Evaluation of the effect of sulfur poisoning on the performance of Ni/CGO based SOFC anodes

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SOFC Degradation

Bundesministerium für Bildung und Forschung

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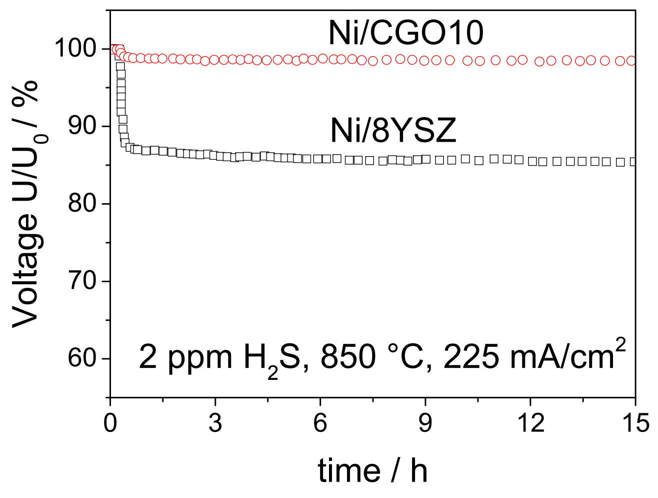
Outline

- Motivation and aim of the work
- Experimental procedure
- Results
  - Short-term sulfur poisoning
  - Long-term sulfur poisoning
- Summary and conclusions

Motivation and aim of the work

- Sulfur-containing impurities in natural gas and biogas
- Higher sulfur tolerance of Ni/CGO than Ni/YSZ
- CGO: MIEC + catalytically active for H2 oxidation [2 – 4]
- Mechanism is not fully understood



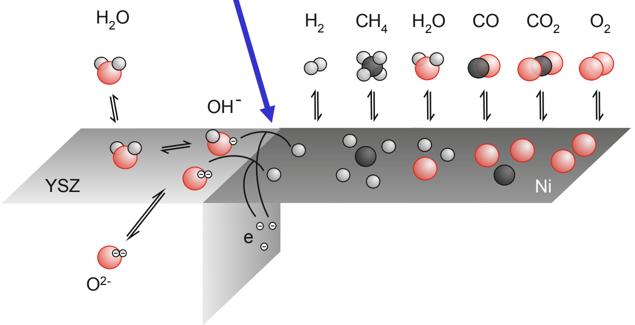
Goal: Elucidation of sulfur poisoning and underlying hydrogen oxidation mechanism on Ni/CGO-based anodes

[1] Kavarucu et al., *Journal of Power Sources*, 217, (2012), 364; [2] Primdahl, Mogensen, *Solid State Ionics*,152, (2002), 597; [3] Nakamura, *J.Electrochem. Soc.*, 155, (2008), B563; [4] Chueh et al., *Nat. Mater.*, 11, (2011), 155

