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

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Motivation

Natural Gas

- Ni based cermet SoA electrocatalysts
- Ni surface posioned with H_2S

Sulfur compounds

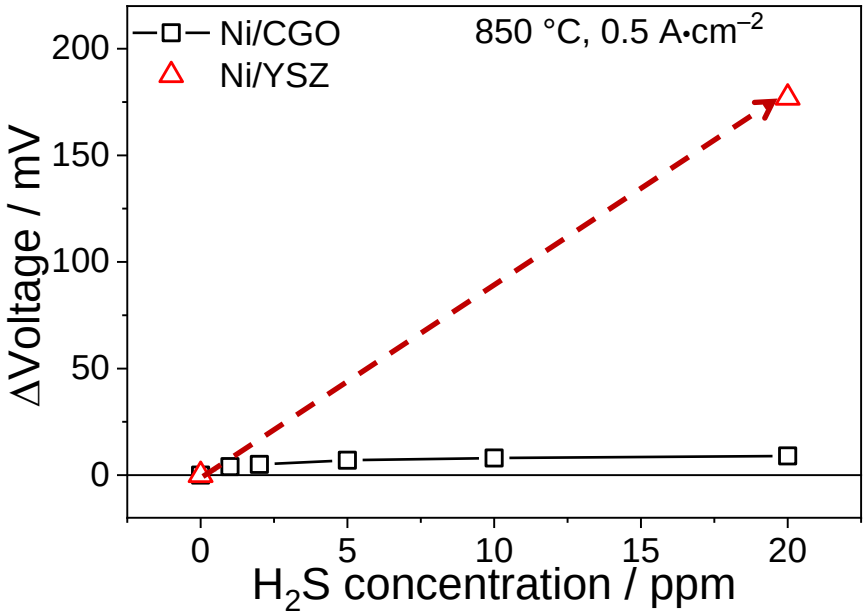
Diesel

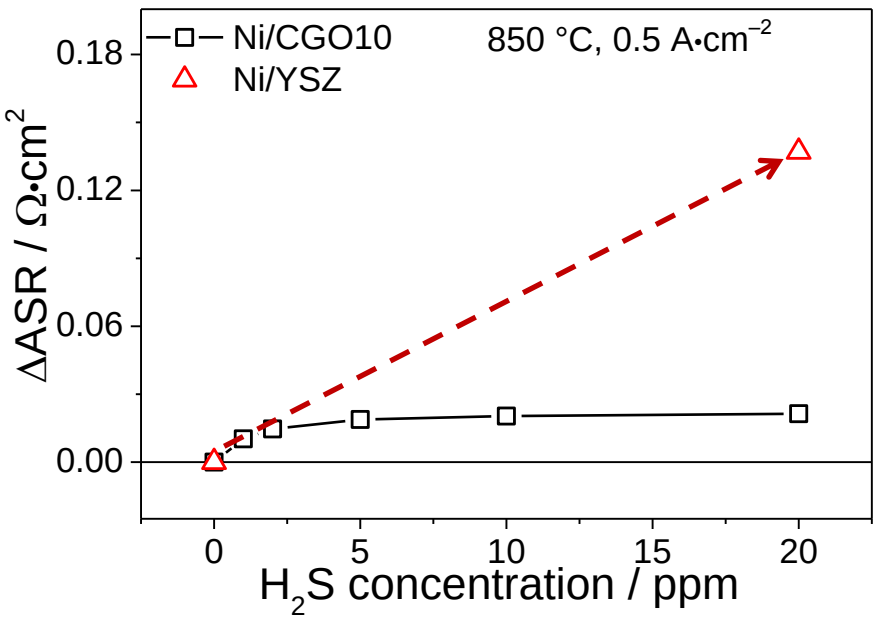
- Upstream desulfurizing unit
- **Failure of desulfurizing unit?**

Investigation of sulfur poisoning in reformate fuels on Ni/CGO in ESC configuration

