Understanding electro-catalysis to design perovskite based electrodes for Solid Oxide Cells

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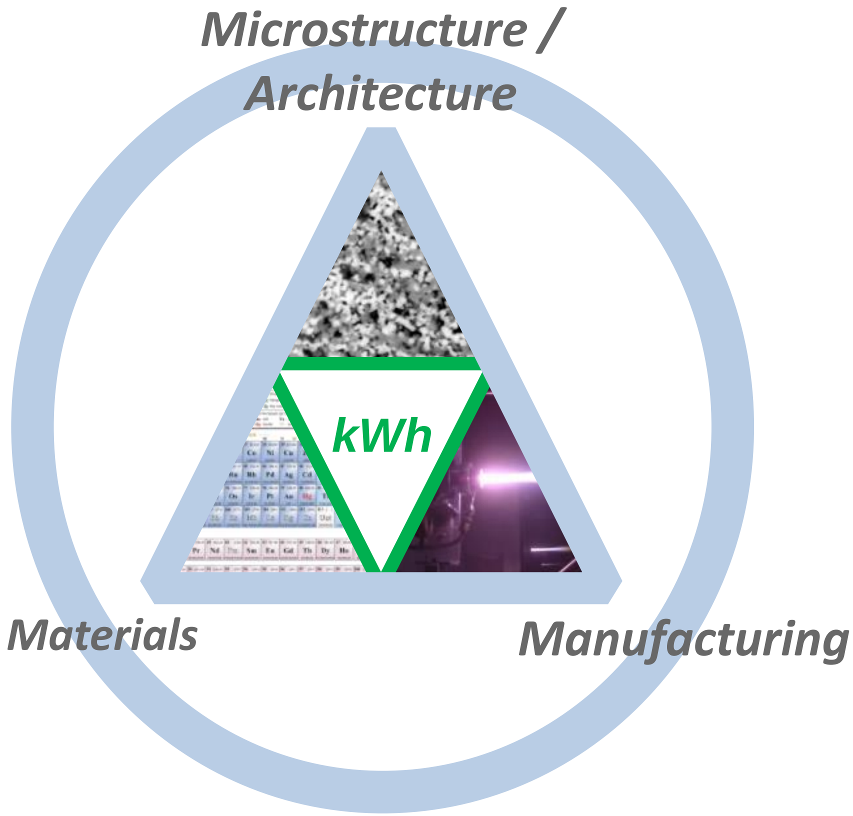
High Temperature Solid Oxide Cells

- Conversion at high efficiency
- Power Generation **(> 60 % net)**
- Possibility to co-electrolyse **H_2O / CO_2** into syngas
- **SOC are reversible**
  Same materials/catalysts for SOFC & SOE operation



Do SOFC perform well in Electrolysis? Specific degradation mechanisms? May optimized SOFC be further optimized for SOE operation?

Motivation – *Power generation*

Natural Gas

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

Sulfur compounds

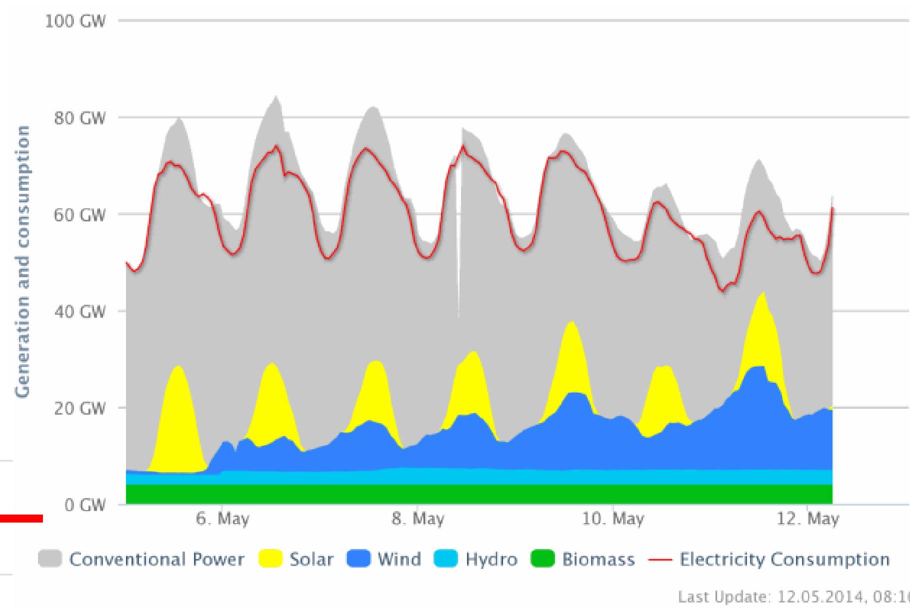
Diesel

➢ Upstream desulfurizing unit
➢ **Failure of desulfurizing unit?**

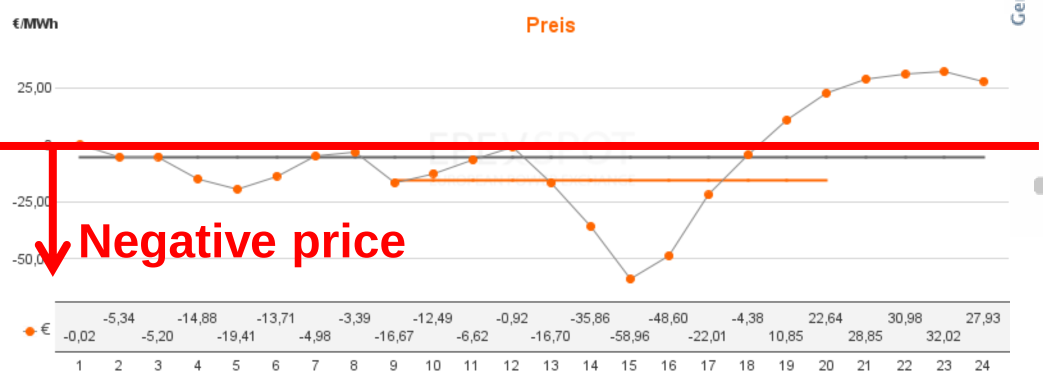
Motivation – *Power-to-X* ?

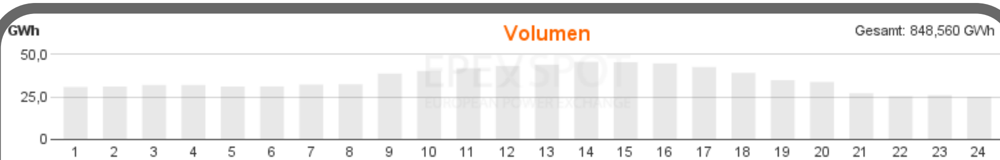
High penetration of renewables induces mismatch between electricity generation and electricity consumption

Generation and Consumption of electricity in Germany 5th-12th of May 2014



Electricity price on the DE-AT market on ***1st of May 2018*** *(Source EPEX)*





ca. 849 GWh at – 5€/MWh

The energy transition requires large energy storage capacities

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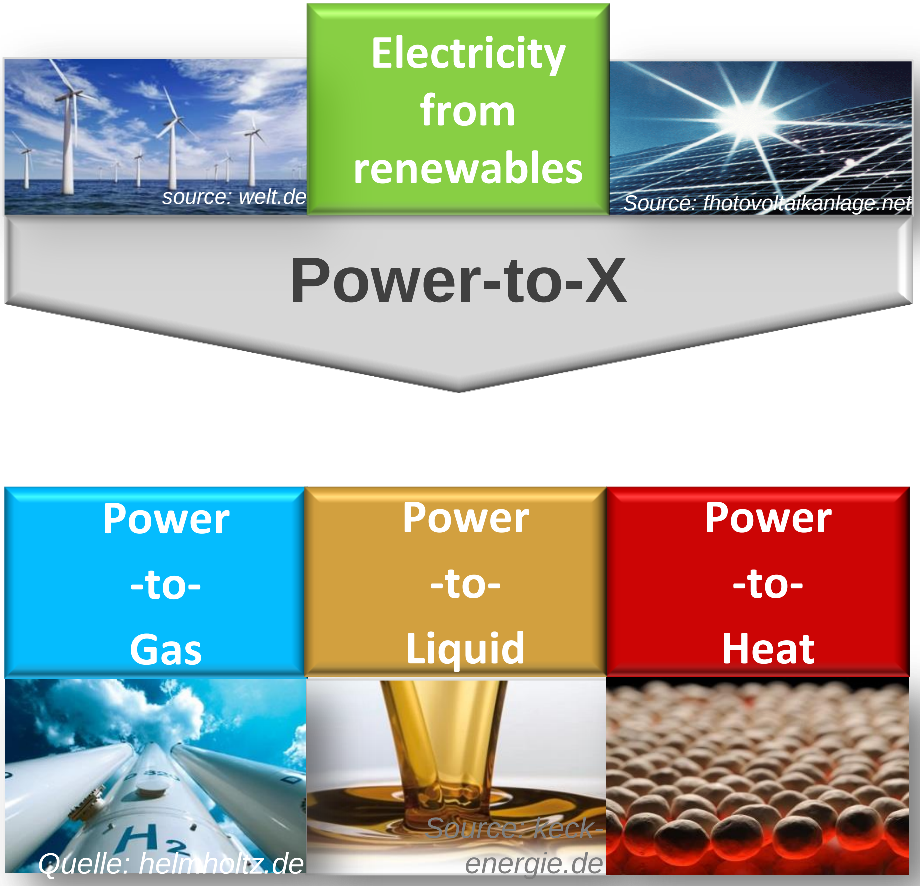
Power-to-X – What is beyond the X ?

