Lifetime and Performance Prediction of SOFC Anodes Operated with Trace Amounts of Hydrogen Sulfide

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Overview

- Motivation and aim of the work
- Computational methods
- Results
  - Reaction mechanism development
  - Sulfur poisoning in H_2/H_2O fuels
  - Sulfur poisoning of internal methane steam reforming
- Summary and conclusions

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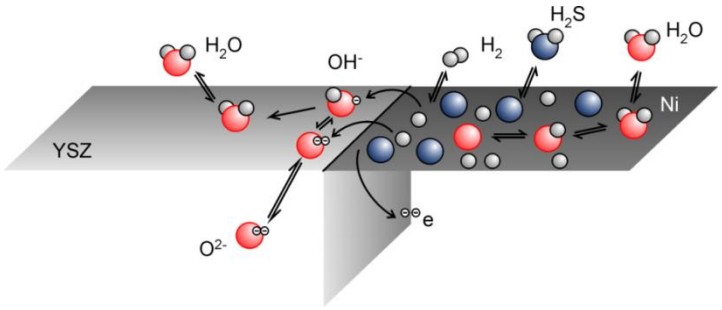
Motivation and aim of the work

- Ni/YSZ anode poisoning with H_2S

- Despite extensive experimental and theoretical investigation, still no validated mechanism for sulfur poisoning

- Identification of underlying processes with elementary kinetic modeling

- Derivation of thermodynamic and kinetic data



Goal: ➢ Building of a reaction mechanism and identification of the elementary processes leading to sulfur poisoning of Ni/YSZ anodes

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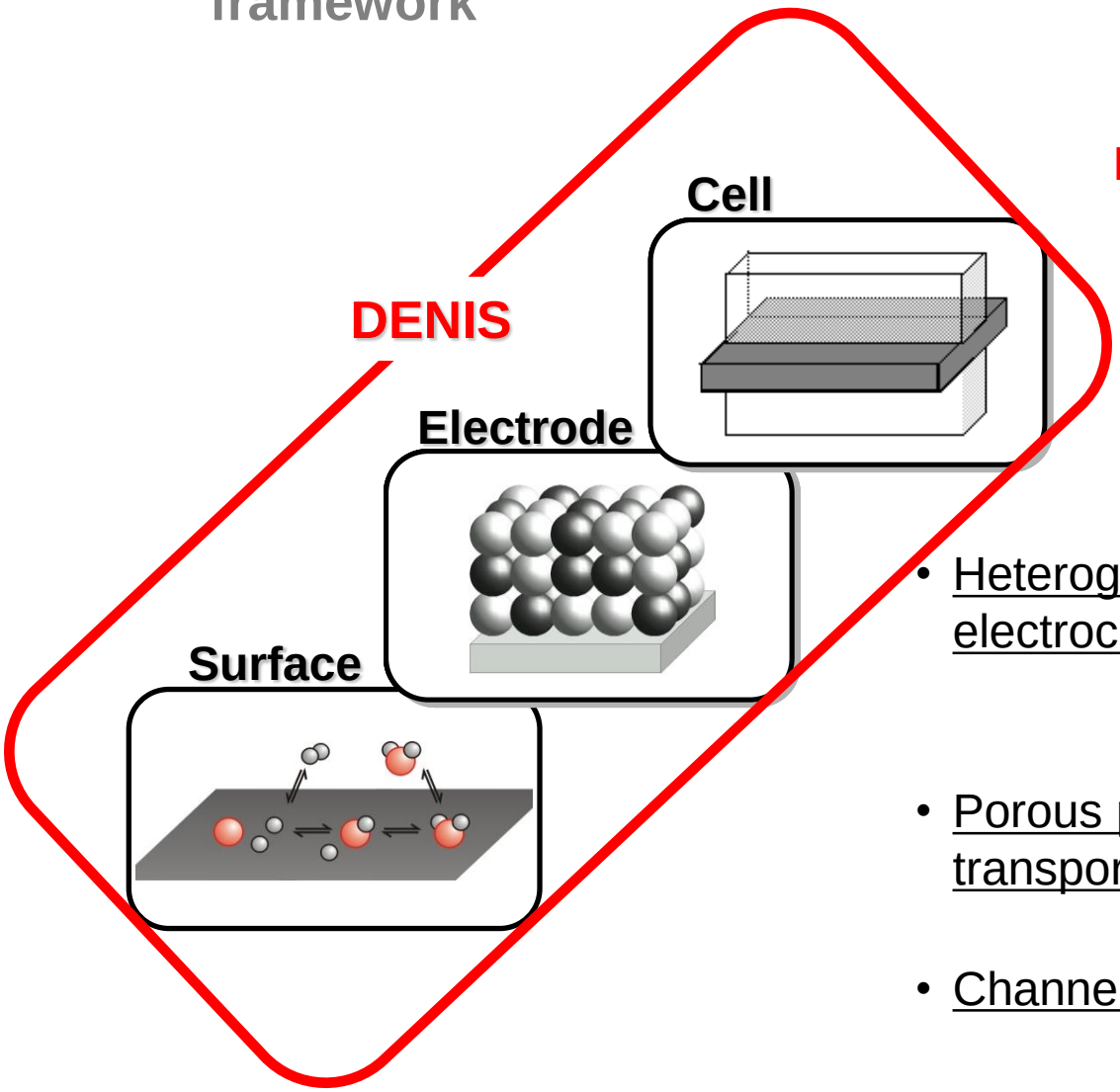
Computational methods: Elementary kinetic modeling framework



