Sulfur poisoning effect on Ni/CGO anodes

Matthias Riegraf

German Aerospace Center (DLR), Stuttgart, Germany

12.10.2016

SOFC Degradation

Bundesministerium
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Outline

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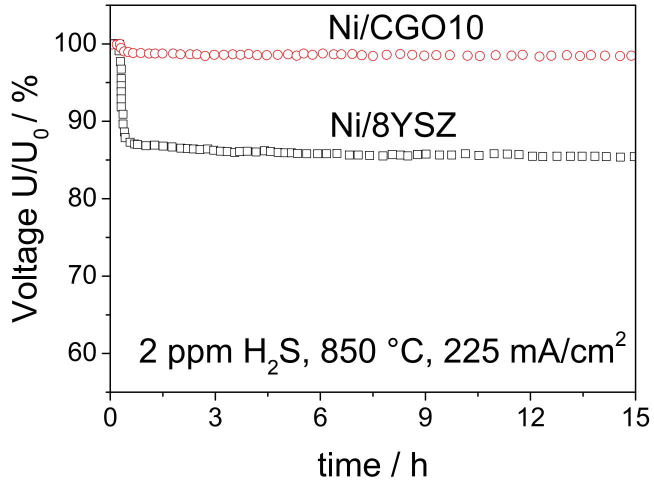
Motivation and aim of the work

- Sulfur-containing impurities in diesel reformate used for APU
- Ni-based anodes in state-of-the-art MSC
- Higher sulfur tolerance of Ni/CGO than Ni/YSZ
- CGO: MIEC + catalytically active for H2 oxidation [2 – 4]
- Mechanism is not fully understood



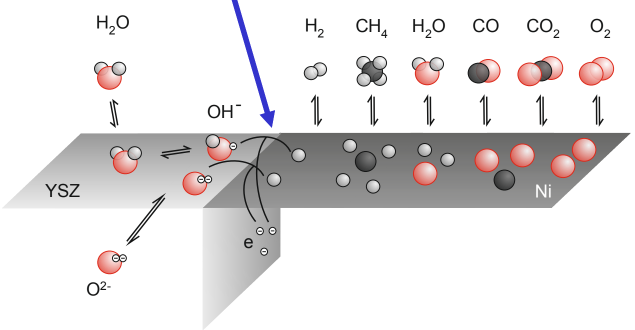
Goal: Elucidation of sulfur poisoning mechanism on Ni/CGO-based anodes

[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

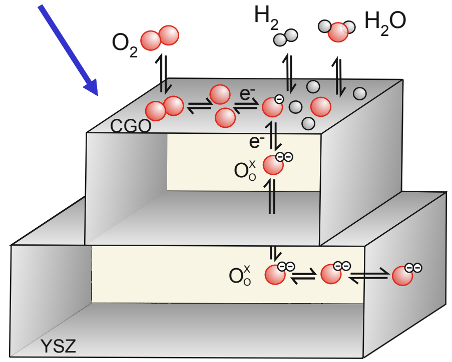
Ni/YSZ based anodes

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;

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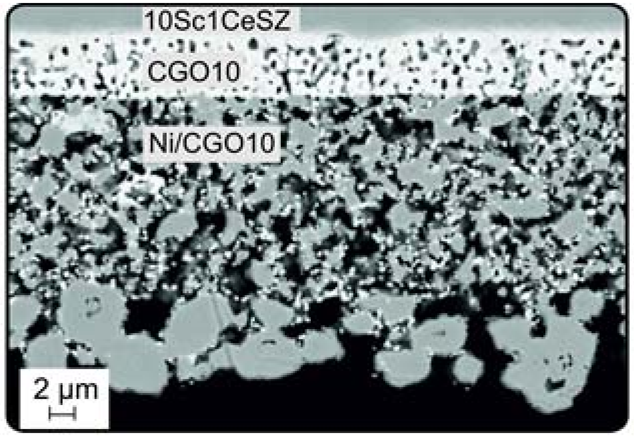
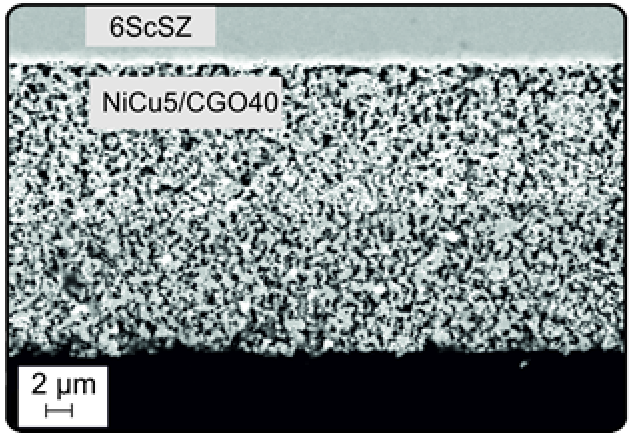
Experimental Procedure





