A3PS

Rethinking Propulsion.

Influence of Operating Conditions on Membrane Ageing in PEFC

- Viktor Hacker, Eva Wallnoefer

Hybrid and electric vehicles, energy storage technologies and control systems

National and international R&D-projects, research institutions and funding programs

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Ein Unternehmen der Austrian Research Centers

Fuel Cells - Challenges

- Cost
- Stack durability
- Cruising range
- Power density
- High temperature operation

Content

OVERVIEW

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- **thermal degradation**
- **mechanical degradation**
- **chemical degradation**
- **H_2O_2 formation**
- **influence of operating conditions**
  - membrane thickness
  - gas pressure
  - temperature
  - gas humidity
  - cell potential

IN SITU DEGRADATION STUDIES

- **operating conditions**
- **characterisation methods**
  - hydrogen diffusion - pinhole detection
  - potential curves
    - cell performance
    - maximum power density
    - OCV
  - fluoride emission rate
  - EIS - membrane resistance
  - SEM
    - membrane degradation
    - membrane thickness
- **conclusions**

Degradation of PEMFC Membranes

impacts of degradation

- membrane decomposition (release of HF, SO_2, CO_2, CO, C-F-compounds)
- membrane thinning
- higher gas permeability
- platinum particle deposition in the membrane
- performance loss of the MEA
- decrease of life time

causes

- thermal degradation
- mechanical degradation
- chemical degradation

influencing factors

- material properties
- cell assembling
- operating conditions

Thermal and Mechanical Degradation

thermal degradation

- under normal operating condition (T < 100 °C), the thermal degradation of the membrane is low
- but: the temperature of the cell strongly influences the chemical degradation
- a local heating of the membrane, caused by different contact resistances, may cause local degradation
  - avoiding of rough MEA surfaces
  - ensure a uniform pressure of the bipolar plates on the MEA

mechanical degradation

- tensions on edges of the MEAs
- particles in the active layer or gas diffusion layer may damage the membrane
- swelling and shrinking of the membrane caused by changes in humidity

Chemical Degradation - Causes

H_2

- creates C-H bonds (replaces F with H)
- causes moderate membrane degradation

H_2O_2 and its radicals $^{\bullet}OH$ and $^{\bullet}OOH$

- are created under certain conditions
- the radicals, ("damaging species") cause rapid membrane degradation

existing or created C-H-bonds

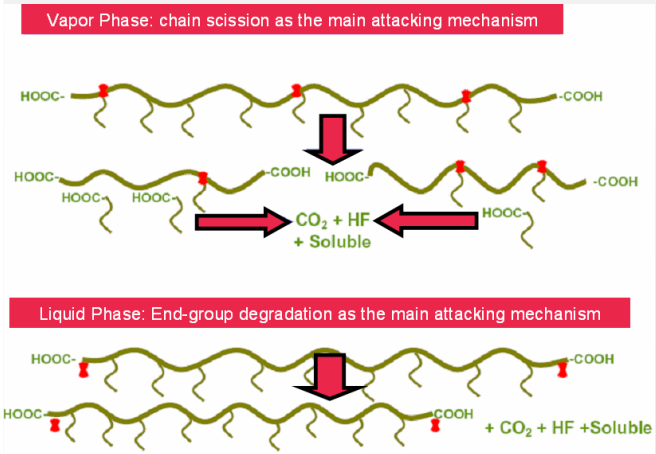
- are a possible point of attack of chemical degradation
- exist in the membrane in a certain extend
- are created by chemical degradation caused by radicals or H_2 → chain reaction

metal ion impurities

- catalyse the formation of •OH and •OOH
- block proton conductive site groups in the membrane

$Fe^{2+} >> Cu^{2+} >> TiO^{2+} > Co^{2+} > Pt^{2} > Ni^{2+} > Al^{3+}$

A.B. LaConti, H. Liu, C. Mittelsteadt, R.C. McDonald, ECS Trans. 1, (8) 199 (2006).