- Store the surplus of energy in alternative vectors ***(hydrogen, fuels, heat…)***
- Delocalize in the space and in the time the release of the energy surplus ***(other infrastructures)***
- Place the kWh of stored energy **on other markets** with higher potential of gains



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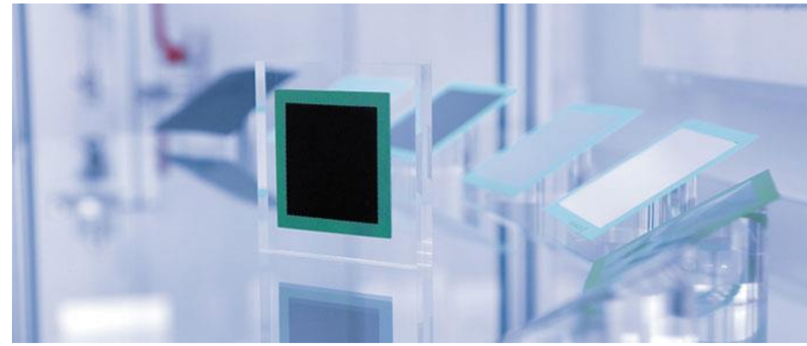
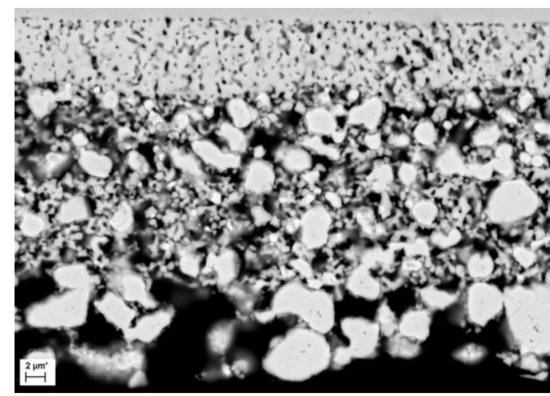
State of the Art

Anode Supported Cell:
Substrate **Ni-3YSZ**: ~ 300µm
AFL **Ni-8YSZ**: ~ 10µm
Electrolyte **8YSZ**: ~ 10 µm
Barrier layer **CGO**: ~ 5µm
Air electrode **LSCF**: ~ 30 µm



Electrolyte Supported Cell
Contact Layer **Ni(CGO)**: ~10µm
AFL **Ni-CGO**: ~ 10µm
Adhesion layer **CGO**: ~ 5µm
Electrolyte **3YSZ**: ~ 90 µm
Barrier layer **CGO**: ~ 5-10µm
Air electrode **LSCF**: ~ 40 µm
Contact Layer **LSMC**:~10µm



ESC from Kerafol GmbH

Do SOFC perform well in Electrolysis? Specific degradation mechanisms? May optimized SOFC be further optimized for SOE operation?

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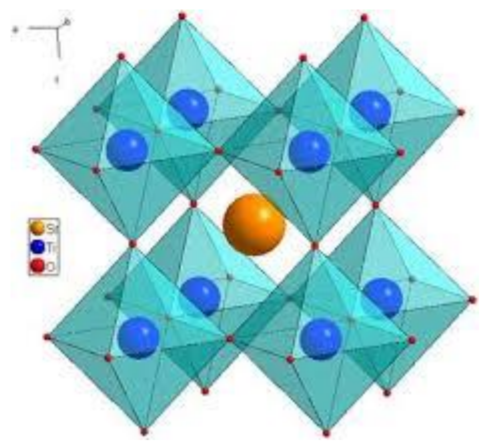
Air Electrode:
Lanthanum Strontium Cobalt Iron perovskite
mixed ionic and electronic conductor