Motivation and aim of the work

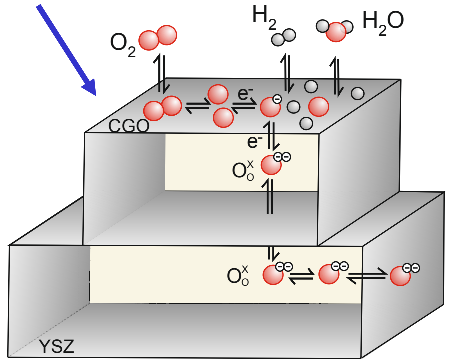
Ni/YSZ based anodes

Active TPB



Ni/CGO based anodes

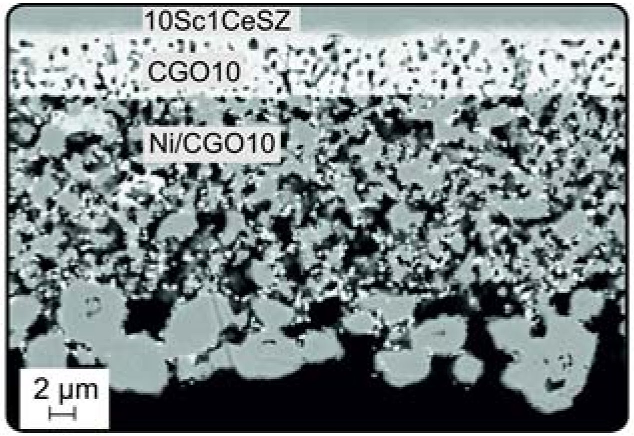
Active surface



- Is Ni pure electronic conductor? [1 – 3]
- Sulfur poisoning of pure CGO electrode possible [4]
- Sulfur poisoning of CGO or Ni?

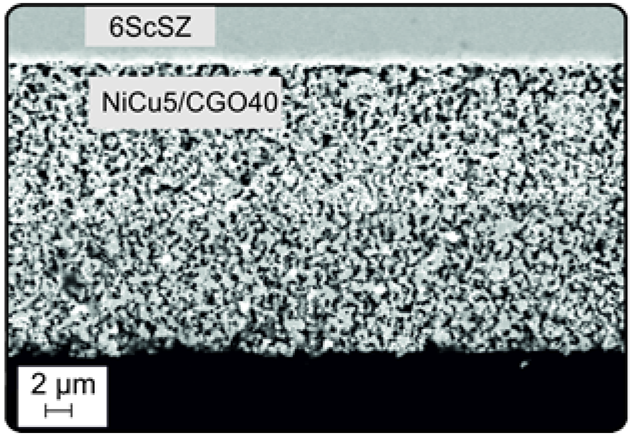
[1] Chueh et al., *Nat. Mater.*, 11, (2011), 155; [2] Feng et al., *Nat. Commun.*, 5, (2014),1; [3] Chueh et al., *Solid State Ionics*, 179, (2008), 1036. [4] Mirfakhraei et al., *J. Power Sources*, 243, (2013), 95;

Experimental Procedure



Ni/CGO10 anode (25 µm)

- 160 µm 10Sc1CeSZ electrolyte
- 65 µm LSM/ScSZ cathode



NiCu5/CGO40 anode (25 µm, HEXIS)

