Zentrum für BrennstoffzellenTechnik GmbH

Impact of air pollutants on HT-PEM fuel cells

Tests with single cell

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Statusworkshop ALASKA
Duisburg, 28.01.2016

Content

- Motivation
- Operating conditions
- Harmful gas tests in 2015
  - NO
  - NO_2
  - NH_3
  - C_2H_6
  - SO_2
- Summary and outlook

ZBT

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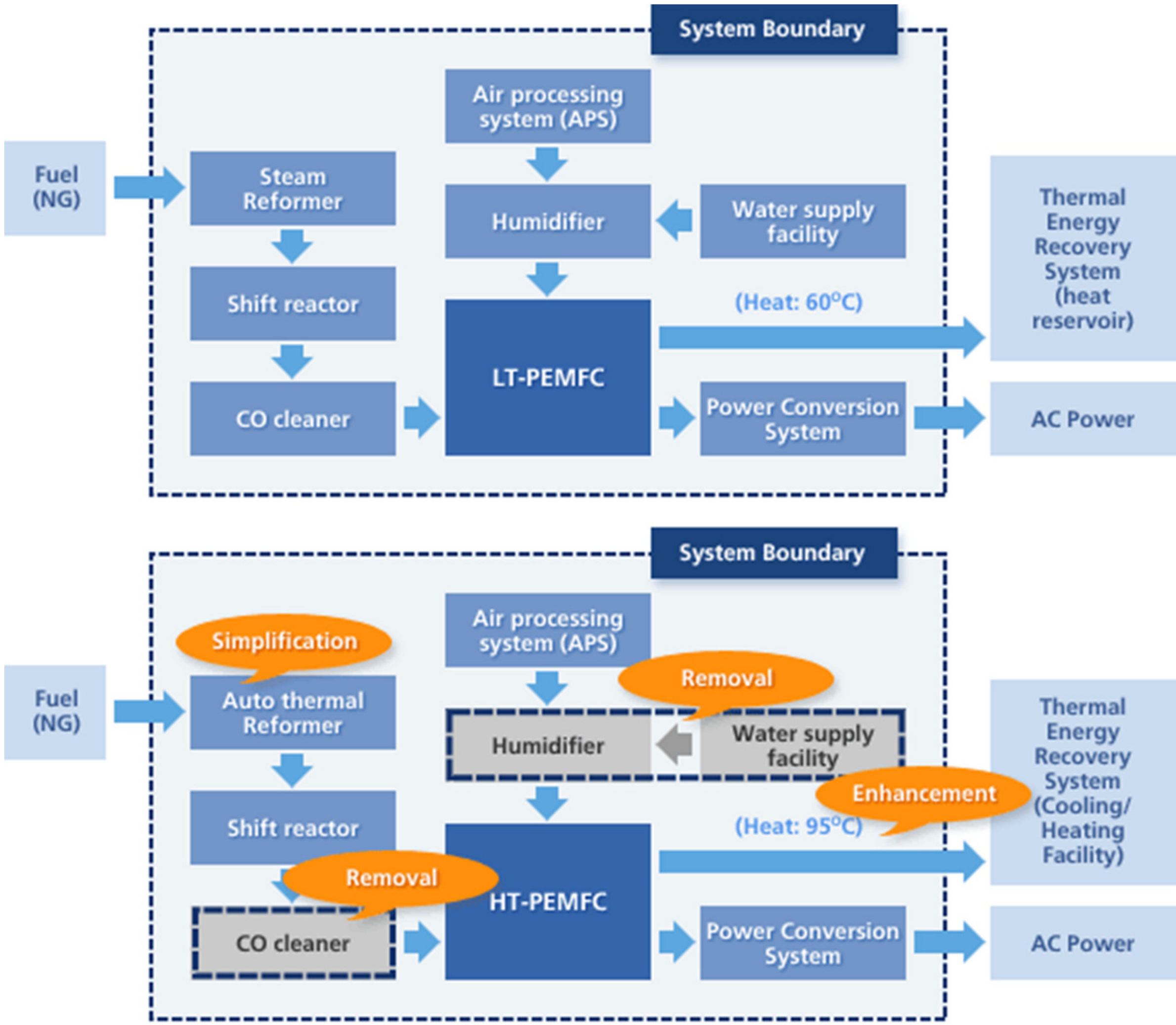
Differences between HT-PEMFC and LT-PEMFC



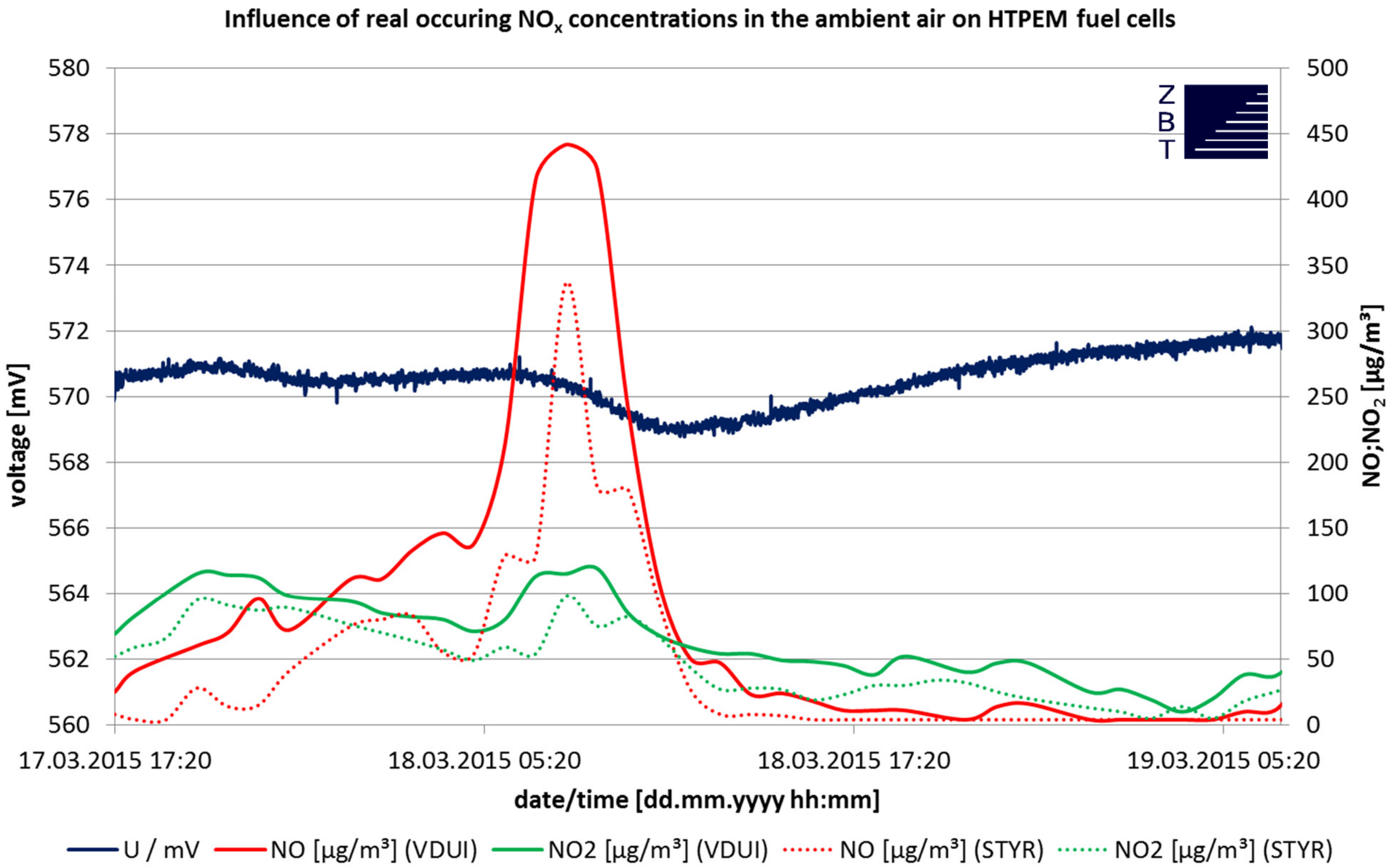
Source: hyosung.sk

- Temperature level
  - LT-PEMFC ≤ 90°C
  - HT-PEMFC 160 – 180°C
- Advantages of HT-PEMFC
  - no external humidification necessary
  - higher tolerance to impurities
    - anode side: CO, H_2S
    - no liquid water during operation
  - available heat at elevated temperature level

Motivation

- Harmful gas influences on the anode of HT-PEMFC have been discovered
- Significant differences between HT-PEMFC and LT-PEMFC
  - membrane
  - proton transport
  - no liquid water during operation
  - phosphoric acid
  - catalyst composition
- Different operating conditions
  - temperature
  - current density
  - stationary operation
  - cell potential

Motivation
influence of NO_x on HT-PEMFC



<u>at standard conditions</u>

NO:

1 ppb = 1,247 µg/m³

NO_2:

1 ppb = 1,912 µg/m³

voltage drop of 3 mV caused by ambient air ZBT lab (loop with particle and oil filter)

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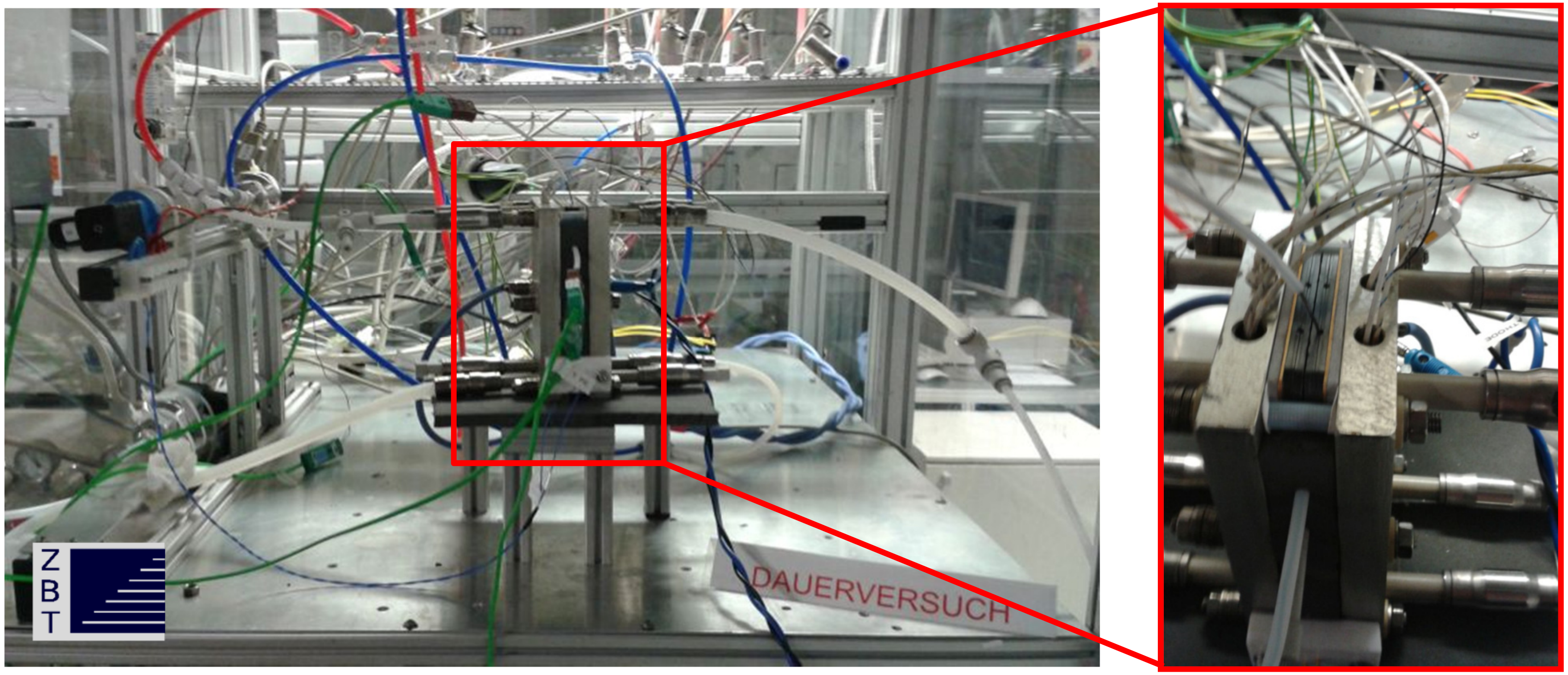
Operating conditions