DENIS: Detailed Electrochemistry and Numerical Impedance Simulation

- Heterogeneous and electrochemistry: Mean-field approach, elementary kinetic description of reactions
- Porous phase transport: Fickian, Knudsen diffusion and Darcy flow
- Channel flow: Navier-Stokes equations

W. G. Bessler, S. Gewies, M. Vogler, *Electrochim. Acta*, 53, 1782 (2007)

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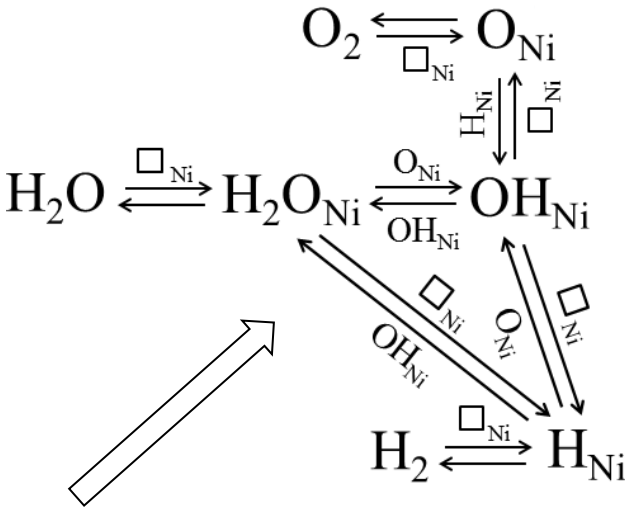
Reaction mechanism development



- H_2 oxidation mechanism validated in previous modeling studies [1,2]
- Assumed to be unaffected by the presence of sulfur

S formation/oxidation at Ni surface:

$$H_2S_g + \square_{Ni} \rightleftharpoons H_2S_{Ni}$$

$$H_2S_{Ni} + \square_{Ni} \rightleftharpoons HS_{Ni} + H_{Ni}$$

$$HS_{Ni} + \square_{Ni} \rightleftharpoons H_{Ni} + S_{Ni}$$

$$S_{Ni} + O_{Ni} \rightleftharpoons SO_{Ni} + \square_{Ni}$$

$$SO_{Ni} + O_{Ni} \rightleftharpoons SO_{2,Ni} + \square_{Ni}$$

$$SO_{2,Ni} \rightleftharpoons SO_{2,g} + \square_{Ni}$$

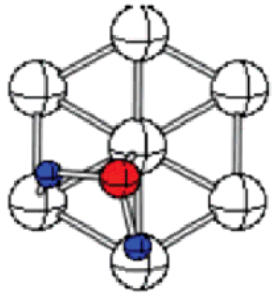
- Extension of original reaction mechanism
- <u>Present work: Derivation of thermodynamic and kinetic data</u>

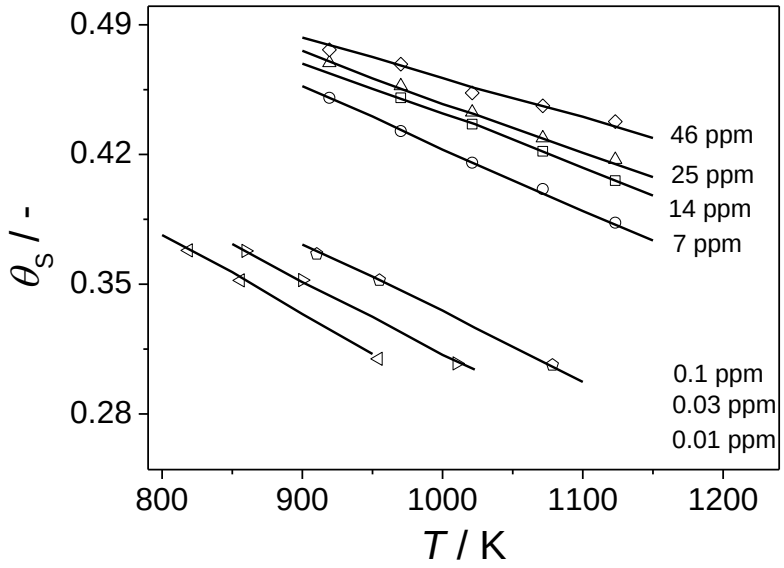
1. Vogler et al., *J. Electrochem. Soc.*,156, (2009),B663; 2. Bessler et al., *Phys. Chem. Chem. Phys*., 12, (2010), 13888