Ni/CGO10 anode (25 µm, Kerafol)

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

NiCu5/CGO40 anode (25 µm, HEXIS)

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

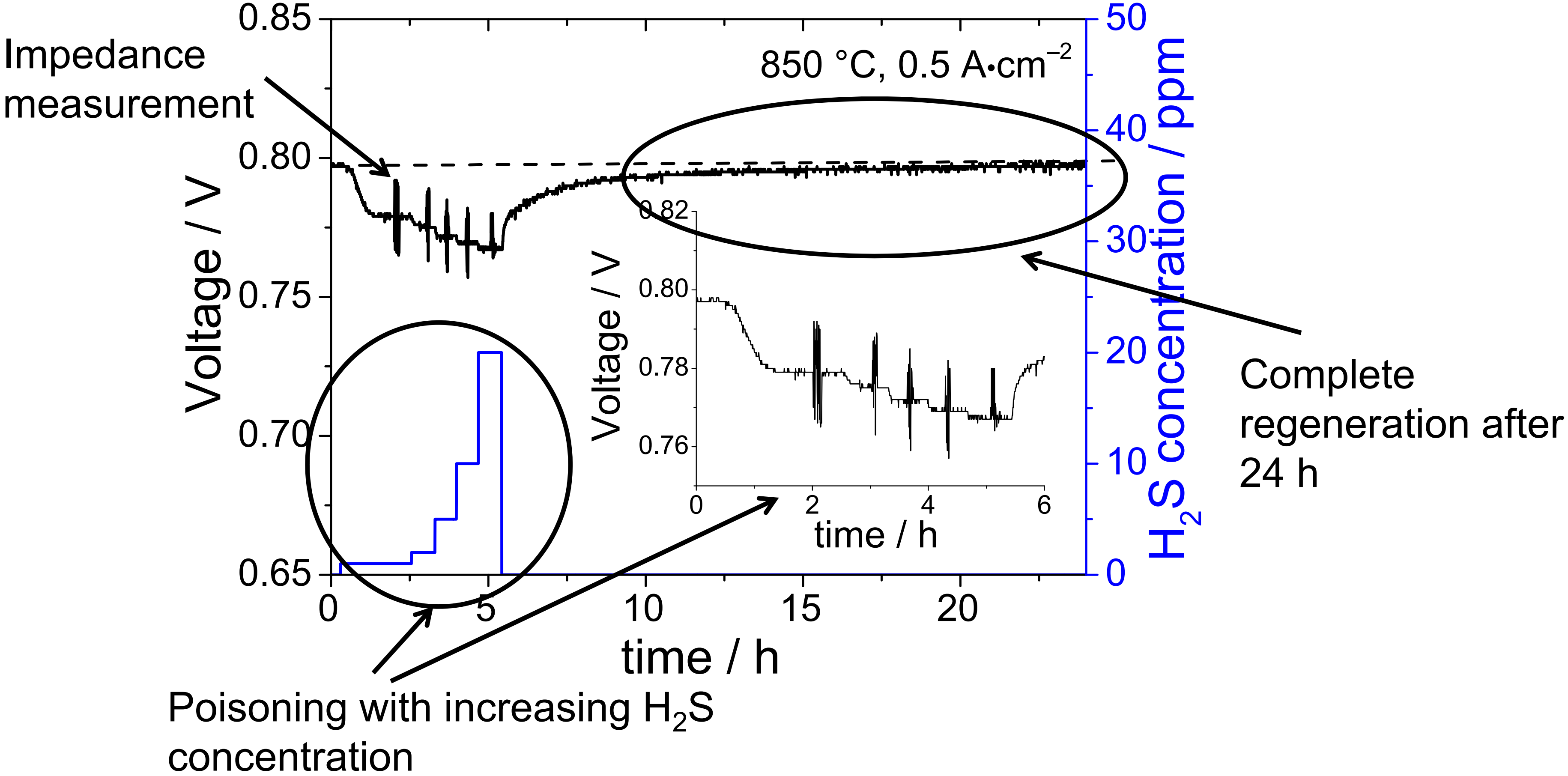
➢ Systematic parameter study of short-term poisoning at different current density and temperatures

