Monitoring of membrane failure due to pinhole formation

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Overview

1. Introduction
   - degradation of PEMFC membranes
   - influence of operating conditions
2. In-situ Degradation Studies
   - operating conditions
   - characterization methods
3. 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

Degradation of PEMFC Membranes – causes

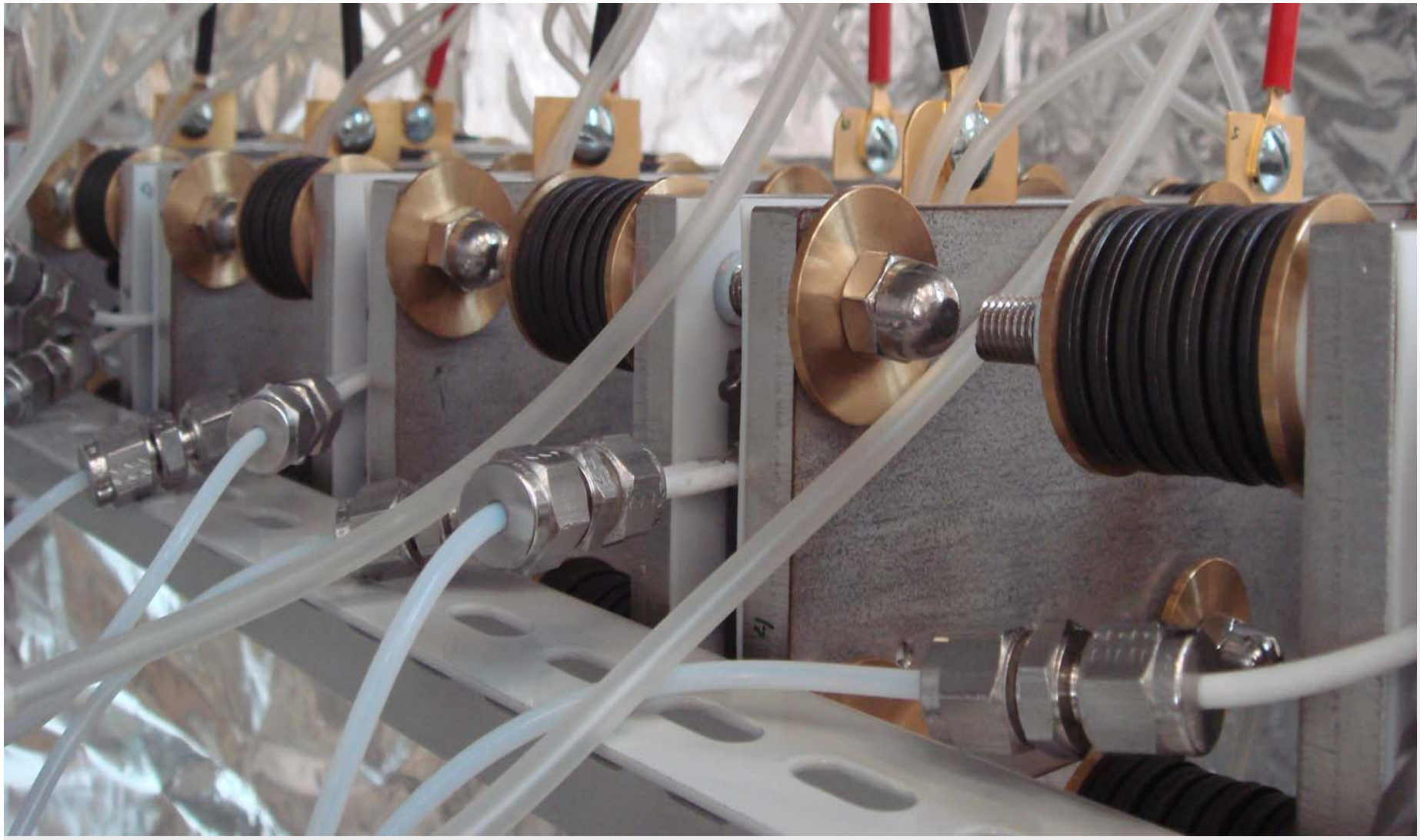
- thermal degradation
- mechanical degradation
- chemical degradation

Degradation of PEMFC Membranes – influencing factors

- material properties
- cell assembling
- **operating conditions**

  - membrane thickness
  - gas pressure
  - temperature
  - gas humidity
  - cell potential