Reaction mechanism development: Data derivation

Thermodynamic and kinetic data from literature:

- Derivation from DFT calculations [1-3]
- Entropy of S_{Ni} is constant: $s(S_{Ni}) = 52\ J \bullet K^{-1} \bullet mol^{-1}$ [3,4]
- Enthalpy of sulfur $h(S_{Ni})$ is dependent on surface coverage [2–5]





Chemical experiments [6]

- H_2/H_2S system on Ni surface

⇨ Validation of chemical mechanism

1. Alfonso, *Surface Science*, 602, (2008) 2758; 2. Galea, *Journal of Catalysis*, 263, (2009), 380
3. Monder et al., *ECS Transactions,* 57, (2013), 2449; 4. McCarty et al., *J.Chem.Phys.* 72, (1980), 12;
5. Wang et al*., Electrochemistry Communications, 9, (2007), 2212;* 6. Alstrup et al., *Applied Catalysis*, 1, (1981), 303

Reaction mechanism development: Complete mechanism for S formation and oxidation

Species, i	h_i (kJ·mol^{-1})	s_i (J·K^{-1}·mol^{-1})
Gas-phase (T = 1023K / T=1073 K)		
H_2S_{gas}	8.6 / 10.9	253.5 / 255.8
$H_{2,gas}$	21.4 / 22.9	166.9 / 168.4
$O_{2,gas}$	23.5 / 25.3	244.4 / 246.0
H_2O_{gas}	-241.9 / -212.8	233.7 / 235.7
$SO_{2,gas}$	-261.1 / -258.4	306.9 / 309.6
Anode surface		
$\square_{Ni}$	0	0
O_{Ni}	–221.6	38.9
H_{Ni}	-31.8	40.7
OH_{Ni}	-192.7	106.4
H_2O_{Ni}	-273.2	130.7
H_2S_{Ni}	-43.2	0
HS_{Ni}	-132.0	0
$SO_{2,Ni}$	-486.0	0
SO_{Ni}	-295.0	0
S_{Ni}	f(θ_S)	52.0
YSZ surface		
$\square_{YSZ}$	0	0
O^{2-}_{YSZ}	–236.4	0
H_2O_{YSZ}	–273.0	97.9
OH^{1-}_{YSZ}	-282.5	67.0
Bulk species		
$O^{\times}_{O\,YSZ}$	–236.4	0
$V^{\cdot\cdot}_{YSZ}$	0	0

- Compilation of thermodynamic and kinetic data from various literature sources
- Thermodynamic data for 21 species
- Kinetic data for 15 elementary reactions

Reaction	k^0 (or s_i^0)	E^{act} (kJ·mol^{-1})
Ni surface reactions		
$H_{2,g} + 2\square_{Ni} \rightleftharpoons 2H_{Ni}$	$9.80\cdot10^{17}$ cm^4·mol^{-2}·s^{-1}	0
$H_2O_g + \square_{Ni} \rightleftharpoons H_2O_{Ni}$	$1.4\cdot10^{10}$ cm^2·mol^{-1}·s^{-1}	0
$H_{Ni} + O_{Ni} \rightleftharpoons OH_{Ni} + \square_{Ni}$	$5.0\cdot10^{22}$ cm^2·mol^{-1}·s^{-1}	97.9
$H_{Ni} + OH_{Ni} \rightleftharpoons H_2O_{Ni} + \square_{Ni}$	$3.0\cdot10^{20}$ cm^2·mol^{-1}·s^{-1}	42.7
$H_2O_{Ni} + O_{Ni} \rightleftharpoons 2OH_{Ni}$	$5.42\cdot10^{23}$ cm^2·mol^{-1}·s^{-1}	209.4
$H_2S_g + \square_{Ni} \rightleftharpoons H_2S_{Ni}$	s_i^0=0.5	0
$H_2S_{Ni} + \square_{Ni} \rightleftharpoons HS_{Ni} + H_{Ni}$	$1.0\cdot10^{22}$ cm^2·mol^{-1}·s^{-1}	14.5
$HS_{Ni} + \square_{Ni} \rightleftharpoons H_{Ni} + S_{Ni}$	$1.0\cdot10^{22}$ cm^2·mol^{-1}·s^{-1}	10.6
$SO_{Ni} + \square_{Ni} \rightleftharpoons S_{Ni} + O_{Ni}$	$1.0\cdot10^{22}$ cm^2·mol^{-1}·s^{-1}	158.2
$SO_{Ni} + O_{Ni} \rightleftharpoons SO_{2,Ni} + \square_{Ni}$	$1.0\cdot10^{22}$ cm^2·mol^{-1}·s^{-1}	61.8
$SO_{2,Ni} \rightleftharpoons SO_{2,g} + \square_{Ni}$	$1.0\cdot10^{10}$ s^{-1}	0
YSZ surface reactions		
$H_2O_g + \square_{YSZ} \rightleftharpoons H_2O_{YSZ}$	$6.595\cdot10^{11}$ cm^2·mol^{-1}·s^{-1}	0
$H_2O_{YSZ} + O^{2-}_{YSZ} \rightleftharpoons 2\,OH^{1-}_{YSZ}$	$1.6\cdot10^{25}$ cm^2·mol^{-1}·s^{-1}	164.0
$O^{\times}_{O\,YSZ} + \square_{YSZ} \rightleftharpoons V^{\cdot\cdot}_{YSZ} + O^{2-}_{YSZ}$	$1.6\cdot10^{22}$ cm^2·mol^{-1}·s^{-1}	91.0
Charge-transfer reaction		
$H_{Ni} + OH^{1-}_{YSZ} - \rightleftharpoons \square_{Ni} + e^- + H_2O_{YSZ}$	$0.34\cdot10^{20}$ cm^2·mol^{-1}·s^{-1}	181.4

