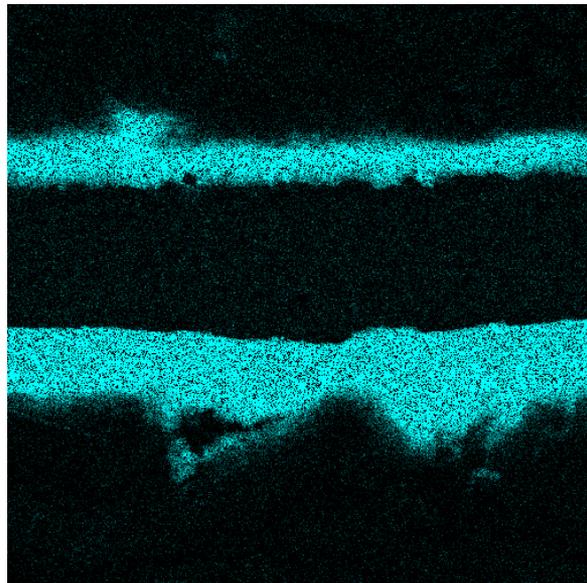


SEM /EDX investigation of the silicon deposition in the membrane-electrode-assembly

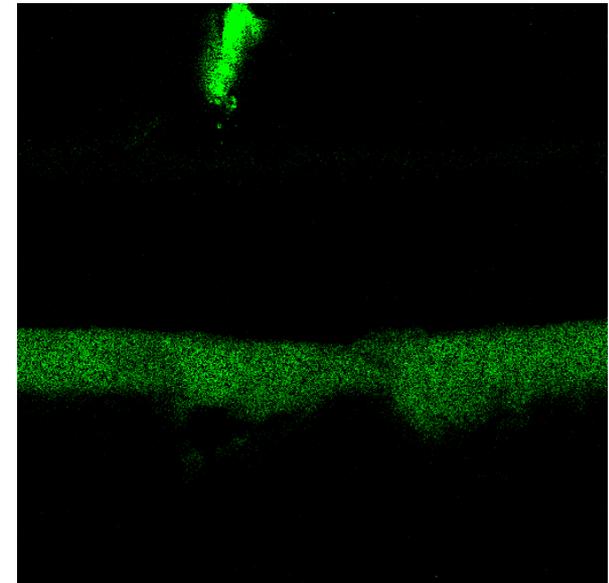
Cross section



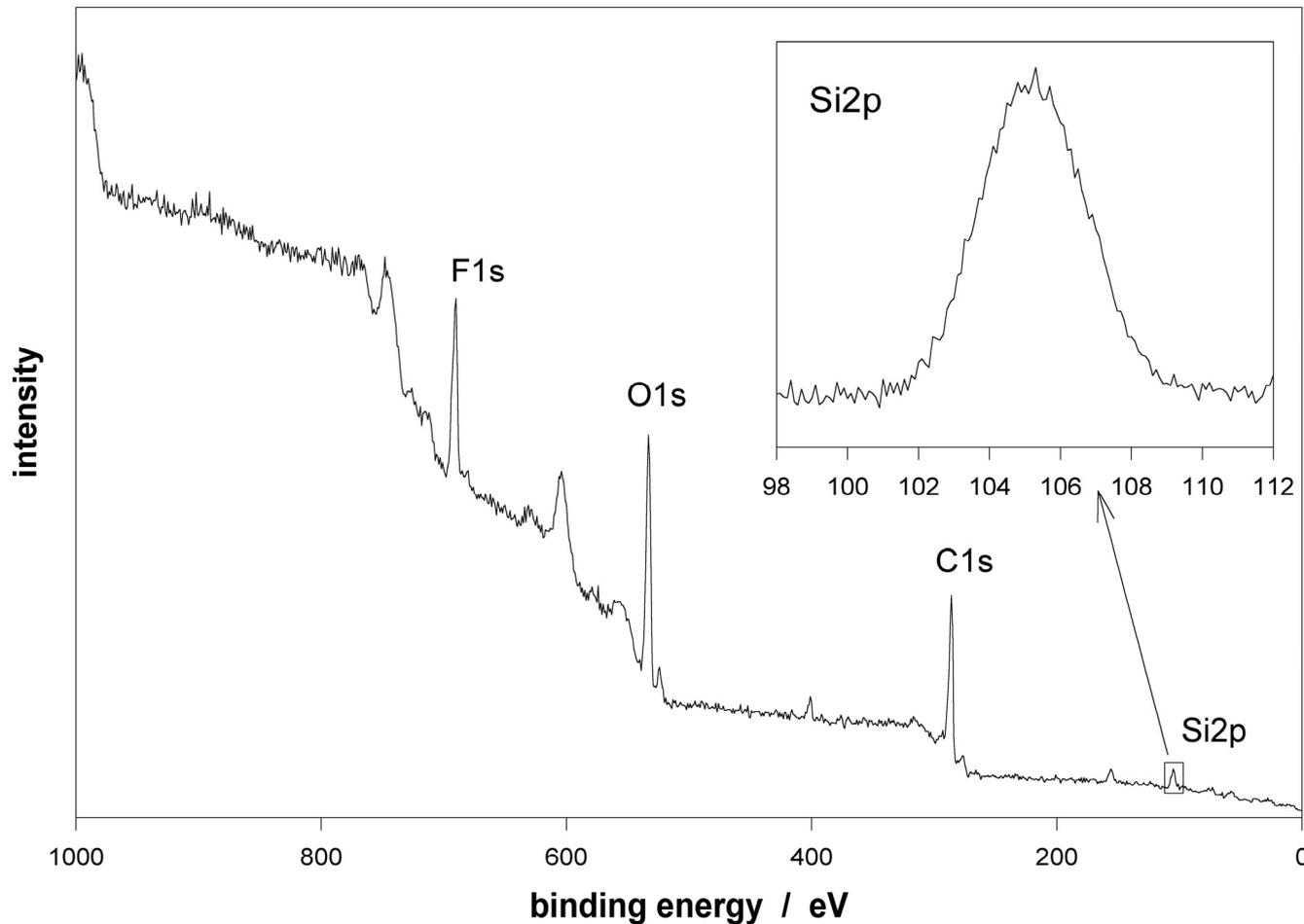
Platinum



Silicon



XPS investigation of the silicon deposition on the anode

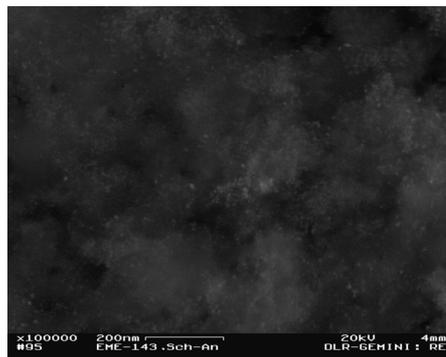
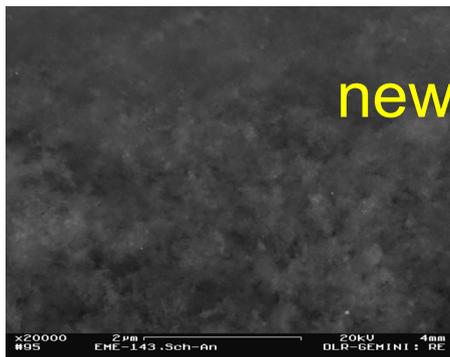




Conclusions

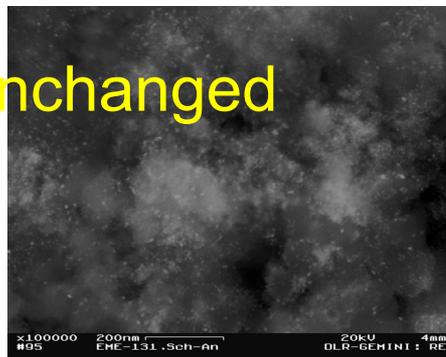
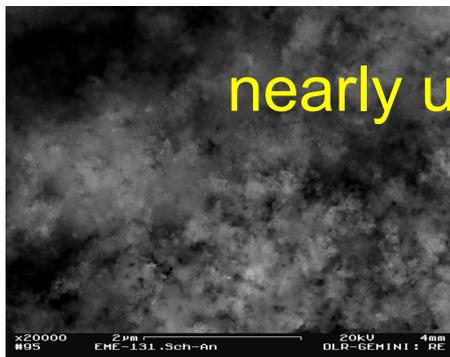
- **The diagnostic and analytic tools can use in order to support the development of components**
- **The diagnostic tools allow to investigate the conditions inside the cell**
- **The combination of various diagnostic and analytic methods yields a better understanding of the fuel cell processes**
- **Diagnostic tools can used for controlling fuel cells in order to optimize the performance as well as to avoid negative operation conditions**

