

Assessment of sulfur poisoning of Ni/CGO-based SOFC anodes

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01.06.2017

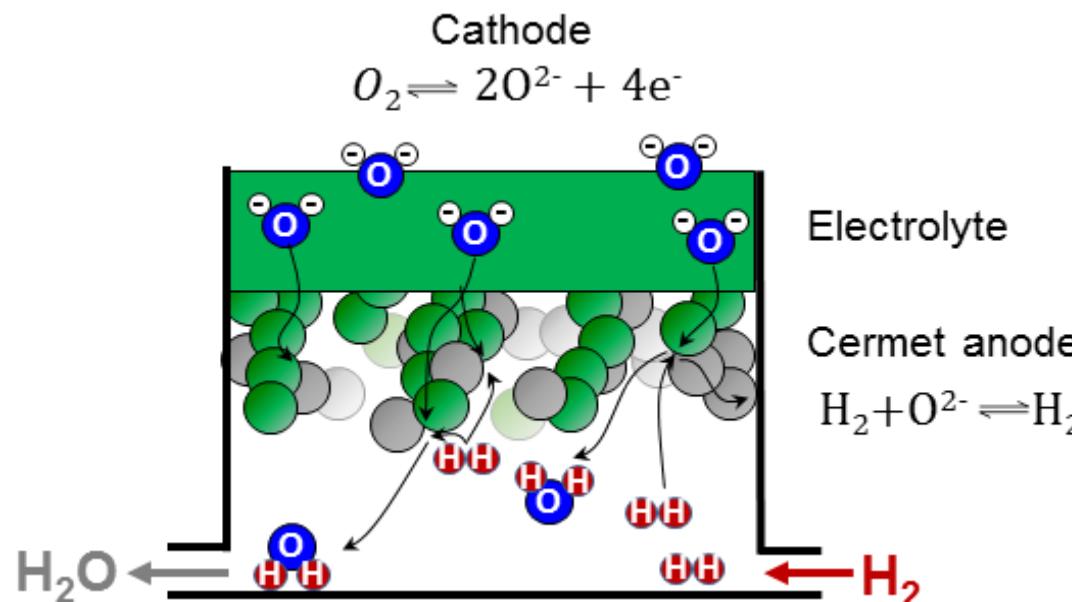


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Knowledge for Tomorrow

Motivation and aim of the work



Ni-based cermet anodes:

- Ni phase as catalyst and electronic conductor
- Ionic conductor:
YSZ (Yttria-stabilized zirconia)
CGO (Gadolinium-doped ceria)
- Reaction at triple phase boundary

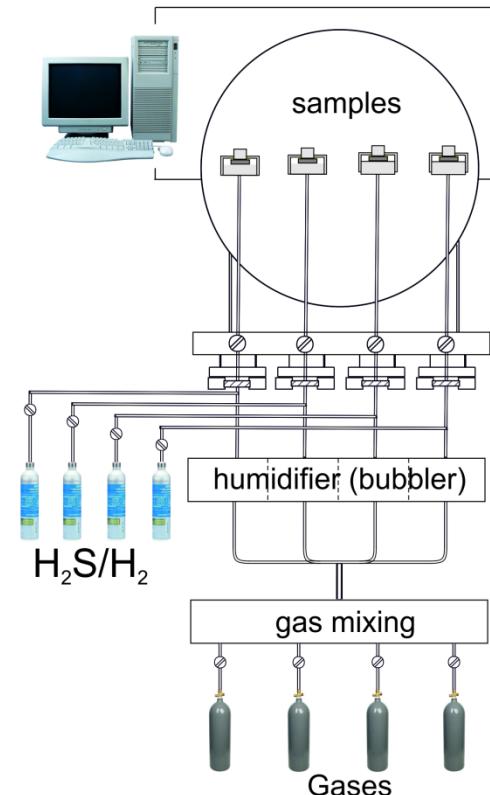
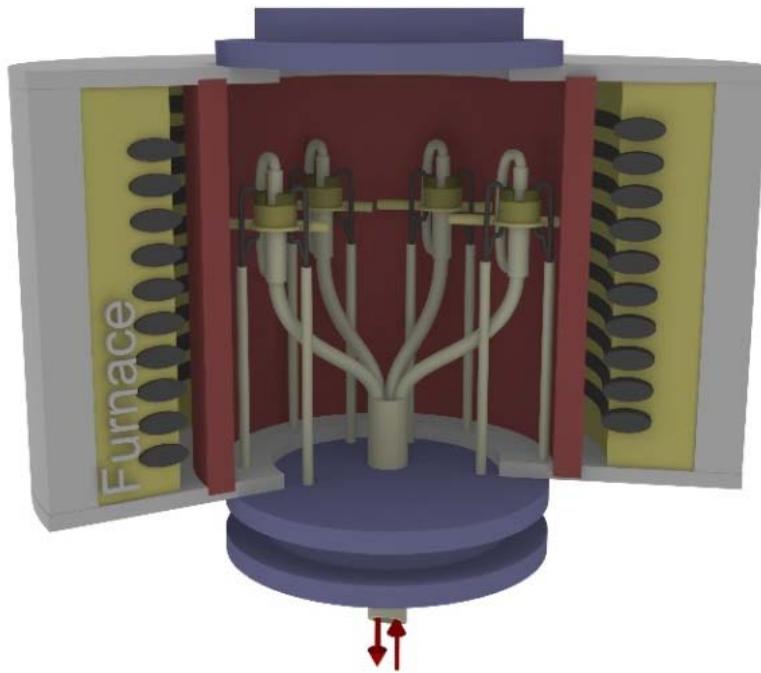
- Sulfur-containing impurities (mainly H_2S) in natural gas and biogas \rightarrow Ni surface poisoning
- Higher sulfur tolerance of Ni/CGO than Ni/YSZ towards H_2 fuels