➢ 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



Experimental Procedure: Testing matrix

- 1 l/min: 97 % H_2, 3 % H_2O + 1, 2, 5, 10, 20 ppm H_2S
- Variation of temperature and current density
- **Ni/CGO10** and Ni/CGO40-based anodes

Current density / A•cm^{-2}

Temperature / °C	OCV	0.25	0.5	0.75
800			X	
850	X	X	X	X
900			X	

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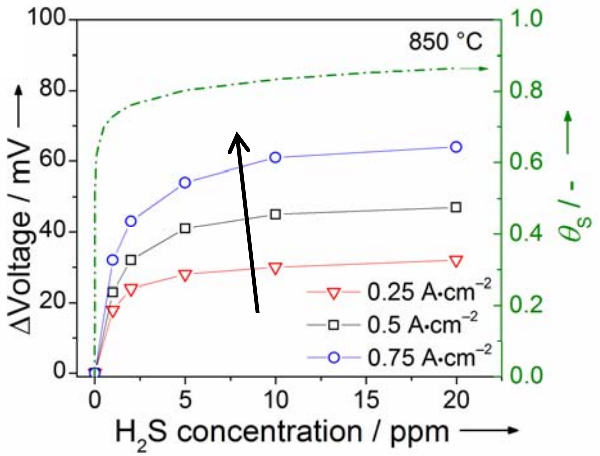
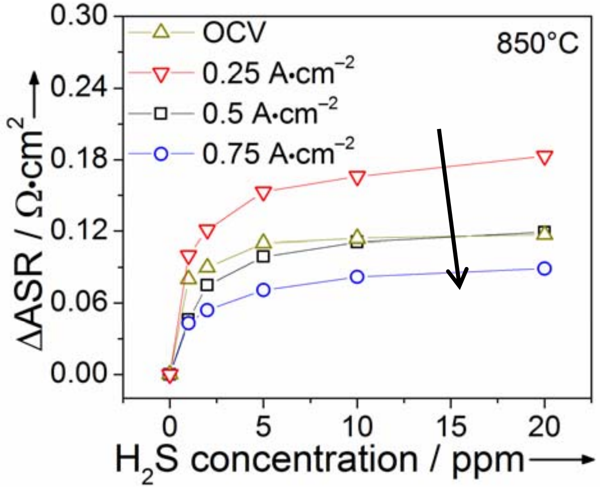
Ni/CGO10: Influence of current density

T = 850°C

Anode gas: 1 l/min: 97% H_2, 3% H_2O + 1, 2, 5, 10, 20 ppm H_2S





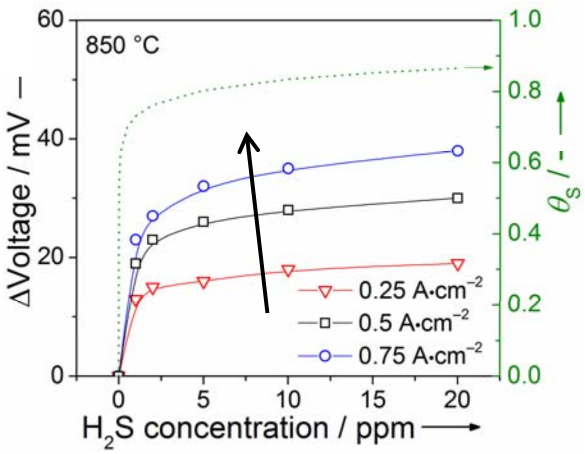
- Saturation effect similar to sulfur coverage on Ni
- Temkin isotherm: $$\frac{p_{H_2S}}{p_{H_2}} = \exp(\Delta h_0^0(1 - a\theta_S)/RT - \Delta s^0/R)$$