Air Electrode

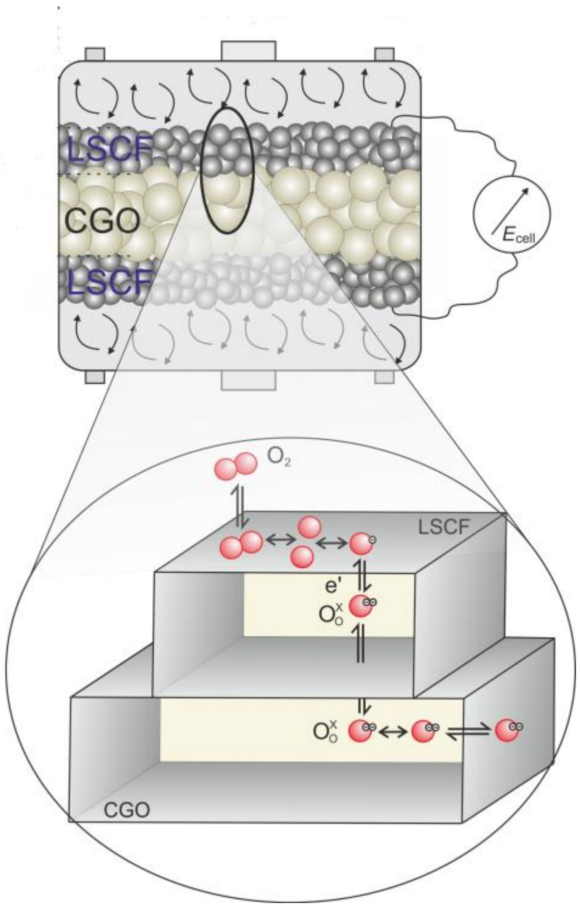
$1/2\ O_2 + 2e^- \rightarrow O^{2-}$

$\sigma_{CGO}\ (e^-) \approx \sigma_{CGO}\ (O^{2-})$

$\sigma_{LSCF}\ (e^-) \geq \sigma_{LSCF}\ (O^{2-})$

Porous Composite Gadolinia Doped Ceria – Lanthanum Strontium Cobalt Iron Oxide

Air Electrode : LSCF-CGO based materials



Reaction mechanism

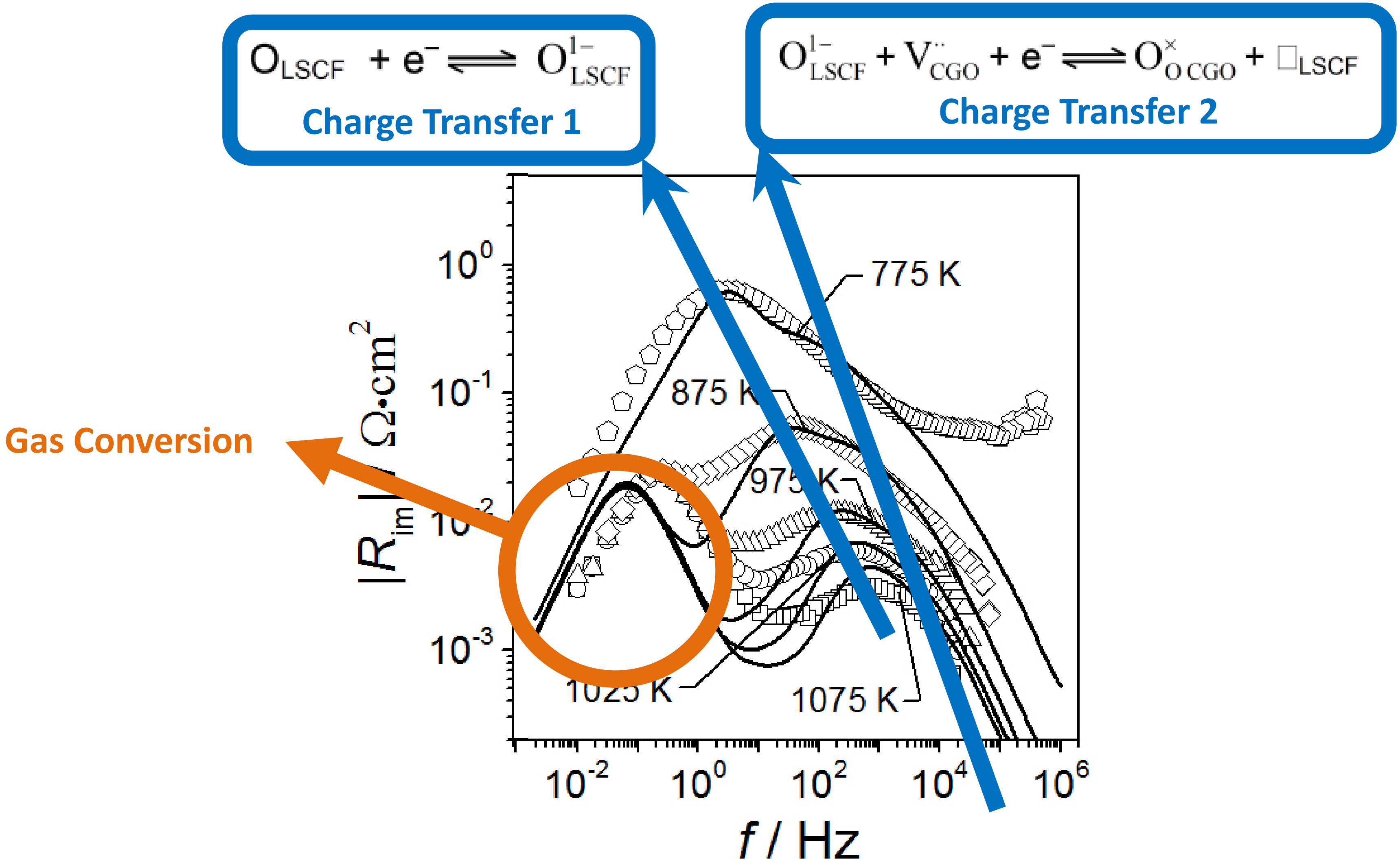
No.	Reaction	k^0 (or s_i^0)	E^{act} (kJ·mol^{-1})
LSCF phase			
R1	$O_2 + \square_{LSCF} \rightleftharpoons O_{2,\,LSCF}$	$s_i^0 = 5.0\cdot10^{-1}$	0
R2	$O_{2,\,LSCF} + \square_{LSCF} \rightleftharpoons 2\cdot O_{LSCF}$	$1.0\cdot10^{22}$ cm^2·mol^{-1}·s^{-1}	20
CGO phase			
R3	$O^{2-}_{CGO} + V^{\cdot\cdot}_{CGO} \rightleftharpoons O^{\times}_{O\,CGO} + \square_{CGO}$	$1.6\cdot10^{22}$ cm^2·mol^{-1}·s^{-1}	90.9
Charge-transfer reactions			
C1	$O_{LSCF} + e^- \rightleftharpoons O^{1-}_{LSCF}$	$1.4\cdot10^{16}$ cm^2·mol^{-1}·s^{-1}	181.4
C2	$O^{1-}_{LSCF} + V^{\cdot\cdot}_{CGO} + e^- \rightleftharpoons O^{\times}_{O\,CGO} +$	$8.9\cdot10^{15}$ cm^2·mol^{-1}·s^{-1}	99.7

Reaction kinetics and thermodynamics derived

Experimental data recorded on ***symmetrical button cell (CGO electrolyte)*** with ***LSCF & LSCF I CGO composite cathodes***

V. Yurkiv *et al*, *JES*, 161(4), F480 (2014)

Air Electrode : LSCF-CGO based materials



V. Yurkiv, *et al.*, *JES*, 161(4), F480 (2014)

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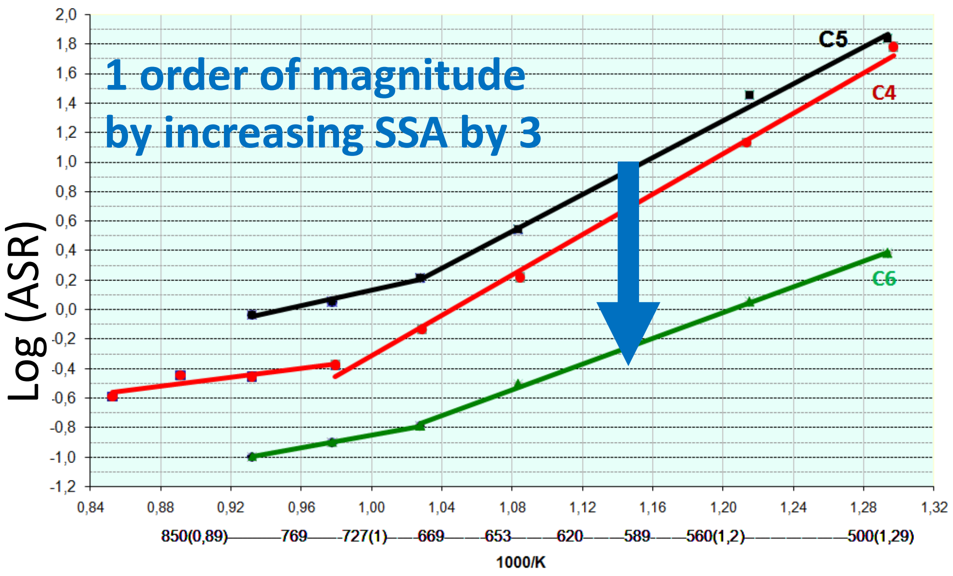
Air Electrode : LSCF-CGO based materials

Performance governed by the surface of exchange between:

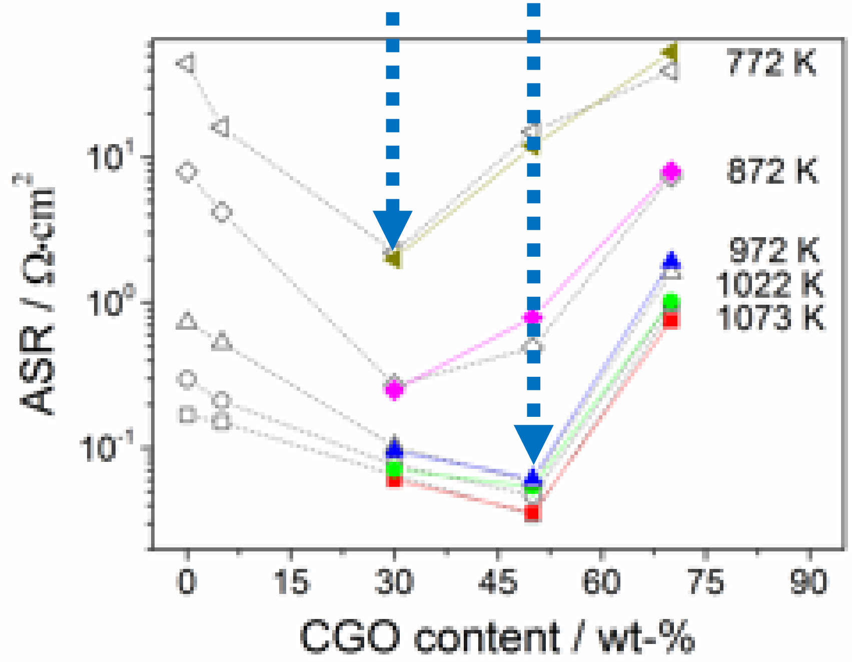
(1) between the LSCF and gas phase : Increase Specific Surface Area of LSCF

(2)between LSCF and CGO : Composite electrode LSCF-CGO

(1)



(2)



>>>> Composite LSCF-CGO with surface modification <<<<
>>>> CGO content to be adapted as a function of op. T <<<<