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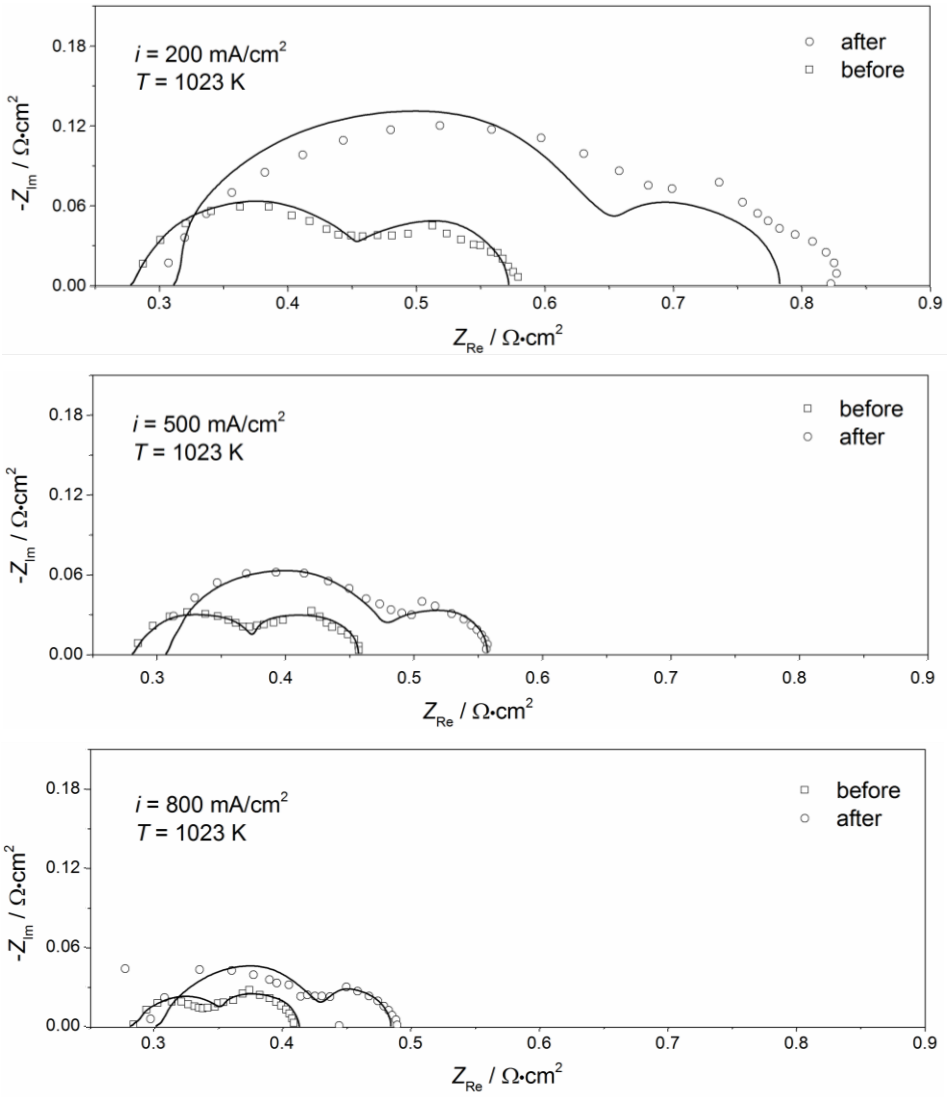
Sulfur poisoning in H_2/H_2O fuels: Impedance modeling