Sulfur poisoning in H_2/H_2O fuels: Ni/CGO vs. Ni/YSZ

850 °C, 0.5 A•cm^{-2}, 97 % H_2, 3 % H_2O + 1, 2, 5, 10, 20 ppm H_2S





Different mechanisms

Electro-oxidation on Ni/CGO anodes

1. Sulfur oxidation to SO_2 via oxygen spillover from CGO to Ni [1,2]
2. Sulfur diffusion into CGO bulk phase [3,4]

} Free Ni surface

3. Catalytic activity of CGO towards H_2 oxidation [5,6] → Activity of CGO

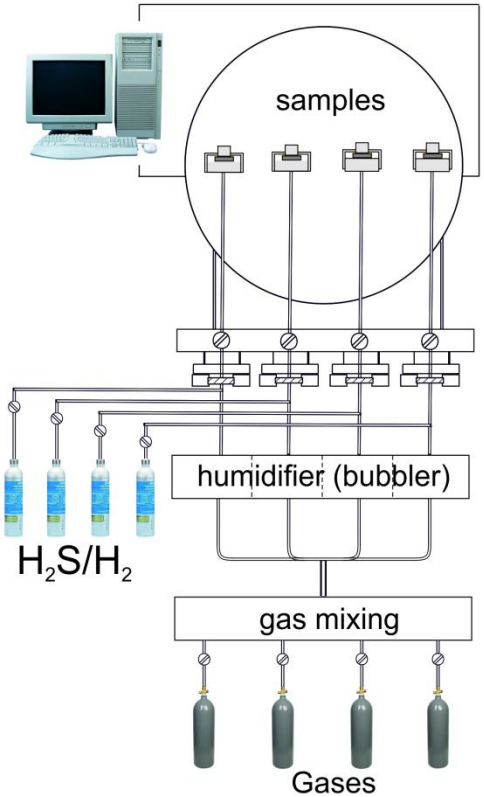
Reformate operation: CO as a fuel

Water gas shift reaction: $$CO + H_2O \rightleftharpoons H_2 + CO_2$$

CO oxidation: $$CO + O^{2-} \rightleftharpoons CO_2 + 2e^-$$

[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)

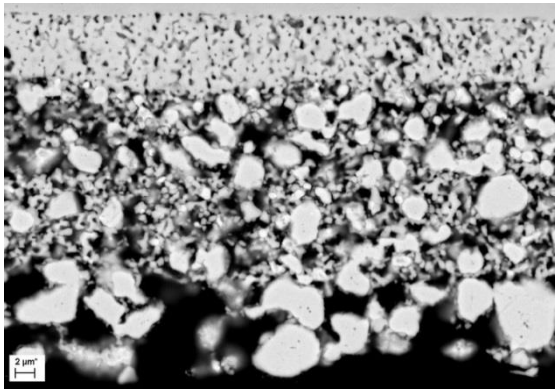
Experimentals



Simultaneous measurement of up to **four cells under variation of pH_2S and current density *i***

ESC from **Kerafol (Ni-YSZ)** & **IKTS (Ni-CGO)**

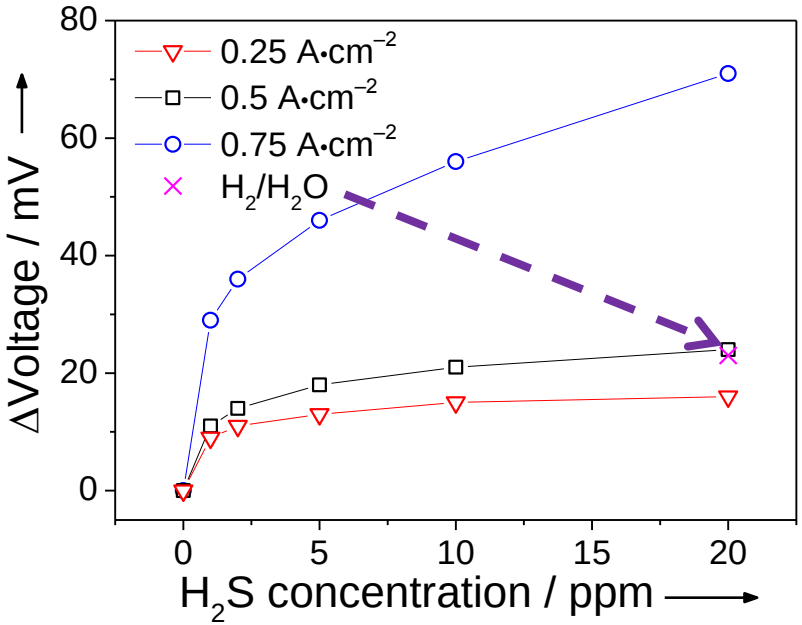
Number of fuel gas mixture	H_2	H_2O	CO	CO_2	N_2	CH_4	Ni/YSZ	Ni/CGO
I	16	14	16	14	40	-	-	Yes
II	32	14	-	-	54		-	Yes
III	7	7	20	20	46	-	Yes	Yes[a]
IV	7	7	-	-	86	-	Yes[a]	Yes[a]
V	-	-	20	20	60	-	Yes	Yes[a]
VI	16	23	-	-	50	11	-	Yes