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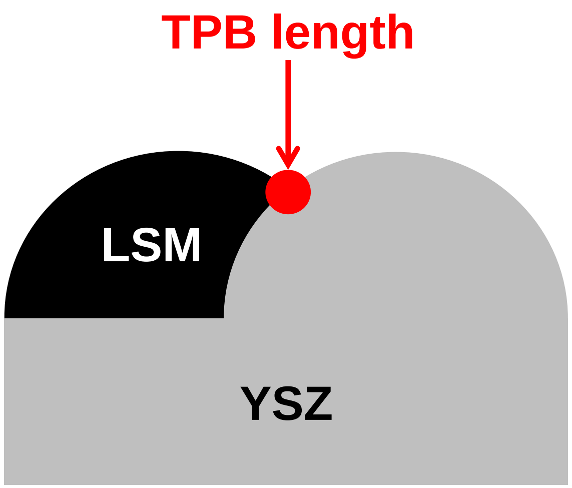
Air Electrode : LSCF - CGO based materials

LSM - YSZ

$\sigma_{YSZ}\,(O^{2-}) >> \sigma_{YSZ}\,(e^{-})$

$\sigma_{LSM}\,(e^{-}) >> \sigma_{LSM}\,(O^{2-})$

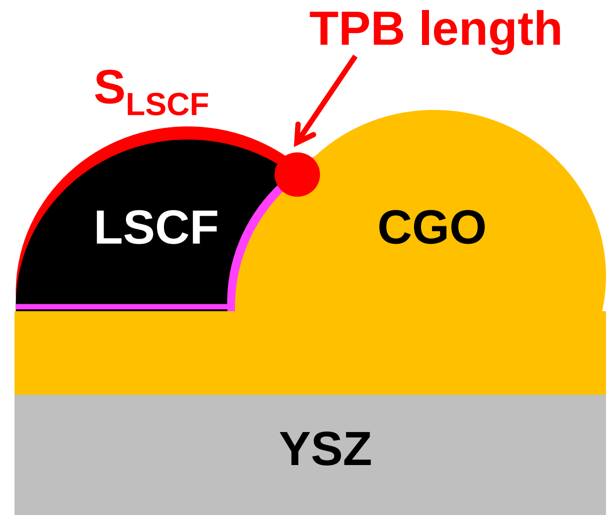


TPB

LSCF - CGO

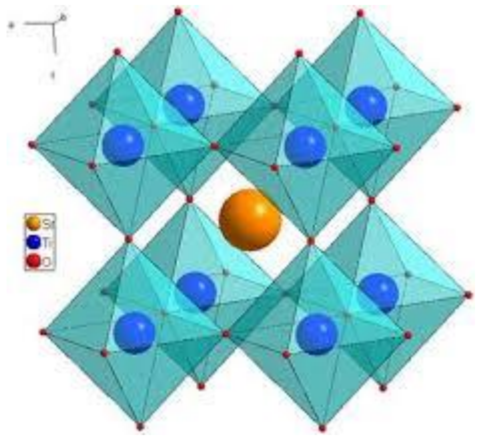
$\sigma_{CGO}\,(e^{-}) \approx \sigma_{CGO}\,(O^{2-})$

$\sigma_{LSCF}\,(e^{-}) \geq \sigma_{LSCF}\,(O^{2-})$



TPB + LSCF surface(s)

Fuel electrode:
Lanthanum doped Strontium Titanate (LST)
"mixed" ionic and electronic conductor



Fuel Electrode

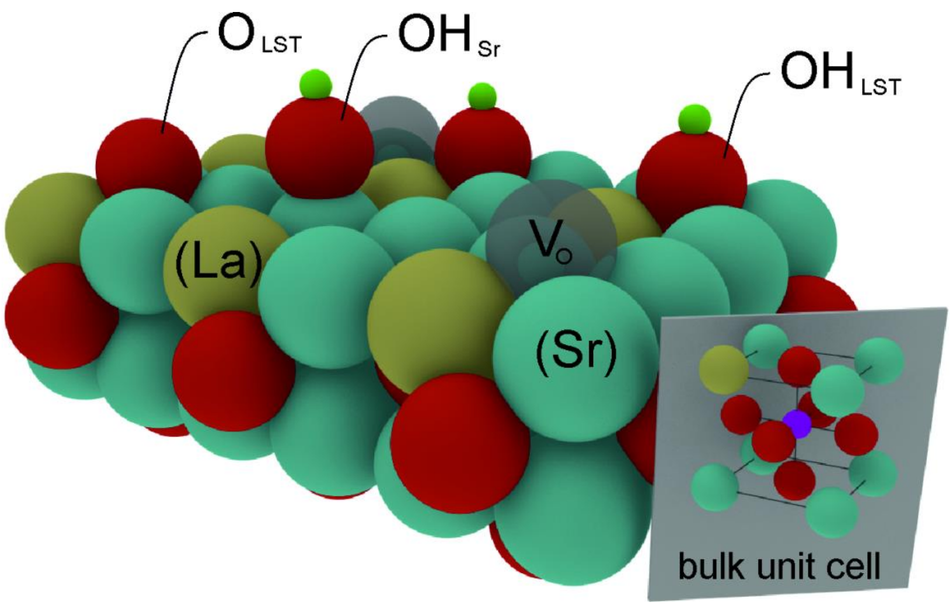
$H_2 + O^{2-} \rightarrow H_2O + 2e^-$

$\sigma_{GDC}\,(O^{2-}) \approx \sigma_{GDC}\,(e^-)$
$\sigma_{LST}\,(e^-) \geq \sigma_{LST}\,(O^{2-})$

Porous Composite Gadolinia Doped Ceria – Lanthanum doped Strontium Titanate

sulfur tolerance
redox stable (dimensionally)

Lanthanum doped Strontium Titanate (LST) Fuel Electrode



$$H_2 + 2\,O_{LST} \rightleftharpoons OH_{LST} + OH_{LST}$$

$$H_2O + O_{LST} + \square_{LST} \rightleftharpoons 2\,OH_{LST}$$

$$O_{LST} + O_{LST} \rightleftharpoons O_2 + \square_{LST}$$

- Perovskite structure with cubic unit cell
- 5 atoms at surface – only one oxygen
- $6.7\cdot10^{18}$ sites·m^{-2} which lead to total surface site density of $1.0\cdot10^{-5}$ mol·m^{-2}
- Types of species:
  - Two types of surface sites O_{LST},
  - Two hydroxyl groups: **OH_{LST}**, OH_{Sr}
  - Theoretically OH group can exist at La surface site
  - Hydrogen adsorbed on Sr site, H_{Sr} (hydride)

V. Yurkiv, G. Constantin, A. Hornes, A. Gondolini, E. Mercadelli, A. Sanson, L. dessemond, R. Costa, J. Power Sources (2015), 287, 58

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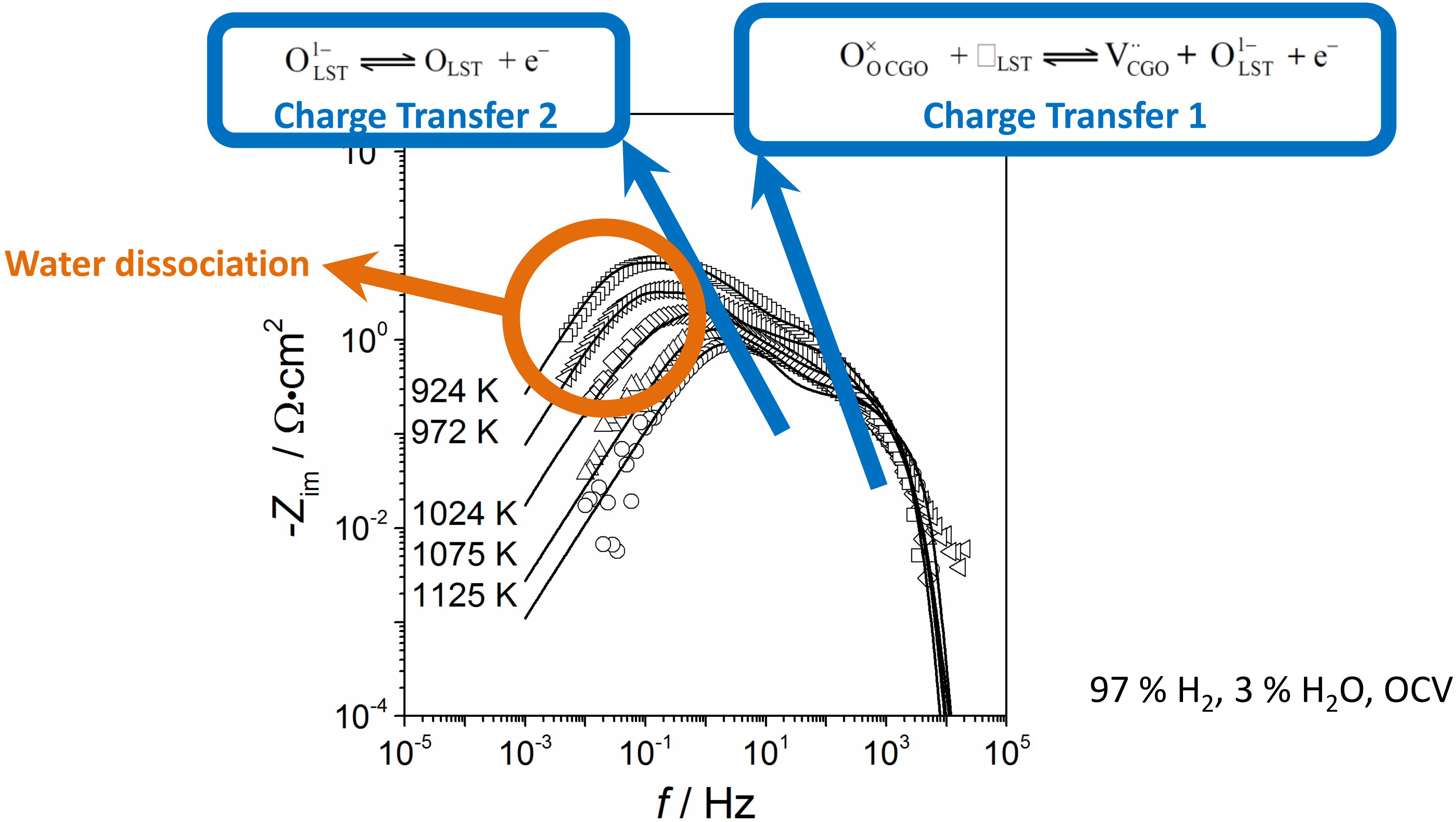
Lanthanum doped Strontium Titanate (LST) Fuel Electrode