W. E. Delaney, W. Liu, ECS Trans. 11, (1) 1093 (2007).

H_2O_2 Formation under Fuel Cell Conditions

at the cathode side

- H_2O_2 is an intermediate product of the formation of water
- no damaging species is formed at the cathode at higher cell potentials

at the anode side

- H_2O_2 is formed at the anode side with H_2 and O_2 at the electrocatalyst at potentials < 0.682 V

$E_0 = 0.682$ V

$H_2O_2 \rightarrow 2\ H^+ + O_2 + 2\ e^-$

- the lower the current density, the lower is the anode potential
- O_2 is present at the anode because of air bleed or diffusion from the cathode side through the membrane
- the presence of an electrocatalyst is needed at least at one side of the membrane to form a damaging species
- metal impurities catalyse radical formation

radical formation $H_2 \rightarrow 2\ \bullet H$ (at the catalyst)

$\bullet H + O_2 \rightarrow \bullet OOH$

recombination $\bullet OOH + \bullet H \rightarrow H_2O_2$

$O_2 + 2\ H^+ + 2\ e^- \rightarrow H_2O_2$

Influence of Operating Conditions

membrane thickness

- a thicker membrane effects a lower gas diffusion rate
- but: most of the studies did not confirm a correlation between membrane thickness and degradation rate
- some studies found a correlation between membrane volume (= thickness) and degradation rate

gas pressure

- a higher gas pressure increases gas diffusion
- gas permeability increases at higher temperatures
- hydrogen partial pressure has a high influence on membrane degradation
- oxygen partial pressure has a lower influence on membrane degradation than hydrogen pressure