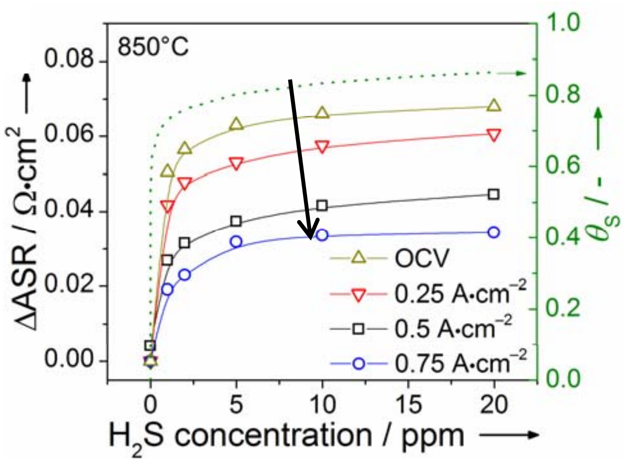
⇨ Sulfur poisoning of Ni surface?

Ni/CGO40: Influence of current density

T = 850°C

Anode gas: 1 l/min: 97% H_2, 3% H_2O + 1, 2, 5, 10, 20 ppm H_2S



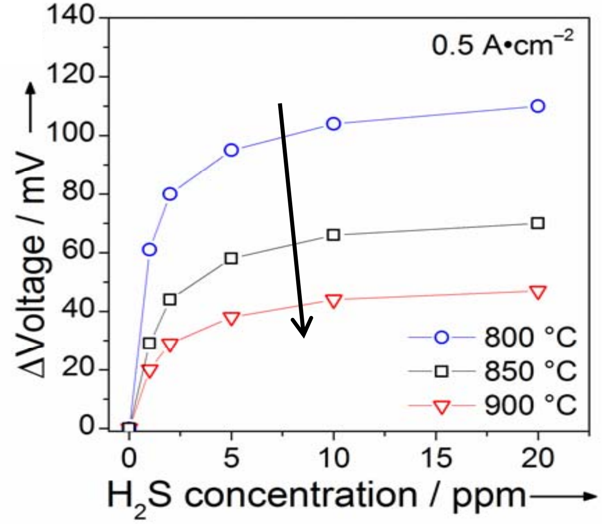


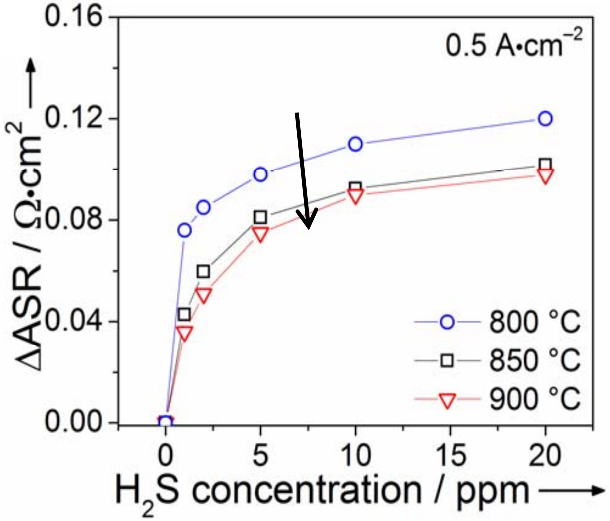
- Mitifation effect at high current densities
- pH_2O decreases charge transfer resistance

Ni/CGO10: Influence of temperature

T = 850°C

Anode gas: 1 l/min: 97% H_2, 3% H_2O + 1, 2, 5, 10, 20 ppm H_2S

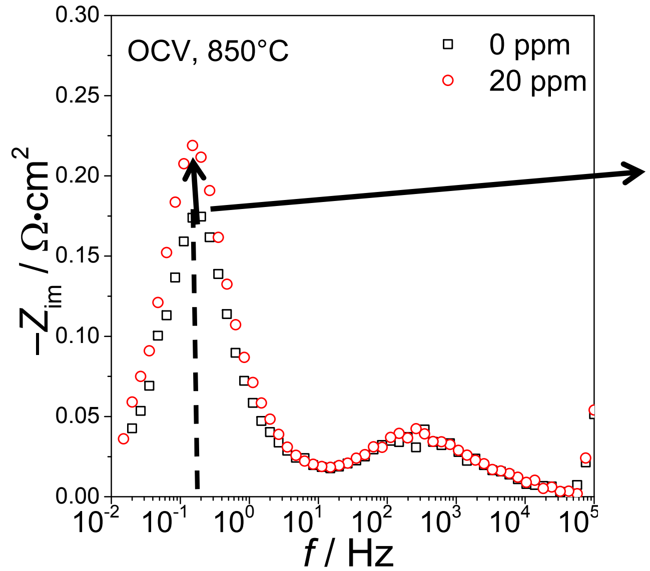




- Temperatur mitigation effect on sulfur poisoning
- Sulfur desorption / Bulk diffusion?