In Situ Degradation Studies

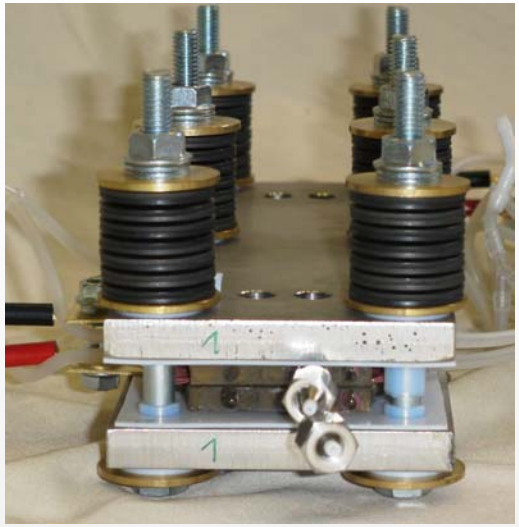


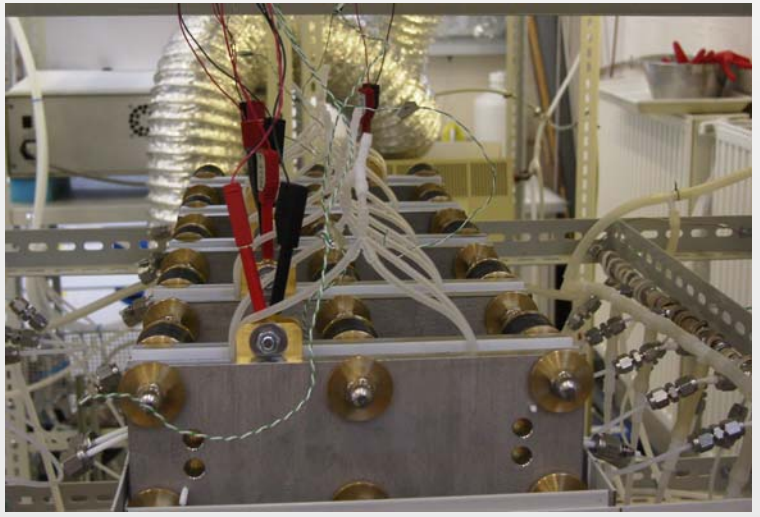
Operating Conditions

- *5 to 1 fuel cells* (in series), 25 cm^2 each operated under the same conditions up to 1300 h
  - permanent operating 24h/day, 7 days/week
  - interruptions only for electrochemical characterizations
  - every one or two weeks, one cell was removed (SEM analysis)

- *gas flow:*
  - H2: $\lambda = 1.5$ (at OCV: 300 ml min^{-1})
  - Air: $\lambda = 2.2$ (at OCV: 300 ml min^{-1})

- *MEAs:*
  - pt loading: A: 0.4 mg cm^{-2}, C: 0.6 mg cm^{-2}
  - membrane: bilayer membrane, reinforced with PTFE, thickness: 35 µm
  - activation of the MEAs (6 h at 0.4 and 0.6 V)



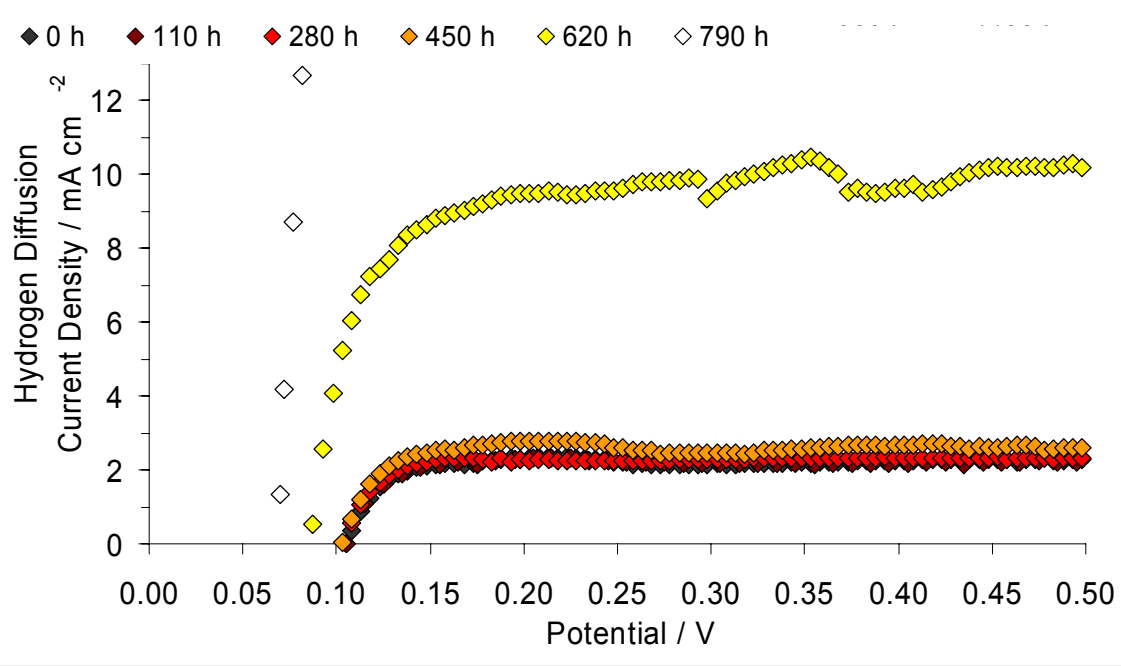


Characterisation Methods

- performance (UI)
- cell potential (CP)
- membrane resistance (MR)
- fluoride emission rate (FER)
- pinhole detection (PD)
- membrane thickness and condition (SEM)