temperature

- a higher temperature accelerates membrane degradation

Influence of Operating Conditions

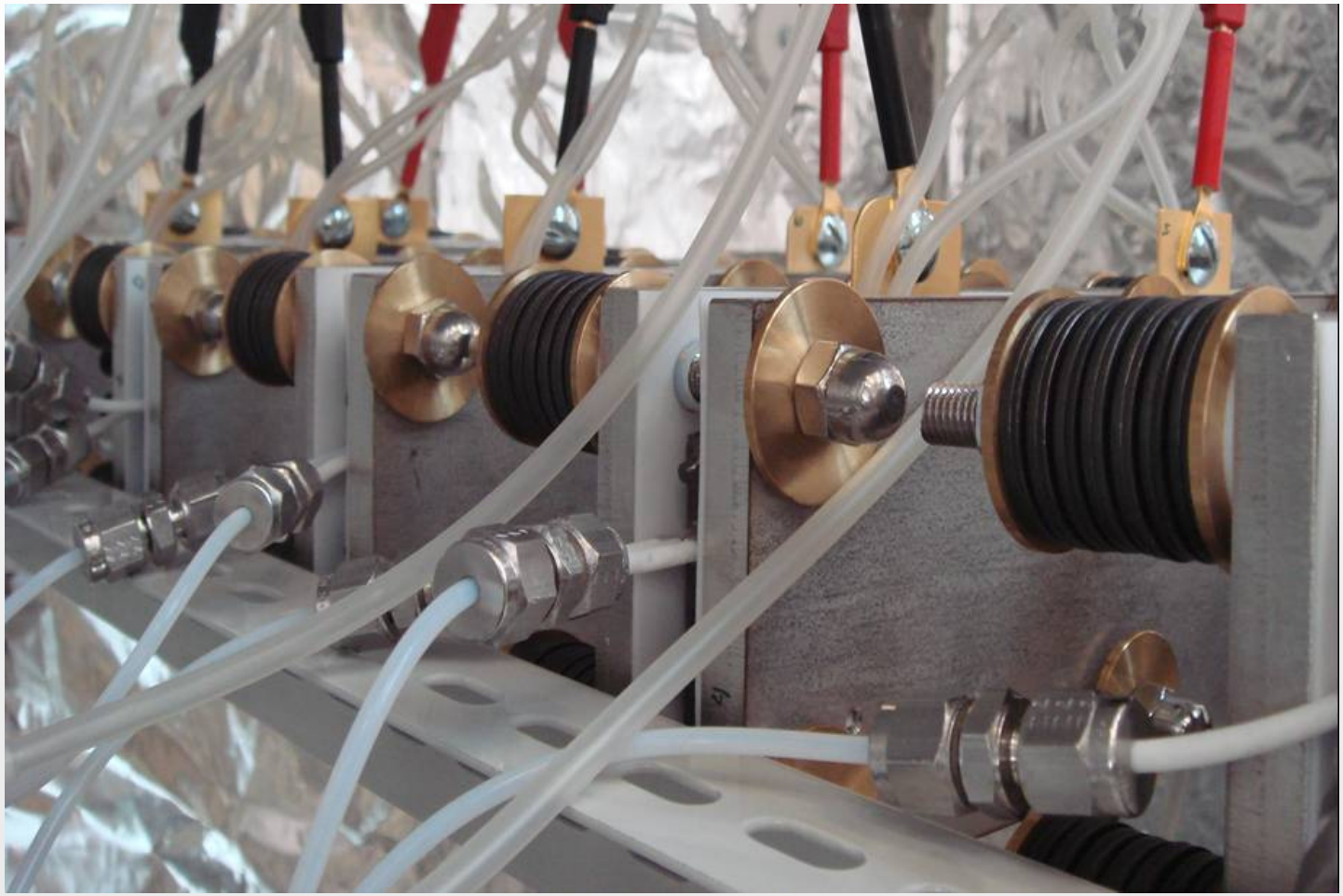
gas humidity

- there are contradictions between
  - more recent studies (= high humidity: lower corrosion rates) and
    former studies (= high humidity: higher corrosion rates)
  - ex situ analysis and studies under real fuel cell operating conditions
- higher gas humidity increases
  - dissolution of metal impurities and their migration in the membrane
  - membrane flexibility
  - mobility of the damaging species
- but: diffusion of oxygen and hydrogen may not be influenced by the humidity of the membrane (apolar gases - polar membrane)

cell potential

- the higher the cell potential, the higher is the stability of H_2O_2 at the anode side and the higher is the membrane degradation rate

In Situ Degradation Studies



Operating Conditions

test series

- *standard conditions*

  0 mA cm^{-2} (OCV)

  70 °C

  90 % rH

- *low humidity*

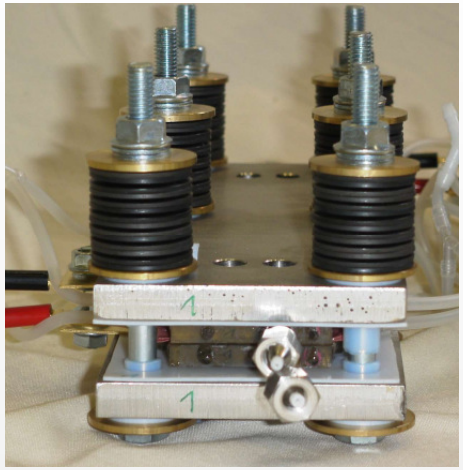
  40 % rH

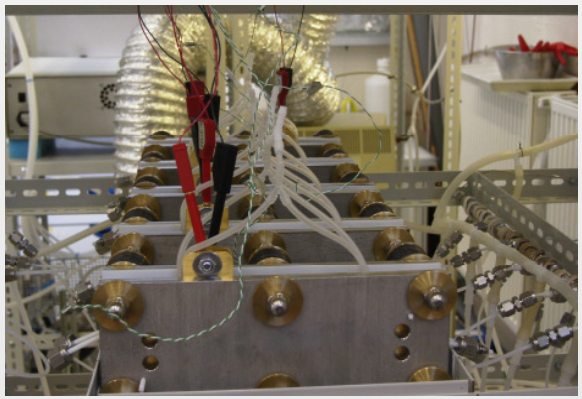
- *low temperature*

  40 °C

- *45 mA cm^{-2}*

- *135 mA cm^{-2}*





Characterisation Methods

performance (UI)

- potential curves
- cumulated
- every 7 days (165 h)

membrane resistance (MR)

- EIS
- individually
- every 7 days (165 h)

pinhole detection (HD)

- H_2 diffusion current measurements
- individually
- every 7 days (165 h)

cell potential (CP)

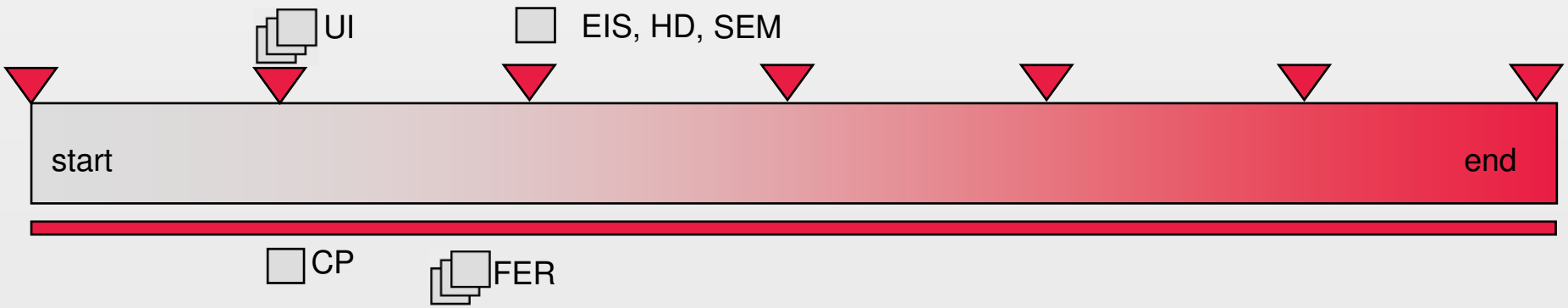
- individually
- continuously

fluoride emission rate (FER)

