Research Activities towards long-term stable SOFCs at Montanuniversitaet Leoben

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Outline

- **Focus**
  - Long-term investigation ($t < 1000\,h$) of oxygen exchange kinetics of SOFC cathodes in real atmospheres
    - H_2O-, CO_2-, SO_2-containing atmospheres
    - surface poisoning by Cr- and Si-compounds

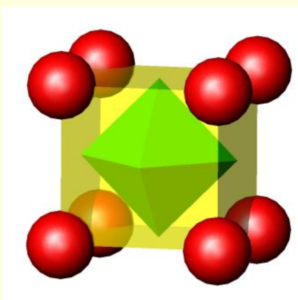
- **Methods**
  - dc conductivity relaxation measurements (k_{chem}, D_{chem}, σ_e)
  - surface and bulk characterisation by XPS and TEM (EDXS, EELS)
  - thermodynamic calculations

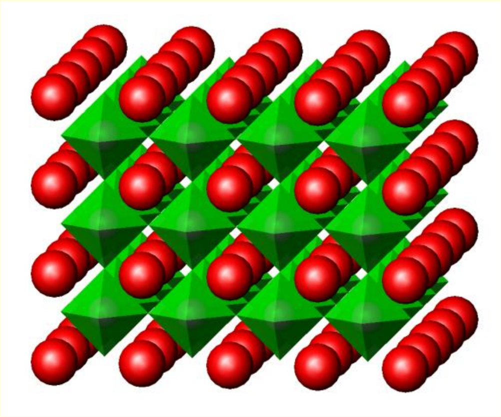
- **Materials**
  - $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF)
  - $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ (LSC)
  - $Nd_2NiO_{4+\delta}$ (NNO)

SOFC cathodes

Perovskites ($ABO_{3-\delta}$):

A=La,Sr,Ba and B=Co,Fe,Mn
δ... oxygen nonstoichiometry
(oxygen vacancies)

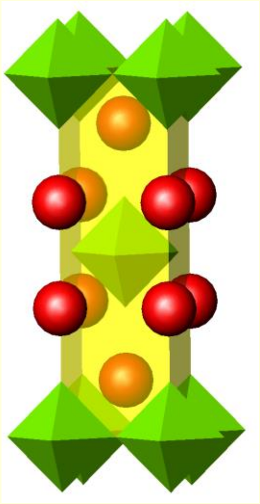


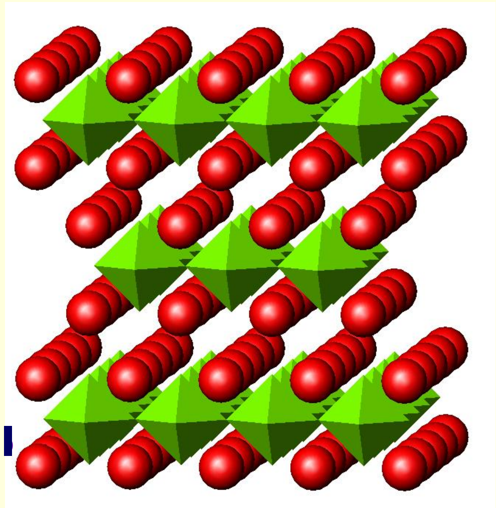


A-site ions (red)
BO_6-octahedra (green)

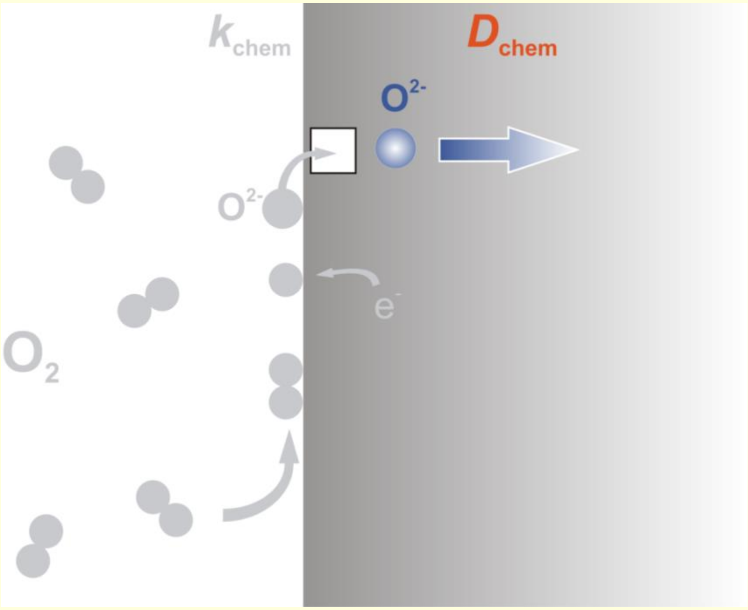
K_2NiF_4-type oxides (A_2BO_{4+d}):

A=Nd,Pr and B=Ni
δ... oxygen nonstoichiometry
oxygen excess (oxygen interstitials)