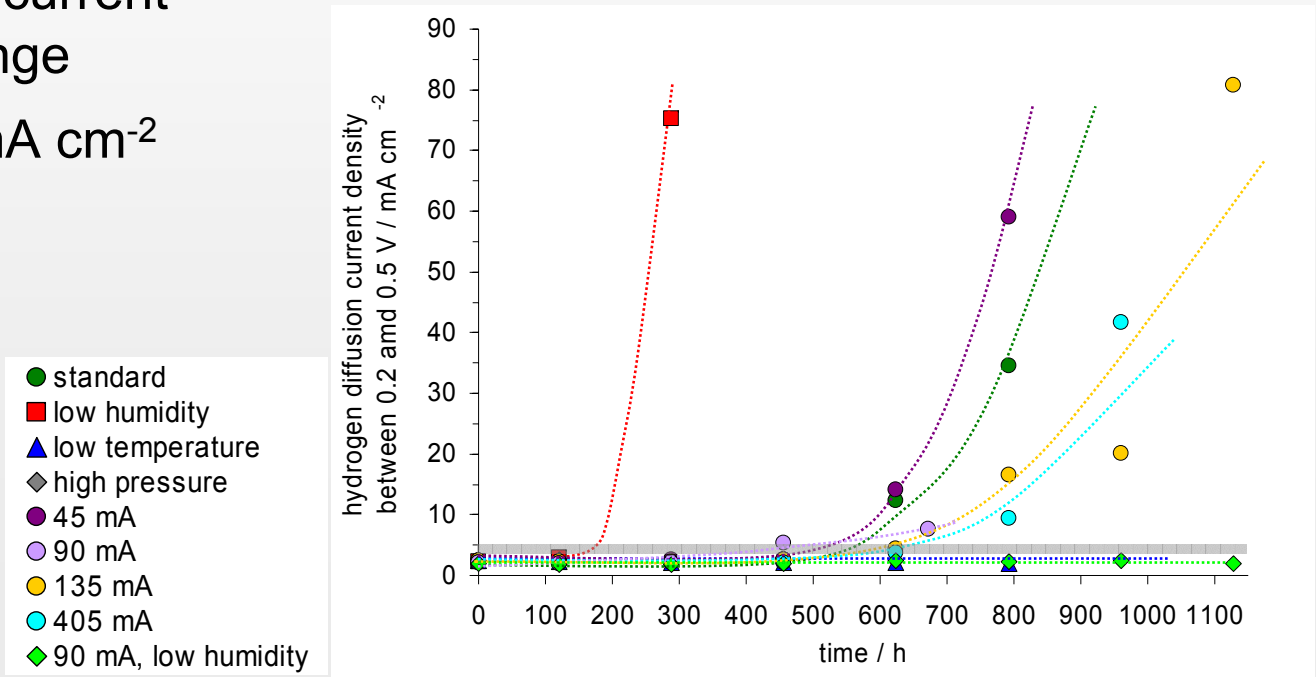
Hydrogen Diffusion

- anode: H_2 flow / cathode: N_2 flow
- standard conditions H_2 diffuses through the membrane and gets oxidised with an increasing potential
- the hydrogen diffusion current is limited by diffusion to < 5 mA cm^{-2}
- if there is a pinhole, the current increases with increasing potential