Goal:

- Investigation of sulfur poisoning in reformate fuels
- Derivation of a reaction mechanism



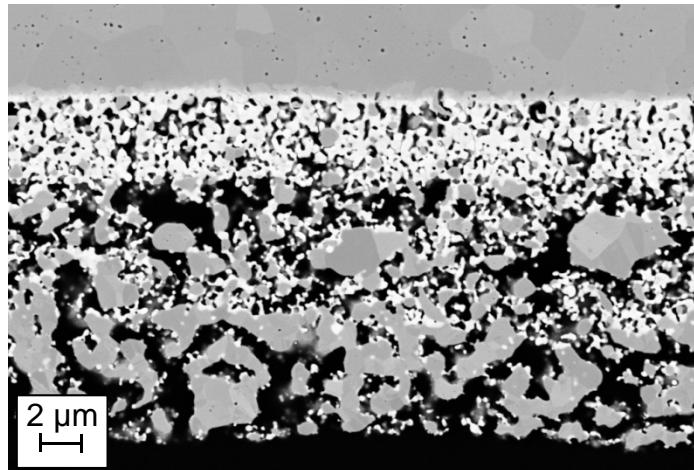
Methodology



- Simultaneous measurement of up to four cells under variation of $p\text{H}_2\text{S}$ and current density i
- Comprehensive parameter studies possible

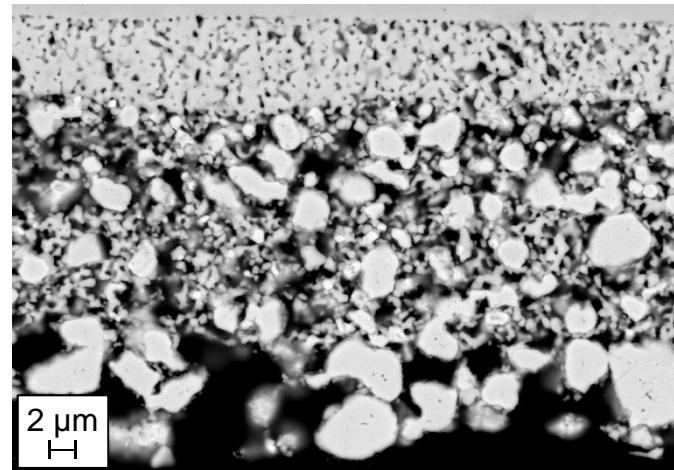


Methodology



Ni/CGO10 anode (20 μm)

- Fraunhofer IKTS, Germany
- 160 μm 10Sc1CeSZ electrolyte
- 65 μm LSM/10Sc1CeSZ cathode
- 5 μm CGO10 barrier layer