- Impedance measurements of ASC at 1023 K and different *i*



- Button cell configuration with
  - 500 µm Ni/YSZ anode
  - 10 µm YSZ electrolyte
  - 30 µm LSCF cathode

- Gas phase composition:

50 % H_2, 1.5 % H_2O, 48.5 % N_2

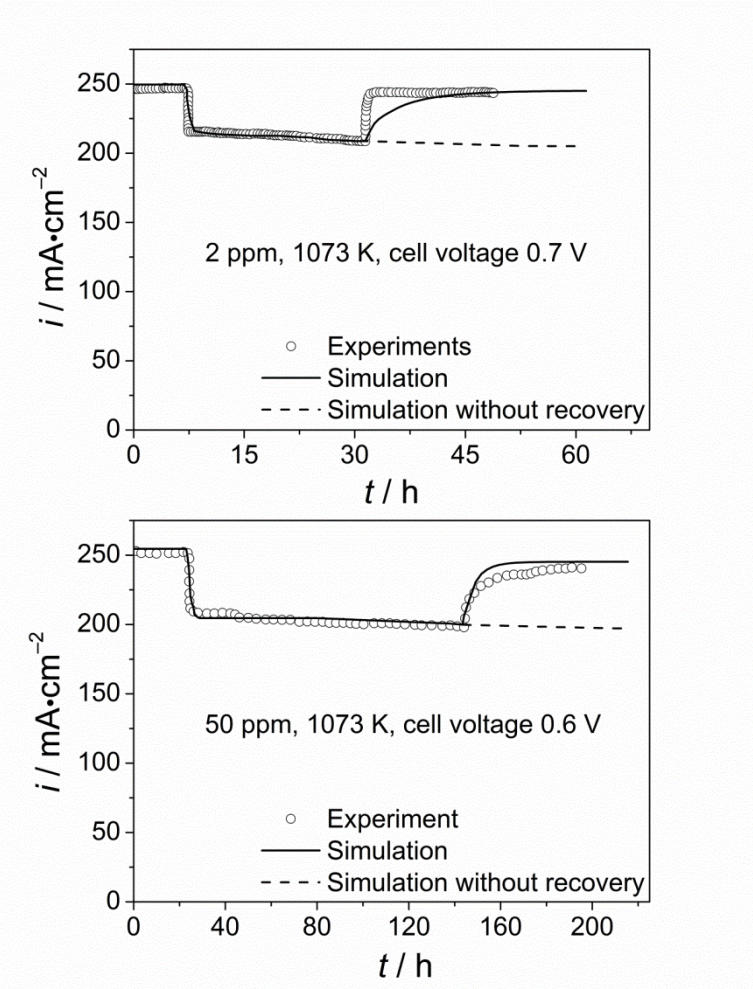
1 ppm H_2S

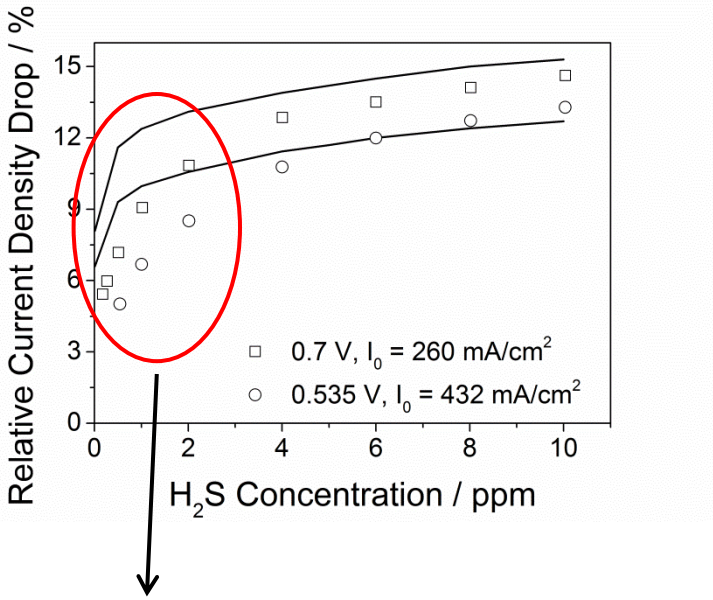
- Good agreement between simulations and experiments for systems with and without sulfur

Exp.: Yang et al., *Energy & Environmental Science*, 3, (2010) 1804

Sulfur poisoning in H_2/H_2O fuels: Performance drops

- Button cell configuration with 50 µm Ni/YSZ, 250 µm YSZ and 50 µm LSM
- Gas composition: 50 % H_2, 1.5 % H_2O, 48.5 % N_2, T = 1073 K