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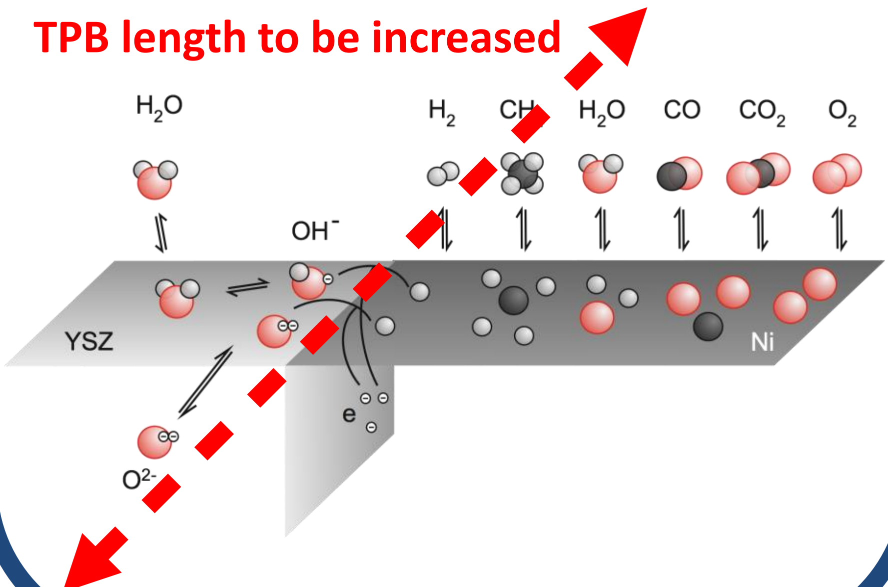
Ni-YSZ vs LST-CGO anode / CGO not MIEC

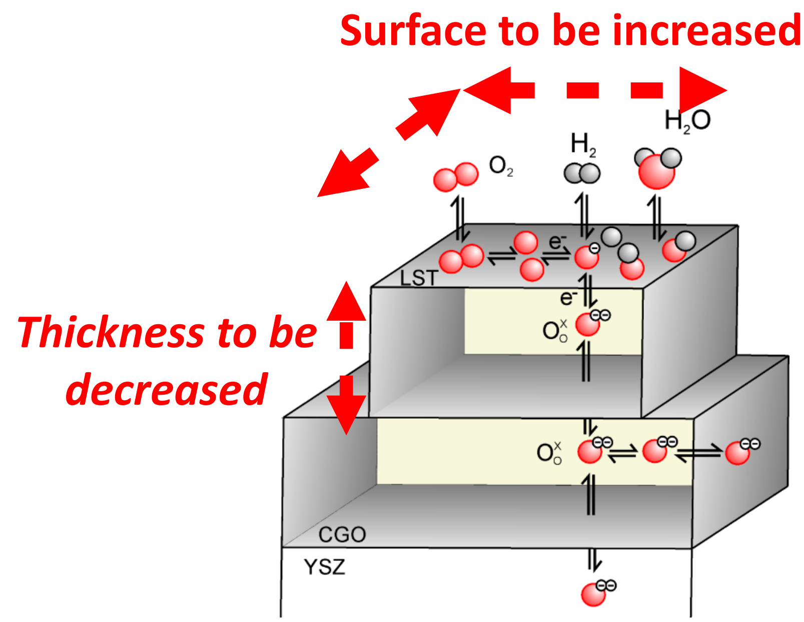
Ni-YSZ

- Hydrogen Charge Transfer is the rate limiting step
- Performance is governed by the length of triple phase boundaries



LST-CGO

- Oxygen Charge Transfer is rate limiting
- Performance is governed by surfaces of exchange (LST I CGO & LST I Gas)