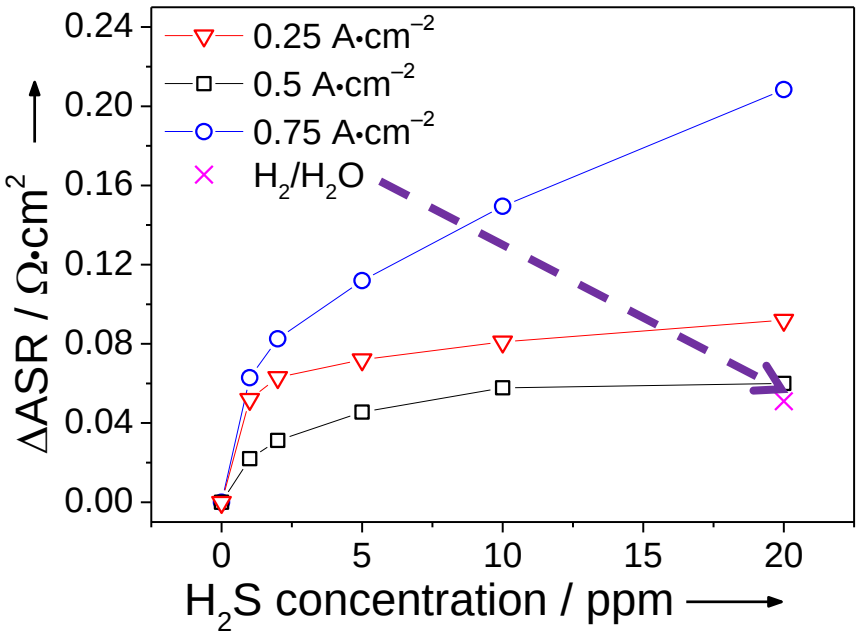


ESC from Kerafol

Reformate operation on Ni/CGO

16 % H_2, 16 % CO, 14 % CO_2, 40 % N_2, 14 % H_2O



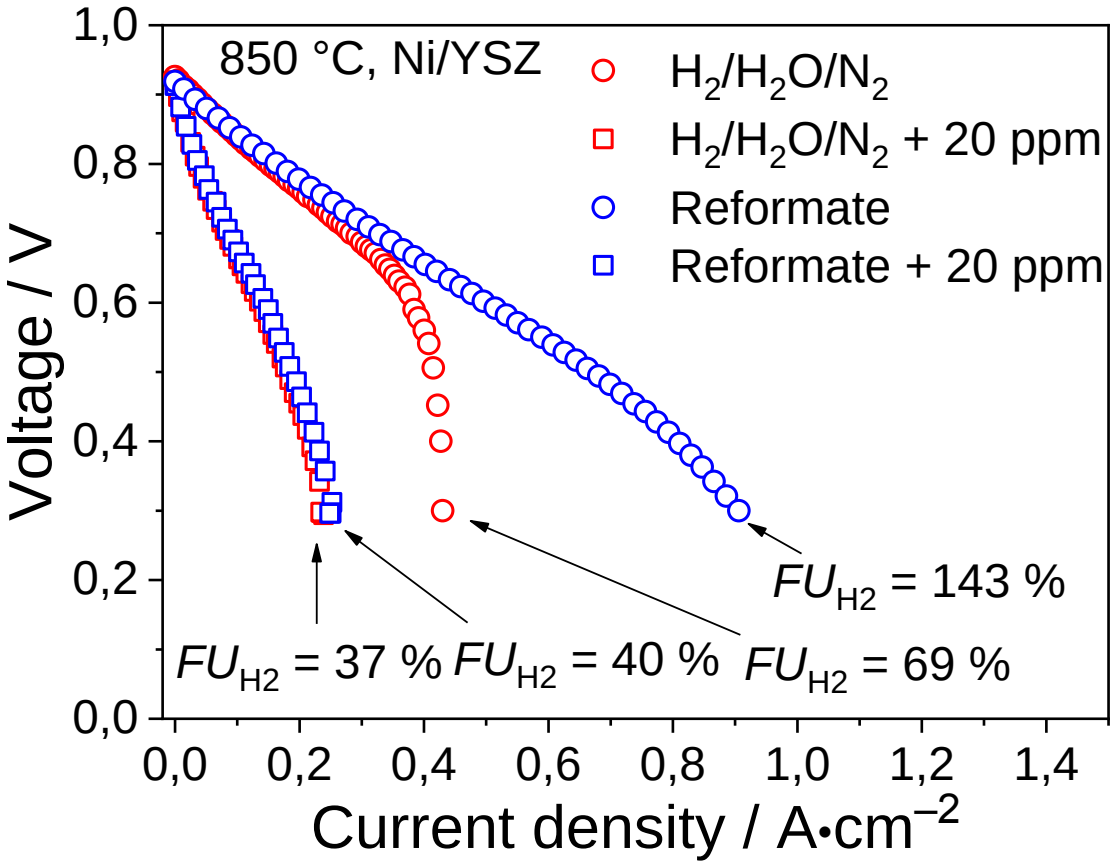


Effect of sulfur poisoning is increased at higher current densities (=higher fuel utilization)

(nearly) no difference between the Reformate Operation and the H_2 operation
H_2/H_2O Chain is mostly affected by the sulfur poisoning