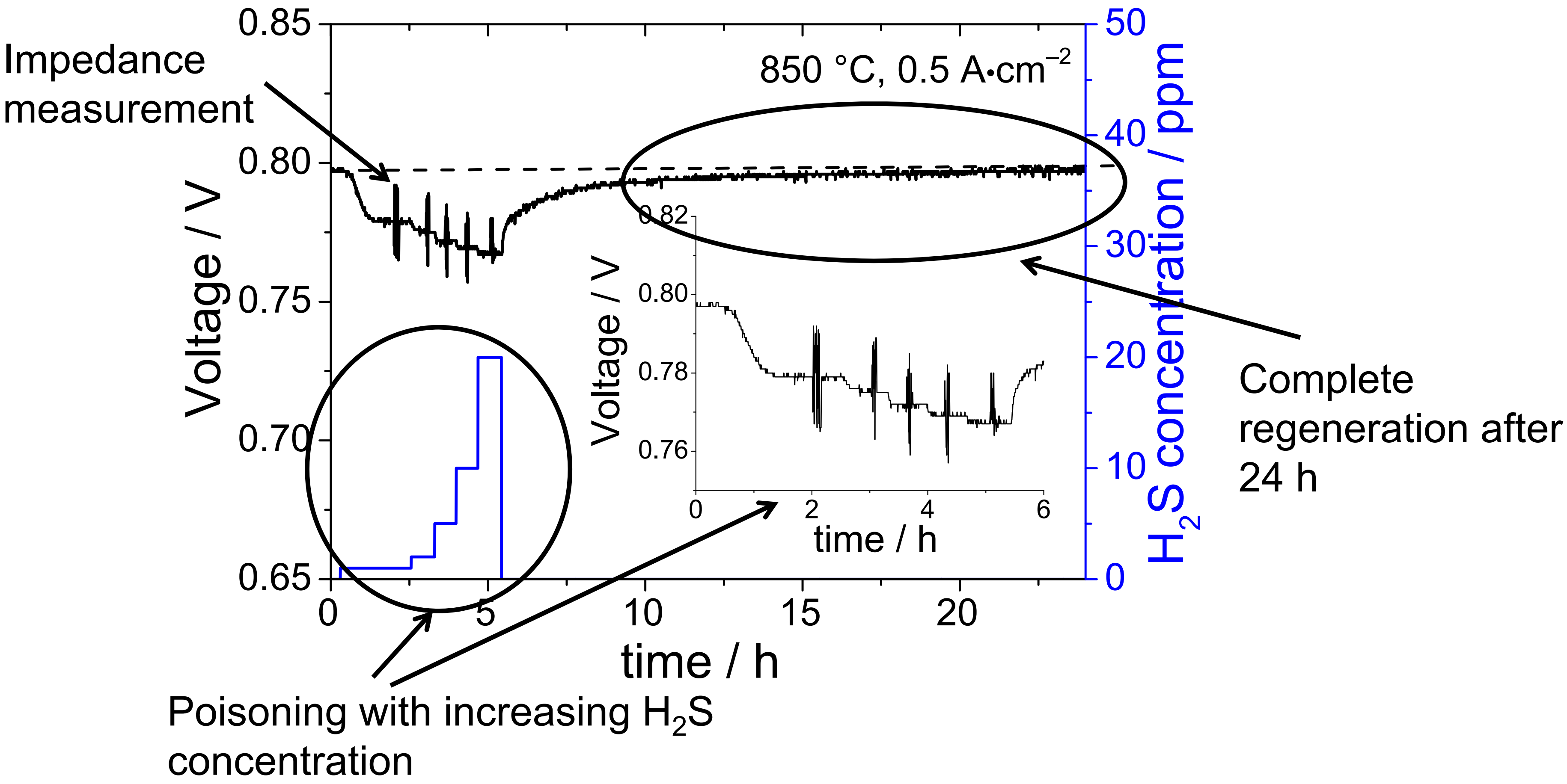
- 160 µm 6ScSZ electrolyte
- 70 µm LSM/ScSZ cathode

- ➢ Systematic parameter study of short-term poisoning at different current density and temperatures
- ➢ Long-term experiments
- ➢ In-situ monitoring with electrochemical impedance spectroscopy

Experimental Procedure:Testing protocol short-term poisoning

T = 850°C , i = 0.5 A•cm^{-2}

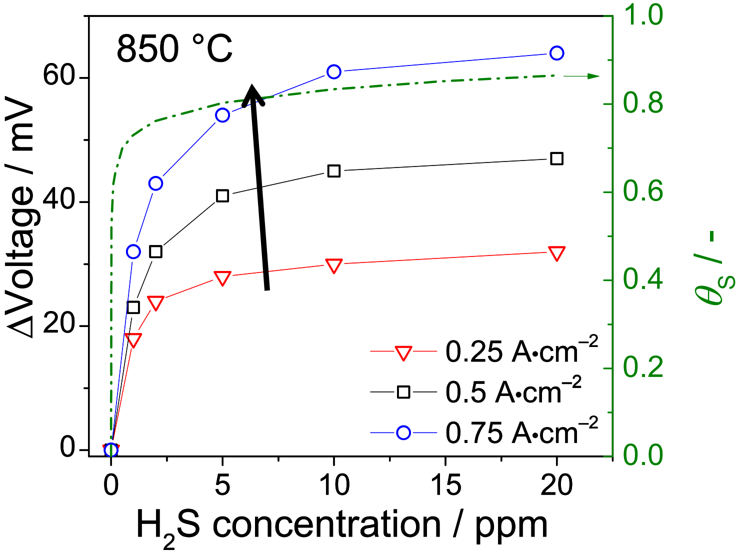
Anode gas: 97 % H_2, 3 % H_2O + 1 – 20 ppm H_2S