Experimental conditions

- single cell ZBT-design: 50 cm² active area
- cell temperature 160°C (140°C)
- stoichiometry cathode/anode: 2.0/1.2
- gases: air on cathode side and H_2 on anode side
- current density: 300 mA/cm²
- MEA: Elcomax

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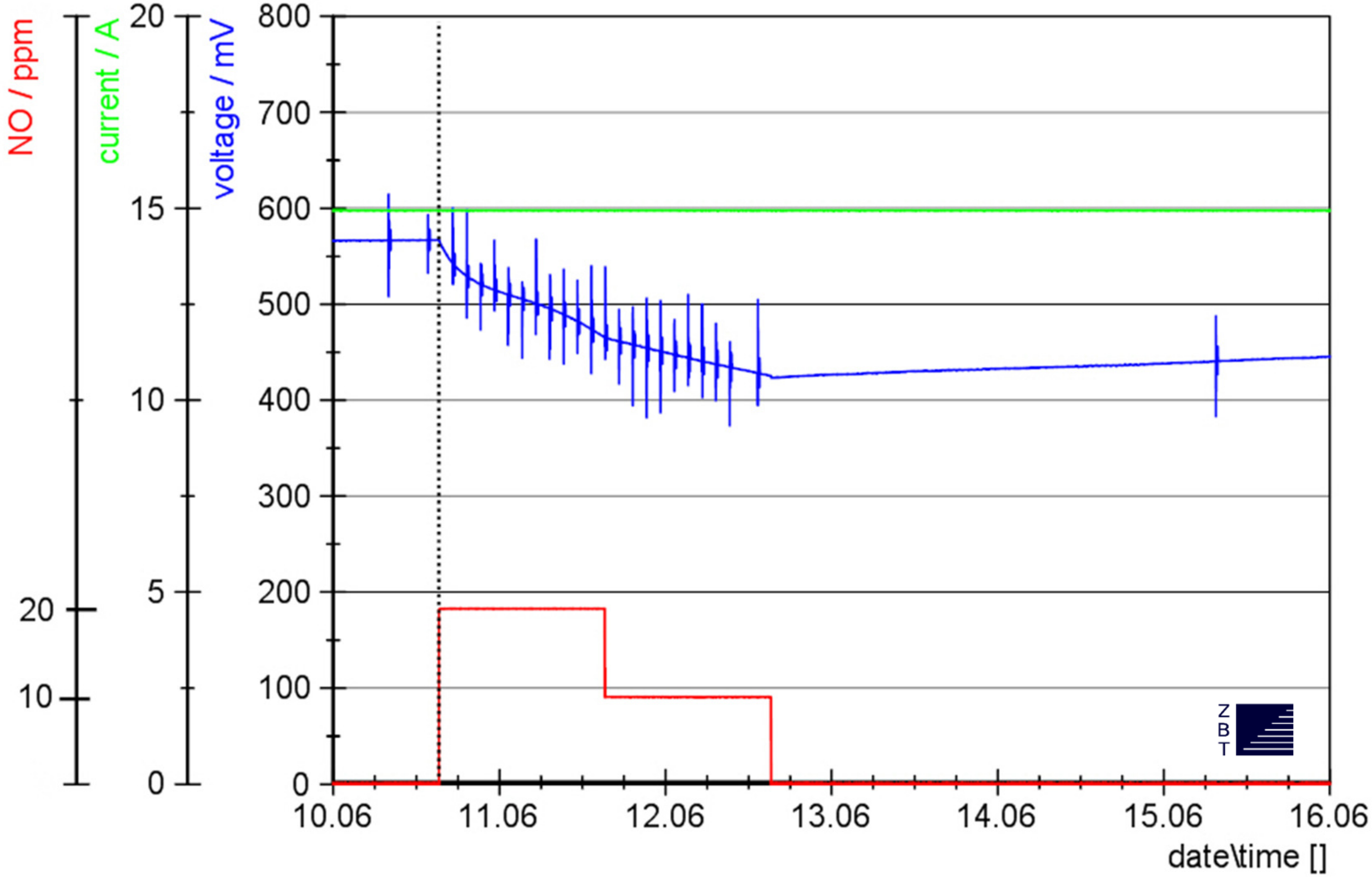
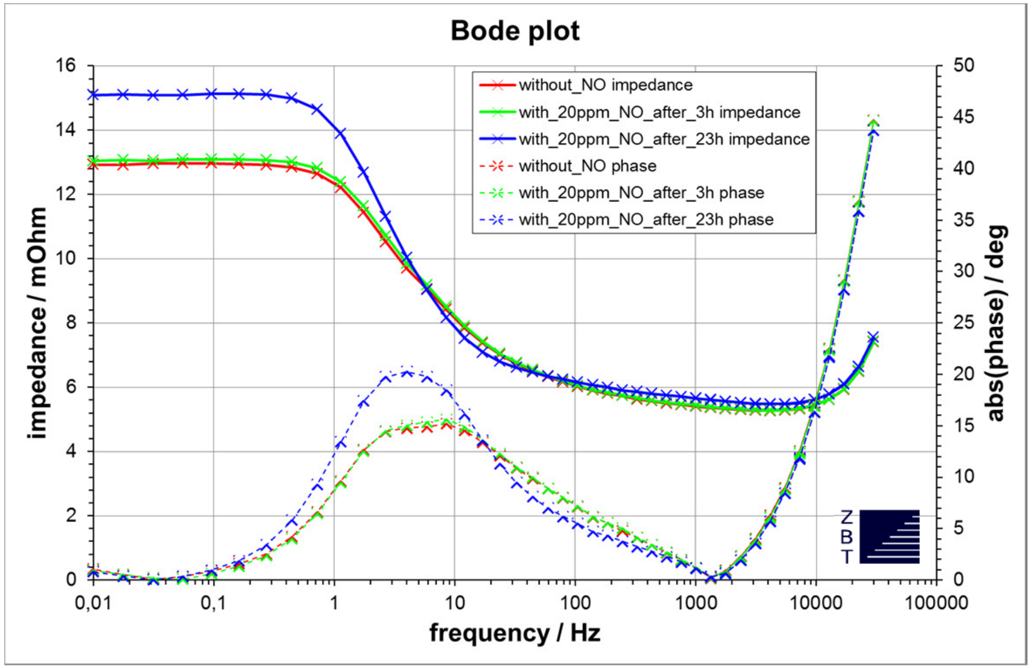
Experiments with nitric oxide (NO) 10 ppm and 20 ppm

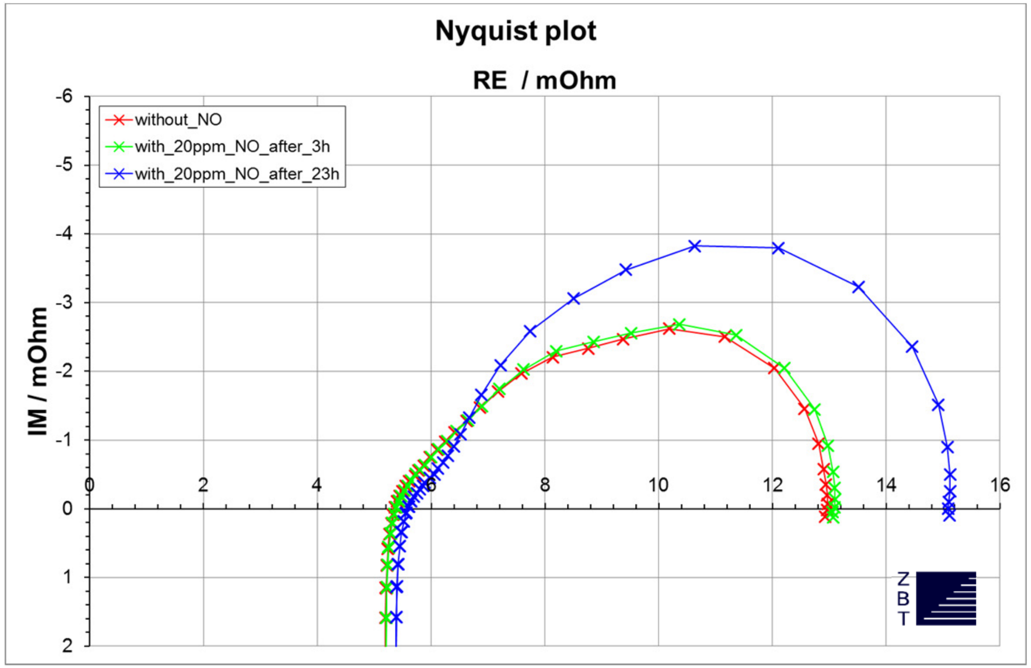


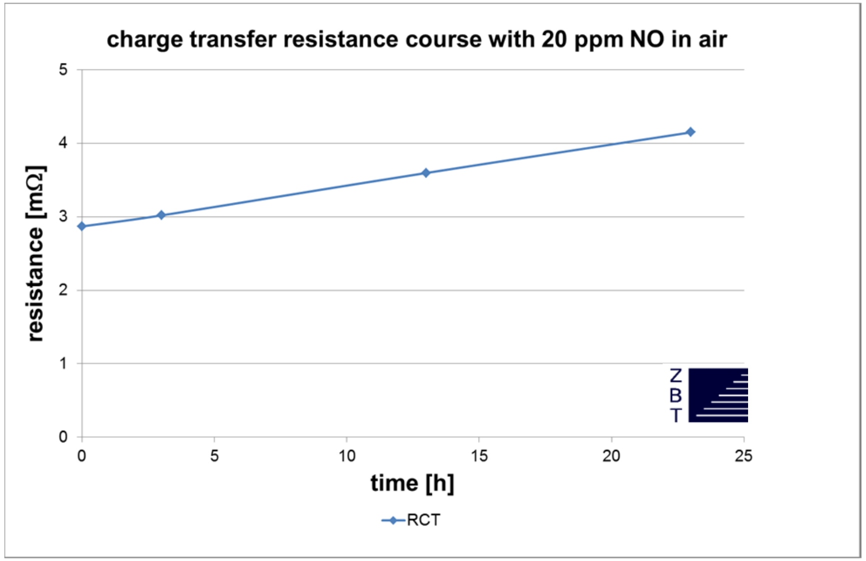
- current density: 300 mA/cm²
- cell temperature: 160°C
- stoichiometry cathode: 2.0