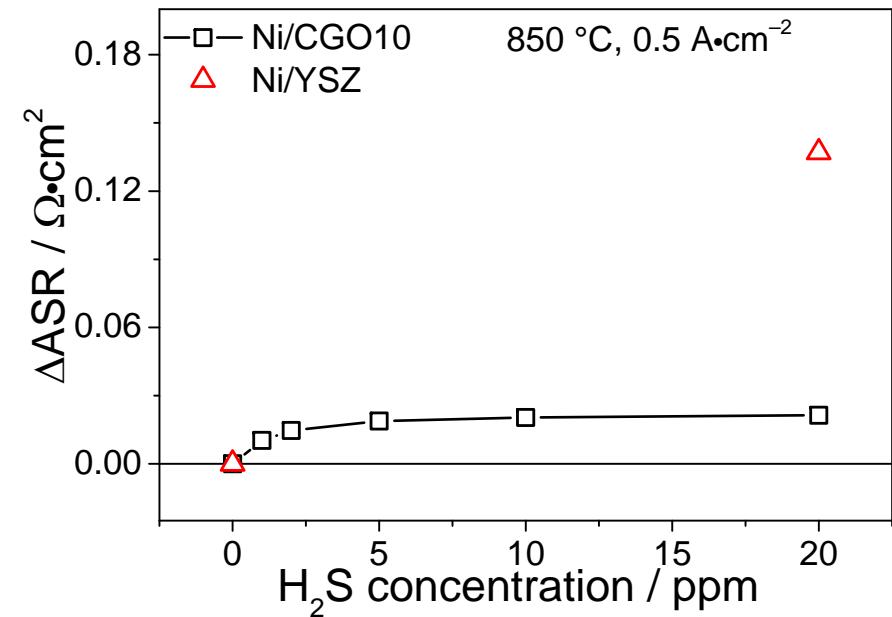
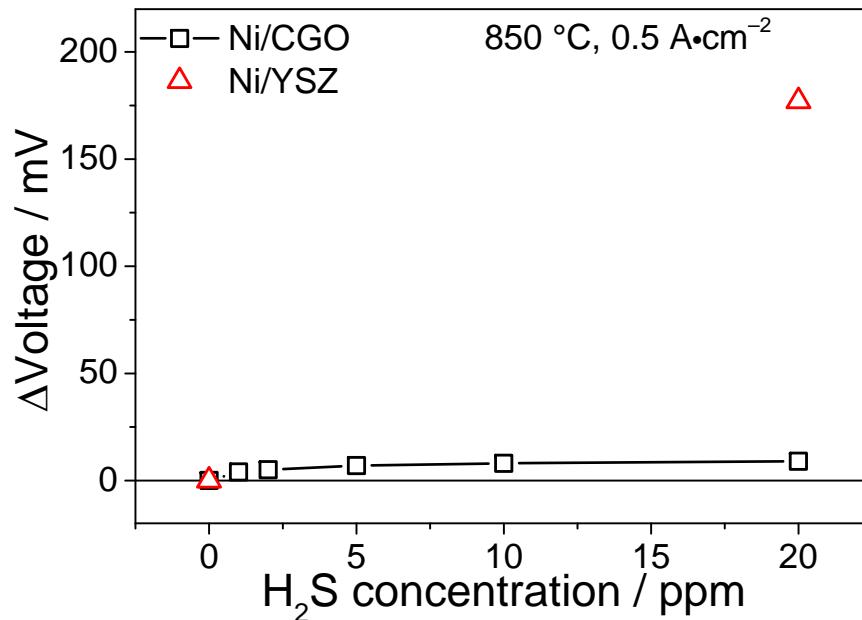
Ni/8YSZ anode (25 μm)

- Kerafol, Germany
- 160 μm 10Sc1CeSZ electrolyte
- 65 μm LSM/10Sc1CeSZ cathode
- 5 μm 8YSZ barrier layer



Sulfur poisoning in H₂/H₂O fuels: Ni/CGO vs. Ni/YSZ

850 °C, 0.5 A•cm⁻², 97 % H₂, 3 % H₂O, + 1, 2, 5, 10, 20 ppm H₂S



- Despite same Ni content, significantly larger resistance increase for Ni/CGO anodes! → Reaction mechanisms mu



Mechanism of Ni/CGO

Literature theories for high sulfur tolerance:

1. Sulfur oxidation to SO_2 via oxygen spillover from CGO to Ni [1,2]
 2. Sulfur diffusion into CGO bulk phase [3,4]
 3. Catalytic activity of CGO towards H_2 oxidation [5,6]
- } Free Ni surface → Activity of CGO

[1] Kavarucu et al., *J. Power Sources*, 217, (2012), 364; [2] Xu et al., *J. Electrochem. Soc.*, 158, (2011); [3] Gerstl et al., *Materials*, 9, (2016); [4] Mullins et al., *Surf. Science*, 601, (2016); [5] Chueh et al., *Nat. Materials*, 11, (2011); [6] Nakamura et al., *J. Electrochem. Soc*, 1555, (2008)