- FER in cathode and anode exhaust water
- cumulated
- daily

membrane thickness and condition (SEM)

- SEM
- individually
- every 7 - 14 days



Hydrogen Diffusion

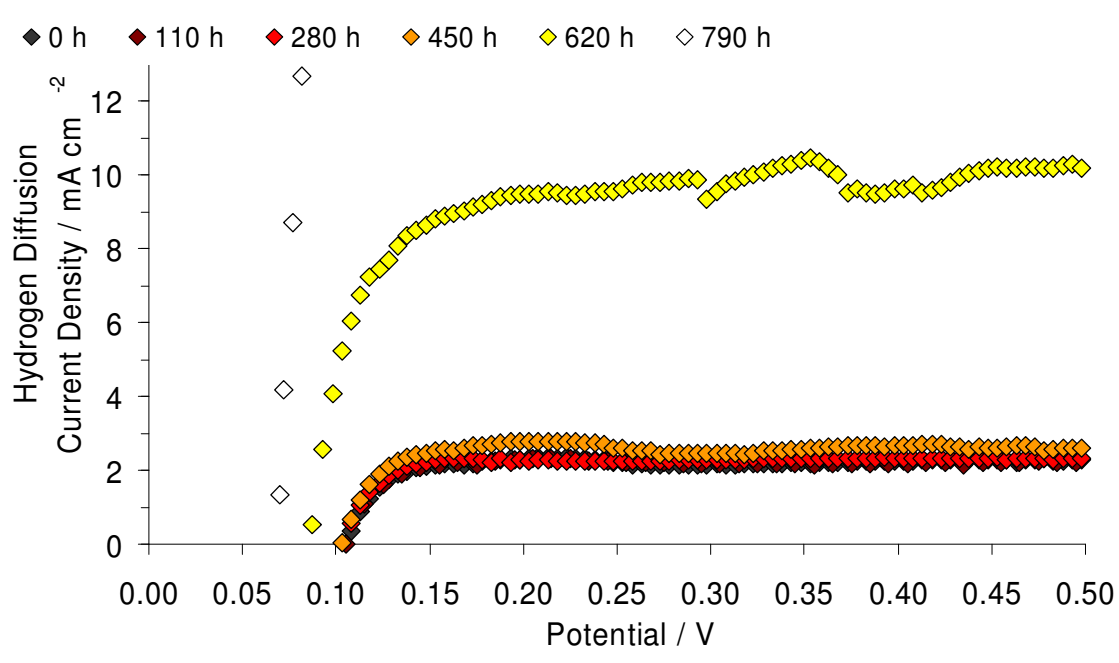
conditions, principle

- anode: H_2 flow
- cathode: N_2 flow

- H_2 diffuses through the membrane and gets oxidised with an increasing potential