Reformate operation on Ni/YSZ

- 7 % H_2, 7 % H_2O, 86 % N_2
- 7 % H_2, 7 % H_2O, 20 % CO_2, 20 % CO, 46 % N_2

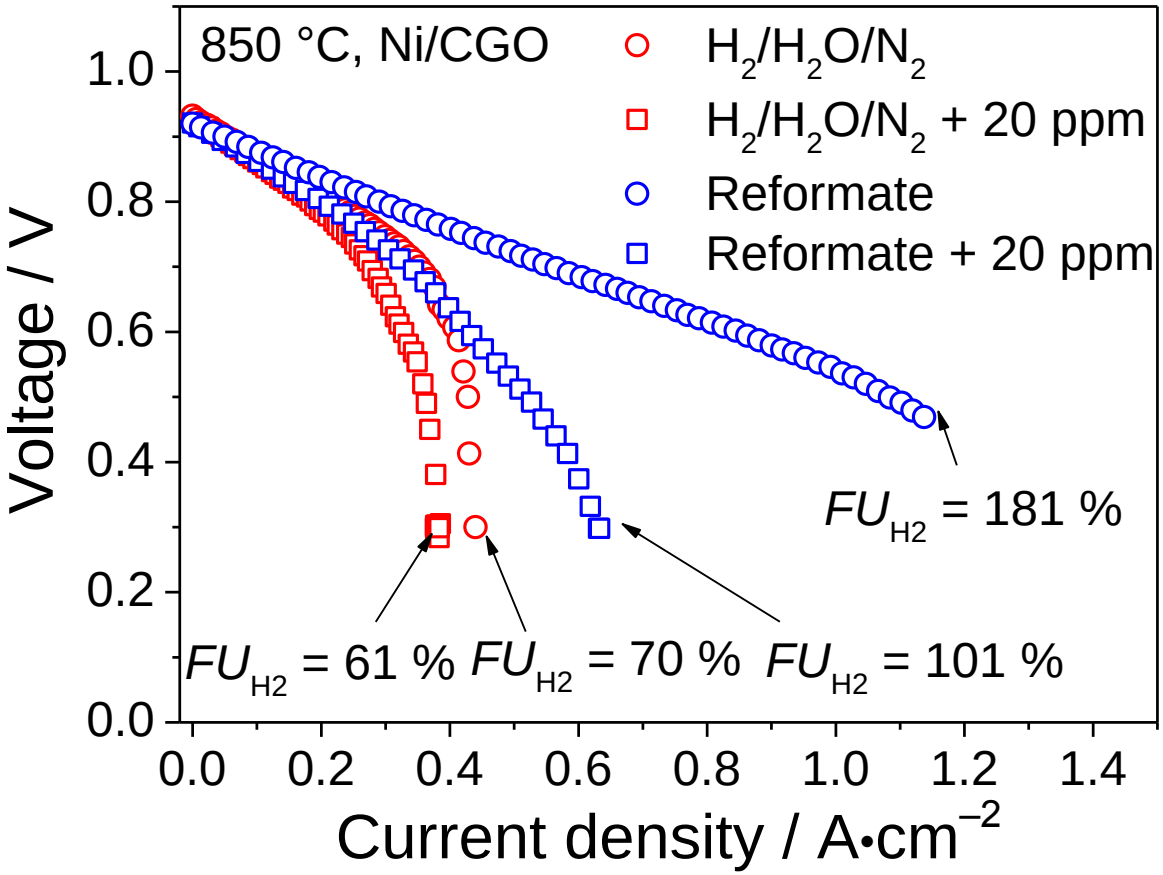


<u>20 ppm:</u>
Same performance in reformate and non-reformate

→ Water Gas Shift reaction and CO oxidation are inhibited