- significant voltage decline
- in contrast to NT-PEM the voltage does not stabilize after some time, but drops linear
- very slow regeneration

Impedance measurements during NO-contamination

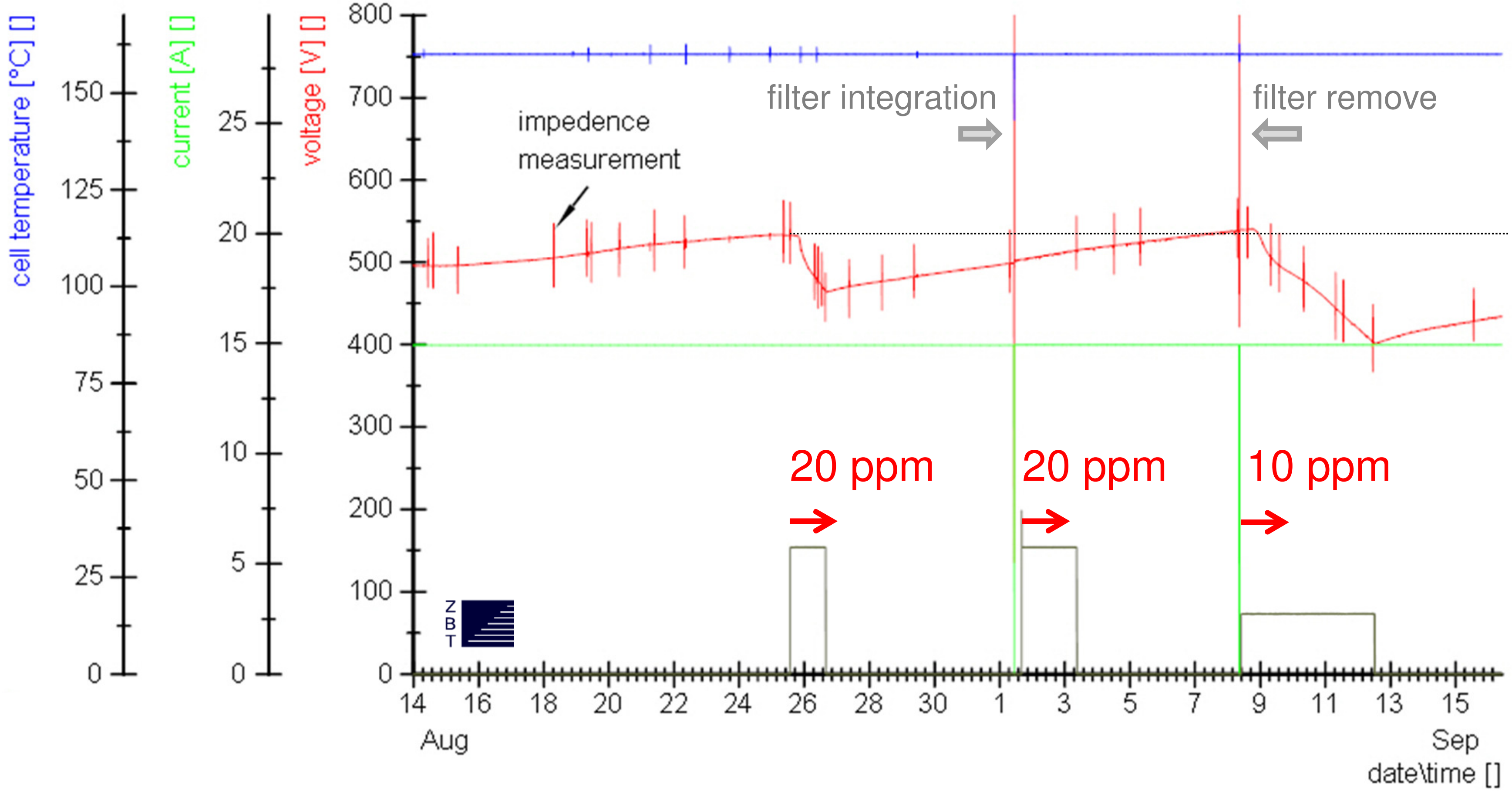






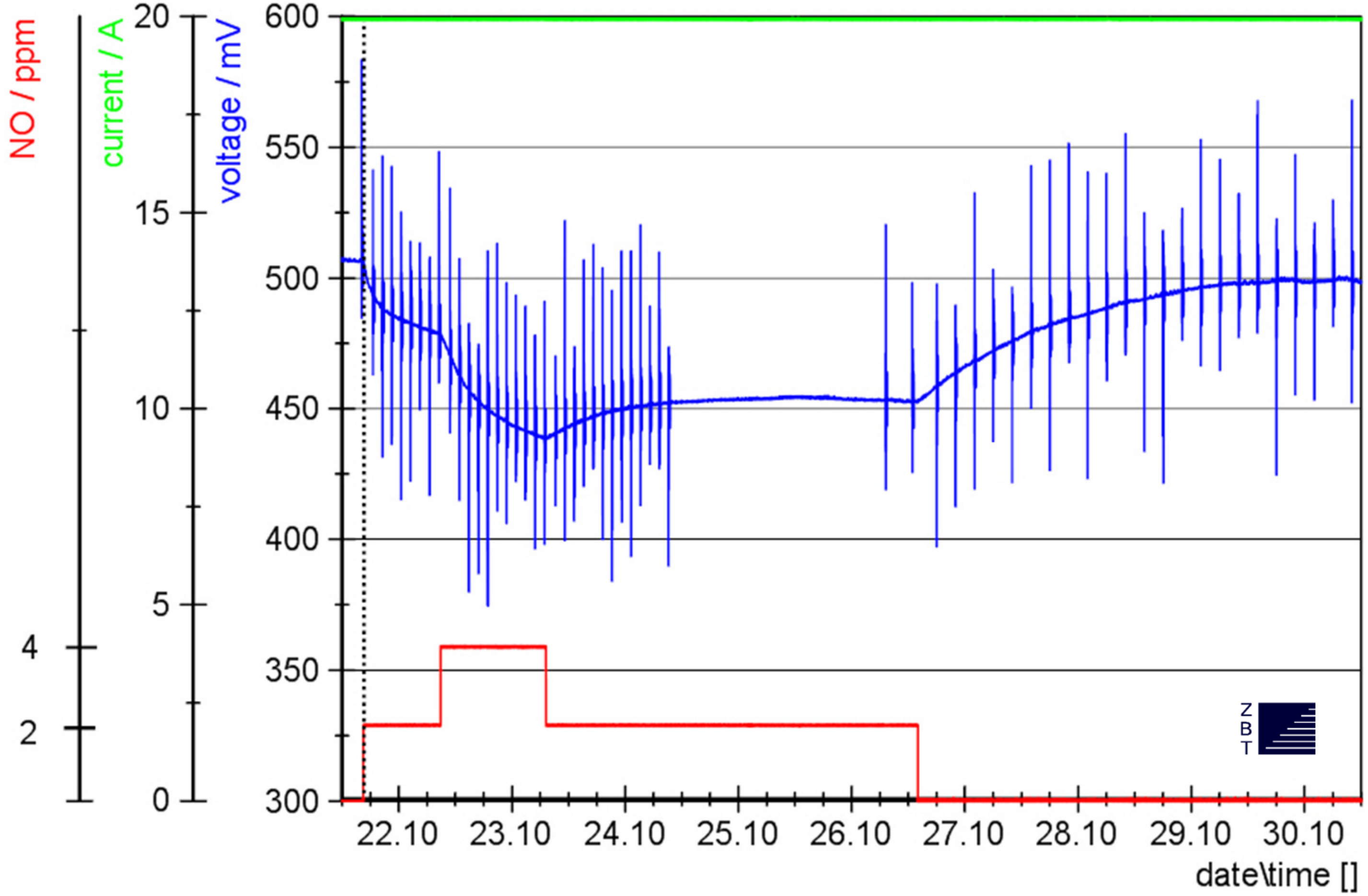
- sharp rise in medium-arc
- charge transfer resistance R_{CT} increases almost linearly
- slight increase in the ohmic resistance
- slight increase of the ionic resistance R_p (ionic resistance of the cathode catalyst layer)

Experiments with nitric oxide (NO) 10 ppm and 20 ppm
efficiency of the filter



- filter is very effective, unchanged regeneration behavior despite harmful gas addition

Experiments with nitric oxide (NO) 2 ppm and 4 ppm



- current density: 400 mA/cm²
- cell temperature: 160°C
- stoichiometry cathode: 3.0

- at 2 ppm voltage loss > 25 mV
- increasing to 4 ppm intensified the voltage drop
- significant regeneration only with uncontaminated air supply → no complete regeneration
- regeneration faster in comparison to the experiments with higher concentration of NO