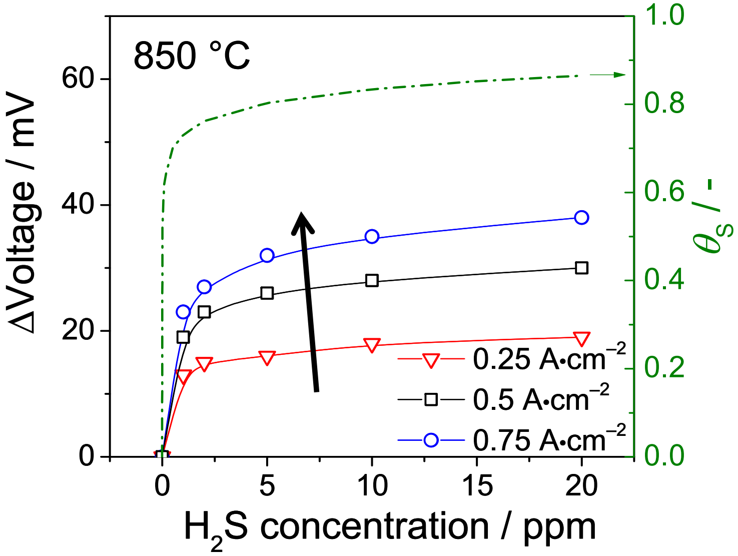
Short-term sulfur poisoning: Effect of current density on performance

i = 0.25 – 0.75 A•cm^{-2}, T = 850°C, 97 % H_2, 3 % H_2O + 1 – 20 ppm H_2S

Ni/CGO10



Ni/CGO40

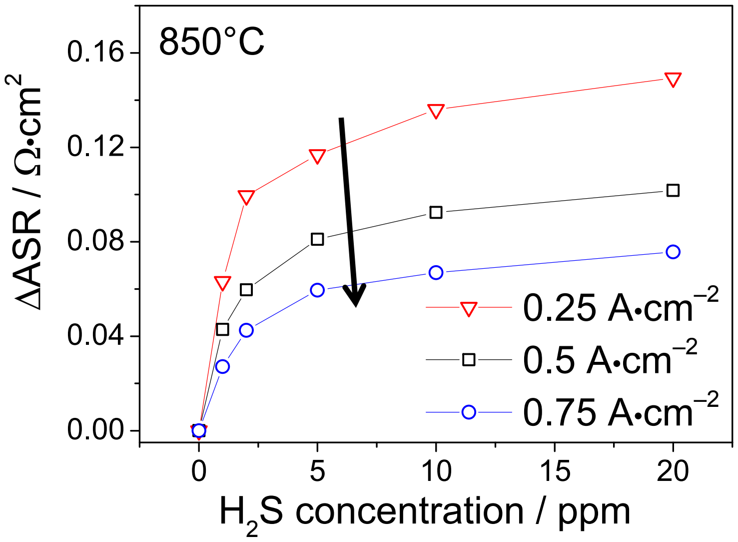


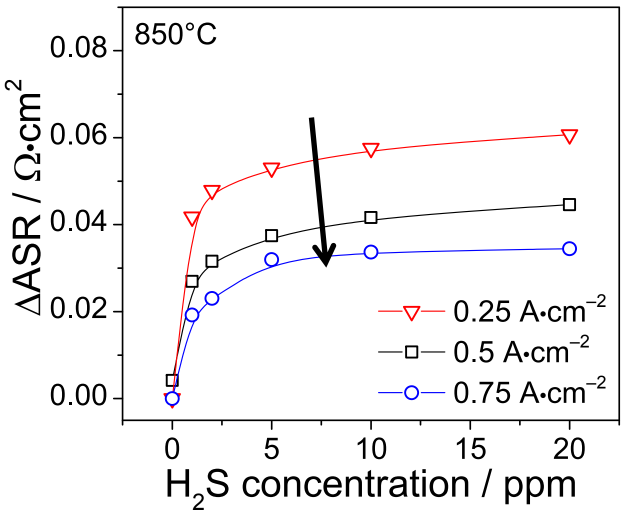
- Saturation effect similar to sulfur coverage on Ni
- Temkin isotherm: $\frac{p_{H_2S}}{p_{H_2}} = \exp(\Delta h_0^0(1 - a\theta_S)/RT - \Delta s^0/R)$

⇨ Sulfur poisoning of Ni surface?