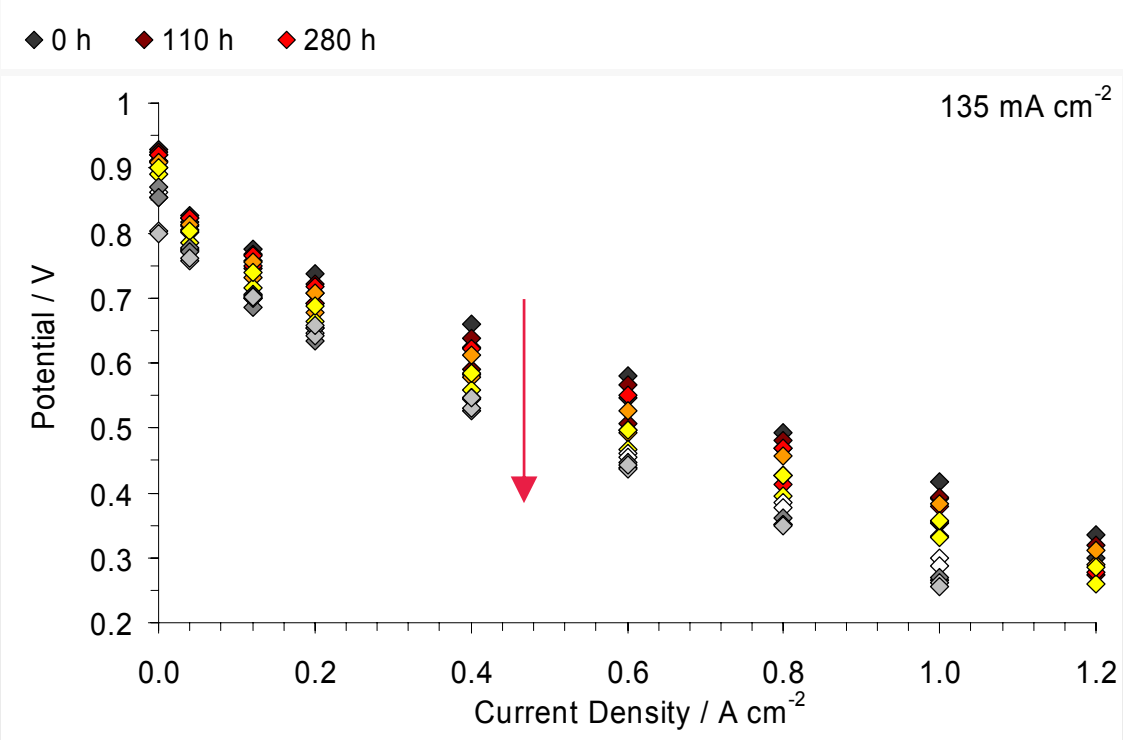
Hydrogen Diffusion - Results

- the formation of a pinhole can not be forecasted
- <u>end of membrane lifetime:</u> time interval, at which the hydrogen diffusion current density is in the range between 4 and 5 mA cm^{-2}



Cell Performance

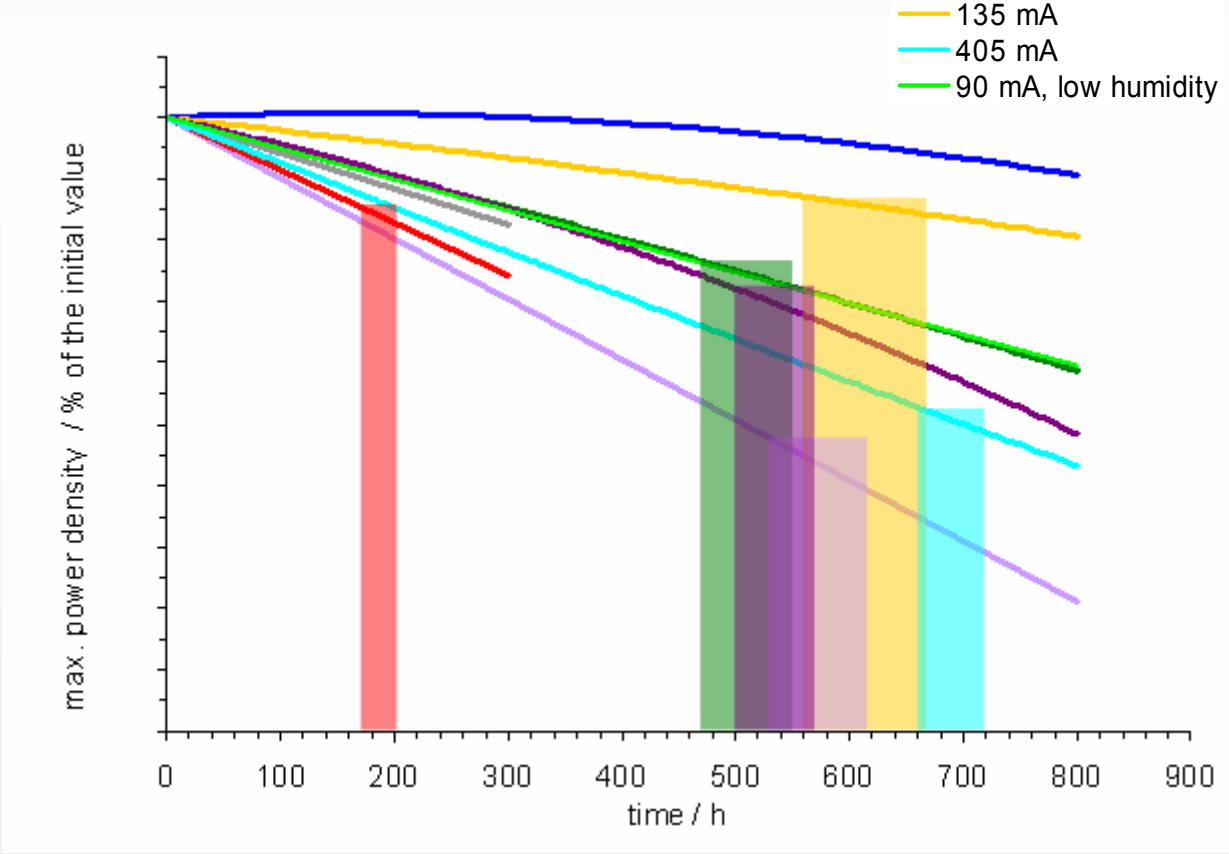
- the cumulated performance of the stack was investigated; H_2: λ = 1.5 / Air: λ = 2.2
- no gas pressure; T: 70 °C
- polarisation curves: changes with operating time