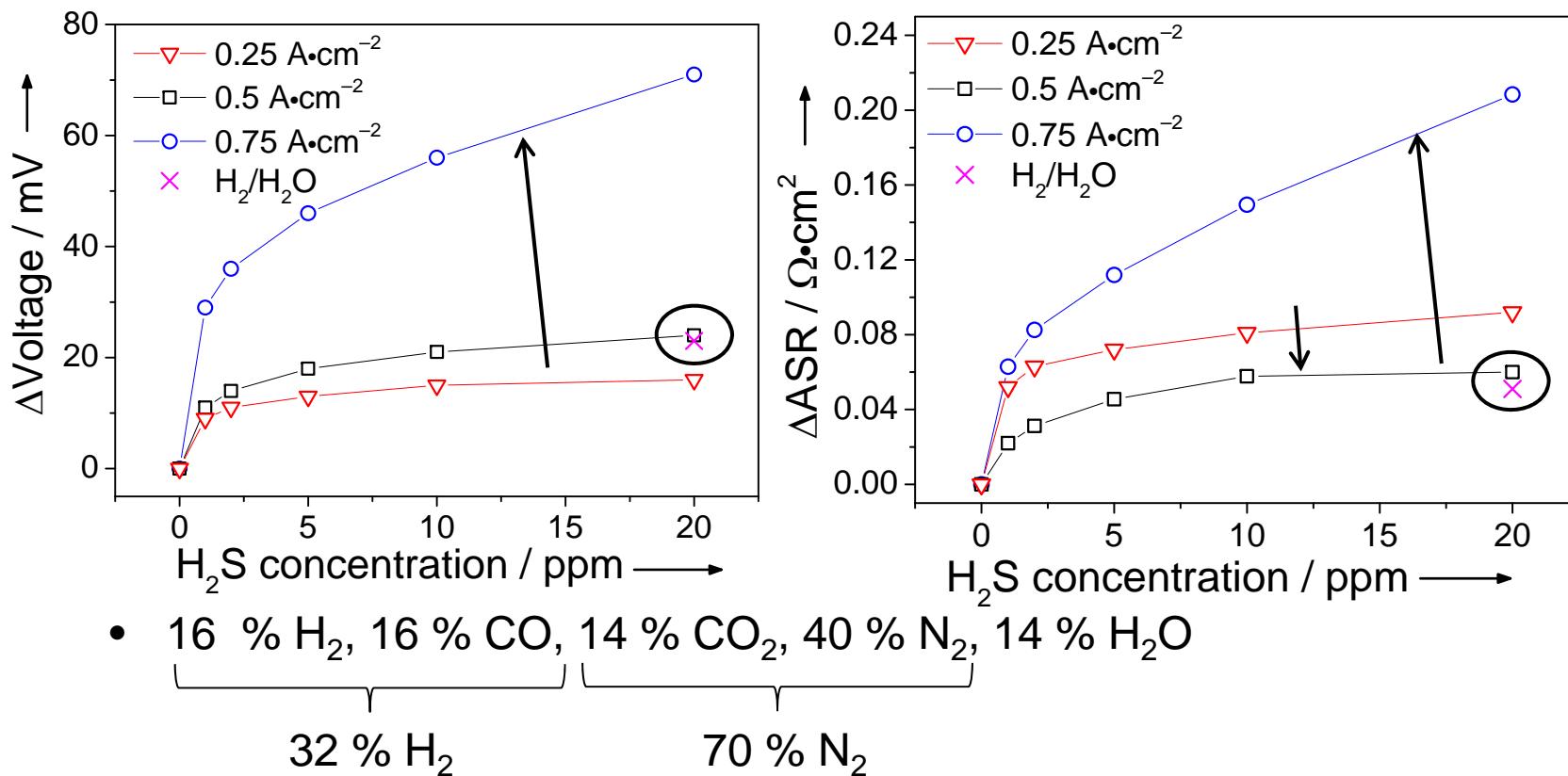


Reformate operation Ni/CGO

- $T = 850 \text{ }^{\circ}\text{C}$, $i = 0.25, 0.5, 0.75 \text{ A} \cdot \text{cm}^{-2}$
- 16 % H₂, 16 % CO, 14 % CO₂, 14 % H₂O, 40 % N₂
- Model diesel reformate for APU application
- Large CO content facilitates investigation of CO conversion