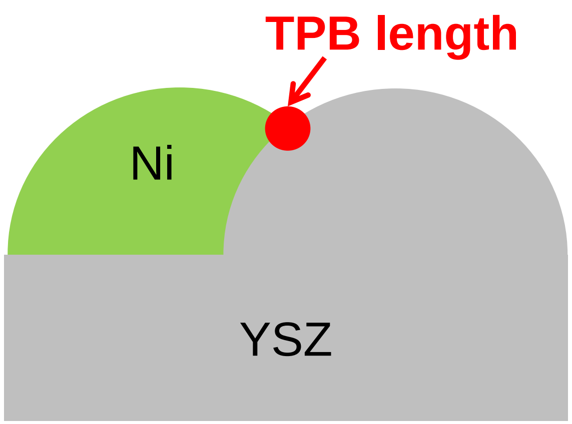


Case Study - Sulfur Poisoning

Ni-YSZ

$\sigma_{YSZ}\,(O^{2-}) >> \sigma_{YSZ}\,(e^{-})$

$\sigma_{LSM}\,(e^{-}) >> \sigma_{LSM}\,(O^{2-})$

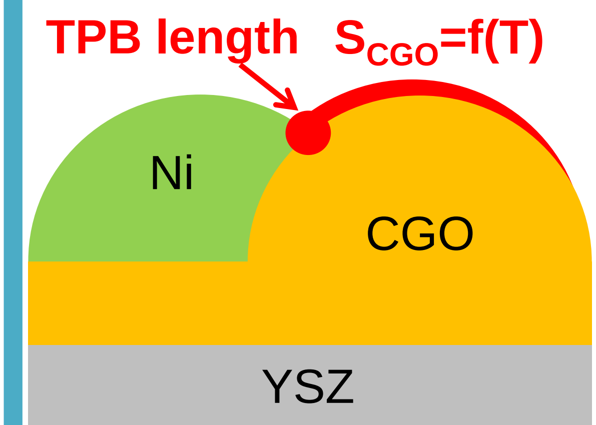


TPB

Ni-CGO

$\sigma_{CGO}\,(O^{2-}) \approx \sigma_{CGO}\,(e^{-})$

$\sigma_{Ni}\,(e^{-}) >> \sigma_{Ni}\,(O^{2-})$

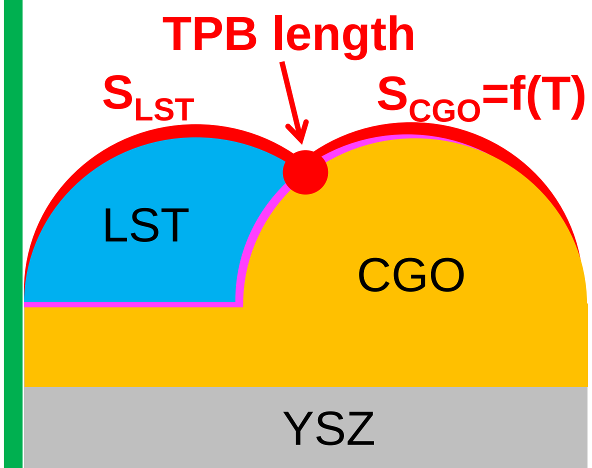


T < 600°C (?)
TPB
T >600°C (?)
TPB + CGO surface

LST-CGO

$\sigma_{CGO}\,(O^{2-}) \approx \sigma_{CGO}\,(e^{-})$

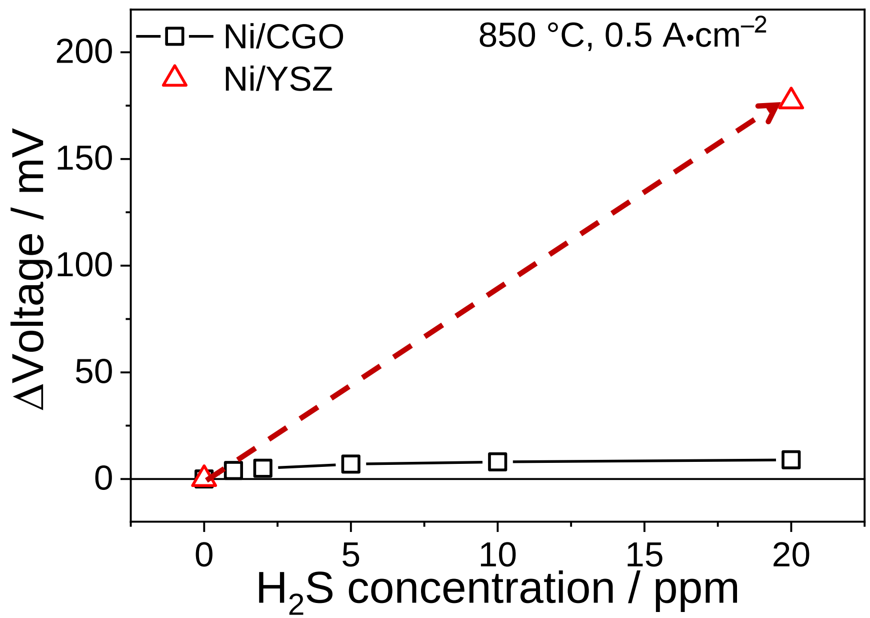
$\sigma_{LST}\,(e^{-}) \geq \sigma_{LST}\,(O^{2-})$

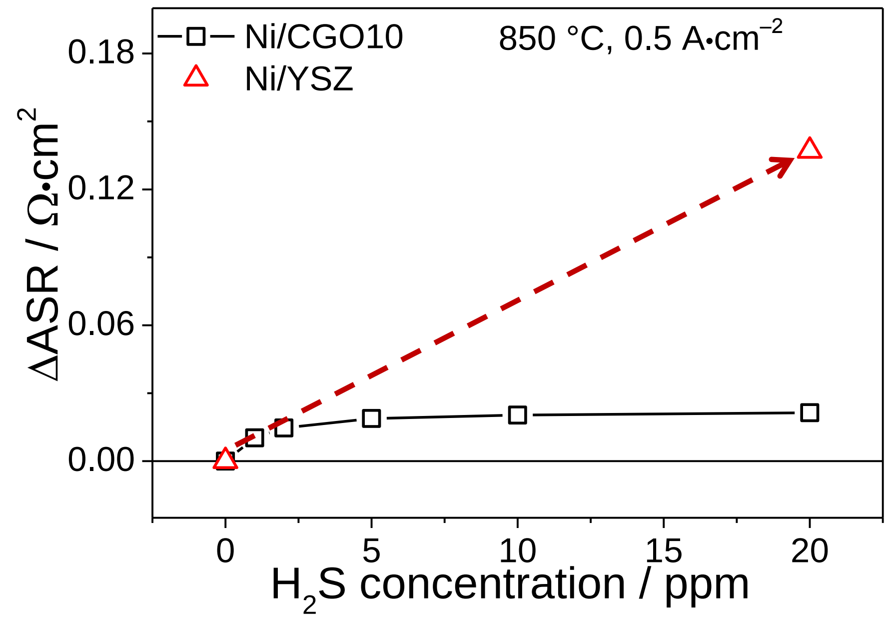


T < 600°C (?)
TPB + LST surface(s)
T > 600°C (?)
TPB + LST surface(s)
+ CGO surface

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

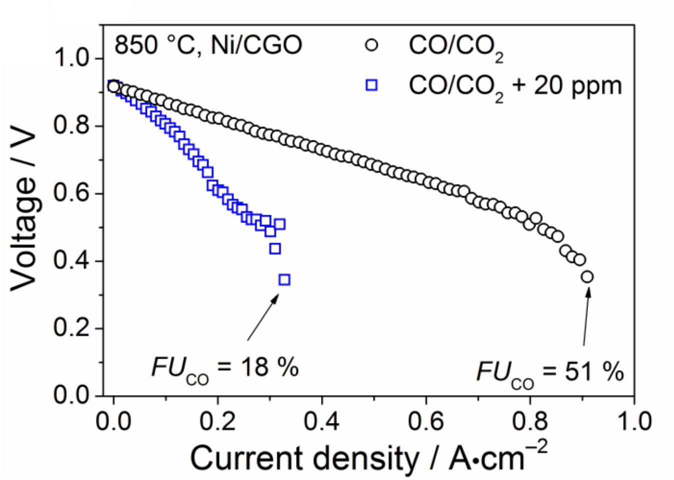
850 °C, 0.5 A•cm^{-2}, 97 % H_2, 3 % H_2O + 1, 2, 5, 10, 20 ppm H_2S

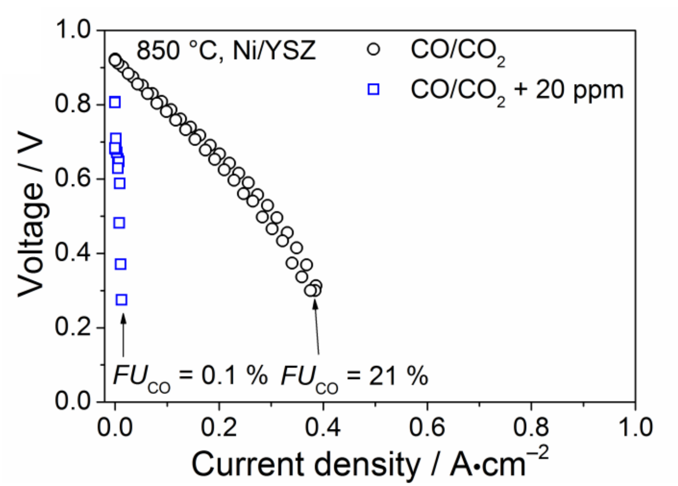




Different mechanisms

CGO as electro-active catalyst





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 sulfur tolerance

Eletrochemical conversion of CO on CGO surface

ACS Catalysis
Research Article
Cite This: ACS Catal. 2017, 7, 7760-7771
pubs.acs.org/acscatalysis

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

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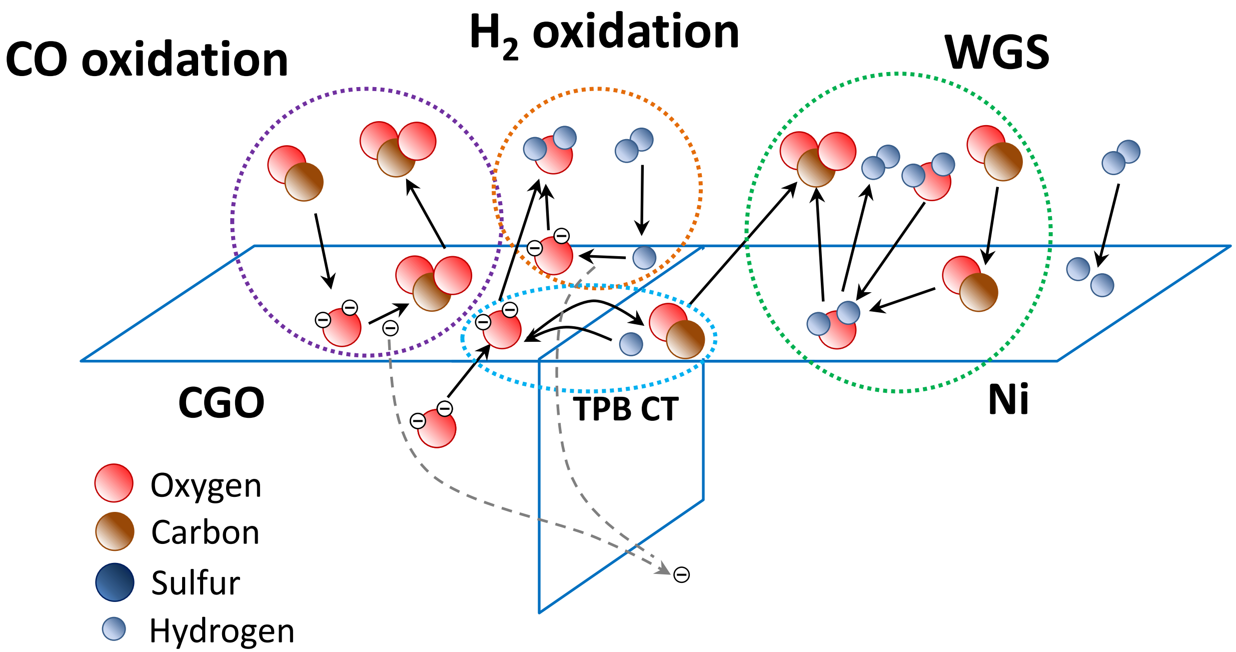
Fuel oxidation mechanism on Ni/CGO