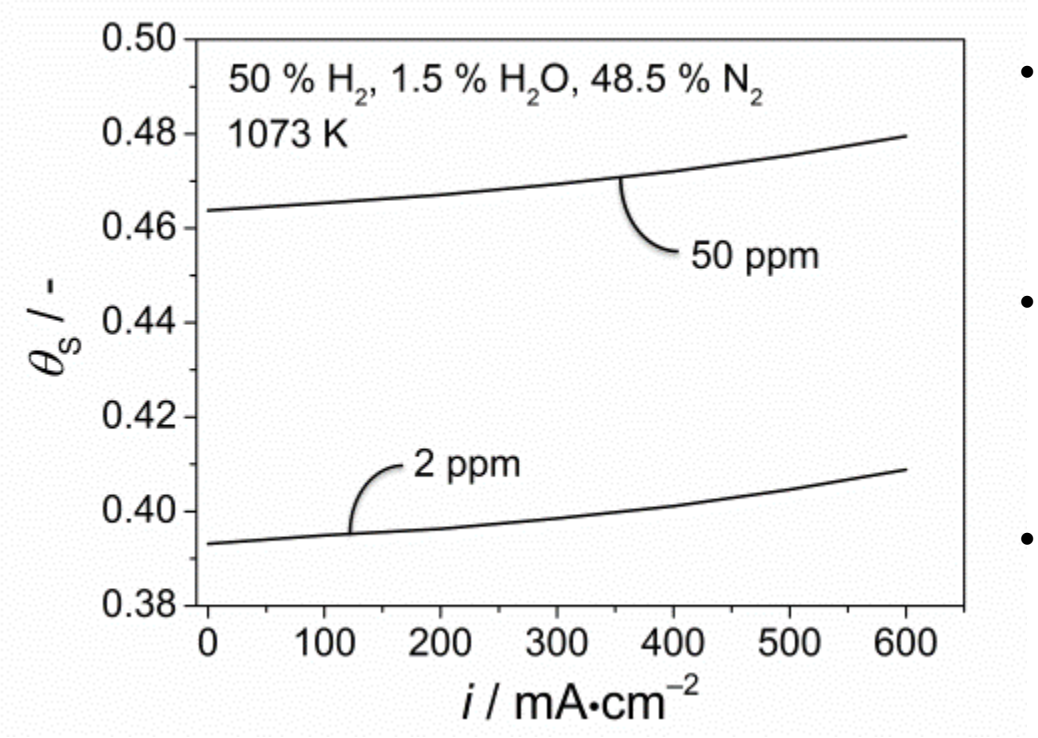


- Deviations for small H_2S concentrations
- <u>Good overall agreement</u>

Exp.: Zha et al., *J. Electrochem. Soc.*, 2007, 154, B201

Sulfur poisoning in H_2/H_2O fuels: Sulfur coverage

- Button cell configuration with 50 µm Ni/YSZ, 250 µm YSZ and 50 µm LSM
- Gas composition: 50 % H_2, 1.5 % H_2O, 48.5 % N_2, T = 1073 K



- Literature [1–3]: Decrease of relative polarization resistance with current density
- Suggestion: Electrochemical oxidation of sulfur

$$S + 2O^{2-} \rightleftharpoons SO_{2,g} + 4e^-$$

- However, sulfur coverage increases with current density

1. Cheng et al., *J. Power Sources*, 172, (2007), 688; 2. Zha et al., *J.Electrochem. Soc*., 154, (2007), B201;
3. Brightman et al., *J.Power Sources*, 196, (2011), 7182;

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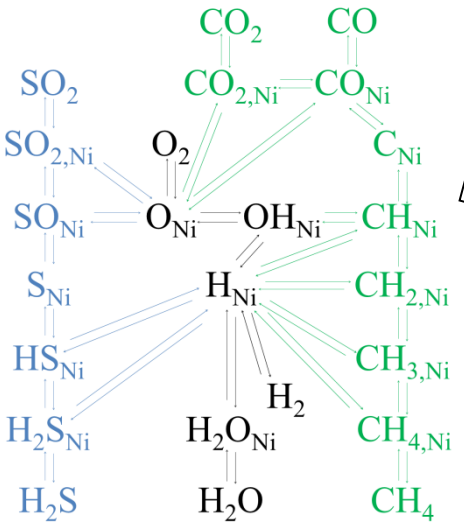
Sulfur poisoning of internal methane steam reforming