Cell Performance - Results

maximum power density

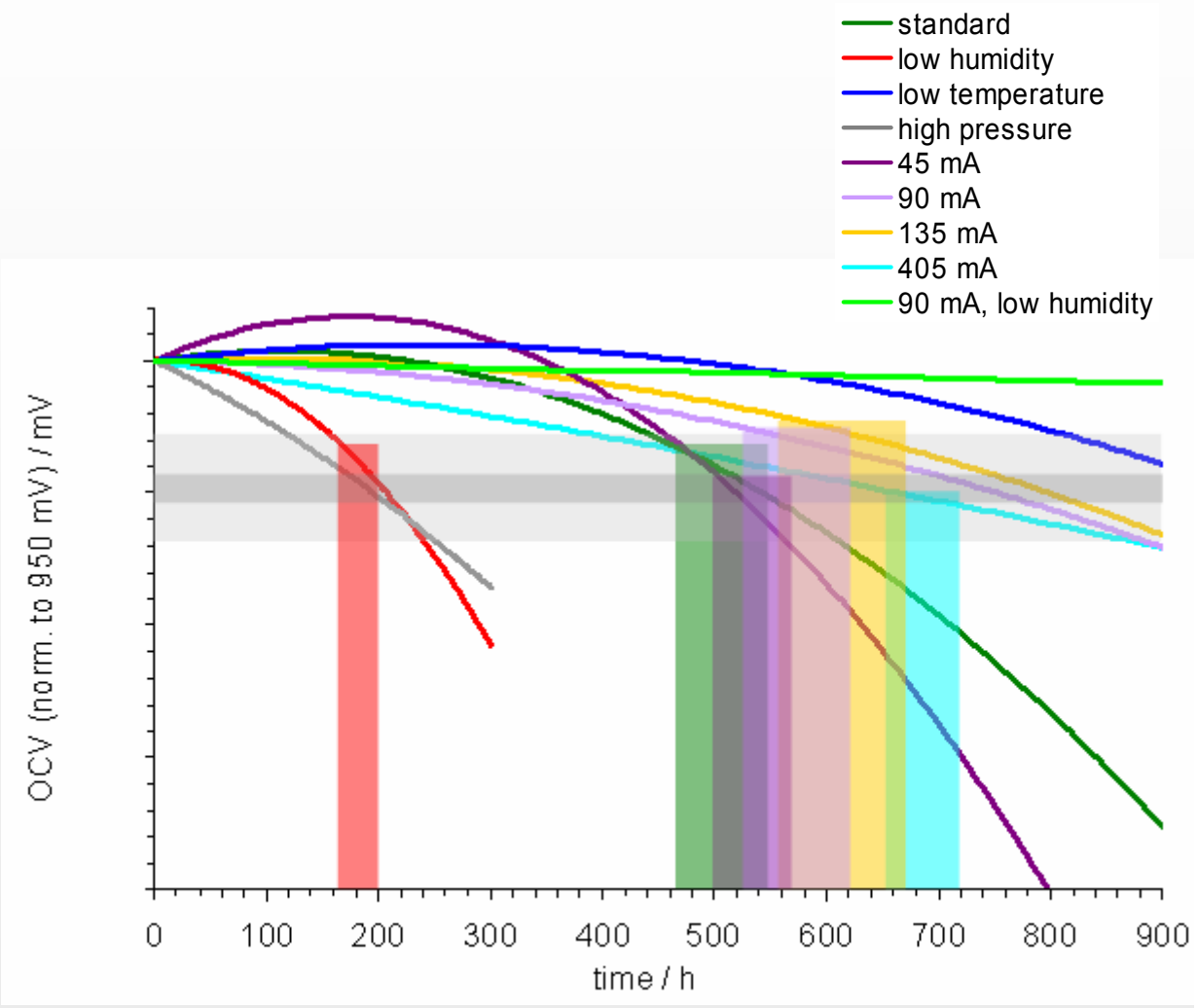
- changes with operating time
- the performance loss is related to the membrane degradation, but also influenced by the electrode degradation
- the formation of the first pinhole is not exactly related to a certain loss of performance