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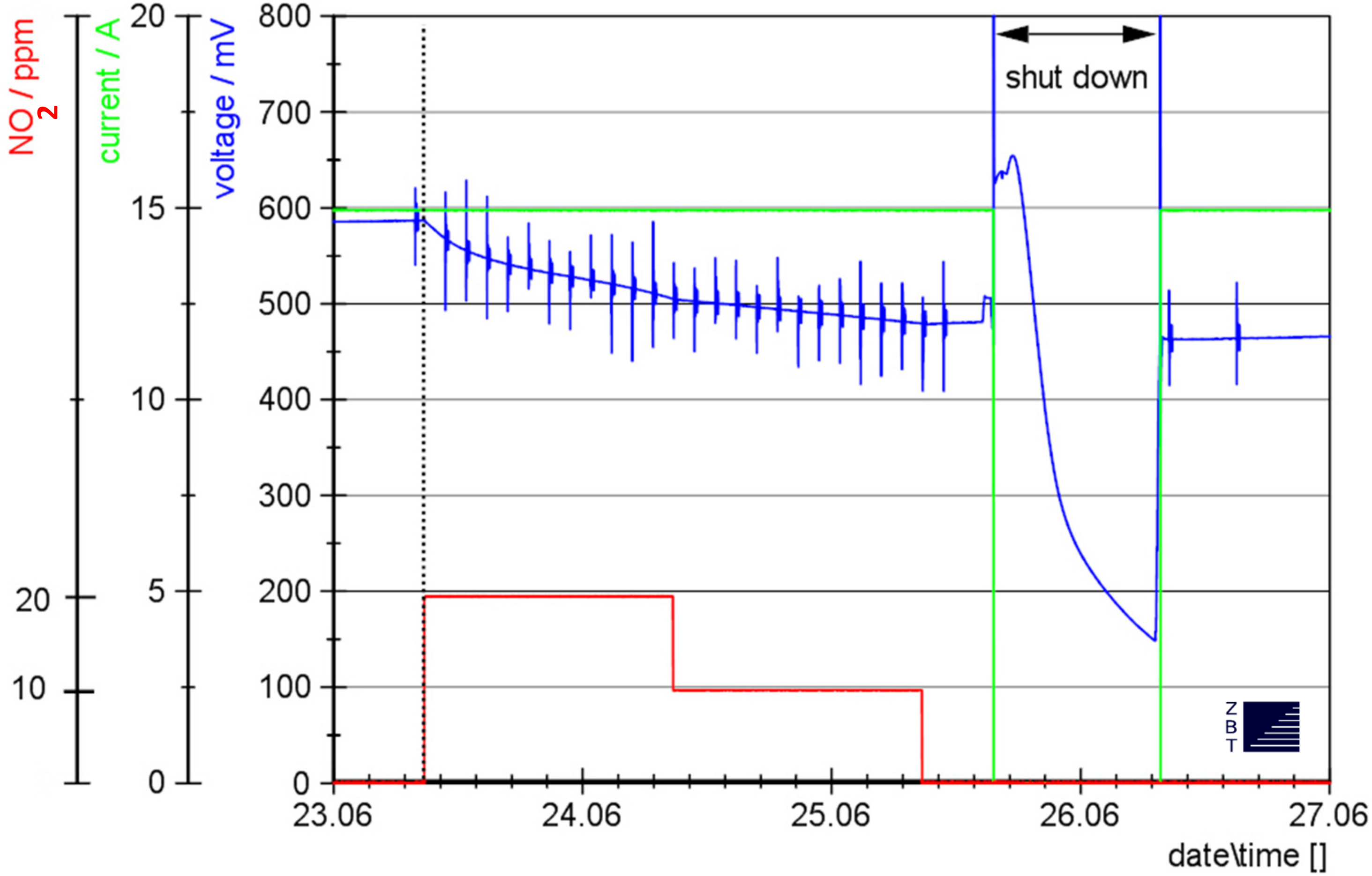
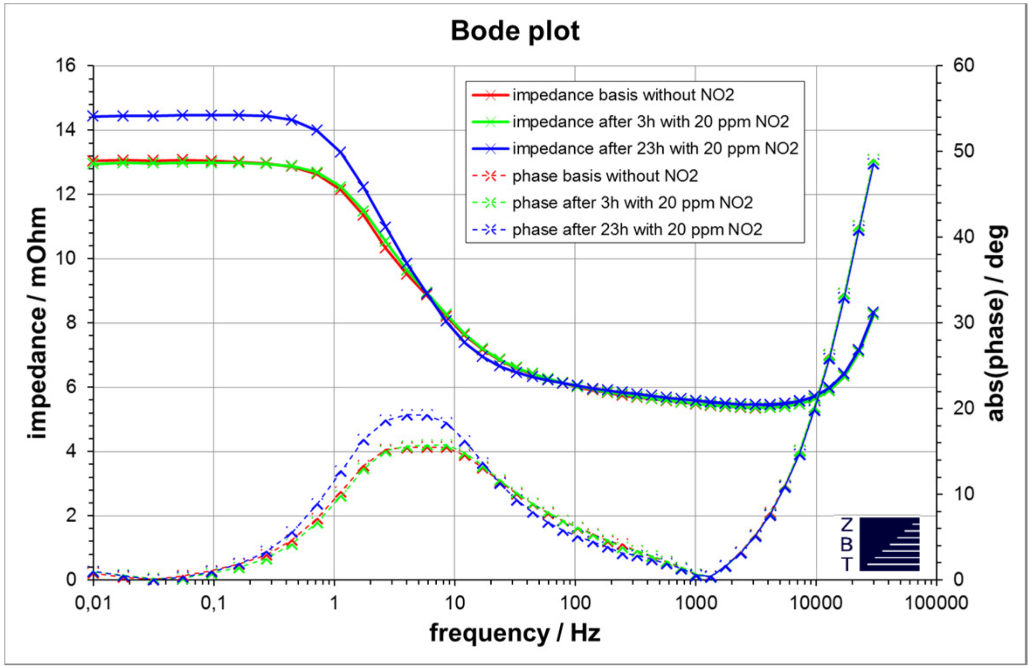
Experiments with nitrogen dioxide (NO_2) 10 ppm and 20 ppm

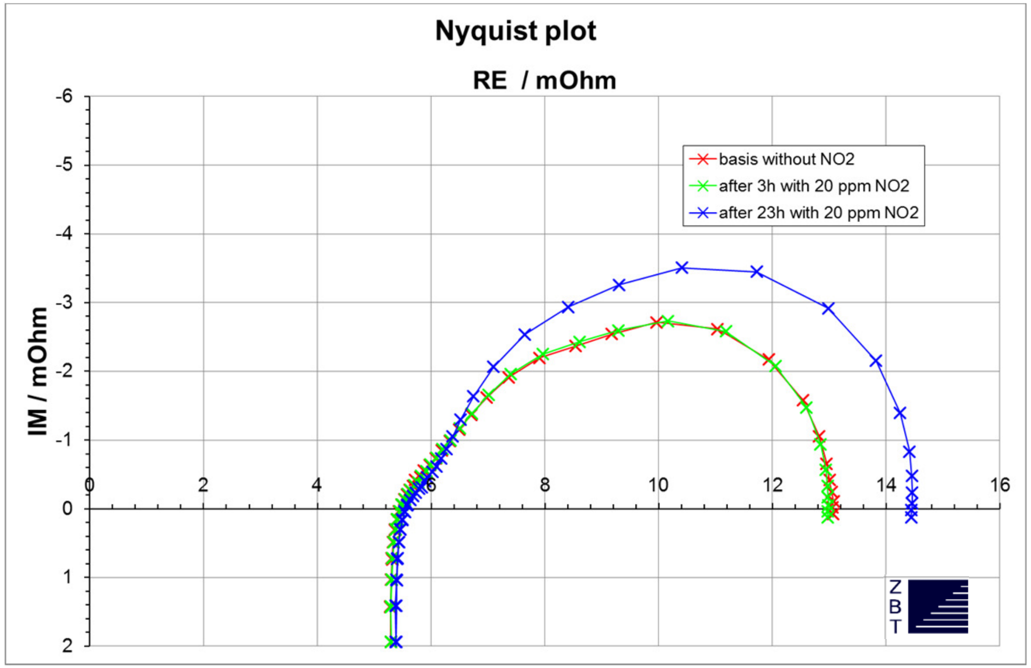


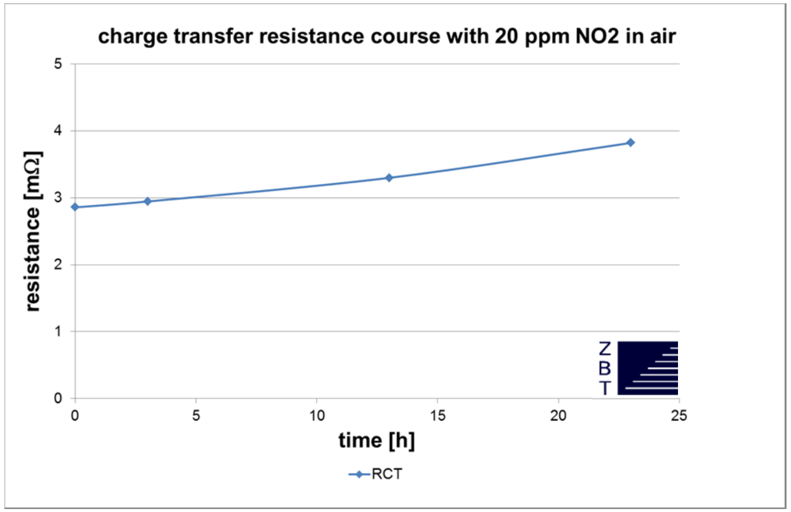
- current density: 300 mA/cm²
- cell temperature: 160°C
- stoichiometry cathode: 2.0

- high voltage loss
- starts with an increased voltage drop, followed by almost linear voltage decline
- shutdown and cooling of the cell do not lead to regeneration

Impedance measurements during NO_2-contamination

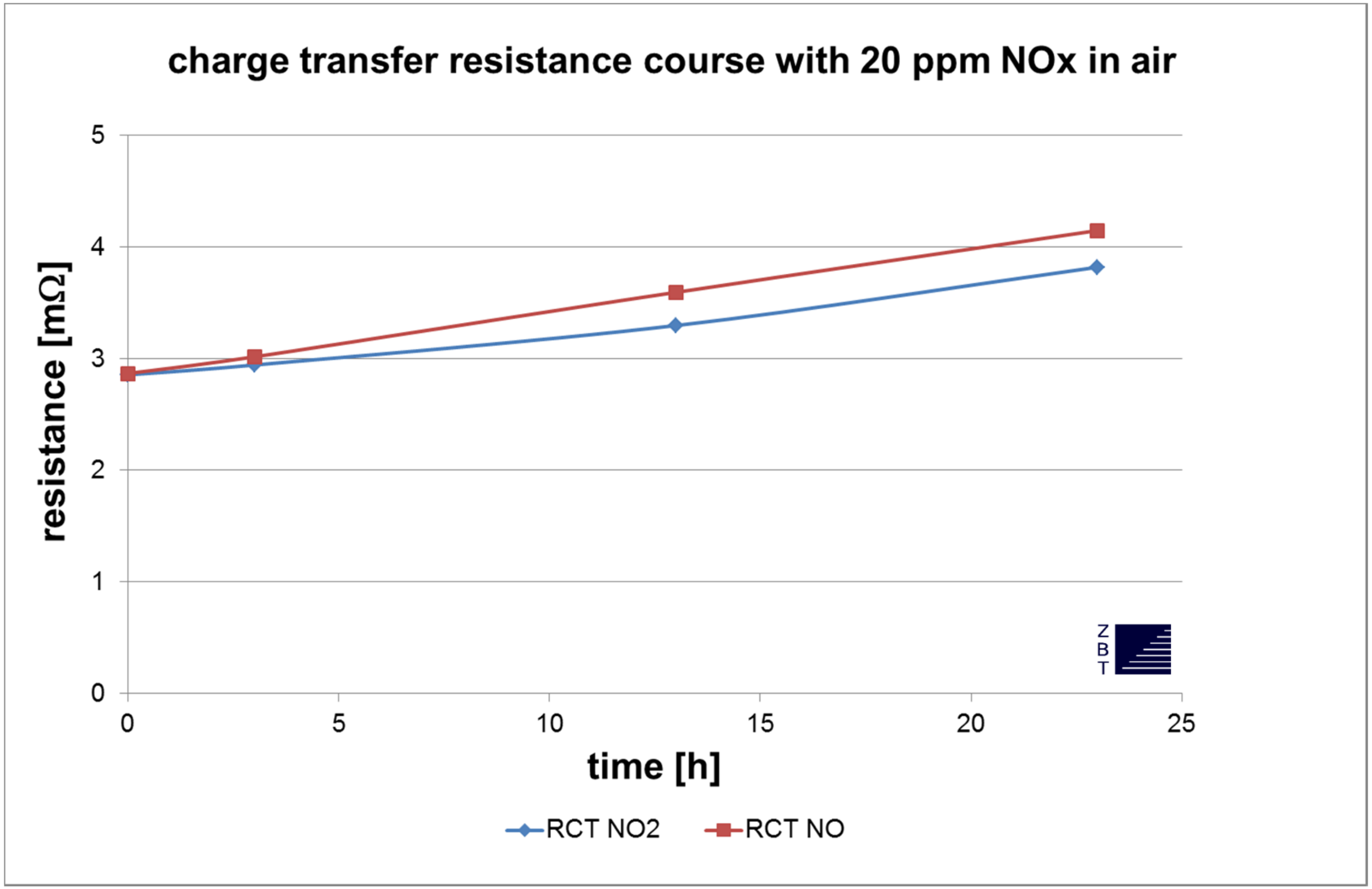






- sharp rise in medium-arc
- charge transfer resistance R_{CT} increases
- very low increase of ionic resistance R_p (ionic resistance of the cathode catalyst layer)