- Reaction mechanism for sulfur poisoning in H_2/H_2O systems

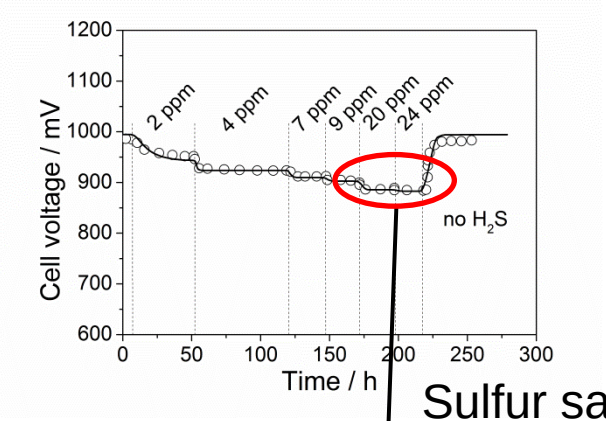
- Elementary kinetic reaction mechanism for methane reforming on Ni/YSZ [1]
- Global reactions:
  - Methane steam reforming
    $$CH_4 + H_2O \rightleftharpoons 3H_2 + CO$$
  - Water gas shift reaction
    $$CO + H_2O \rightleftharpoons H_2 + CO_2$$
  - Methane dry reforming
    $$CH_4 + CO_2 \rightleftharpoons 2H_2 + 2CO_2$$
- 42 surface reactions, 6 gases, 14 surface species

1. Hecht et al., *Appl. Cat. A*, 295 (2005), 40

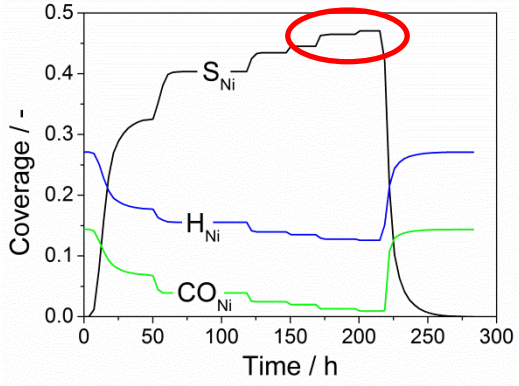
Sulfur poisoning of internal methane steam reforming

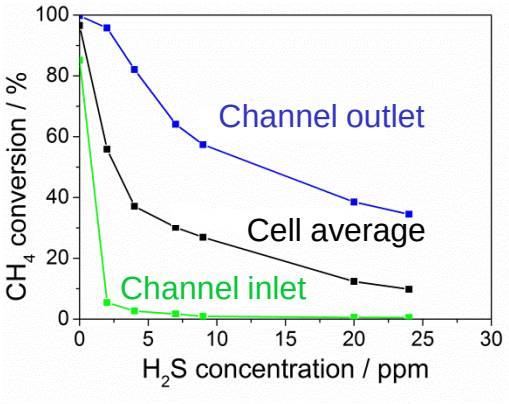
Rasmussen, Hagen [1]:

- Sulfur poisoning of methane steam reforming in ASC at T = 850°C
- Transient poisoning experiments <u>at OCV</u>



Sulfur saturation on Ni surface



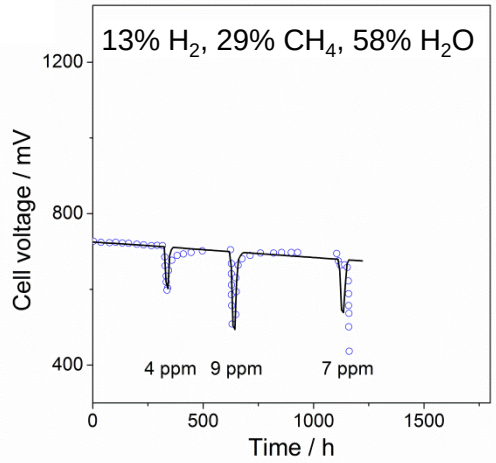


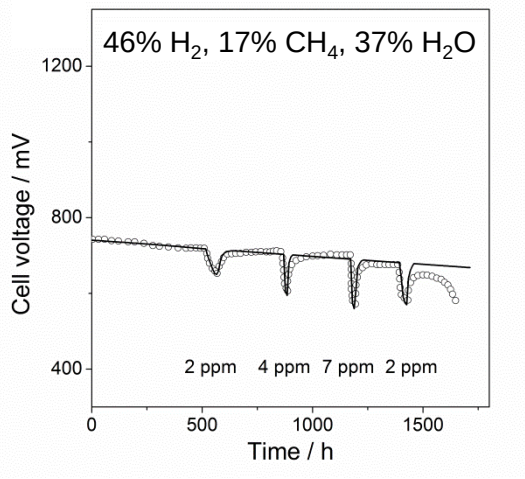
- CH_4 conversion is nearly fully blocked at channel inlet
- Still significant reforming activity at channel outlet