Reformate operation Ni/CGO

- 7 % H_2, 7 % H_2O, 86 % N_2
- 7 % H_2, 7 % H_2O, 20 % CO_2, 20 % CO, 46 % N_2



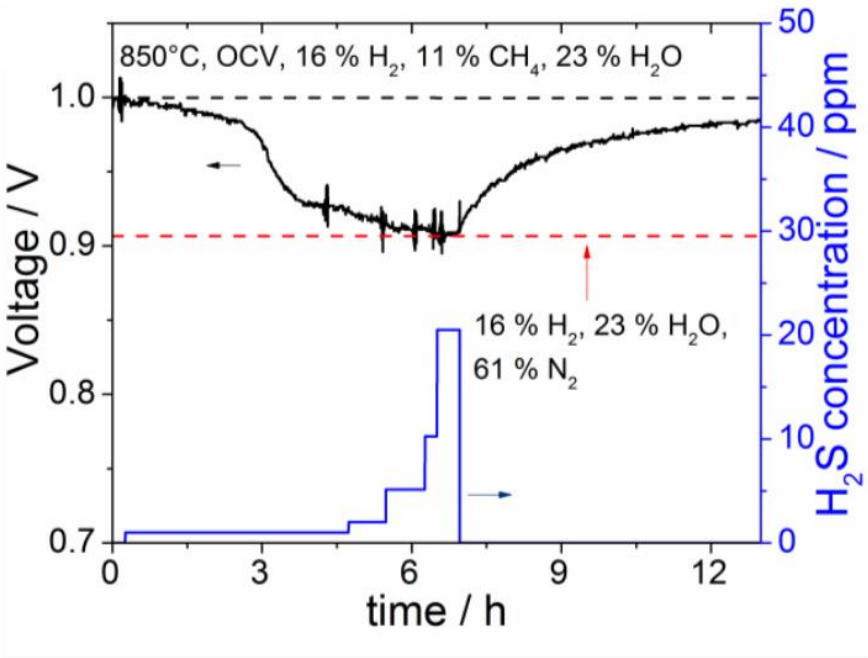
20 ppm:
Different behaviors

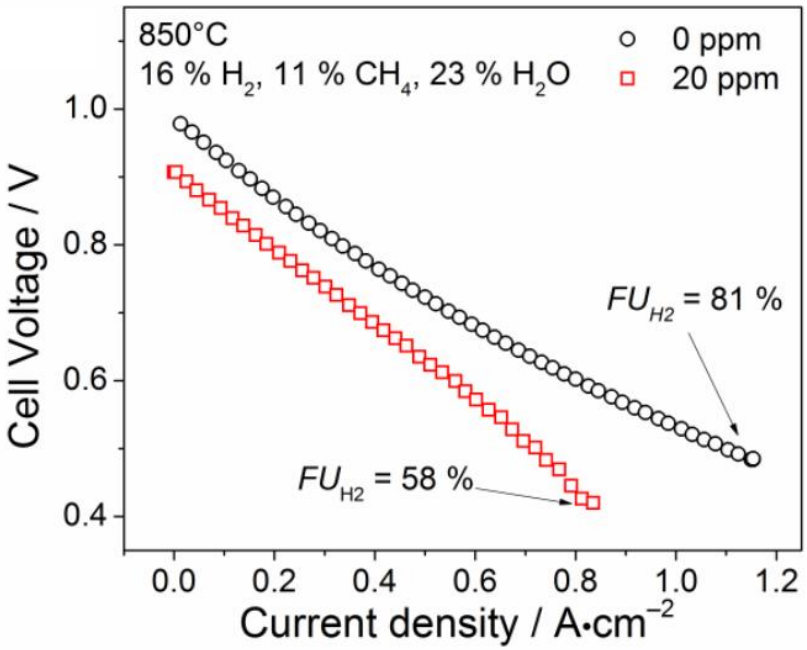
→ **Enhanced sulfur tolerance of Ni/CGO also valid under reformate operation**