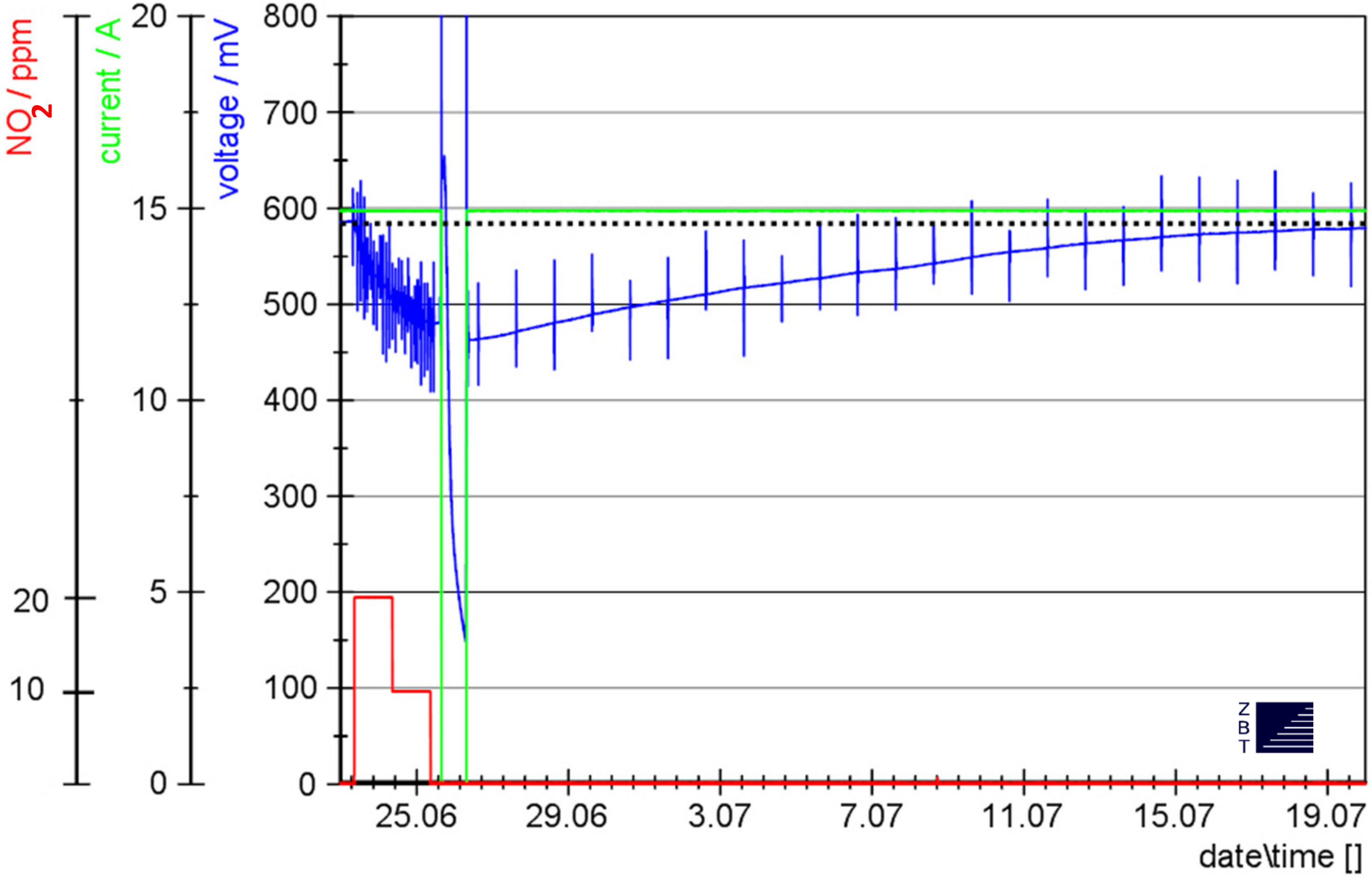
Course of charge transfer resistance NO vs. NO_2



- slower increase of R_{CT} is consistent with the slightly reduced voltage drop while addition of NO_2 compared to NO (with the same concentration and period of time)

Experiments with nitrogen dioxide (NO_2) 10 ppm and 20 ppm

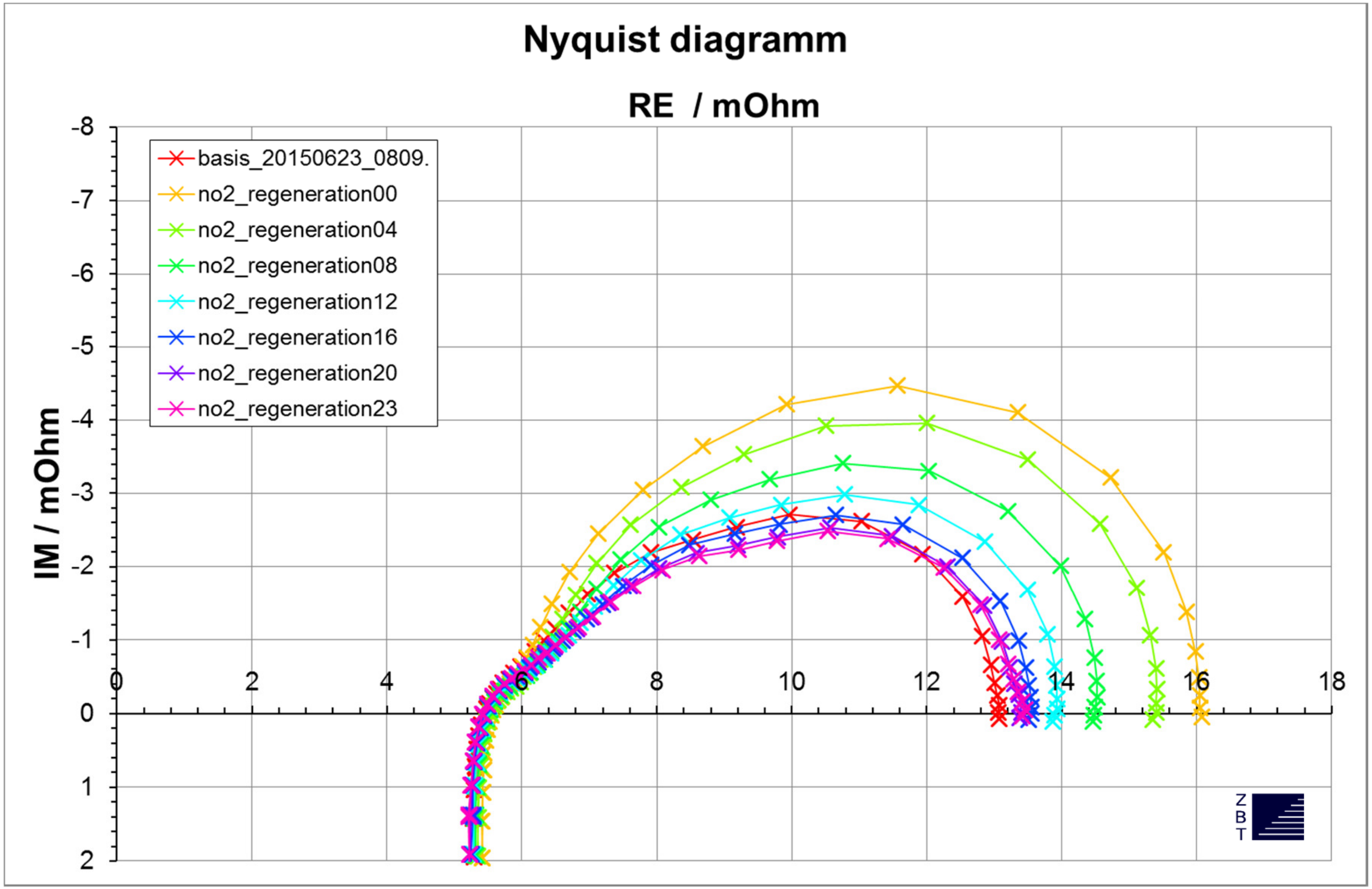
recovery



- current density: 300 mA/cm²
- cell temperature: 160°C
- stoichiometry cathode: 2.0

- regeneration very slow > 3 weeks
- initial voltage is nearly reached

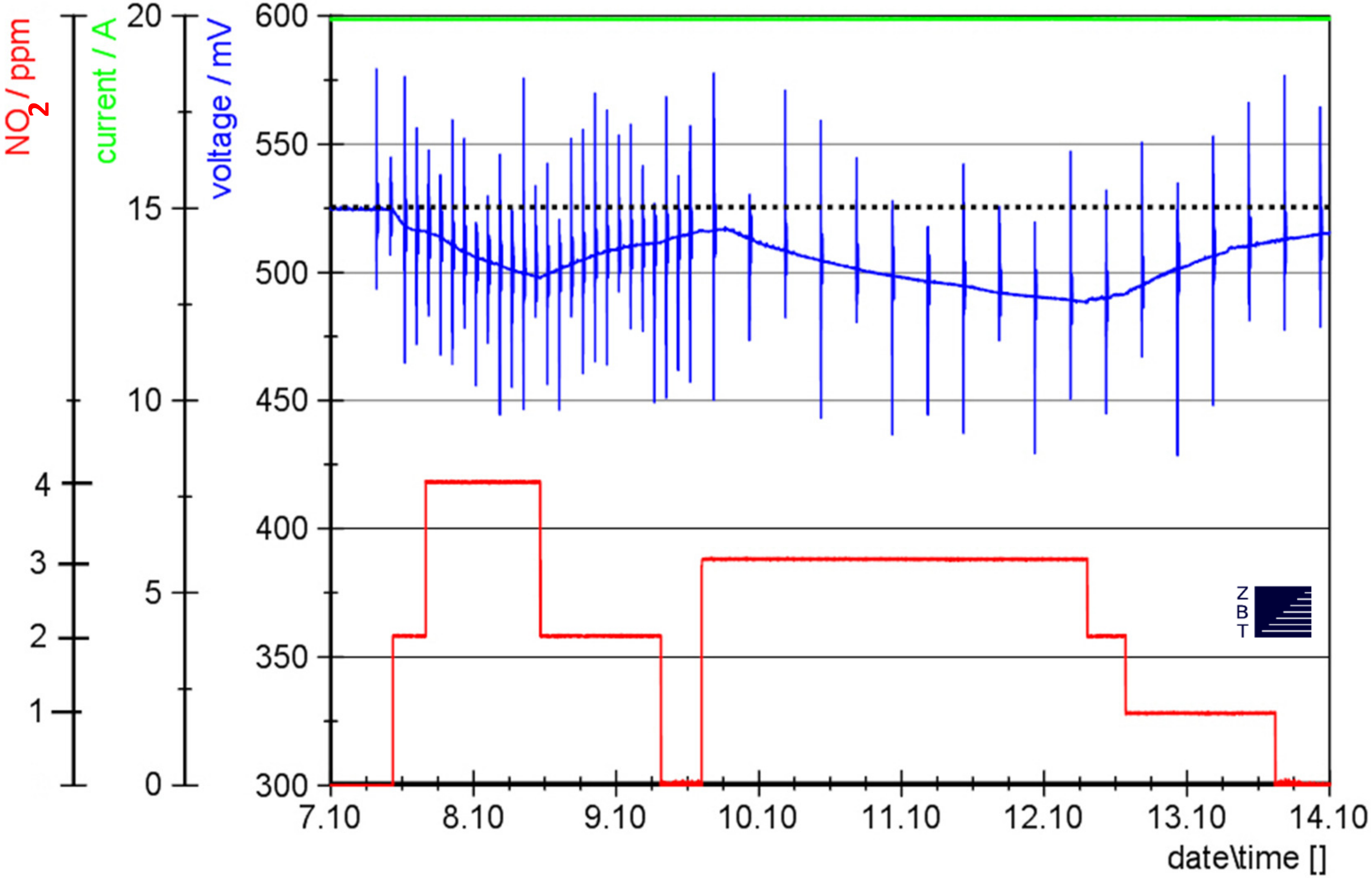
Impedance measurements during regeneration after NO_2 contamination