Degradation of the platinum catalyst



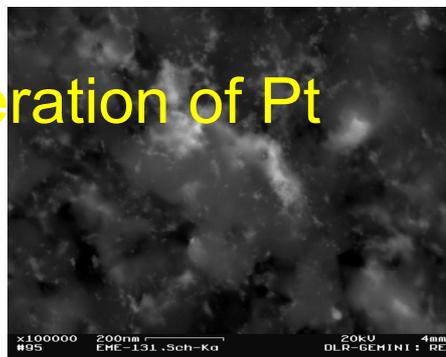
reaction layers in MEAs, prepared by the DLR dry spraying technique

on top: **new** electrode



middle: **anode** reaction layer of an used MEA, normal operation

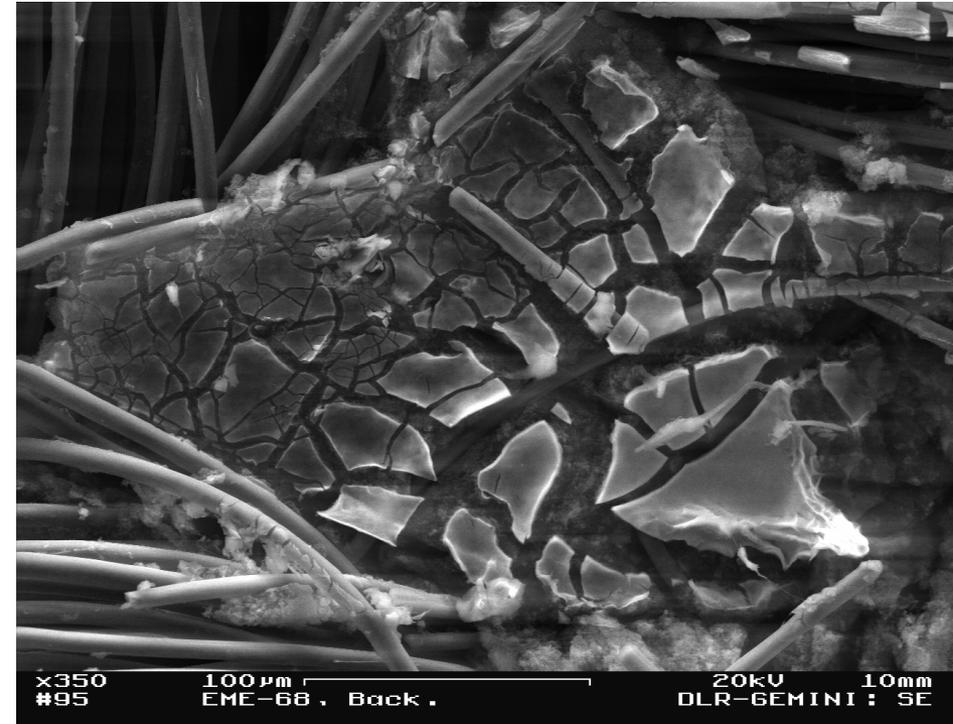
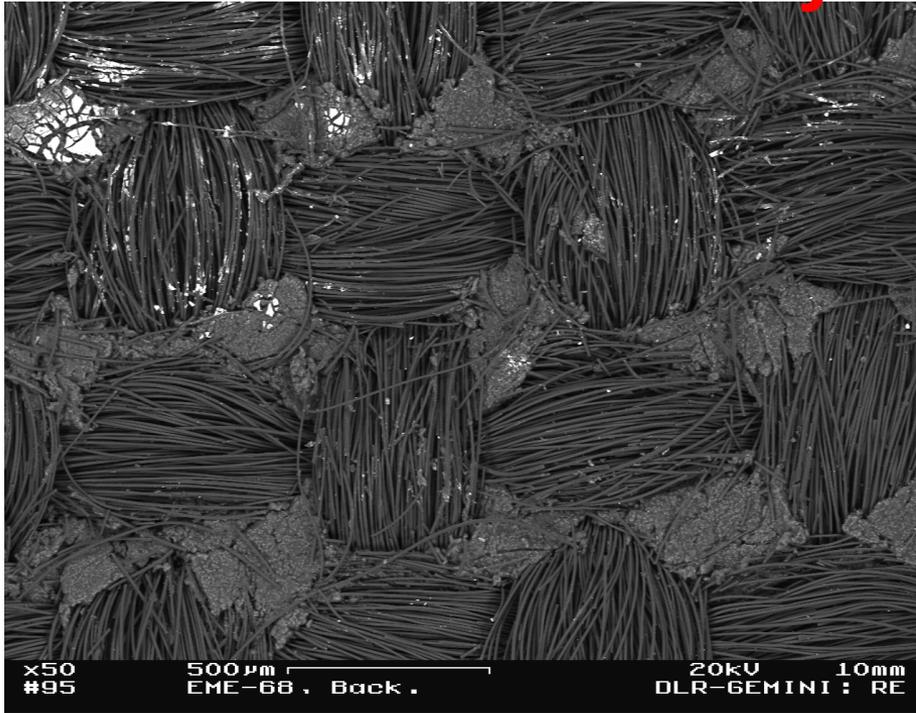
bottom: **cathode** reaction layer of an used MEA, normal operation