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

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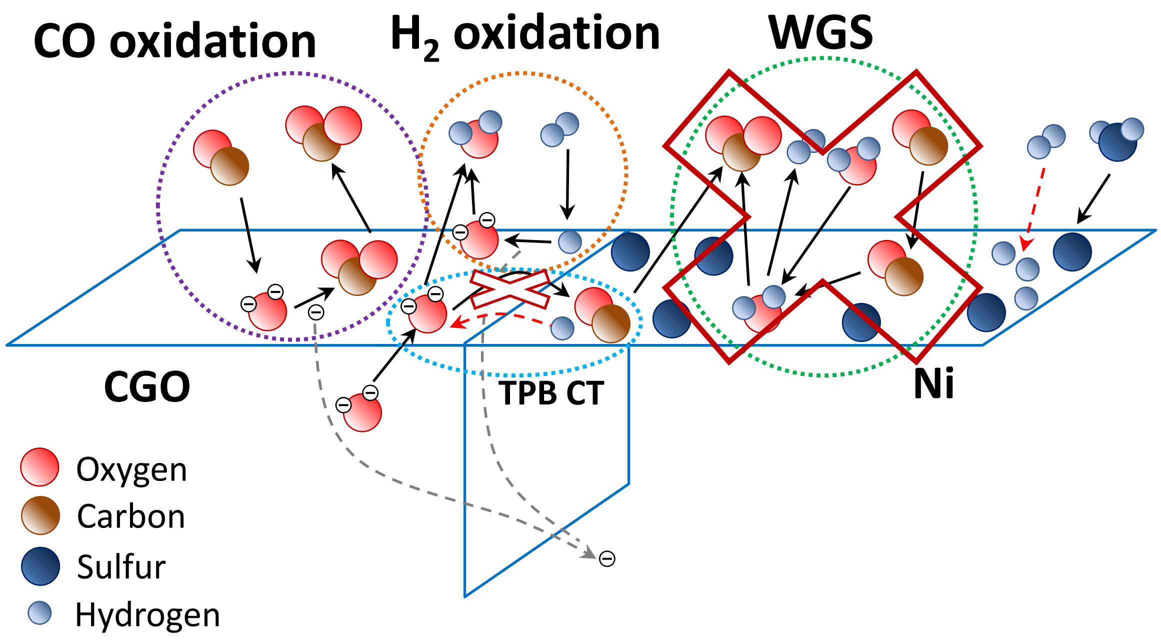
Fuel oxidation mechanism on Ni/CGO under Sulfur poisoning



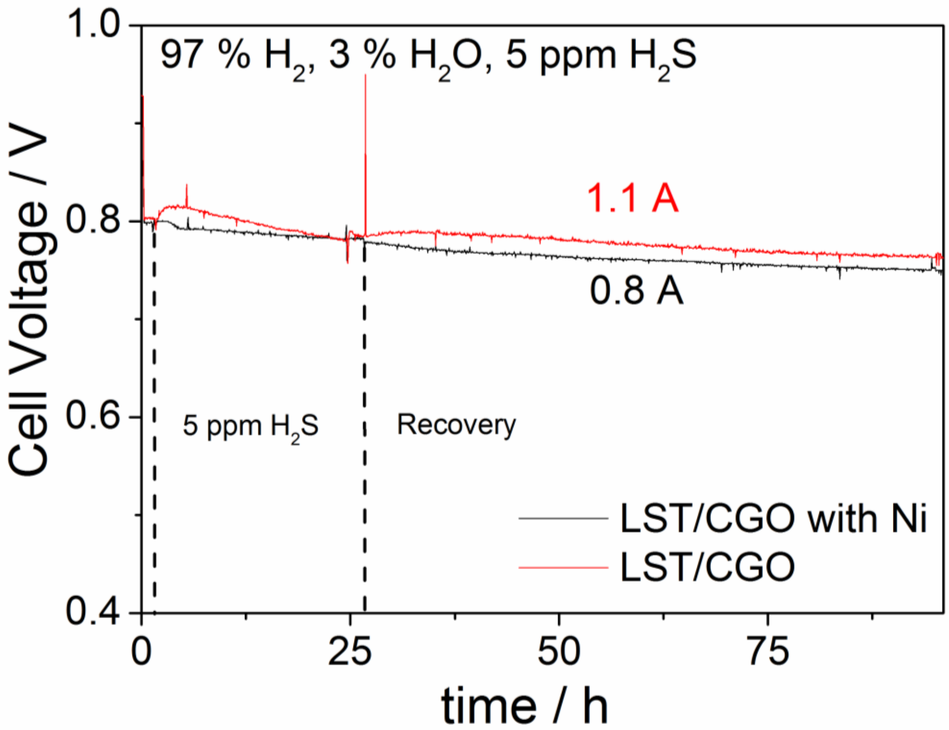
Ce^{4+} / Ce^{3+}

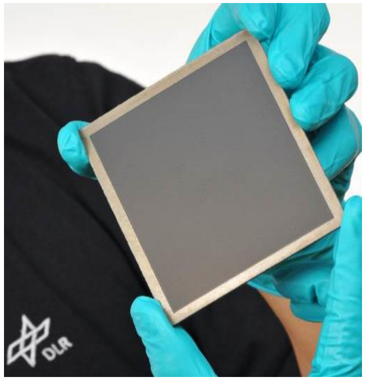
Ni surface is blocked → CO oxidation at TPB deactivated
Surface process on CGO is still active

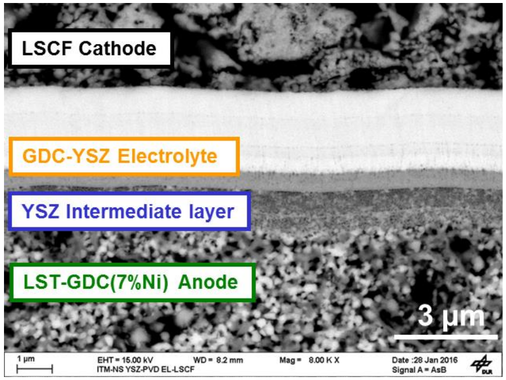
H_2 oxidation at TPB may still be active (smaller atom diameter)

Fuel oxidation mechanism on Ni/LST/CGO: Sulfur poisoning

Metal Supported Cell







LST – CGO seems to react faster to poisoning, higher degradation rate

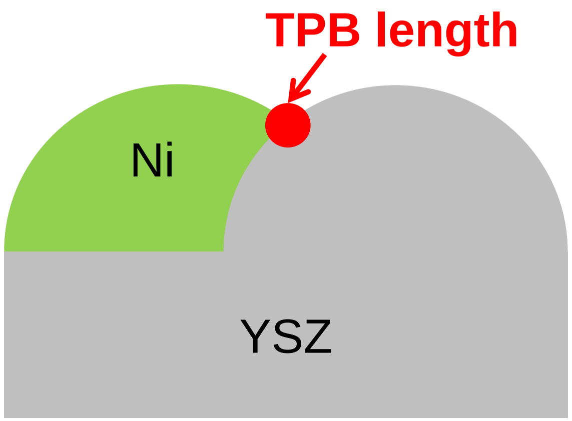
LST – CGO – Ni seems more stable under poisoning conditions