→ **CO is converted**

Methane steam reforming

Poisoning of Ni/CGO at OCV with 1 - 20 ppm H_2S
16 % H_2, 11 % CH_4, 23 % H_2O, 50 % N_2



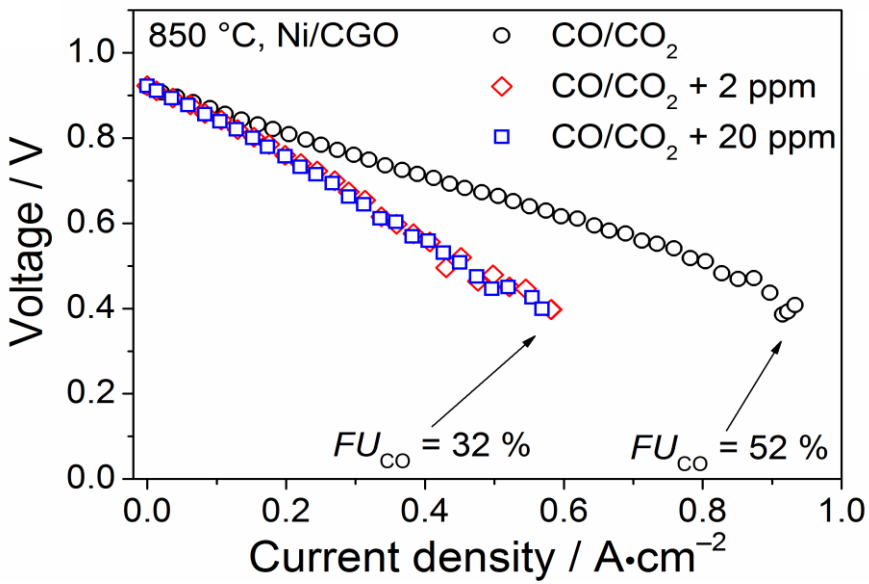


Similar poisoning behavior of WGS and methane steam reforming on Ni/YSZ
Methane Steam Reforming affected by the poisoning

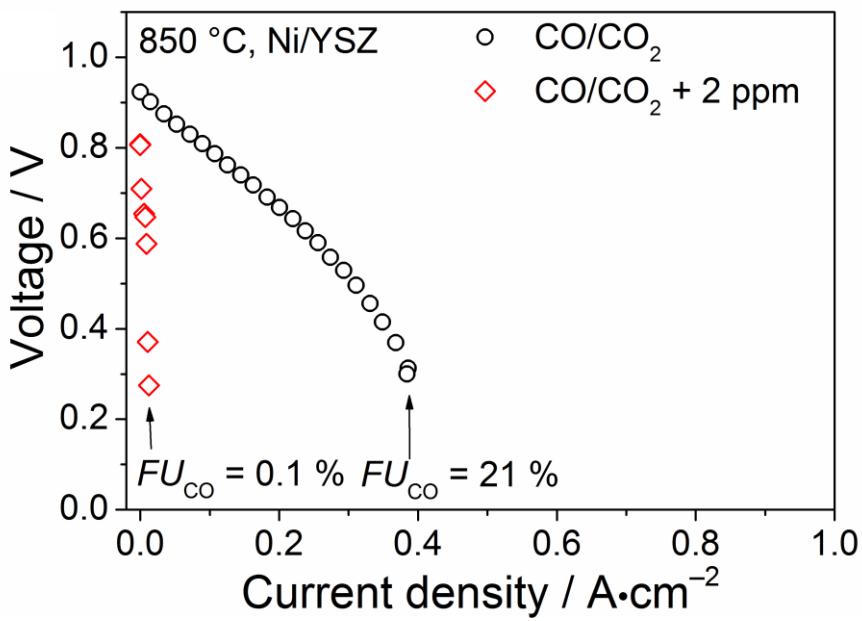
Ni surface poisoned & CGO surface may not be active towards Methane Steam Reforming

CO oxidation on Ni/CGO & Ni/YSZ ?