left side:
20000 fold magnification

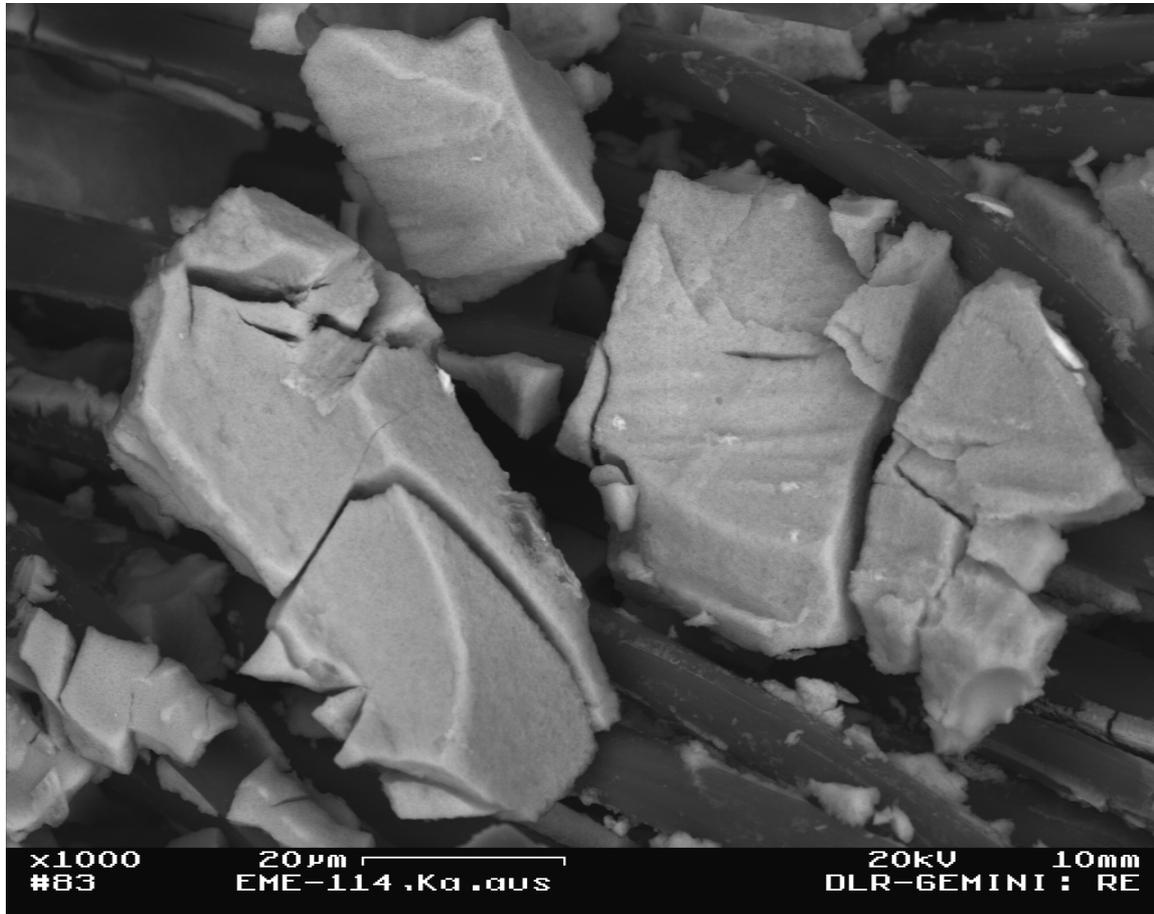
right side:
100000 fold magnification

Pt - particle on the backside of the cathode gas diffusion layer after operation



Gas diffusion layer and flow fields were partially **flooded by the reaction water** during operation