Reformate operation Ni/CGO

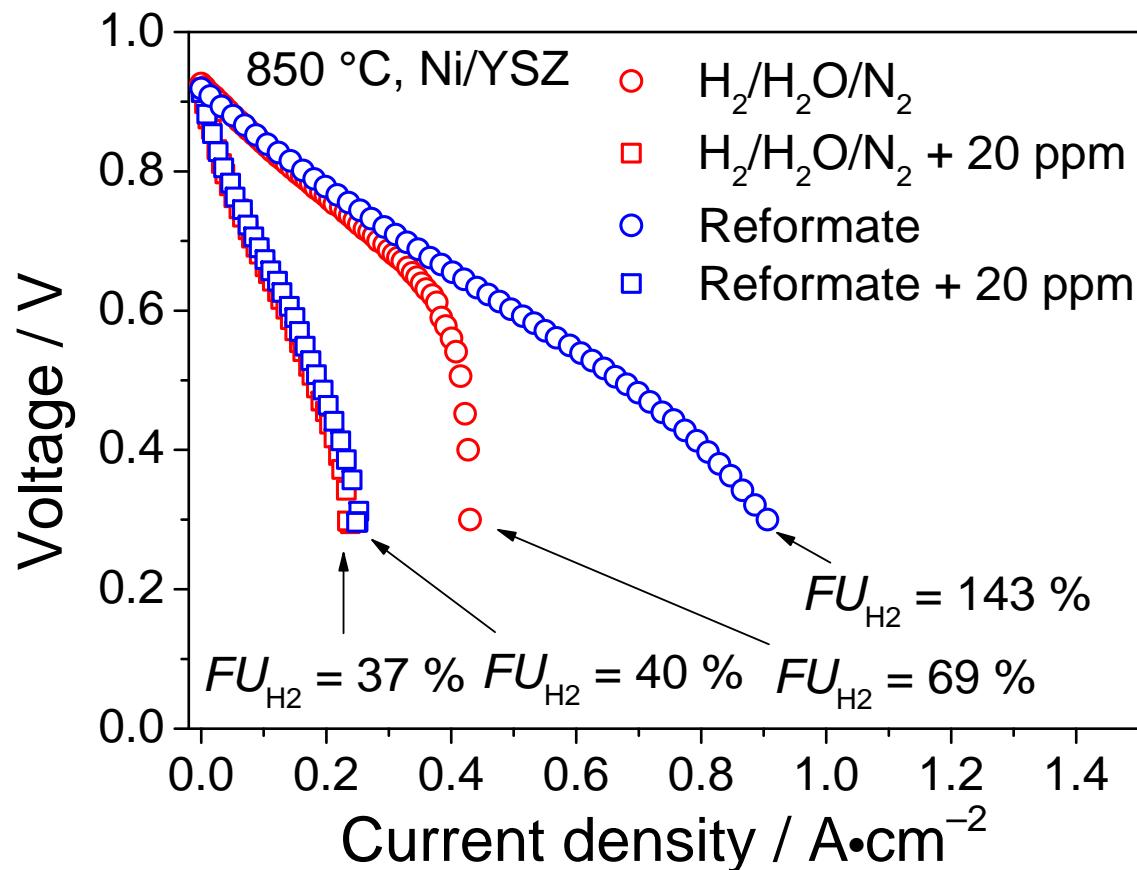


- 16 % H₂, 16 % CO, 14 % CO₂, 40 % N₂, 14 % H₂O
 - 32 % H₂
 - 70 % N₂
- Comparison with H₂/H₂O fuel at 0.5 $\text{A} \cdot \text{cm}^{-2}$ → H₂ content defines performance drop
- More severe effect of sulfur poisoning at higher current densities (=higher fuel utilization) → inhibited CO conversion



Reformate operation Ni/YSZ

- 7 % H₂, 7 % H₂O, 86 % N₂
- 7 % H₂, 7 % H₂O, 20 % CO₂, 20 % CO



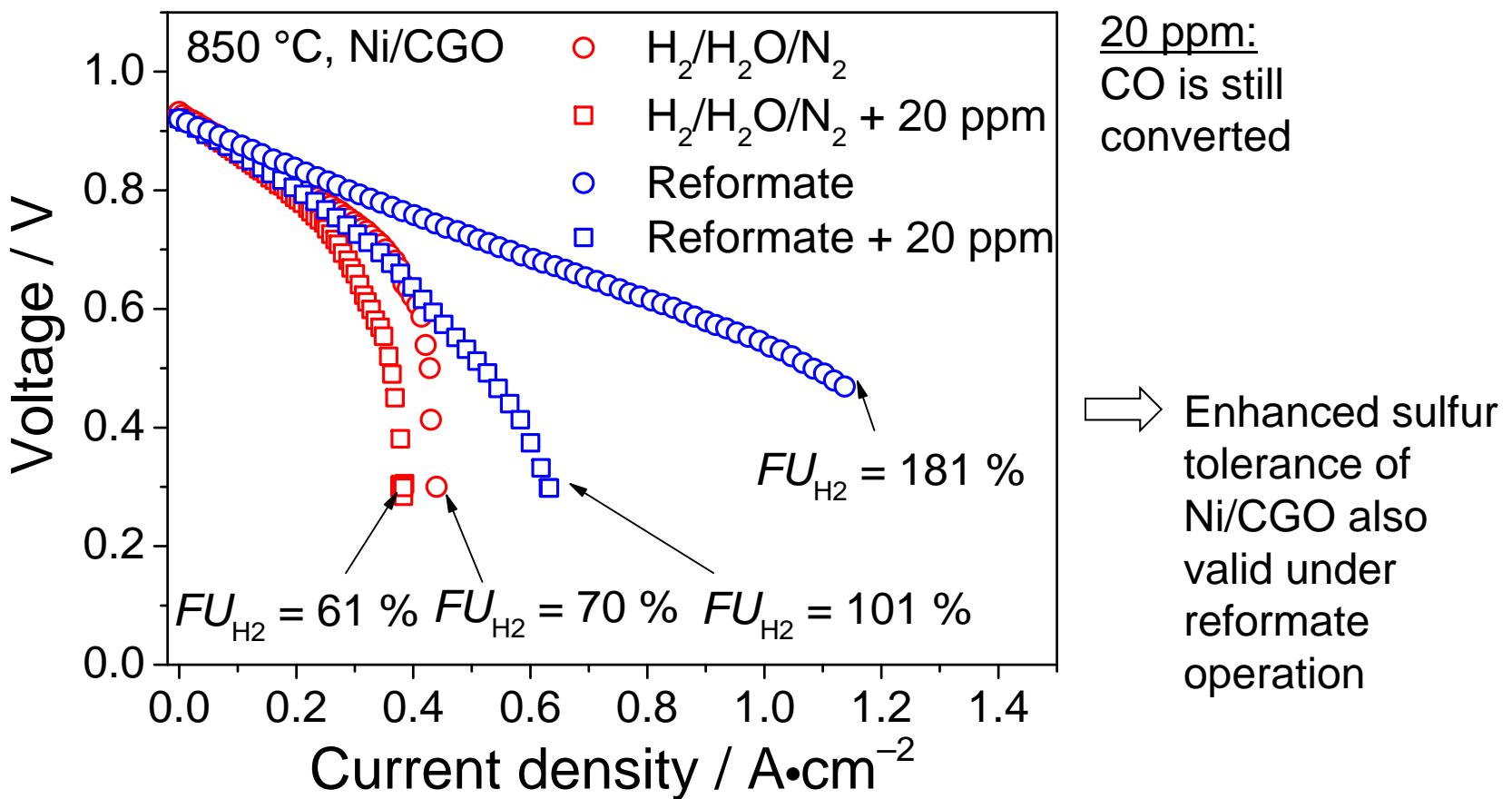
20 ppm:
Same performance in reformate and non-reformate