Ni/CGO



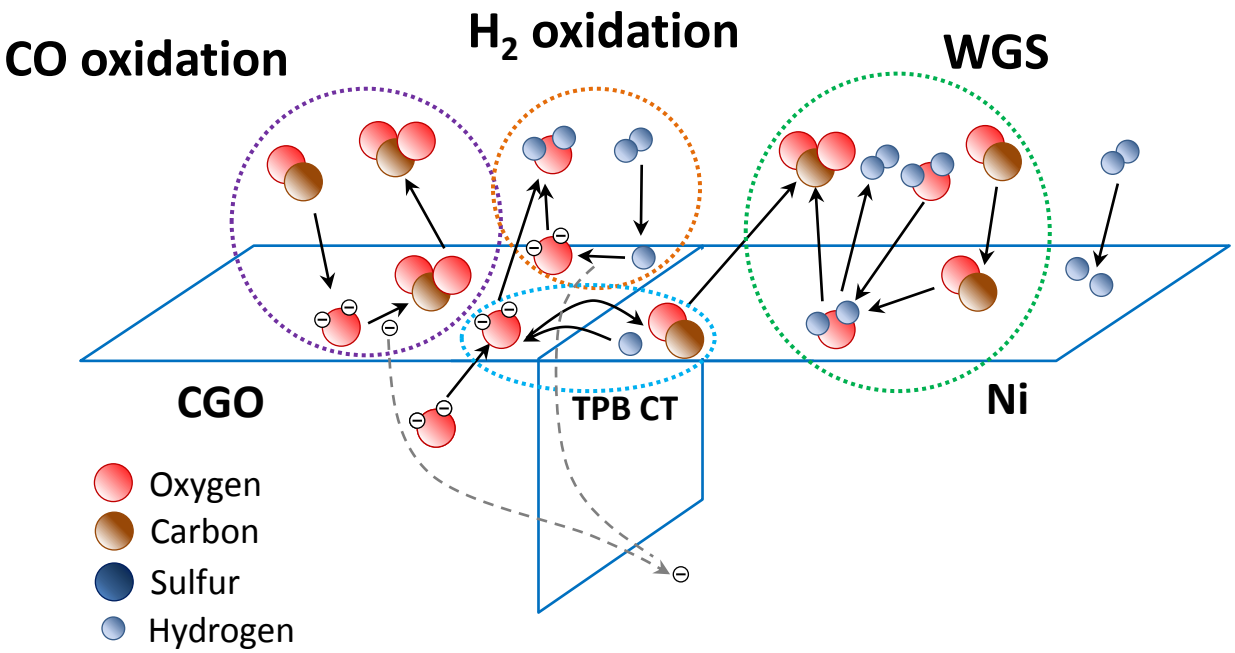
Ni/YSZ



Ni/YSZ: electrochemical CO oxidation inhibited
Ni/CGO: electrochemical CO oxidation poisoned, but still active

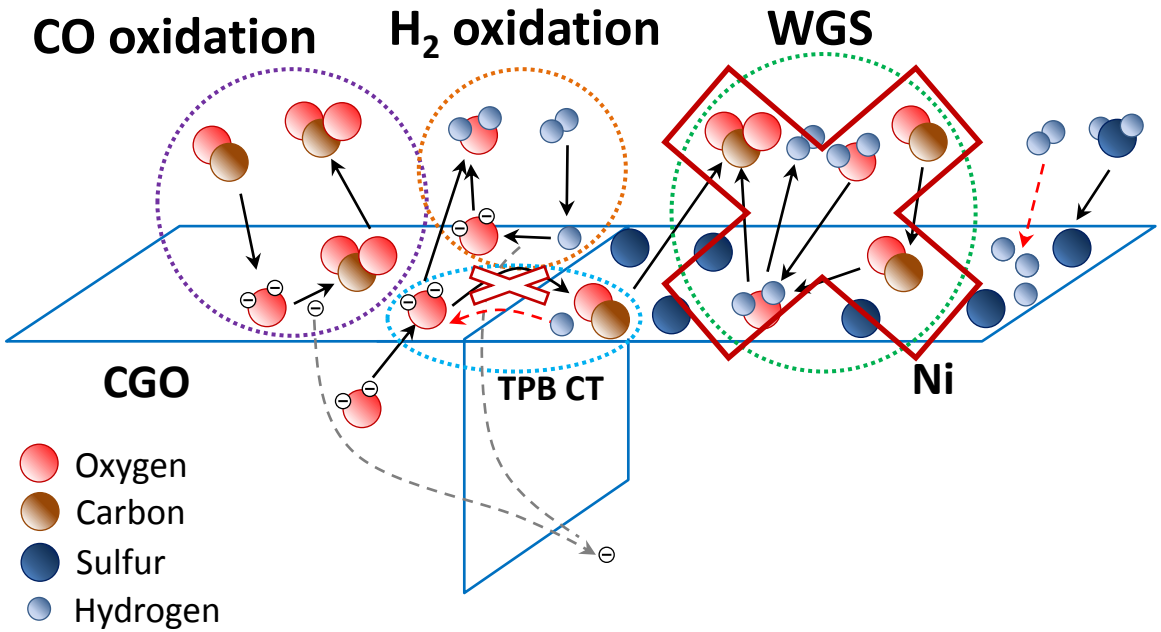
Water gas shift deactivation, electrochemical CO conversion on CGO ?