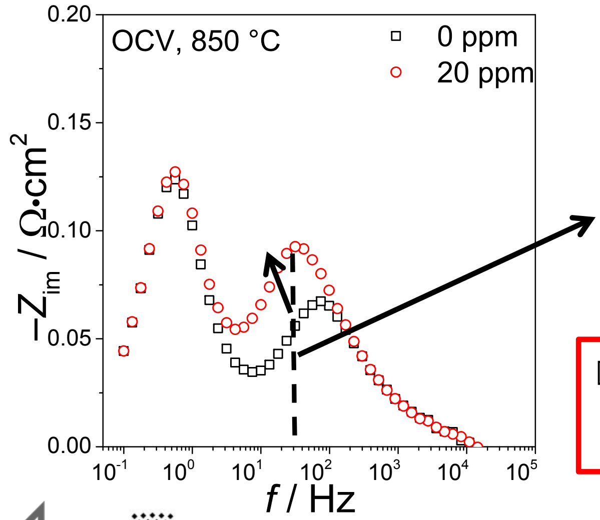
Ni/CGO10 vs. Ni/CGO40: Impedance analysis

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



<u>Ni/CGO10-based cell:</u>

- 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



<u>Ni/CGO40-based cell:</u>

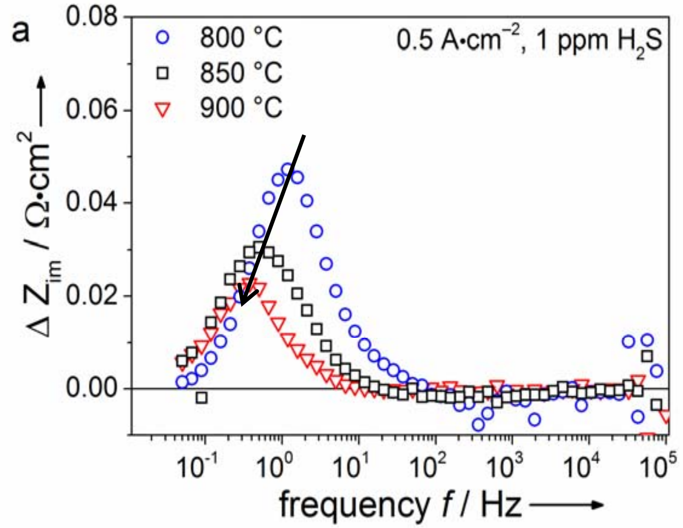
- Influence of sulfur on anode surface process at ~ 50 Hz
- No influence on LF process

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

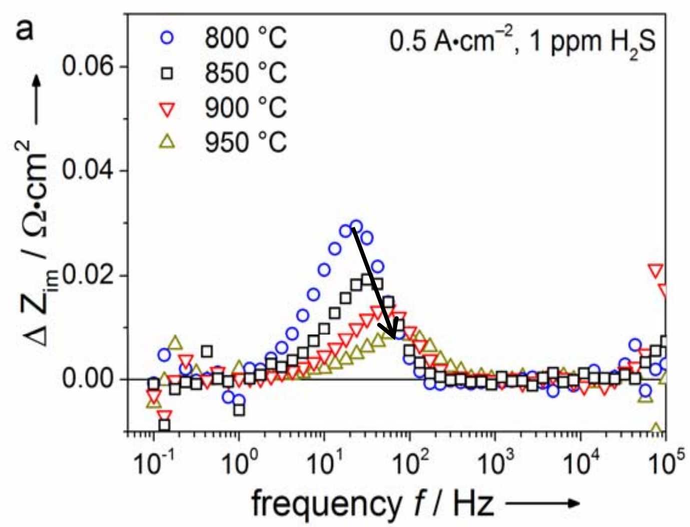
Ni/CGO10 vs. Ni/CGO40: Influence of temperature

- Differential imgainary impedance plot Z_{im}(1 ppm)-Z_{im}(0 ppm)
- Isolation of sulfur influence on anode charge transfer resistance