→ Water gas shift reaction and CO oxidation are completely blocked



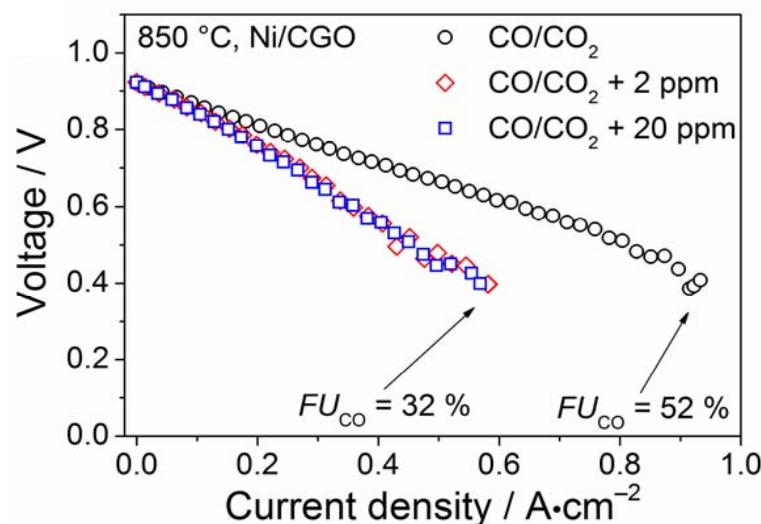
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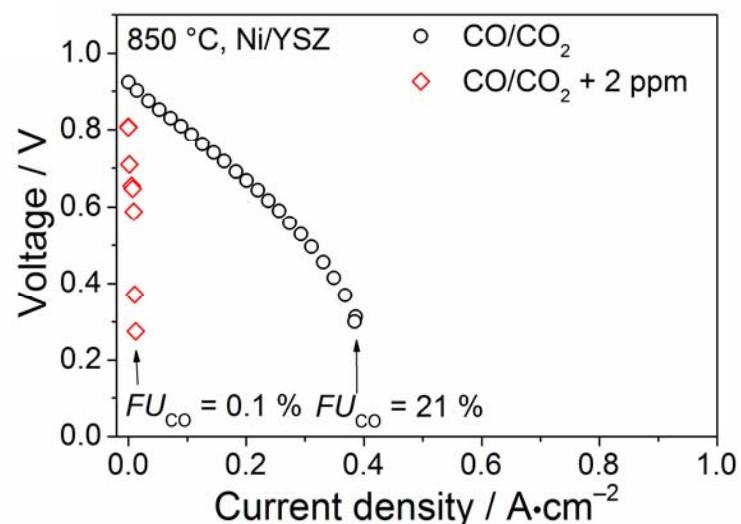