Expected tolerance to Sulfur Poisoning

Ni-YSZ

$\sigma_{YSZ}\,(O^{2-}) >> \sigma_{YSZ}\,(e^{-})$

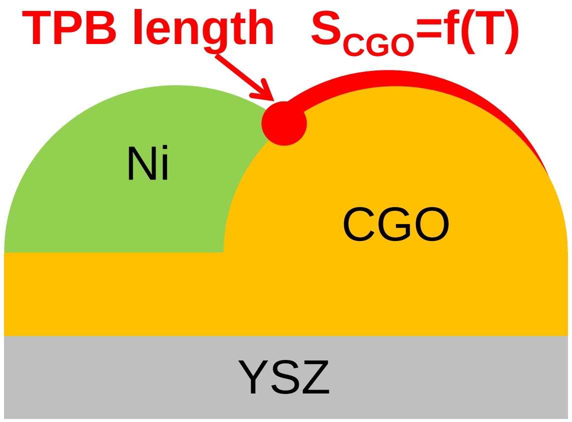
$\sigma_{LSM}\,(e^{-}) >> \sigma_{LSM}\,(O^{2-})$



Ni-CGO

$\sigma_{CGO}\,(O^{2-}) \approx \sigma_{CGO}\,(e^{-})$

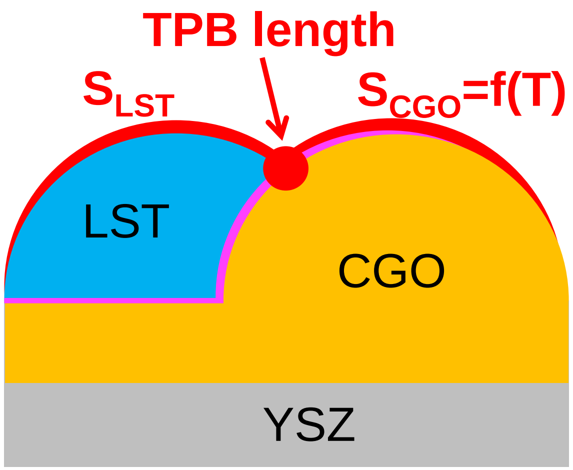
$\sigma_{Ni}\,(e^{-}) >> \sigma_{Ni}\,(O^{2-})$



LST-CGO-Ni

$\sigma_{CGO}\,(O^{2-}) \approx \sigma_{CGO}\,(e^{-})$

$\sigma_{LST}\,(e^{-}) \geq \sigma_{LST}\,(O^{2-})$

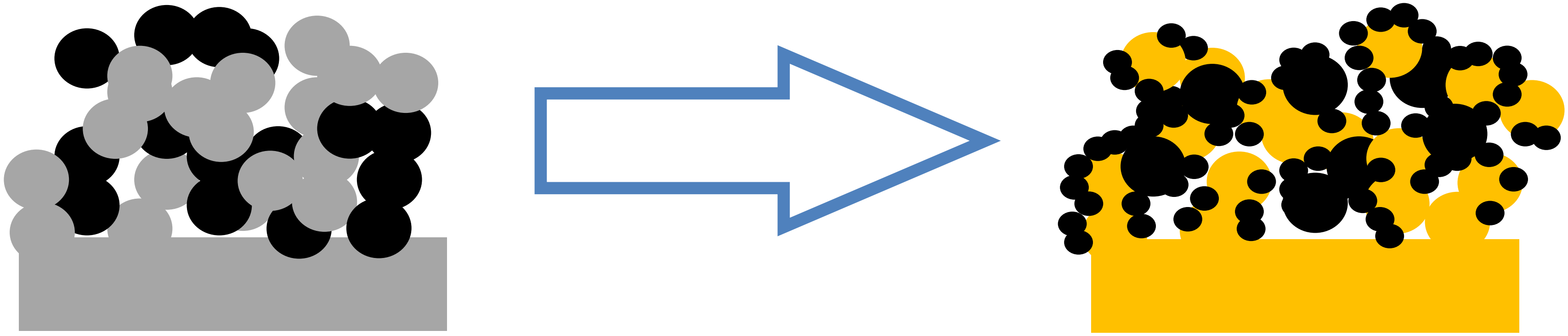


Ni-YSZ	Ni-CGO	LST-CGO-Ni
---	O / +	(++) *tbc*

Summary and conclusions

- **MIEC** materials offer increased electrochemically surfaces
- **TPB length** is not „always“ the critical parameter to control
- **Optimal microstructure may differ depending on operating temperature**

- ***Multiplying reactive surfaces and the nature of those surfaces (metal, oxide) is a key to enhance tolerance of electrodes towards poisons***



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EVOLVE FUEL CELL

FCH FUEL CELLS AND HYDROGEN JOINT UNDERTAKING

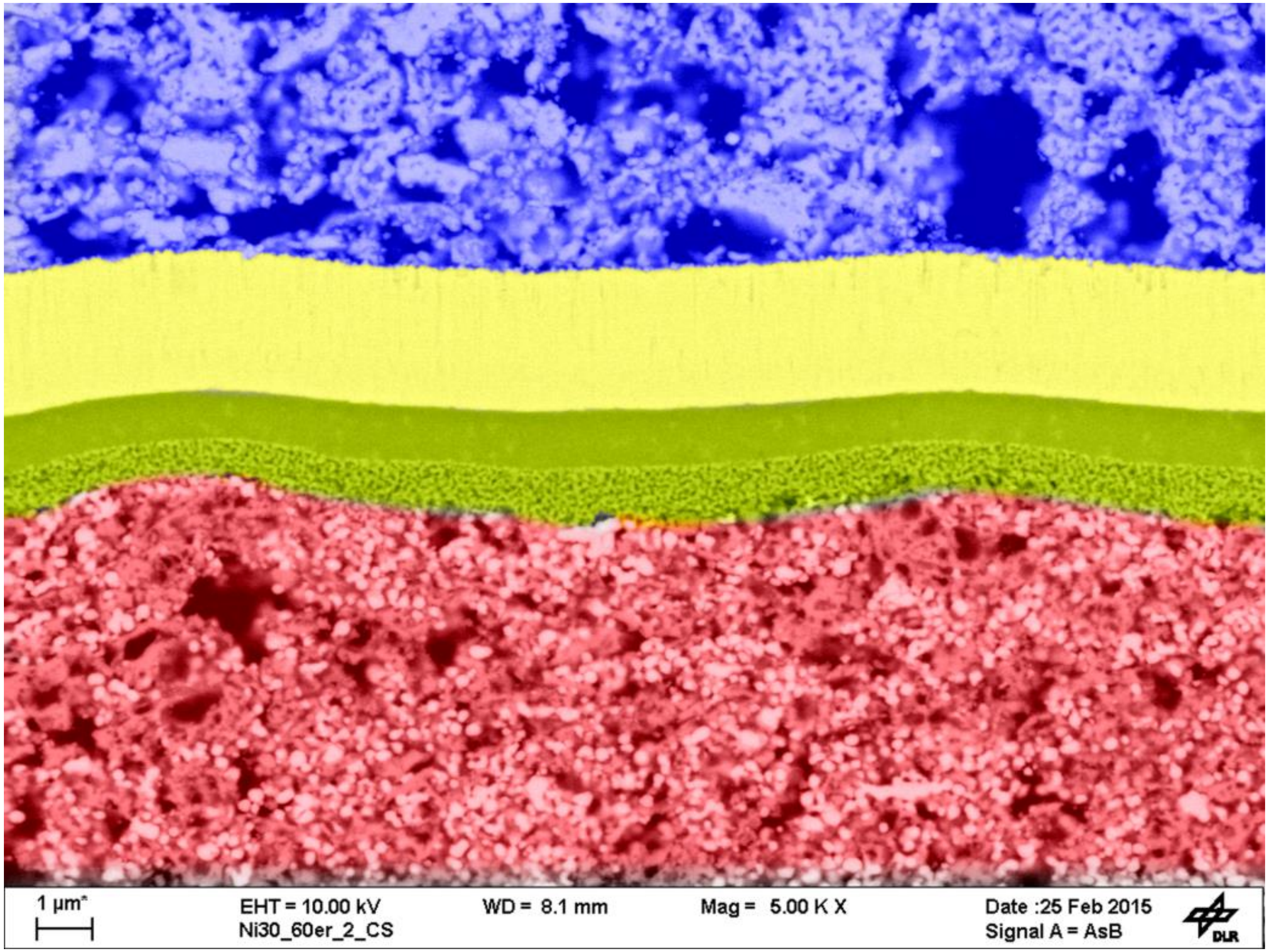
German Federal Ministry for Economy and Industry (BMWi)

Supported by:

Federal Ministry for Economic Affairs and Energy

on the basis of a decision by the German Bundestag

Thanks for your attention!



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