Ni/CGO10



Ni/CGO40

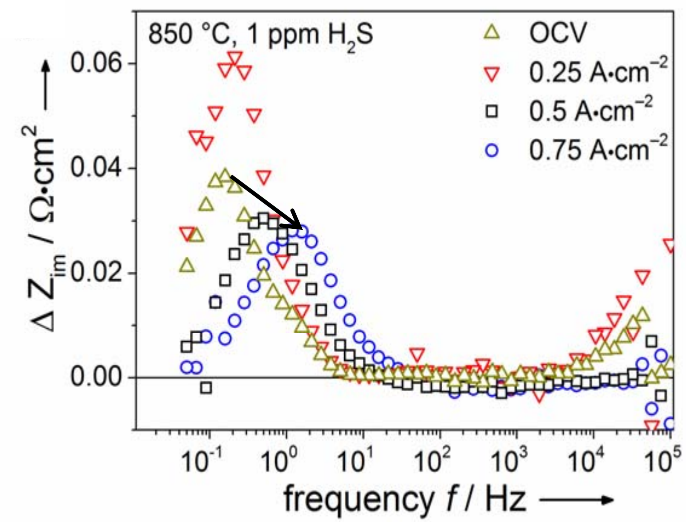


- Ni/CGO10: $f = 1/(2\pi RC)$
- $T\uparrow R\downarrow \rightarrow f\uparrow$
- Ni/CGO10: $f\downarrow \rightarrow C\uparrow$ = Capacitance is strongly temperature-dependent

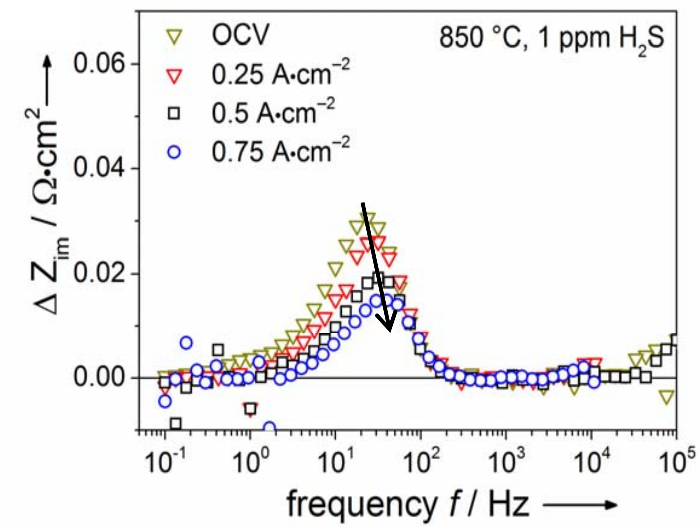
Ni/CGO10 vs. Ni/CGO40: Influence of current density

- Differential imgainary impedance plot Z_{im}(1 ppm)-Z_{im}(0 ppm)
- Isolation of sulfur influence on anode charge transfer resistance

Ni/CGO10



Ni/CGO40



- Ni/CGO10: Larger frequency shift (>1 order of magnitude)
- Capacitance is also dependent on pO_2

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]

Ce^{3+} Ce^{4+}

- Ce^{3+} concentration in CGO10 bulk increases with temperature and decreasing pO_2 [3,4]

- 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; [3] Chueh et al. *Phys. Chem. Chem. Phys.* 11, (2009), 8144 [4] Decaluwe, *J. Phys. Chem. C, 114* (**2010)**,19853.