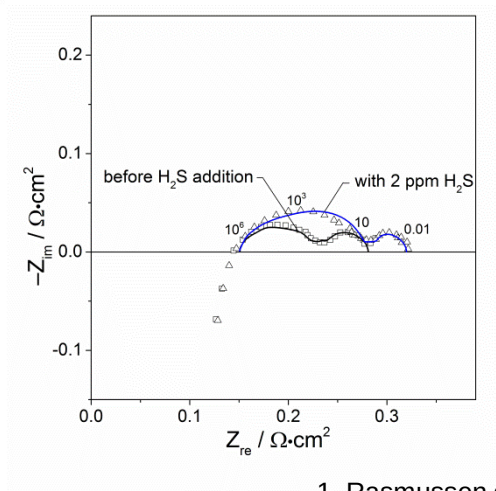
1. Rasmussen et al., *Fuel Cells*, 10, 2010, 1135

Sulfur poisoning of internal methane steam reforming

- Transient poisoning experiments under current load (i =1 A•cm^{-2})
- Impedance spectroscopy measurements





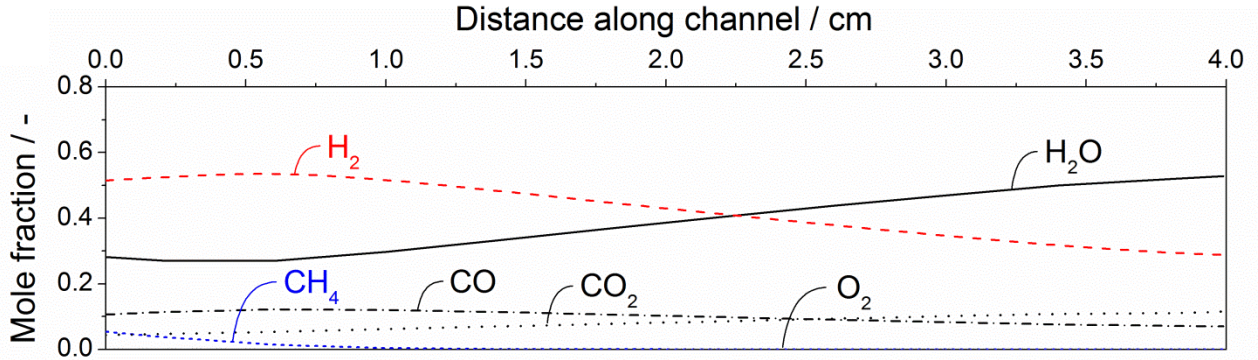


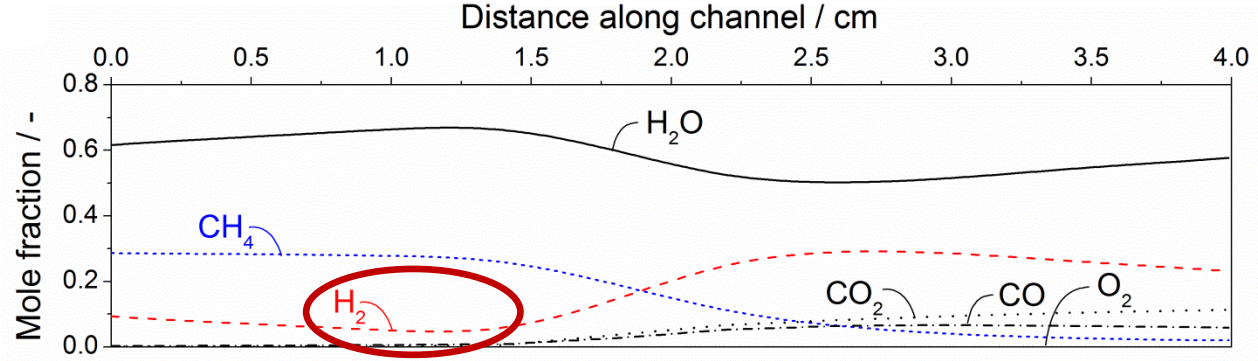
- Successful reproduction of experiments at OCV and under polarization

1. Rasmussen et al., *Fuel Cells*, 10, 2010, 1135

Sulfur poisoning of internal methane steam reforming: Gas phase species distribution

Detailed analysis: Gas phase distribution along the channel
T = 850 °C; i =1 A•cm^{-2}; 13 % H_2, 29 % CH_4, 58 % H_2O





- Without H_2S
- Rapid CH_4 reforming

- 2 ppm H_2S
- Danger of fuel starvation

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Summary and conclusions

- An elementary kinetic reaction mechanism has been developed and validated for sulfur poisoning of Ni/YSZ anodes
    - H_2/H_2O systems
    - Internal methane steam reforming
- A thermodynamic and kinetic data set has been compiled
- Sulfur coverage increases with increasing current density
- Own experiments are required for more profound investigation

Acknowledgments

- German network project: “*SOFC Degradation*”
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Thank you for your attention!

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