- the H_2 diffusion current is limited by diffusion to < 5 mA cm^{-2}

- if there is a pinhole, the current increases with increasing potential

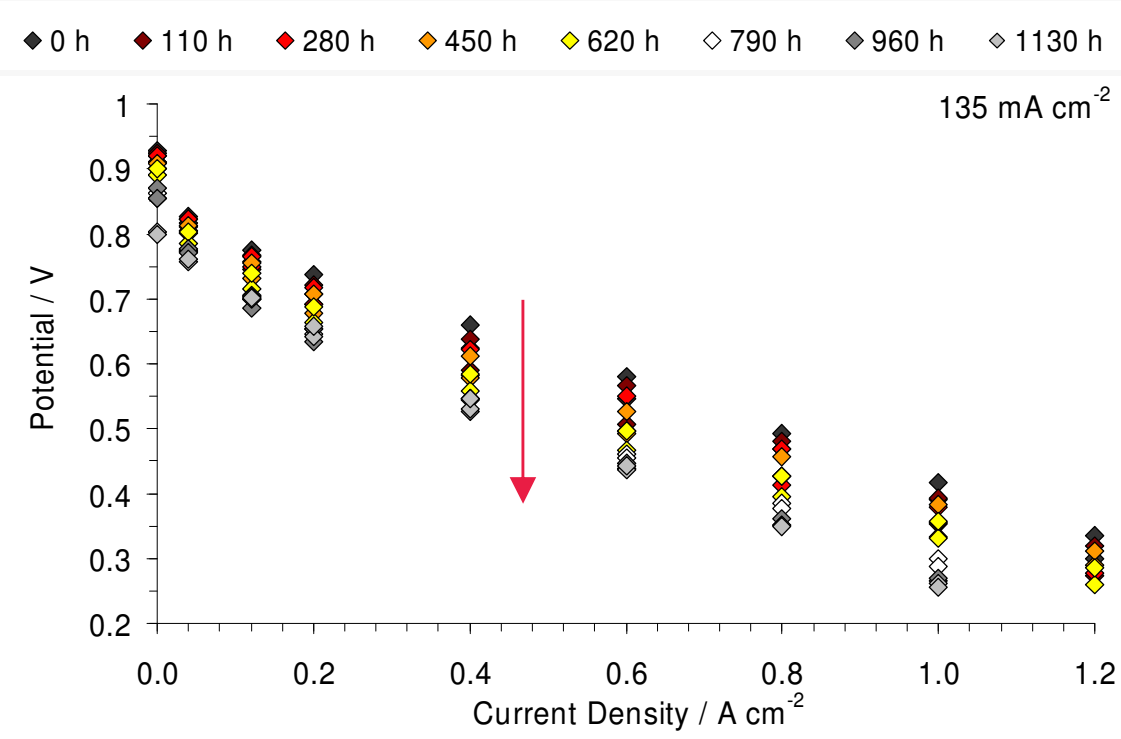


Cell Performance

results

polarisation curves

- changes with operating time

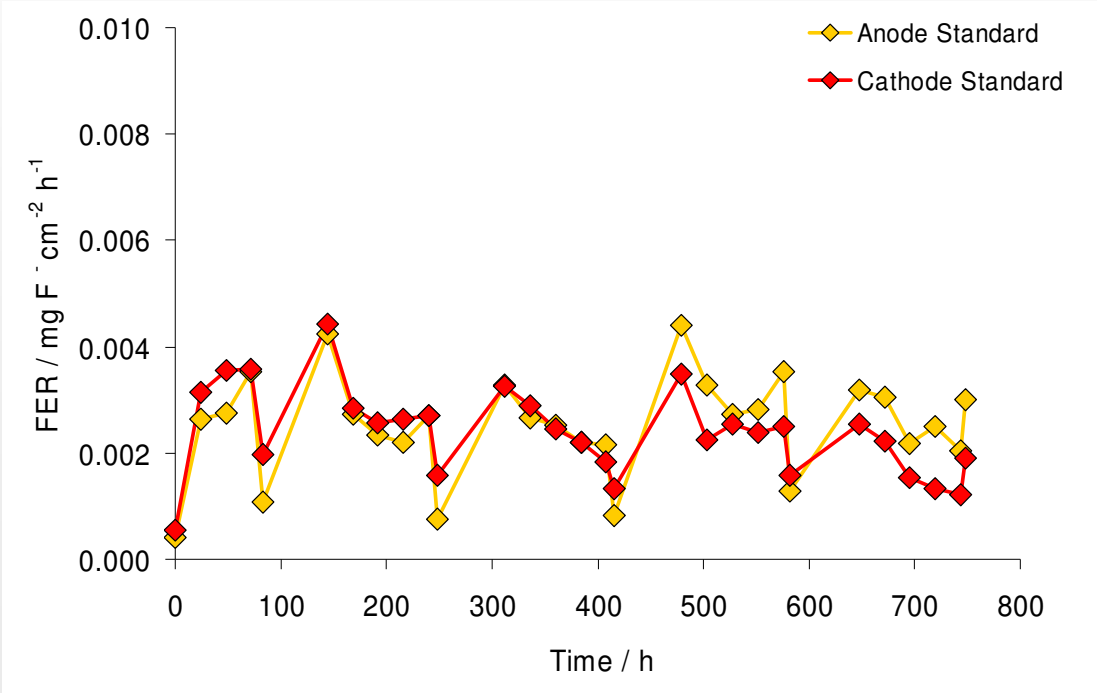


Fluoride Emission Rate

results

- FER in the anode and cathode exhaust water was nearly the same, even though the degradation of the anode side was higher (→ SEM investigations)