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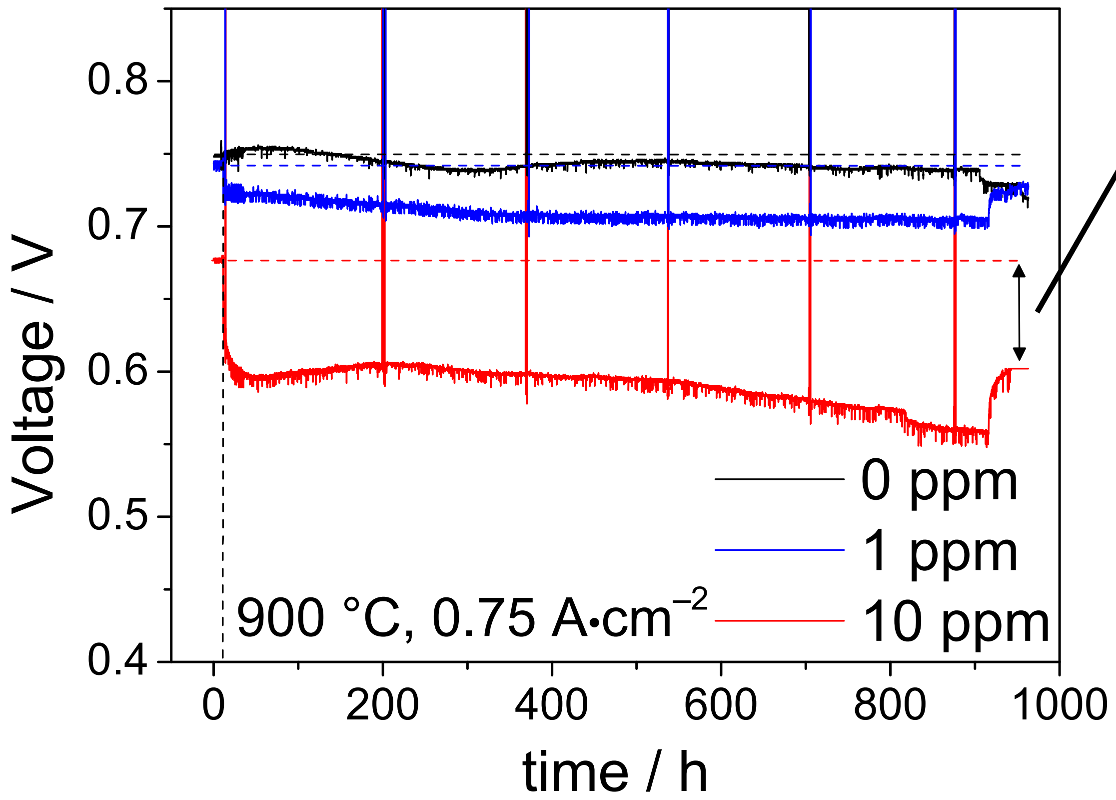
Long-term sulfur poisoning

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

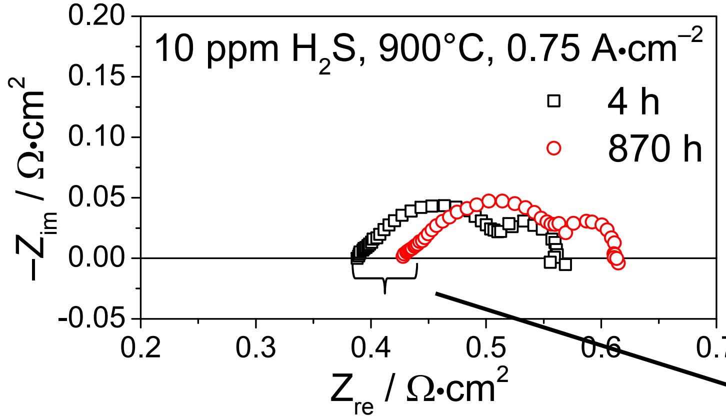


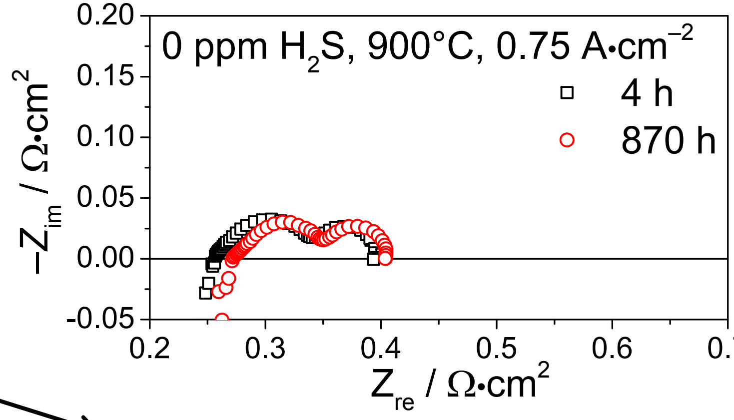
- Sulfur-induced irreversible degradation
- 10 ppm > threshold?
- Combination of low potential and sulfur influence?