Short-term sulfur poisoning: Effect of current density on ASR

$\underline{i = 0.25 - 0.75\ A{\bullet}cm^{-2}}$, T = 850°C, 97 % H_2, 3 % H_2O + 1 – 20 ppm H_2S

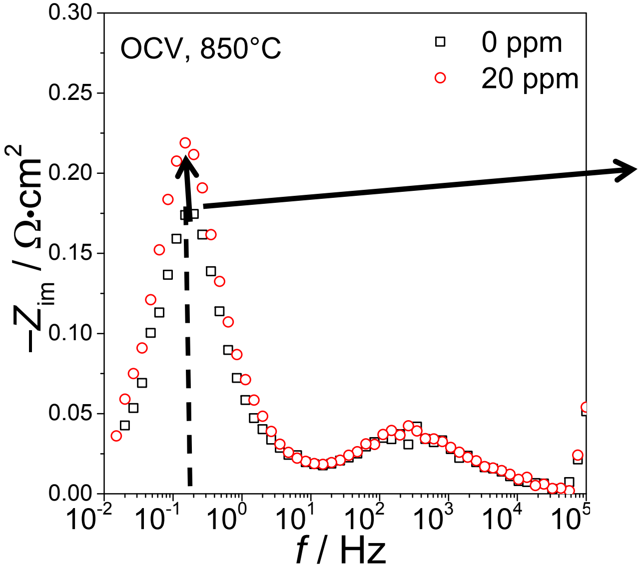


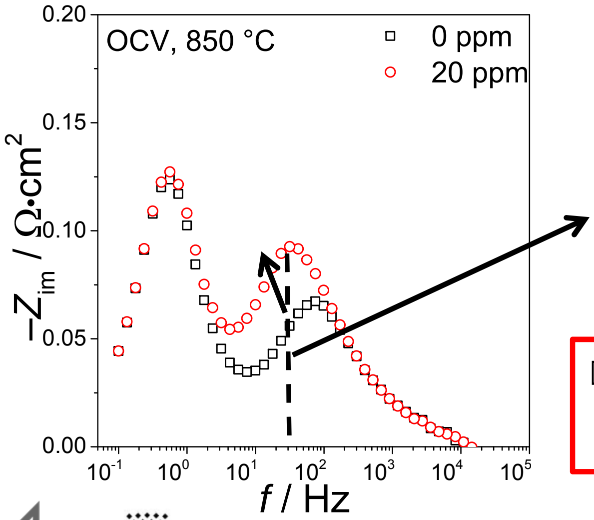


- Mitigation effect at high current densities
- Reason: increasing water content?
- Conclusions about sulfur poisoning mechanism remain difficult

Ni/CGO10 vs. Ni/CGO40: Impedance analysis

T = 850°C, OCV, 97 % H_2, 3 % H_2O + 1 – 20 ppm H_2S





Ni/CGO10-based cell:

- Sulfur influence at ~ 0.2 Hz
- TPB charge transfer process of Ni/YSZ: ~ 10^3 Hz
- Characteristic frequency of surface charge transfer process of pure CGO10

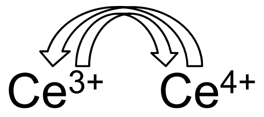
Ni/CGO40-based cell:

- Influence of sulfur on anode surface process at ~ 50 Hz
- No influence on LF process

⇨ Change of peak frequency of sulfur-affected process by 2 orders of magnitude

Discussion: Ni/CGO

- Chemical capacitance at CGO surface due to mixed valent Ce ions and charged adsorbates (e.g. OH^-)
- Rate-limiting step:
  $Ce^{4+} + OH^{-}_{CGO} \rightarrow Ce^{3+} + OH_{CGO}$ [1,2]