Cell Performance - Results

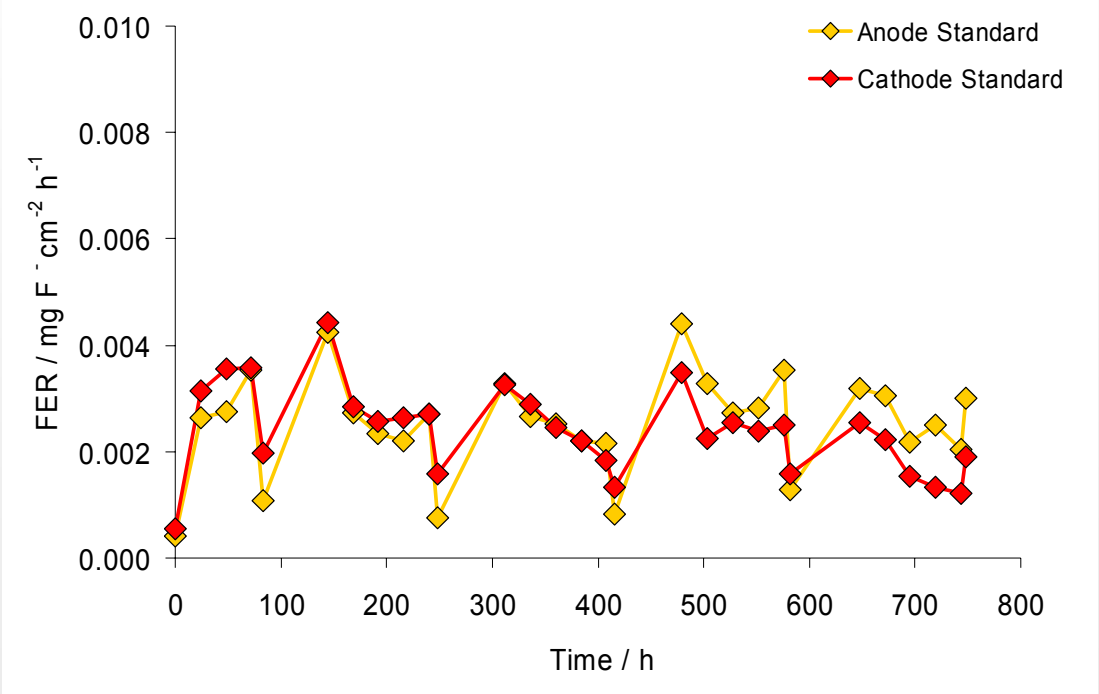
OCV

- OCV decreases with the operating time (non-linear)
- normalised OCV (to 0.95 V)
- the formation of the first pinhole is related to a loss of 30 - 70 mV (mostly ~ 50 mV) of the initial OCV of the “stack” because of the increasing gas diffusion through the degradated membrane
- a certain influence of the electrode degradation may exist