- with regeneration significant decrease of medium-arc
- even slight decrease of the ohmic resistance and the ionic resistance Rp

Experiments with nitrogen dioxide (NO_2)

regeneration under contaminated air



- current density: 400 mA/cm²
- cell temperature: 160°C
- stoichiometry cathode: 3.0

- partial regeneration at reduction of NO_2 concentration in the supply air

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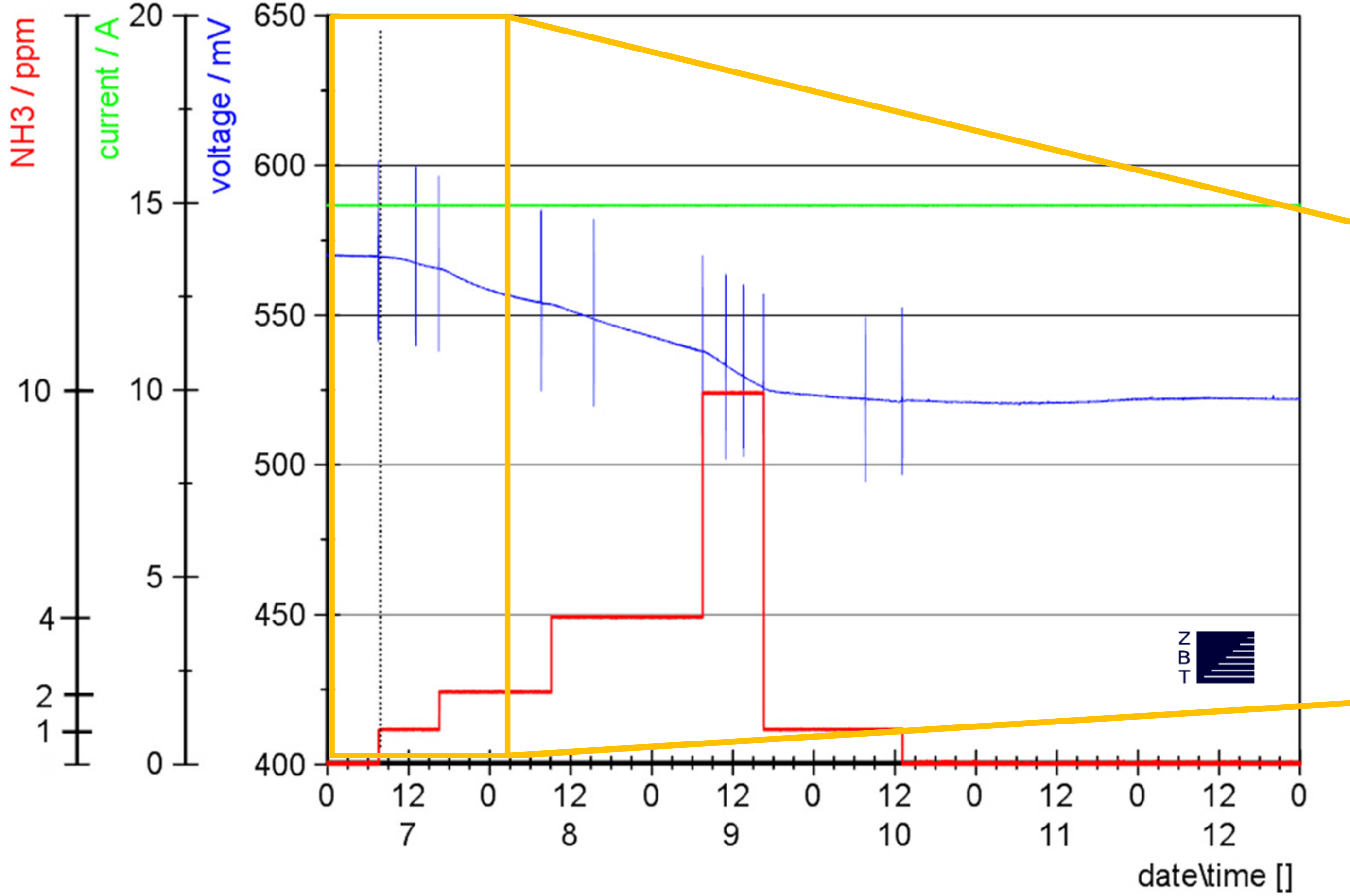
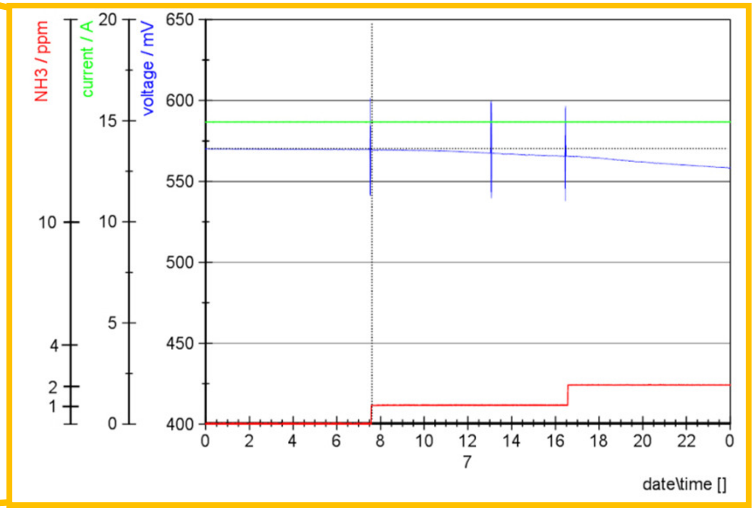
Experiments with ammonia (NH_3)



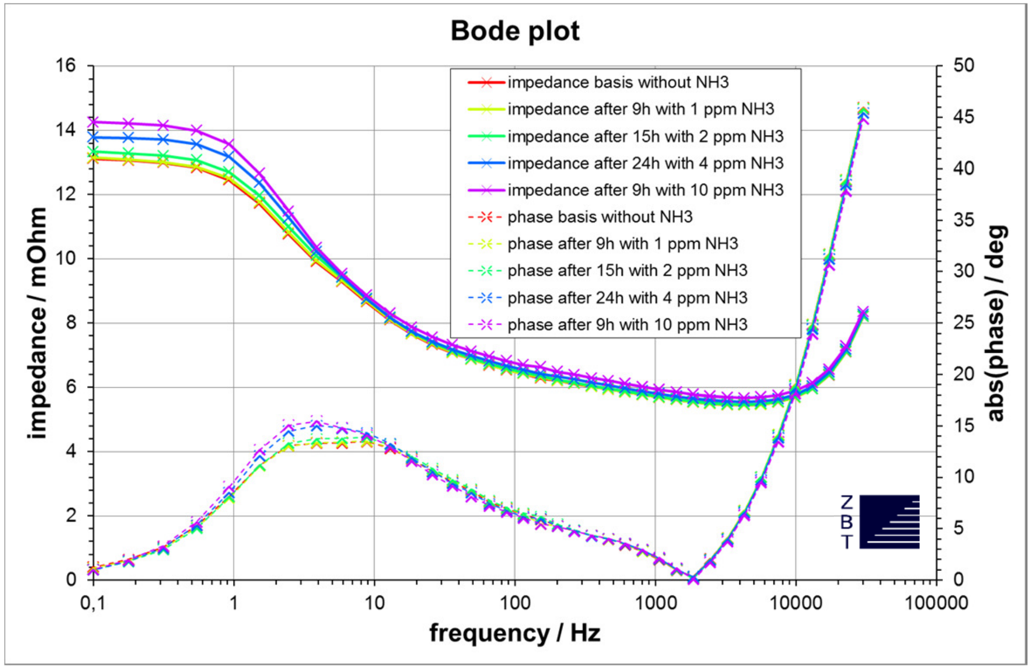
- current density: 300 mA/cm²
- cell temperature: 160°C
- stoichiometry cathode: 2.0

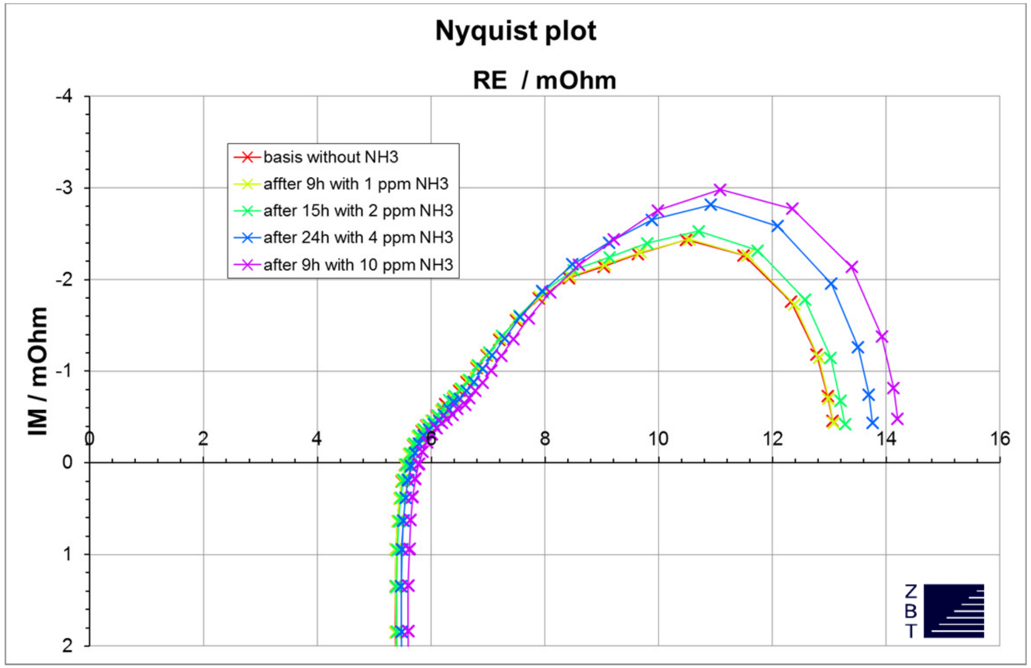


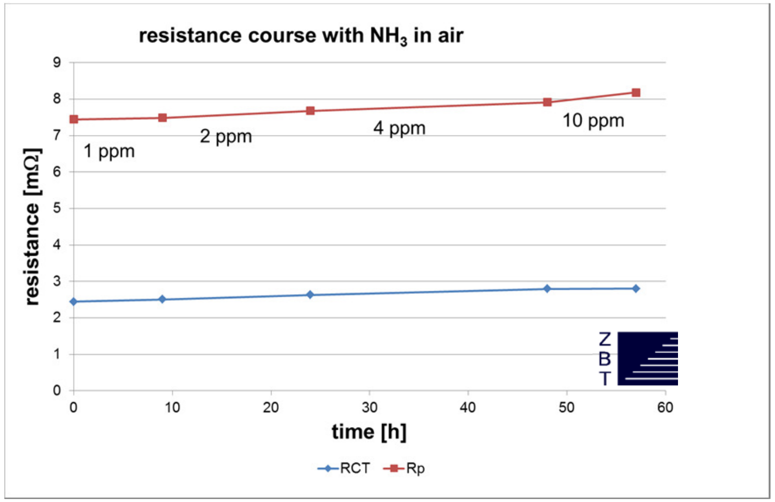
- voltage decrease is delayed

- voltage decrease already at a concentration of 1 ppm NH_3 in air
- stronger voltage drop with increased concentration
- voltage decline almost linear - no approach to a limit value
- in case of reducing the concentration of NH_3 in the feed air, the voltage falls more slowly
- regeneration can not be seen