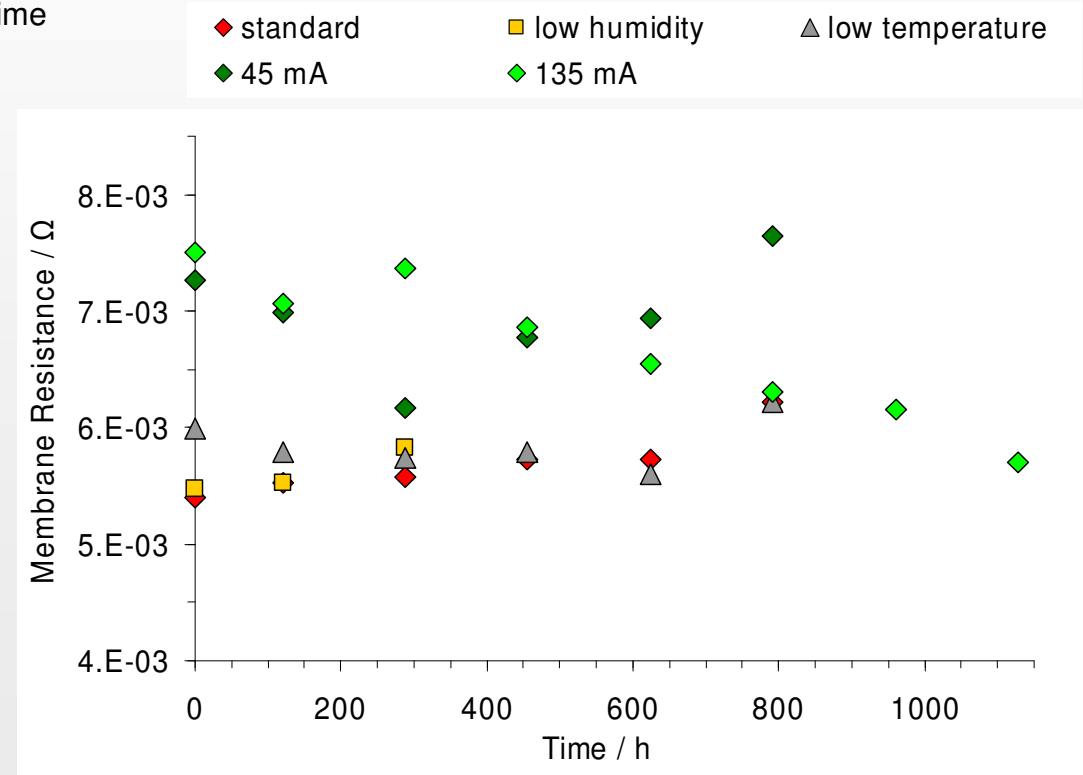
- FER was slightly decreasing with operating time



Membrane Resistance

results

- change of the resistance with the operating time
- the resistance does not correlate clearly to
  - operating conditions
  - operating time
  - pinhole formation
  - membrane thickness (SEM)
- a slight increase of the resistance could be observed at higher degradation/ long operating time in most cases
- the resistance is influenced by
  - the loss of proton conducting, hydrophilic functional groups
  - the structural changes of the hydrophobic phase
  - the thinning of the membrane