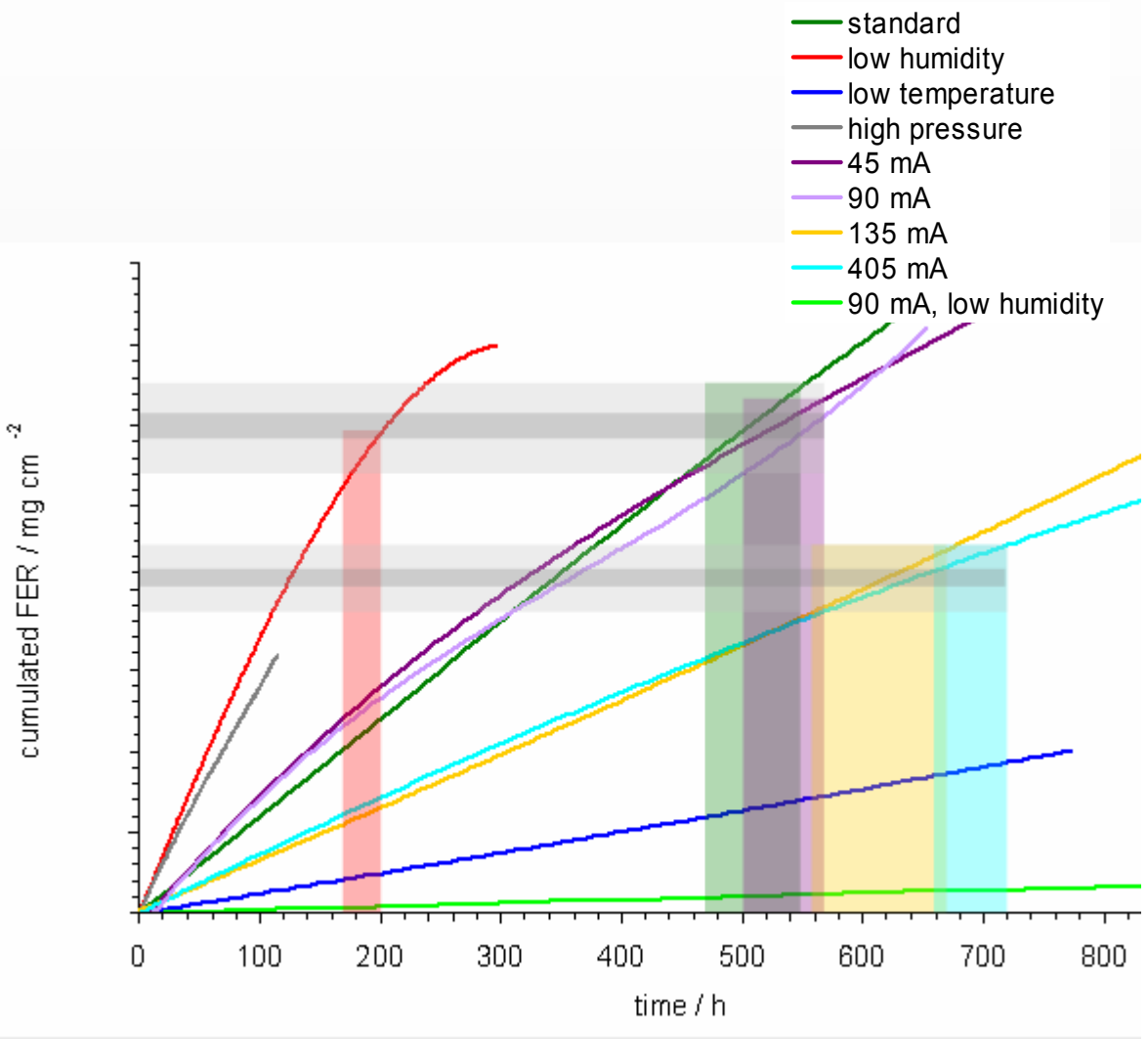
Fluoride Emission Rate - Results

- 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



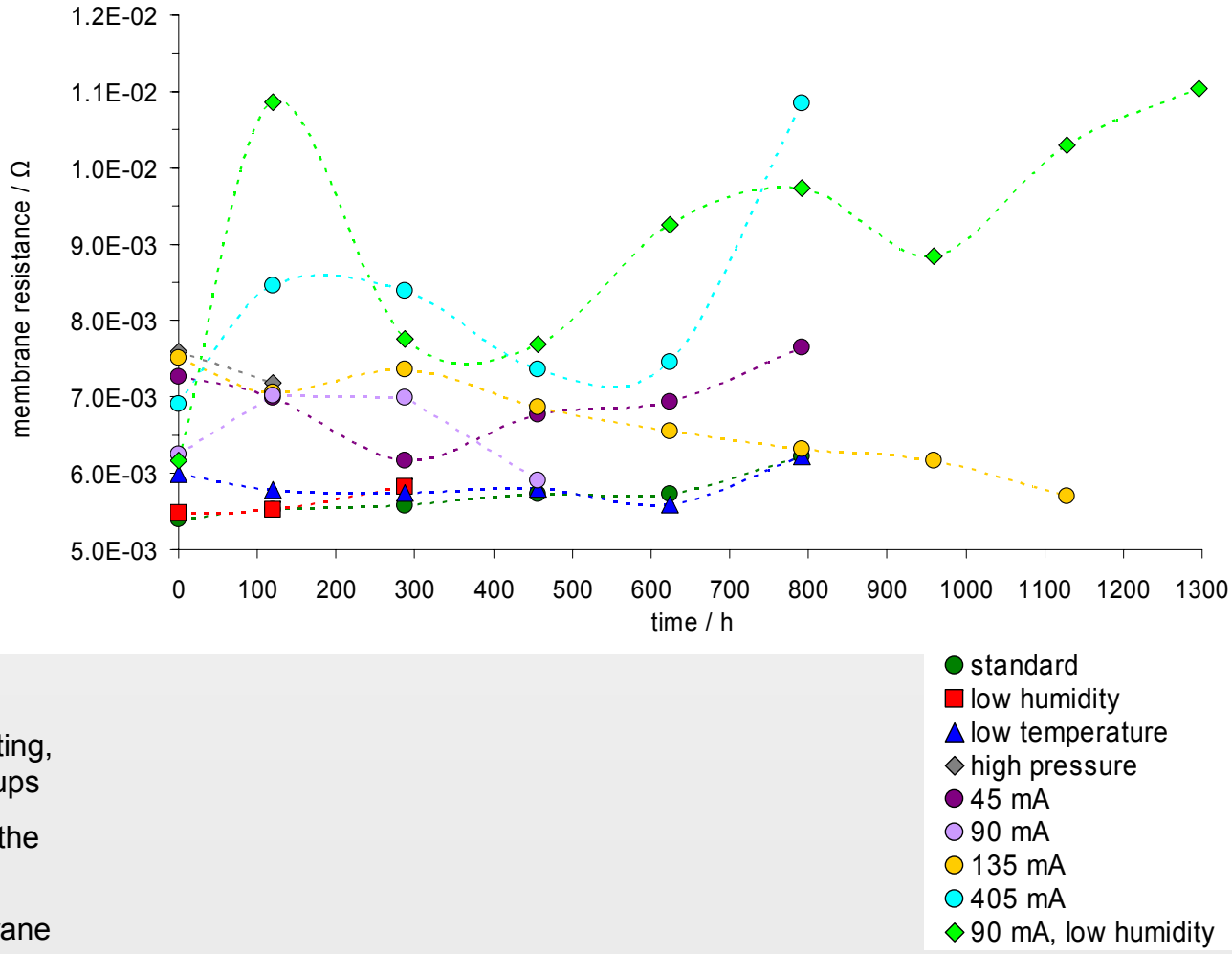
Fluoride Emission Rate - Results

- accumulation of the total anode and cathode FER:
- the formation of the first pinhole is related to a certain cumulated FER:



Membrane Resistance - Results

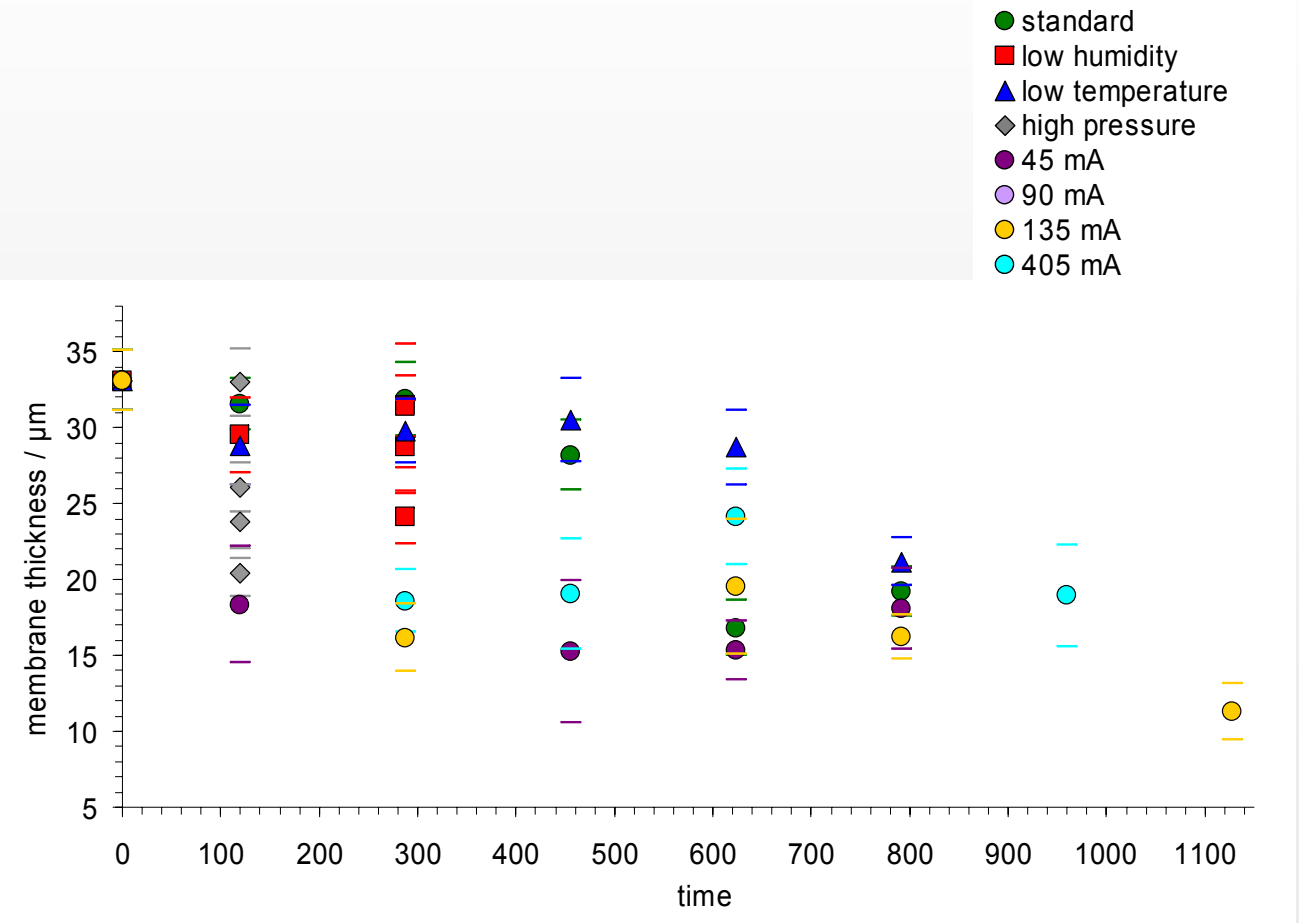
- change of the resistance with the operating time
- the resistance does not correlate clearly to
  - operating conditions
  - operating time
  - pinhole formation
  - membrane thickness (SEM)
- a slight increase of the resistance could be observed at higher degradation/ long operating time in most cases
- 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

membrane thickness

- the thinning of the membrane is not clearly related to operating conditions
- membrane thinning occurs under moderate and harsh conditions
- pinhole formation is not related to a significant membrane thinning



Conclusions

- a low cell current and a low gas humidity accelerate membrane degradation
- a lower temperature and higher cell currents slow membrane degradation
- the current density influences the impact of other parameters (e.g. gas humidity)
- the end of lifetime of the MEA was indicated by the detection of the first pinhole (at moderate performance losses)
- 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 membrane resistance did not correlate clearly to the membrane degradation, the formation of pinholes and the membrane thinning

future research activities

- evaluate and understand the complex interactions of fuel cell operating conditions, membrane parameters and membrane lifetime
- observe membrane and electrode degradation separately
- find a (simple) analysis instrument to observe membrane ageing during fuel cell operation

thank you for your kind attention!