CO oxidation

Ni/CGO



Ni/YSZ

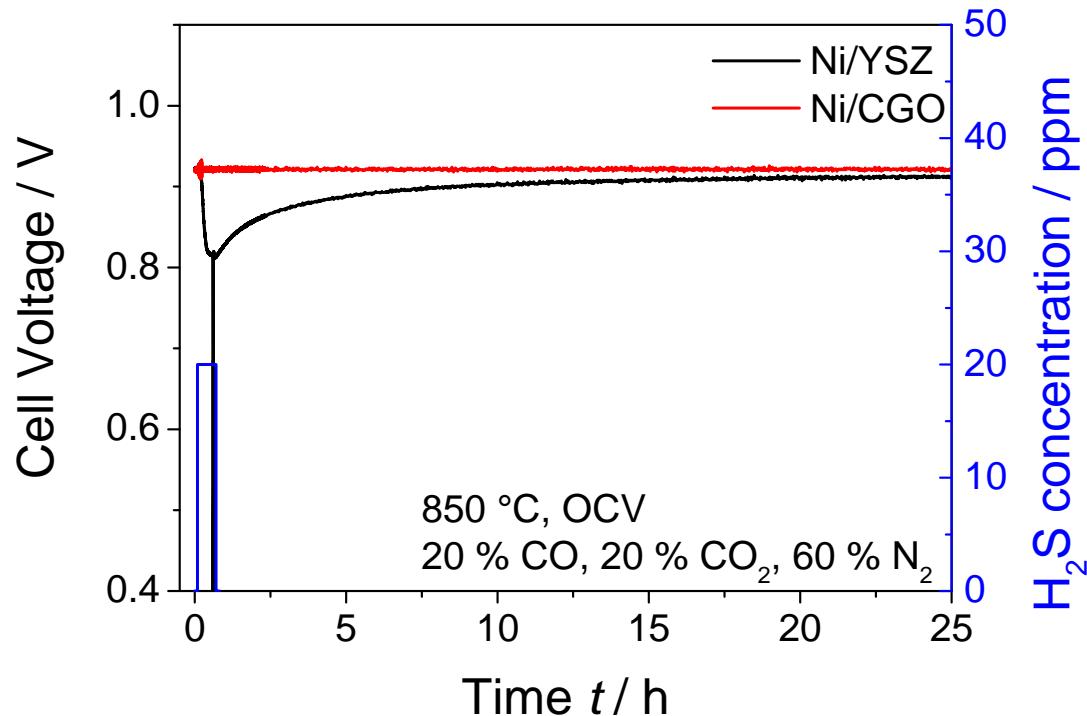


- Ni/YSZ: electrochemical CO oxidation fully blocked
 - Ni/CGO: electrochemical CO oxidation poisoned, but still active
- Water gas shift deactivation, electrochemical CO oxidation on CGO



CO oxidation

Poisoning of both cells at OCV with 20 ppm H₂S

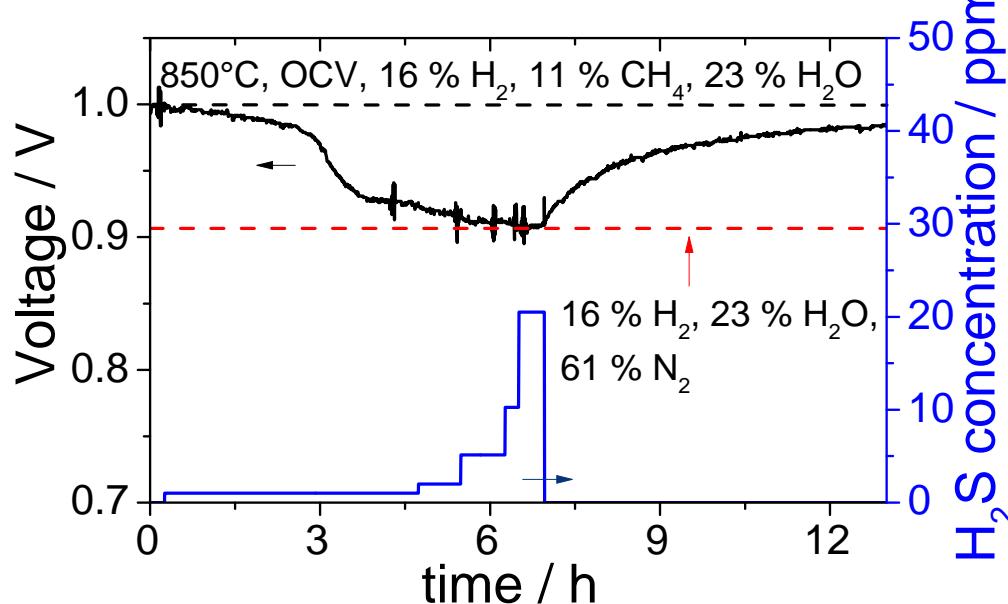


- OCV drop for Ni/YSZ
- CO oxidation is fully deactivated due to Ni surface poisoning



Methane steam reforming

Poisoning of Ni/CGO at OCV with 1-20 ppm H₂S



- Complete poisoning of Ni surface also on Ni/CGO
 - Similar poisoning behavior of WGS and methane steam reforming on Ni/YSZ [1,2]
- Ni surface also fully deactivated for CO adsorption on Ni/CGO



Mechanism of Ni/CGO

Literature theories for high sulfur tolerance:

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Deactivation Methane
steam reforming
~~Free Ni surface~~