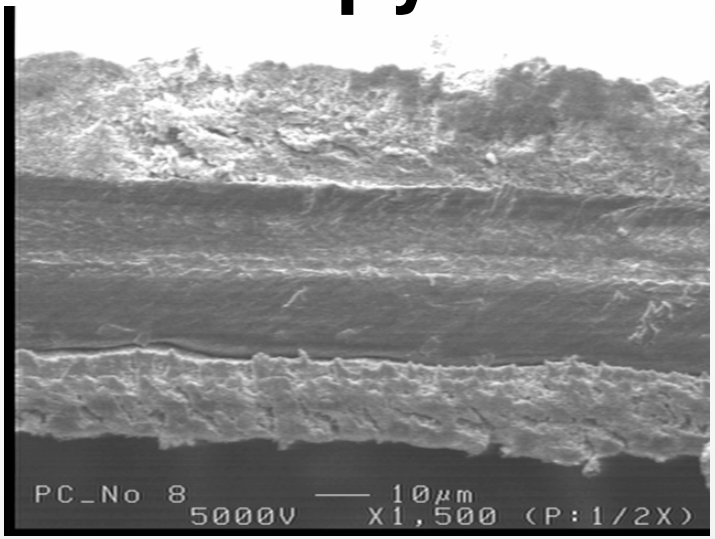


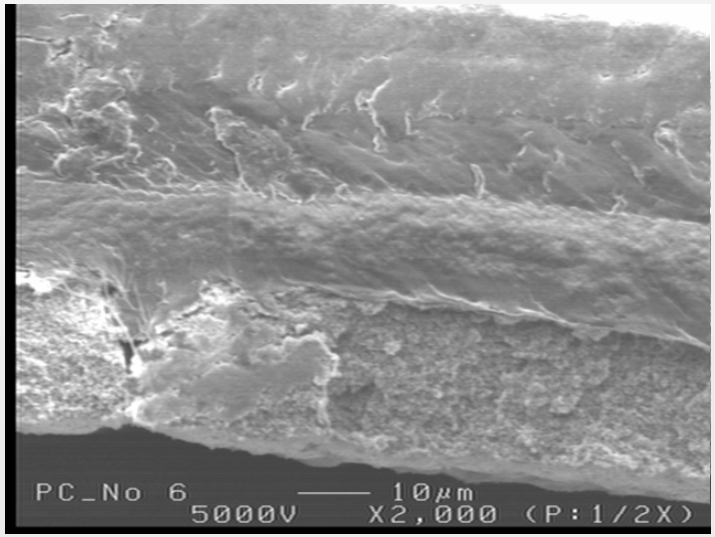
Scanning Electron Microscopy

results

untested, activated membrane

- bilayerd membrane with different orientation of the layers
- membrane thickness: 35 µm
- ~ 5 - 10 % experimental standard deviation of the membrane thickness
- this deviation might be higher than the influence of the operating conditions on the membrane thickness
- even untested electrodes MEA have cracks in the electrodes, indruded by the membrane





Scanning Electron Microscopy

results

degradated membrane under OCV conditions

- thinning of the anode side of the membrane

  after short-time operation under harsh conditions

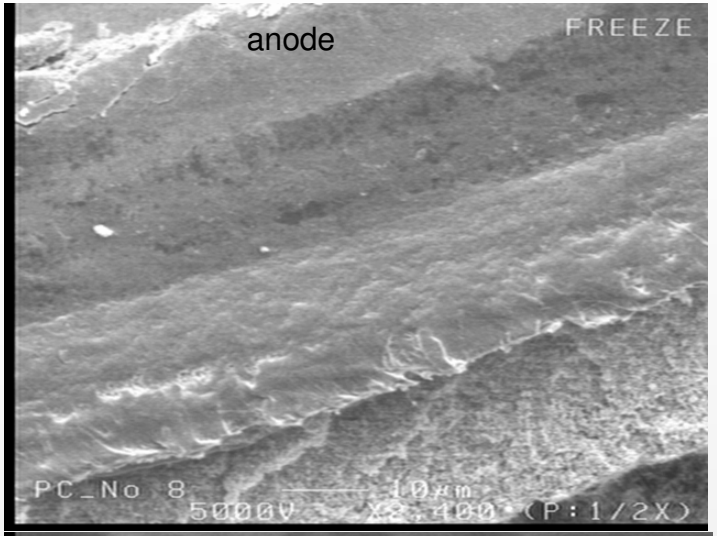
- thinning of the anode side and formation of a porous structure

  after short-time operation under harsh conditions

- platinum particle deposition in the porous membrane

  after short-time operation under harsh conditions

low humidity conditions after 280 h



low humidity conditions after 280 h

Conclusions

- low cell currents and a low gas humidity accelerate membrane degradation
- low operation temperatures and high cell currents slow membrane degradation
- the end of lifetime of the MEA was indicated by the detection of the first pinhole
- an exceed of a certain value of cumulated FER could indicate the formation of pinholes
- a drop of OCV below a certain value could indicate the formation of pinholes
- membrane thinning at the anode side occurred at long-time operation even under moderate operating conditions
- the formation of porous structures and platinum particle deposition at the anode side of the membrane occurred at harsh conditions
- the membrane resistance did not correlate clearly to the membrane degradation, the formation of pinholes and the membrane thinning

Thank you for your kind attention!