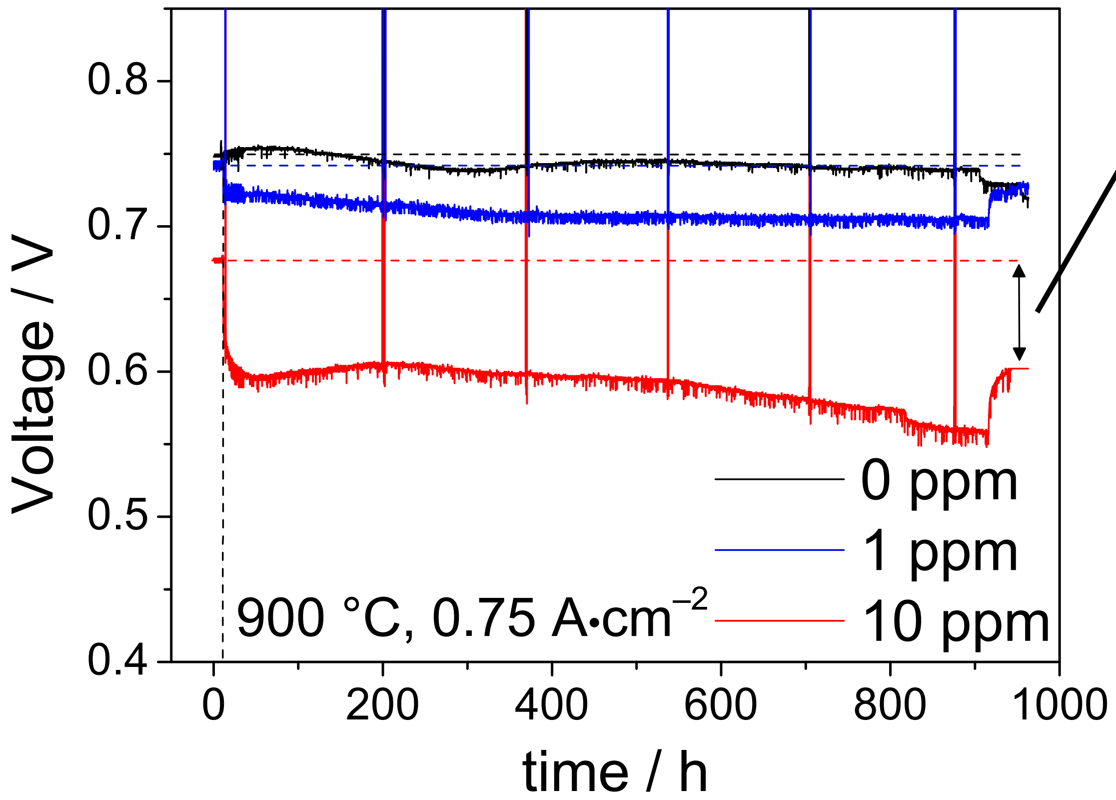
- Gd doping reduces amount of Ce^{3+} through stabilization of Ce^{4+}
- Reflected by lower electronic conductivity
- Reason for lower capacitance value?

⇨ Peak frequency shift of <u>the same process</u> by 2 orders of magnitude

[1] Feng et al., *Nat. Commun.*, 5, (2014),1; [2] Chueh et al., *Solid State Ionics*, 179, (2008), 1036.

Long-term sulfur poisoning

T = 900 °C, 0.75 A•cm^{-2} , 97 % H_2, 3 % H_2O + 0, 1, 10 ppm H_2S
NiCu5/CGO40 anode