Fuel oxidation mechanism on Ni/CGO



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

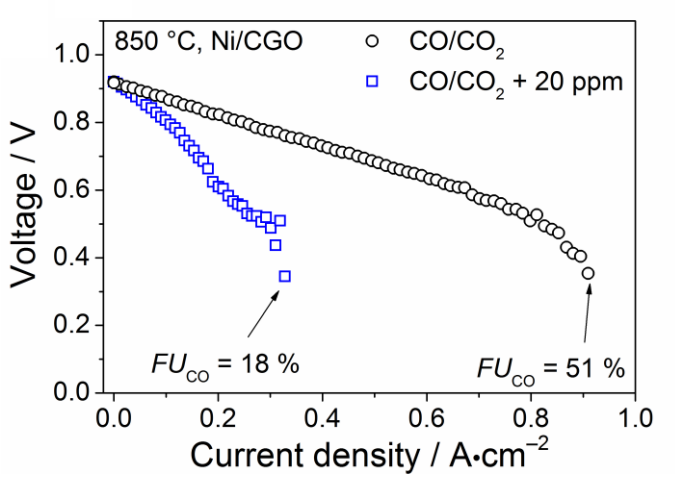
Fuel oxidation mechanism on Ni/CGO: Sulfur poisoning

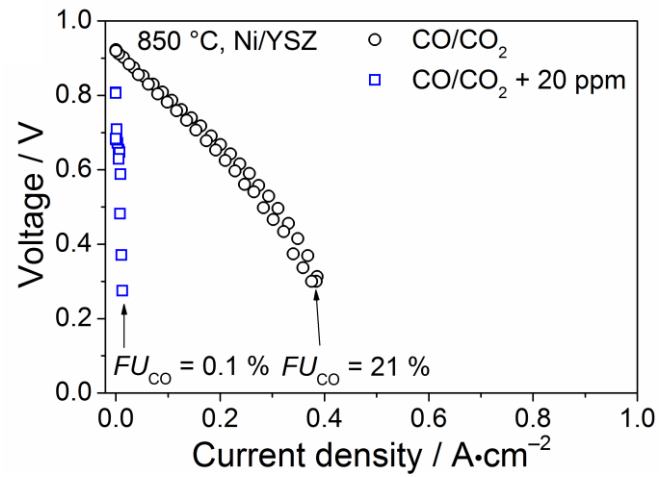


Ni surface is blocked → CO oxidation at TPB deactivated
Surface process on CGO is still active (Mars-van-Krevelen mechanism)

H_2 oxidation at TPB may still be active (smaller atom diameter)

Summary and conclusions





Investigation of sulfur poisoning during reformate operation (CO/CO_2, $CO/CO_2/H_2/H_2O$, CH_4/H_2O)

Reversible short exposure poisoning

Methane steam reforming is inhibited under S-poisoning

CO Oxidation on Ni/CGO still possible even with 20 ppm H_2S (Not on Ni/YSZ) → higher sulfer tolerance

Eletrochemical conversion of CO on CGO surface

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Sulfur Poisoning of Electrochemical Reformate Conversion on Nickel/Gadolinium-Doped Ceria Electrodes

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Thank you for your attention!

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