Impedance measurements during regeneration after NH_3 contamination







- overlay of medium- and low-frequency bow
- increase of diffusion resistances, especially at elevated concentrations
- charge transfer resistance R_{CT} increases slightly
- slight increase in ionic resistance R_p (ionic resistance of the cathode catalyst layer)
- ohmic resistance (membrane resistance) increases slightly, particularly at elevated concentrations

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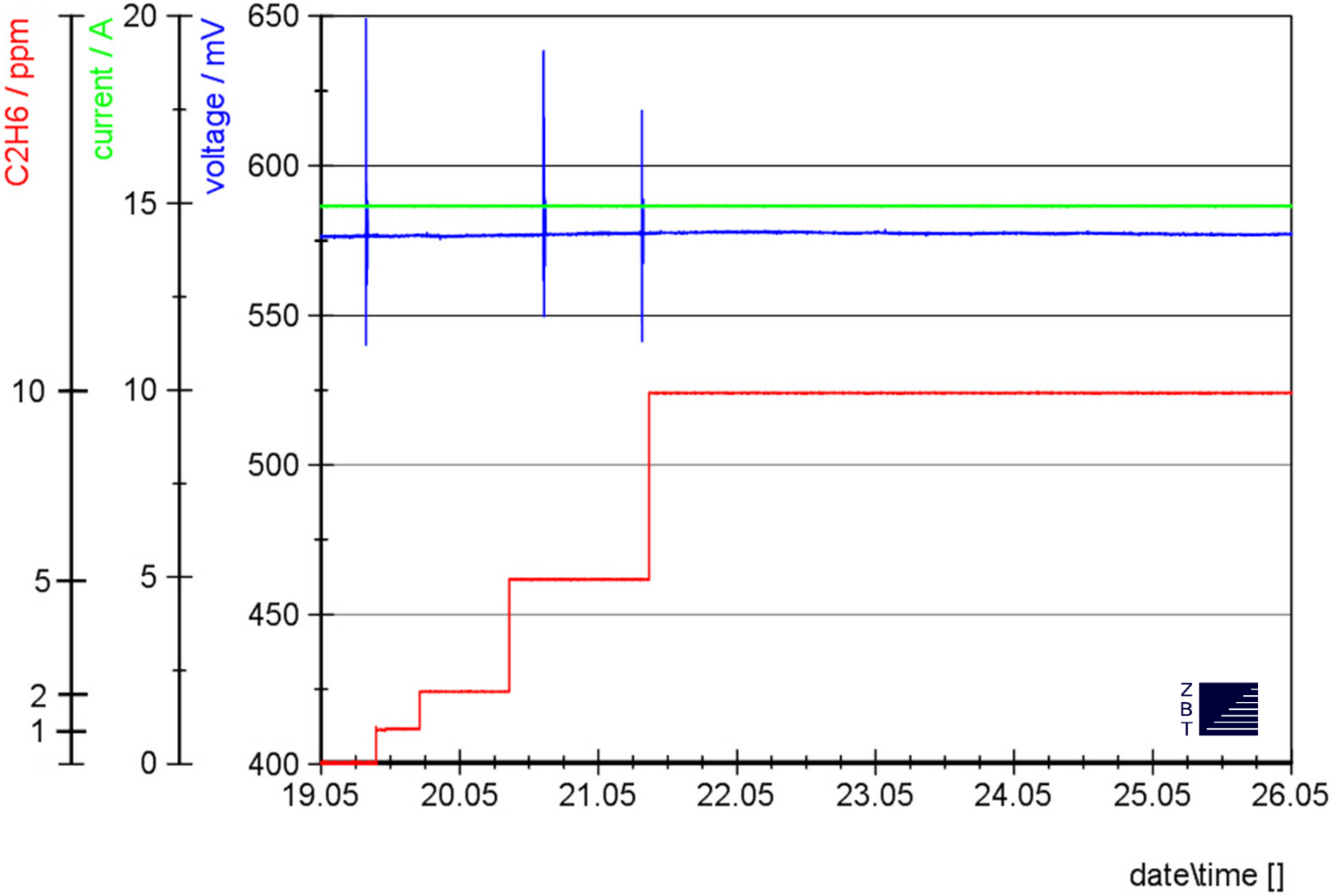
Experiments with ethane (C_2H_6)



- current density: 300 mA/cm²
- cell temperature: 160°C
- stoichiometry cathode: 2.0

- ethane is a constituent of natural gas
- saturated hydrocarbon

- no voltage drop even at a concentration of 10 ppm ethane in air supply
- the behavior is similar to the results with the LT-PEMFC

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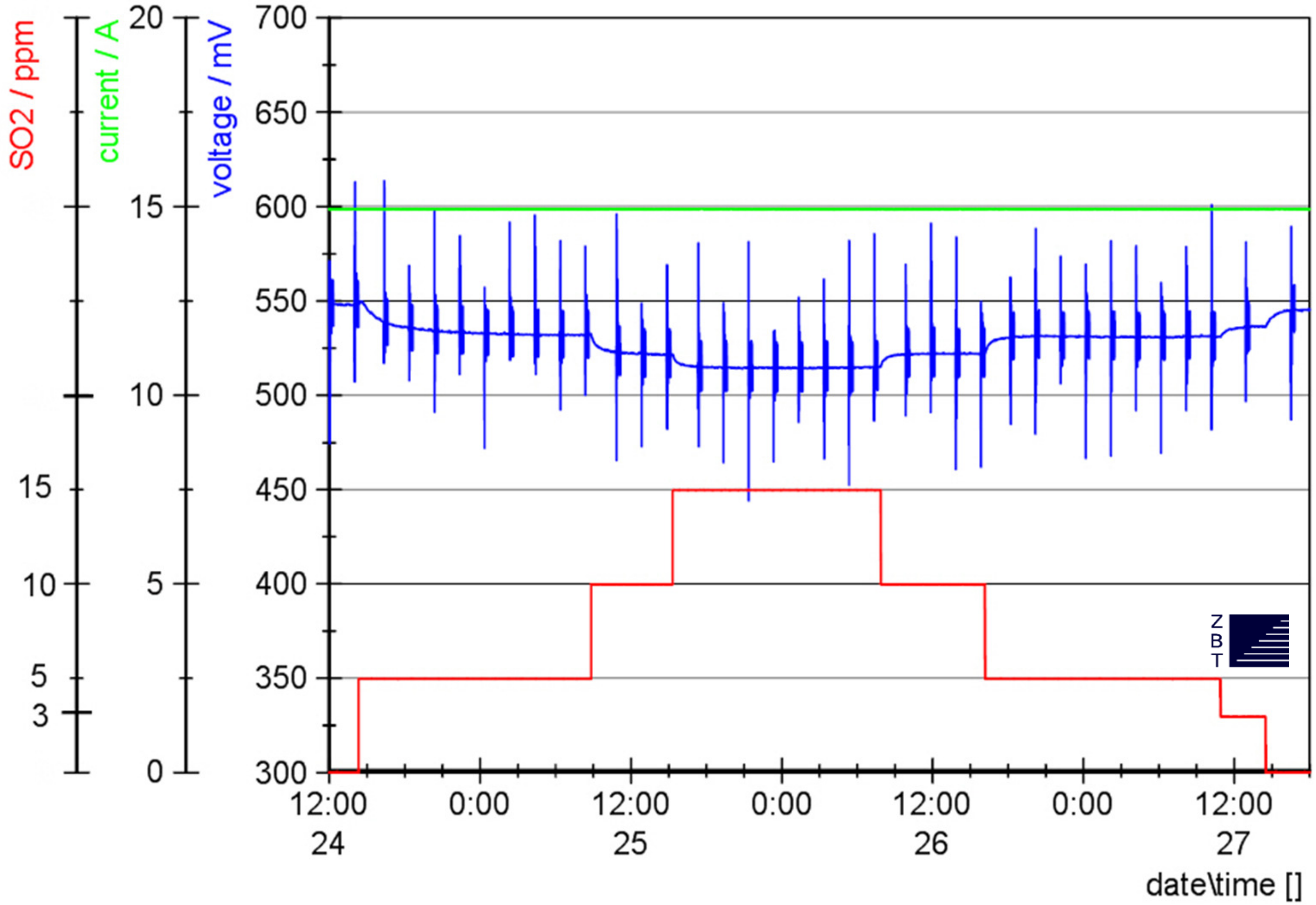
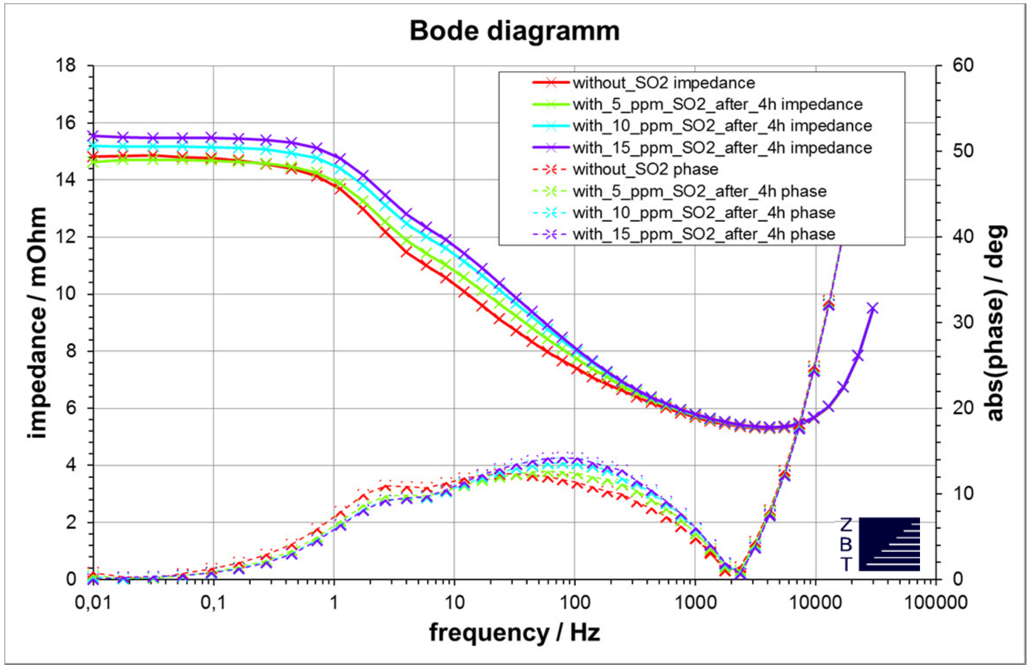
Experiments with sulfur dioxide (SO_2)