Pt - particle on the backside of the cathode gas diffusion layer after operation



Gas diffusion layer and flow fields were partially **flooded by the reaction water** during operation



Investigation of Degradation Processes

XPS-Analysis

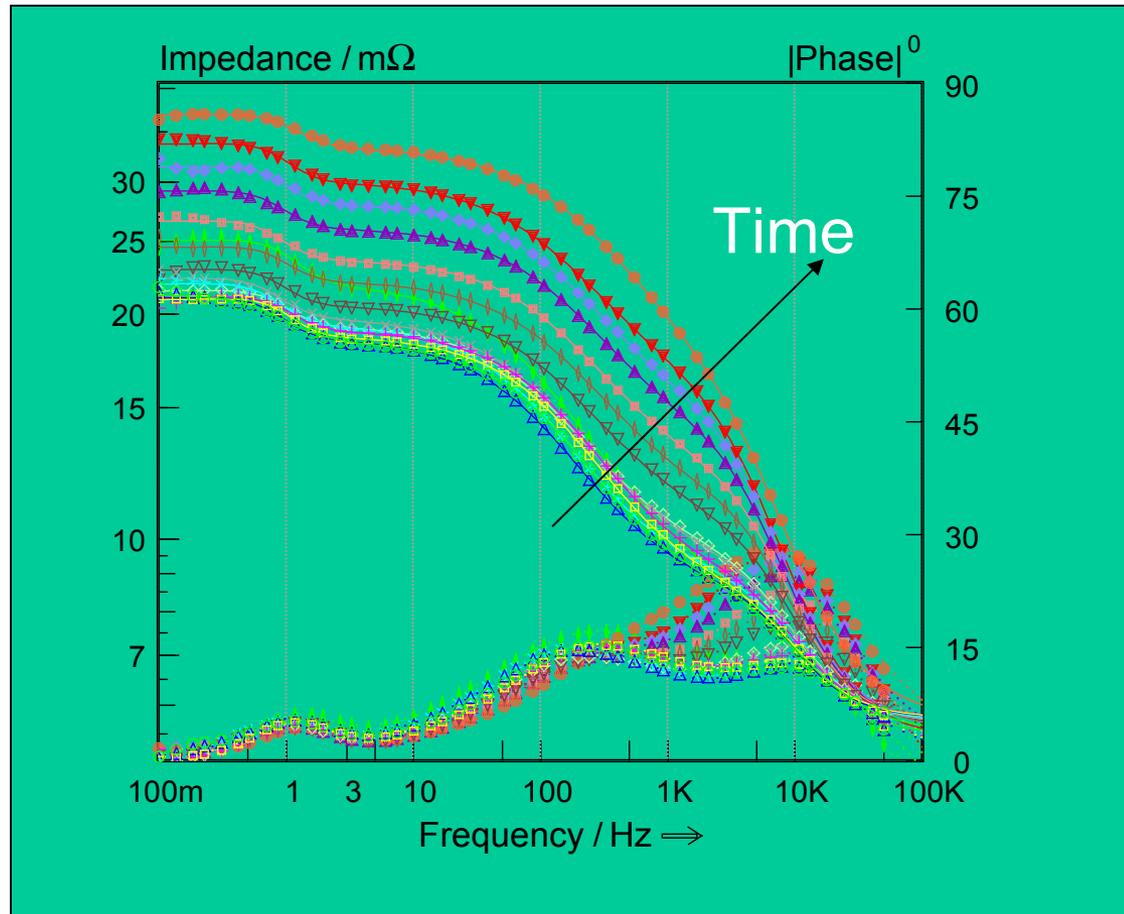
- PTFE degrades
- Hydrophobicity decreases
- Water ballance changes
- Pore system will be flooded