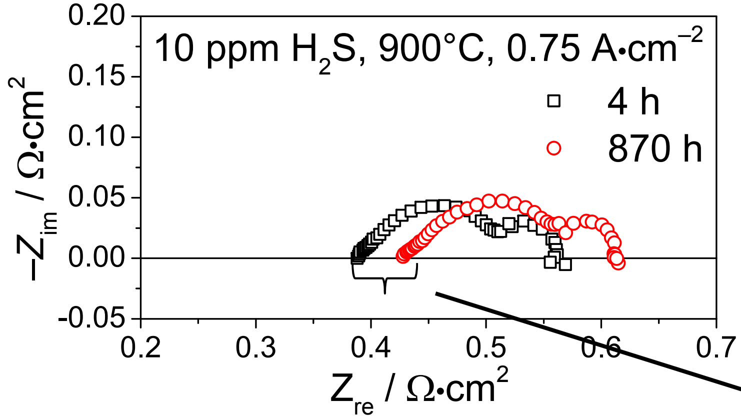
- Sulfur-induced irreversible degradation
- 10 ppm > treshold?
- Combination of low potential and sulfur influence?

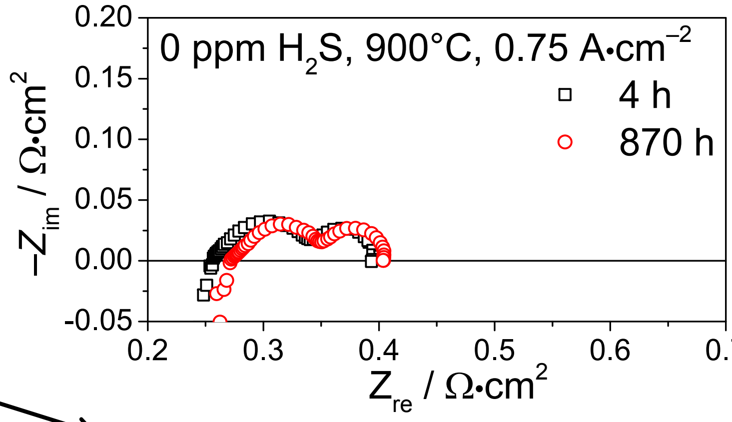
⇨ More experiments needed

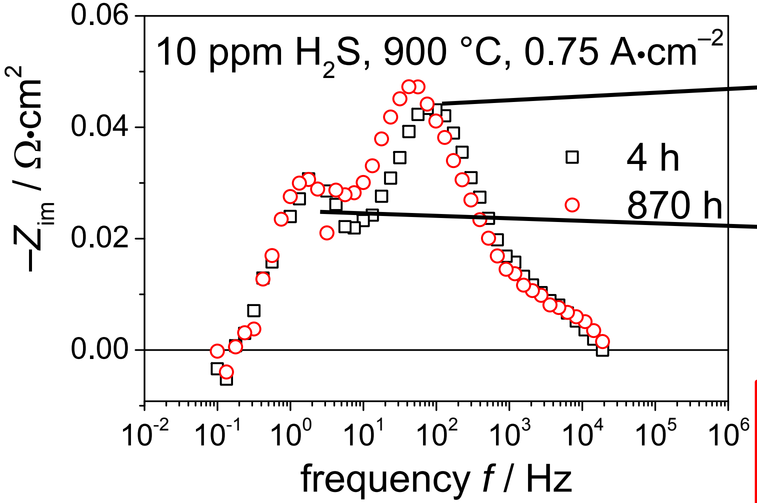
Long-term sulfur poisoning: Impedance analysis

T = 900 °C, 0.75 A•cm^{-2} , 97 % H_2, 3 % H_2O + 0, 1, 10 ppm H_2S

NiCu5/CGO40 anode







- Increasing Ohmic resistance
- Increasing resistance of anode charge transfer process
- No change in LF resistance

⇨ Post mortem analysis necessary for further understanding

Summary and conclusions

- Extensive characterization of sulfur poisoning of Ni/CGO10 and Ni/CGO40-based anodes
- Reversible short-time poisoning
- Ni/CGO10 vs. Ni/CGO40: Capacitance of anode surface process changes by ~ 2 orders of magnitude
- Ni/CGO40: Long-term stability demonstrated for 1 ppm H_2S, irreversible degradation at 10 ppm
- Next step: Sulfur poisoning of reformate-fuelled SOFC
- Investigation of model electrodes required for deeper understanding of the mechanism

Acknowledgments

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Thank you for your attention!

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