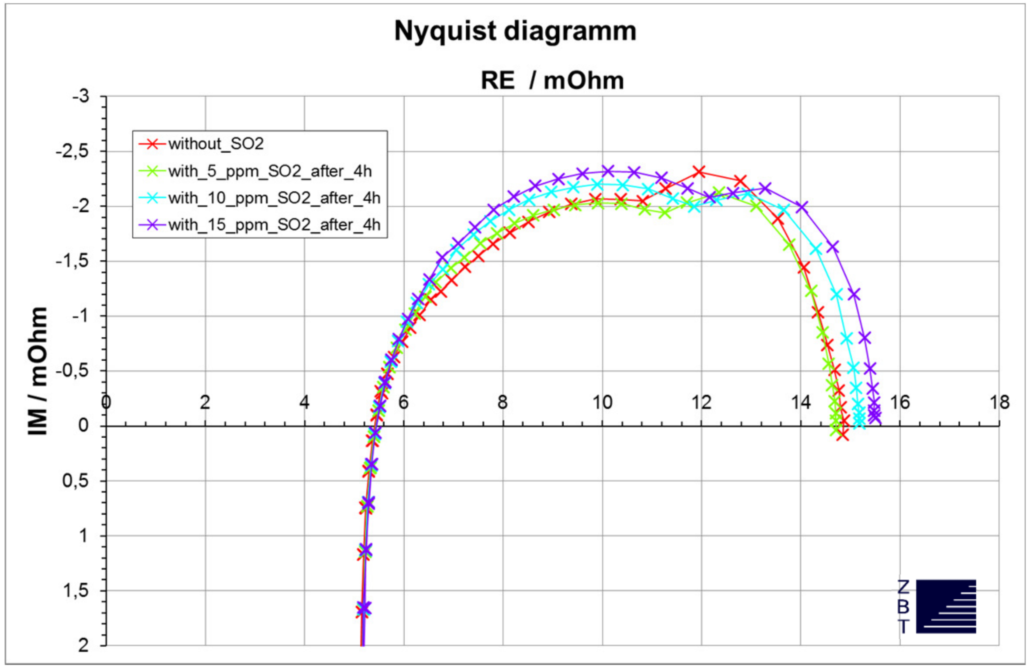


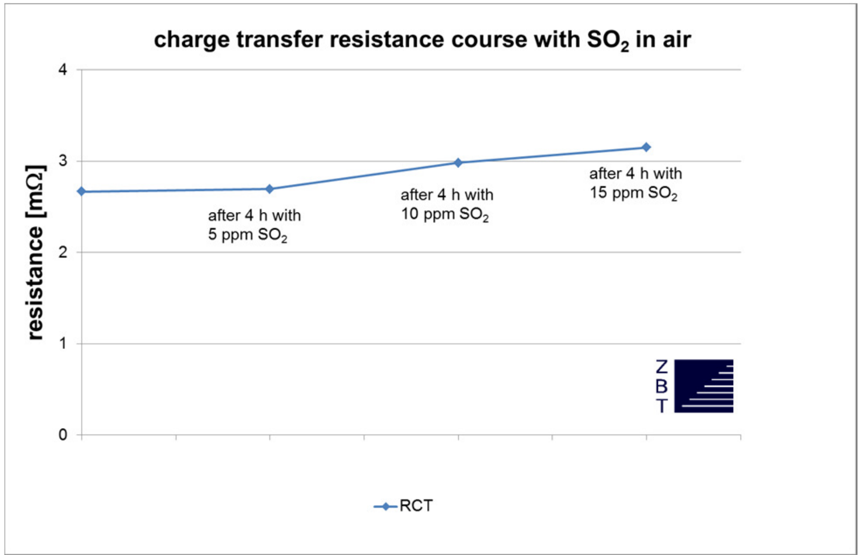
- current density: 300 mA/cm²
- cell temperature: 160°C
- stoichiometry cathode: 2.0

- voltage loss by contamination with 5 ppm SO_2 in air
- the higher the concentration the higher the voltage loss
- after some time the voltage approaches a limit and then remains constant.
- by reducing the concentration a slight recovery takes place
- complete regeneration could not be achieved.

Impedance measurements during regeneration after SO_2 contamination







- increase of medium-arc
- charge transfer resistance R_{CT} increases
- Nernst impedance decreases slightly (diffusion). So far, no explanation for the effect.
- changes in the anode area. Quote from 2. PA: “Leistungsverlust durch SO_2 sei auf Schädigung durch diffusionsbedingte Wanderungen des Gases auf die Anode zu erklären!“

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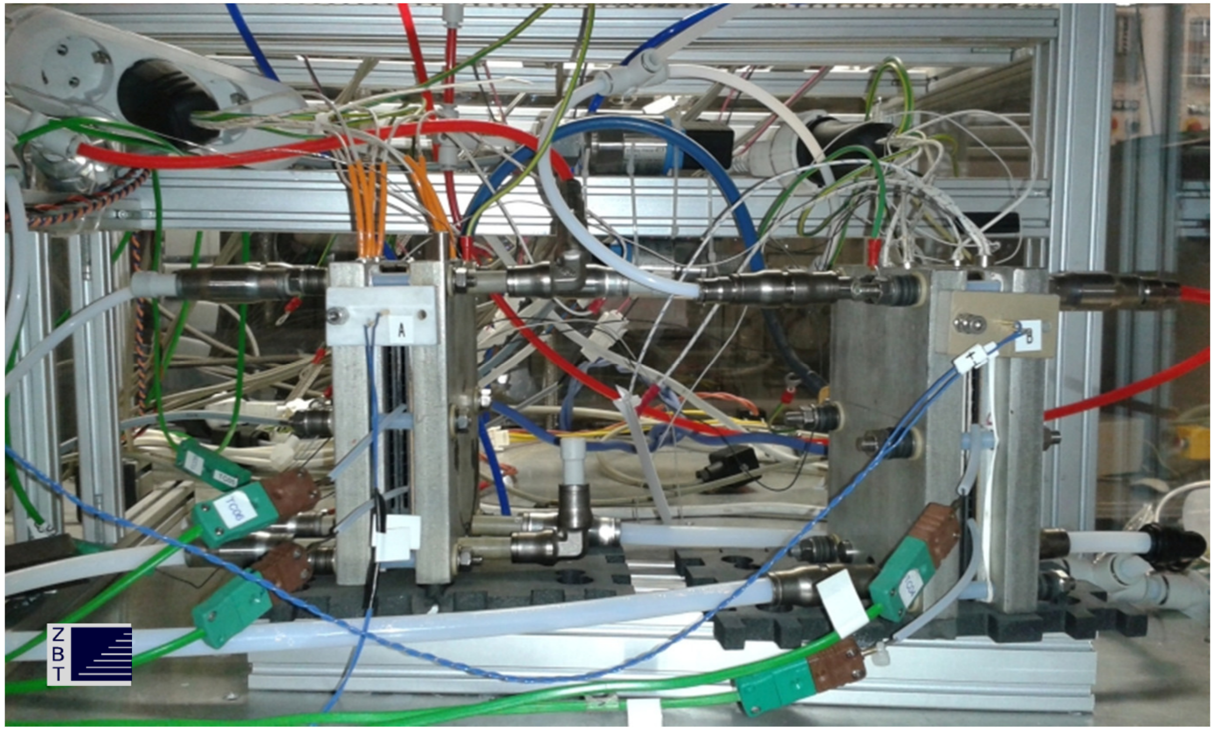
Comparison HT-PEMFC vs. LT-PEMFC

harmful gas	HT-PEMFC contamination	LT-PEMFC contamination	HT-PEMFC recovery	LT-PEMFC recovery
NO	– effect ≥ 360 ppb – almost linear voltage decline	– effect ≥ 100 ppb – approaches to a limit	– very slow – temperature dependent – almost completely	– fast – temperature dependent – completely
NO_2	– effect ≥ 1 ppm – almost linear voltage decline	– effect ≥ 250 ppb – approaches to a limit	– very slow – temperature dependent – Almost completely	– fast – temperature dependent – completely
NH_3	– effect ≥ 1 ppm – effect occurs delayed	– effect ≥ 1 ppm – strong voltage/ current drop	– no recovery	– possible – temperature dependent
C_2H_6	– no effect	– no effect		
SO_2	– effect ≥ 1 ppm	– effect ≥ 100 ppb	– possible, but not completely	– only slight recovery

Summary and outlook

Next steps

- test bench has been extended to an additional measurement place to carry out parallel studies with and without filters
- filter by M+H is present - filter housing was constructed from the ZBT



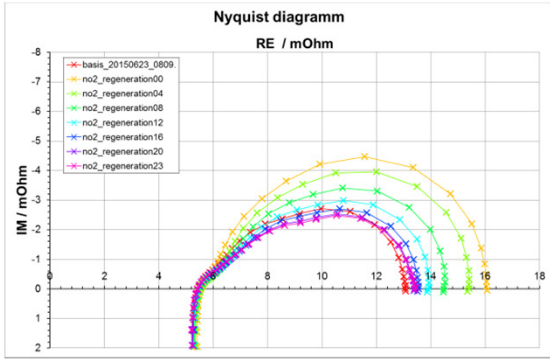
Summary and outlook

- NO, NO_2, NH_3 and SO_2 lead to negative effects already at concentrations in ppm range.
- Influence of NO on HT-PEMFC already at 350 ppb NO in air supply.
- NO, NO_2 and SO_2 cause immediate voltage loss, negative effect of NH_3 is delayed.
- Ethane and salt particles don't cause a negativ effects.
- NO, NO_2 and SO_2 change catalyst property, which is accompanied by an increase in the charge transfer resistance. The activity of the catalyst is reduced.
- With NH_3 the protonic resistance R_p and the membrane resistance R_M rise slightly. NH_3 reacts with the electrolyte. Increase of diffusion resistances, especially at elevated concentrations.
- So far only an experiment with filters. Filter effect is very good.

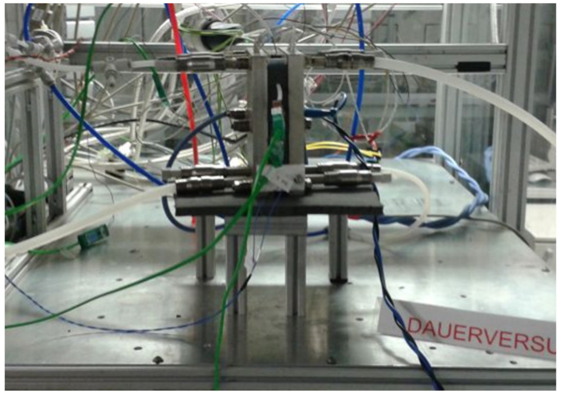
The results show the importance of the harmful gas topic even for HT-PEMFC technology!

⇩

A follow-up project is planned that strengthened to deal with the electrochemical measurements and additional analytical methods!



Thank you for your attention!



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