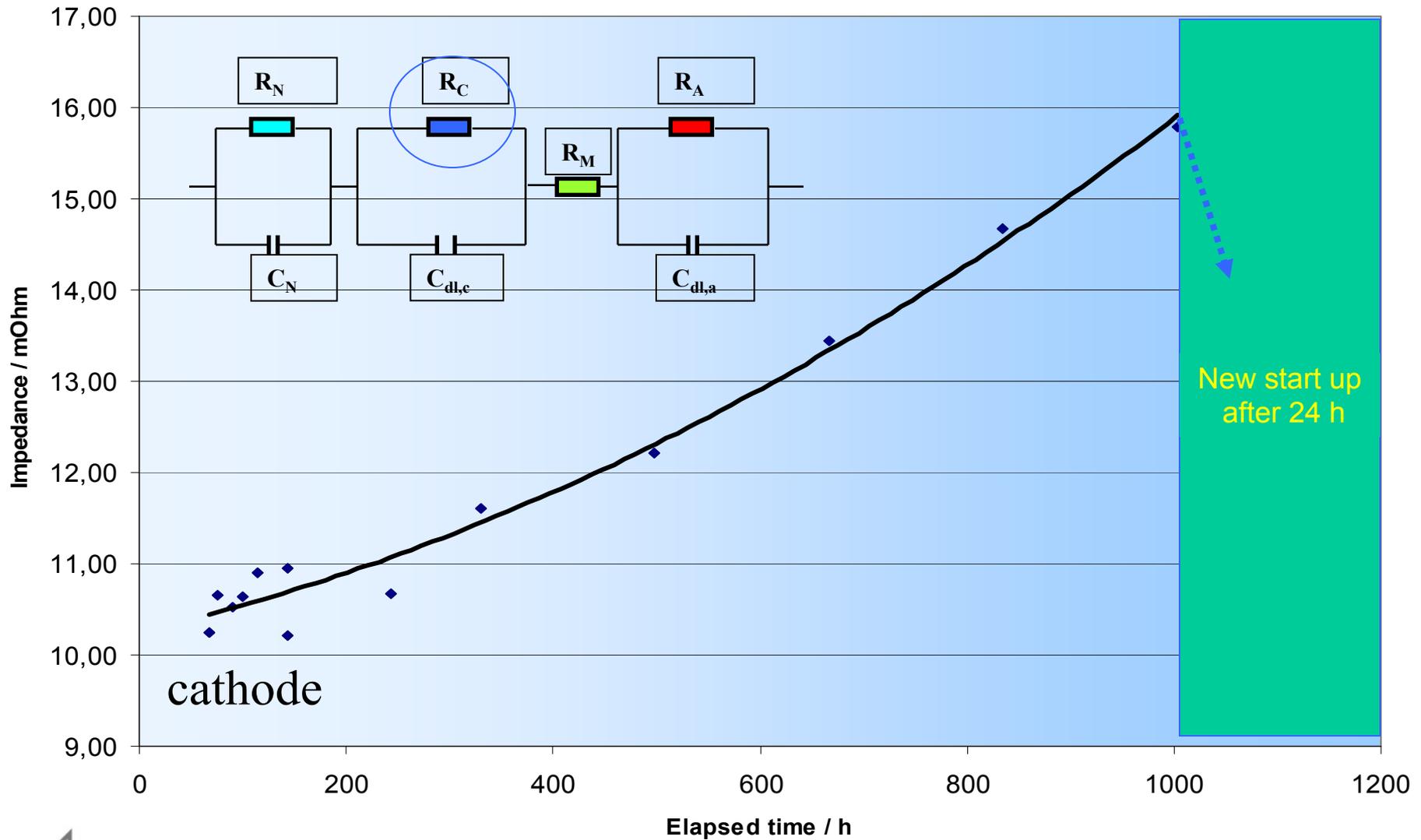
Degradation processes

- **PTFE changes induced by the electrochemical stressing in the start-up procedure as well as during long term operation**
 - **Consequently, the hydrophobicity alters**
 - **The alteration of the PTFE and of the hydrophobicity is more significant at the anode**
- **The platinum catalyst alters during fuel cell operation**
 - **A diffusion of platinum can be observed**
 - **On the cathode the platinum catalyst agglomerates**
 - **Flooding of the electrodes by water enhances the agglomeration of the platinum catalysts**

Bode Plot of EIS measured during PEFC operation at 500 mA cm⁻²



Variation of R_C during PEFC operation at 500 mA cm^{-2}



Variation of R_A during PEFC operation at 500 mA cm^{-2}