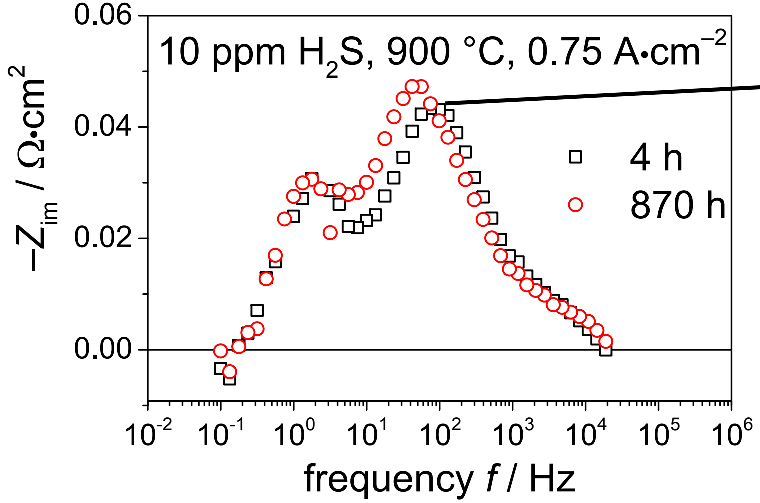
⇨ More experiments needed

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





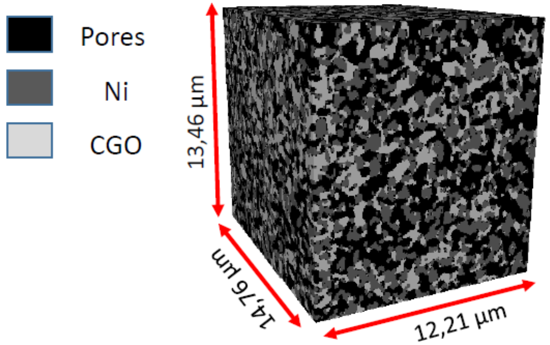


- Increasing Ohmic resistance
- Slight increase in anode charge transfer resistance

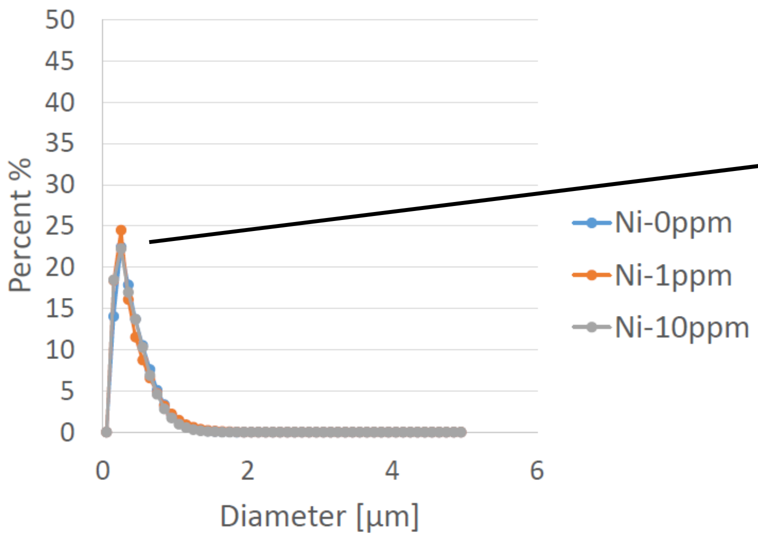
⇨ Post mortem analysis necessary

Long-term sulfur poisoning: FIB/SEM

FIB/SEM analysis and 3D reconstruction by Universität Oldenburg



Test	TPB density [µm^{-2}]	Percolation Ni	Percolati on CGO	Percolation pore
0 ppm	13.75	97.83	98.11	99.31
1 ppm	13.78	96.83	95.25	99.87
	14.07	94.87	96.35	99.64



- No signficant influence of sulfur on anode microstructure
- Electrical Conductivity loss of CGO40 for Redox cycling [1]

⇨ Same for sulfur?

[1] Iwanschitz et al., *PhD Thesis*, RWTH Aachen, (2012)

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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

- Financial support from the German Ministry of Education and Research (BMBF) in the framework of the **“SOFC Degradation”** (Verbundvorhaben SOFC Degradation: Analyse der Ursachen und Entwicklung von Gegenmaßnahmen) project.

Thank you for your attention!

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