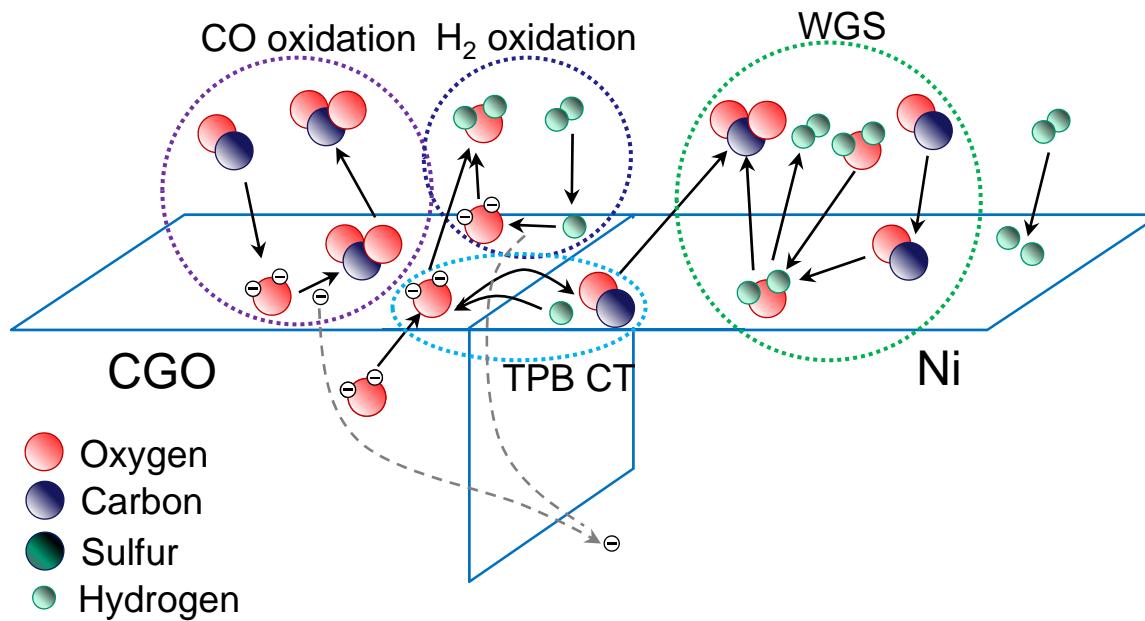


→ Activity of CGO

[1] Kavarucu et al., *J. Power Sources*, 217, (2012), 364; [2] Xu et al., *J. Electrochem. Soc.*, 158, (2011); [3] Gerstl et al., *Materials*, 9, (2016); [4] Mullins et al., *Surf. Science*, 601, (2016); [5] Chueh et al., *Nat. Materials*, 11, (2011); [6] Nakamura et al., *J. Electrochem. Soc*, 1555, (2008)



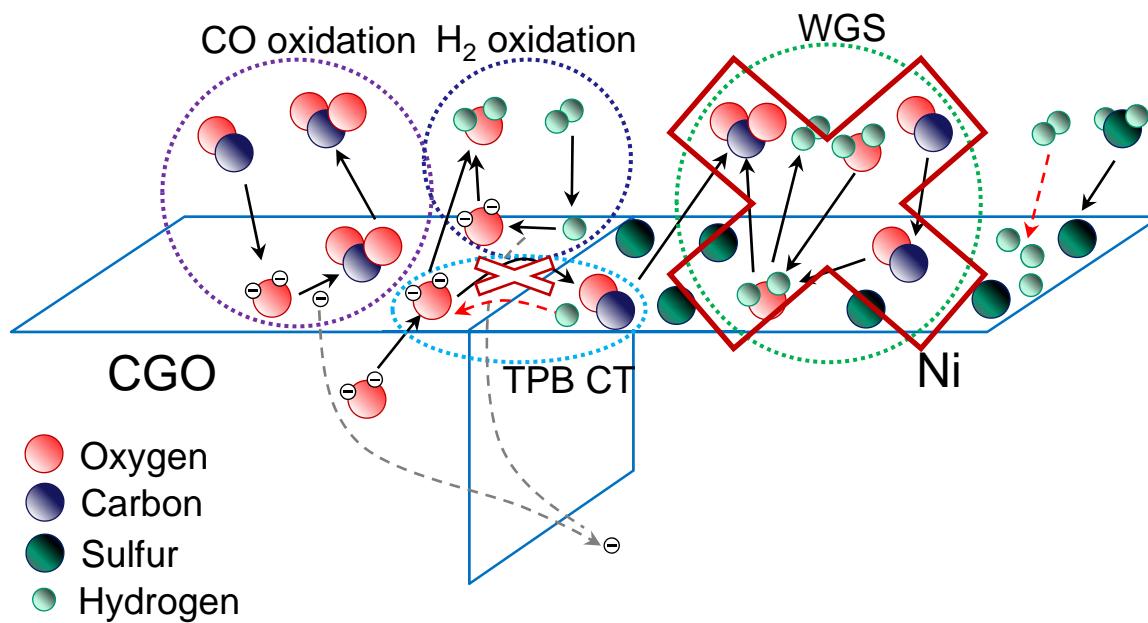
CO oxidation mechanism on Ni/CGO



- CO oxidation on CGO surface possible
- But CO oxidation at TPB dominates, as CO strongly adsorbs on Ni



CO oxidation mechanism on Ni/CGO: Sulfur poisoning



- Ni surface is blocked → CO oxidation at TPB deactivated
- Surface process on CGO is still active (Mars-van-Krevelen mechanism)
- H₂ oxidation at TPB probably still active (smaller atom diameter)



Summary and conclusions

- Characterization of sulfur poisoning of Ni/CGO anodes in a variety of different reformate fuels
- Ni/CGO are able to convert CO even under common sulfur poisoning conditions
- Methan steam reforming on Ni/CGO is completely blocked
- The water gas shift reaction is fully deacivated as well
- Electrochemical CO oxidation on CGO is possible



Acknowledgments

- Dr. Mihails Kusnezoff and Dr. Nikolai Trofimenko from Fraunhofer IKTS for the supply of cells
- High Temperature Materials Division (HTM) sponsored travel grant
- 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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