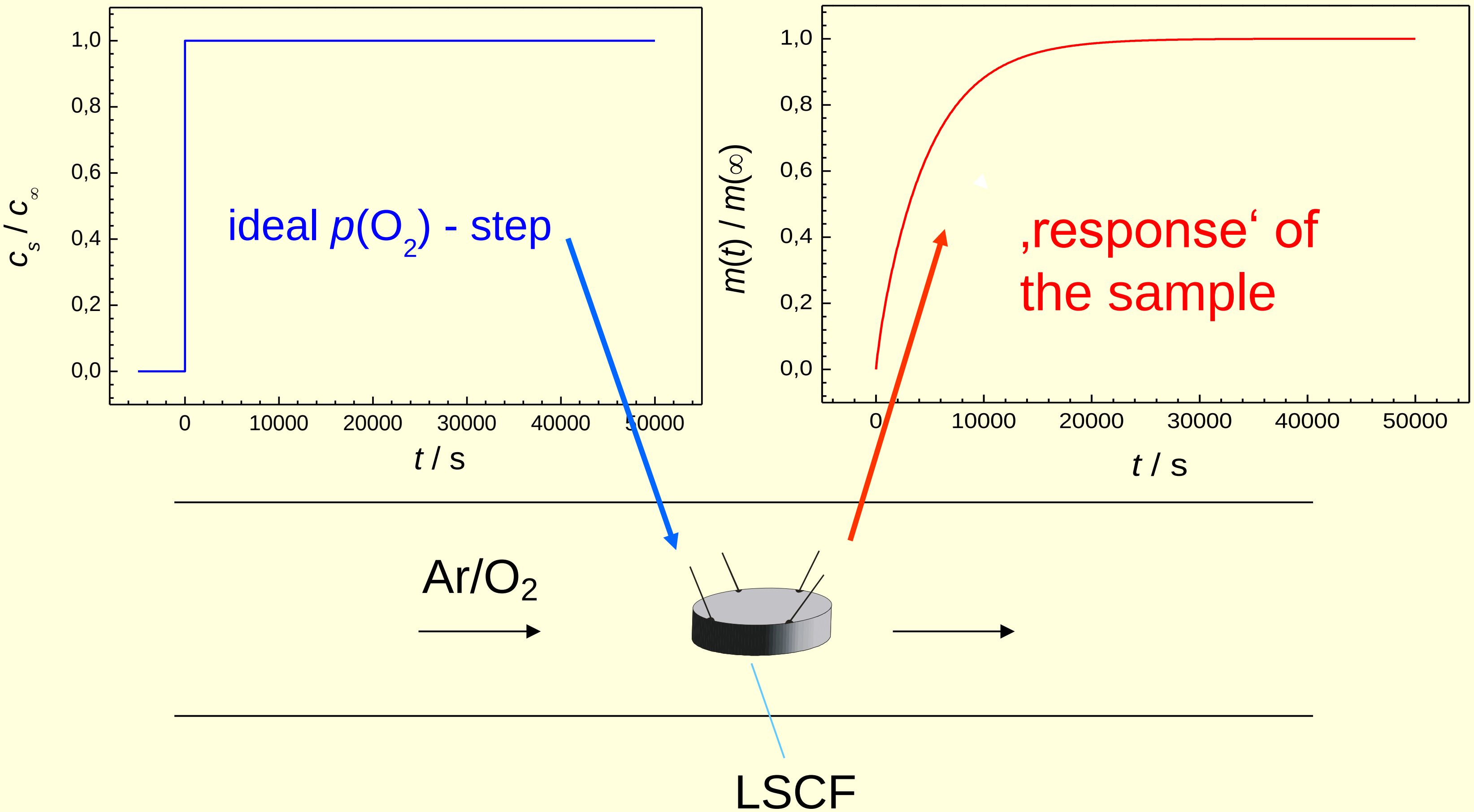
Oxygen exchange kinetics



- oxygen adsorption on surface
  - physisorption: $O_2(g) \rightarrow O_{2,ads}$
  - chemisorption: $O_2(g) \xrightarrow{e^-} O^-_{2,ads}$ or $O_2(g) \xrightarrow{2e^-} O^{2-}_{2,ads}$
- oxygen dissociation on surface (involving oxygen vacancies)
- incorporation of oxygen into the lattice $O^-_{ads} + V_O^{\bullet\bullet} + e' \rightarrow O_O^{\times}$

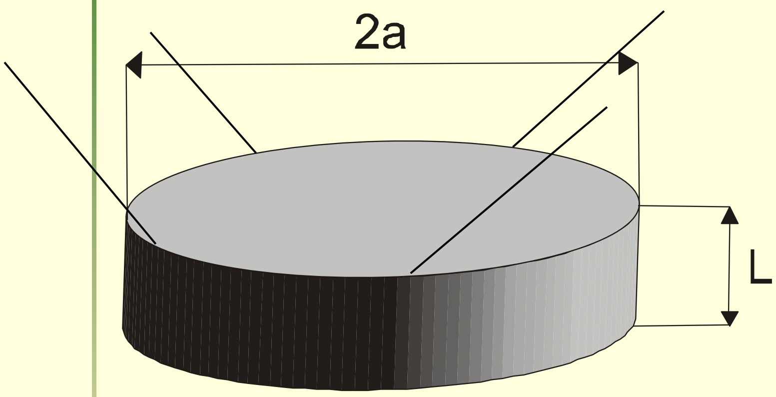
Oxygen exchange kinetics

- dc-conductivity relaxation technique



Oxygen exchange kinetics

- dc-conductivity relaxation technique



$a >> L$

$$\frac{\partial c}{\partial t} = \tilde{D} \frac{\partial^2 c}{\partial x^2}$$

$$\tilde{D} \frac{\partial c}{\partial x} = \pm \tilde{k} (c - c_s) \qquad x = 0, L$$

$\tilde{D}$... chemical diffusion coefficient

$\tilde{k}$ ... surface exchange coefficient

$$\frac{\sigma(t) - \sigma(0)}{\sigma(\infty) - \sigma(0)} = \frac{m(t)}{m(\infty)}$$

van der Pauw method $\longrightarrow \sigma$

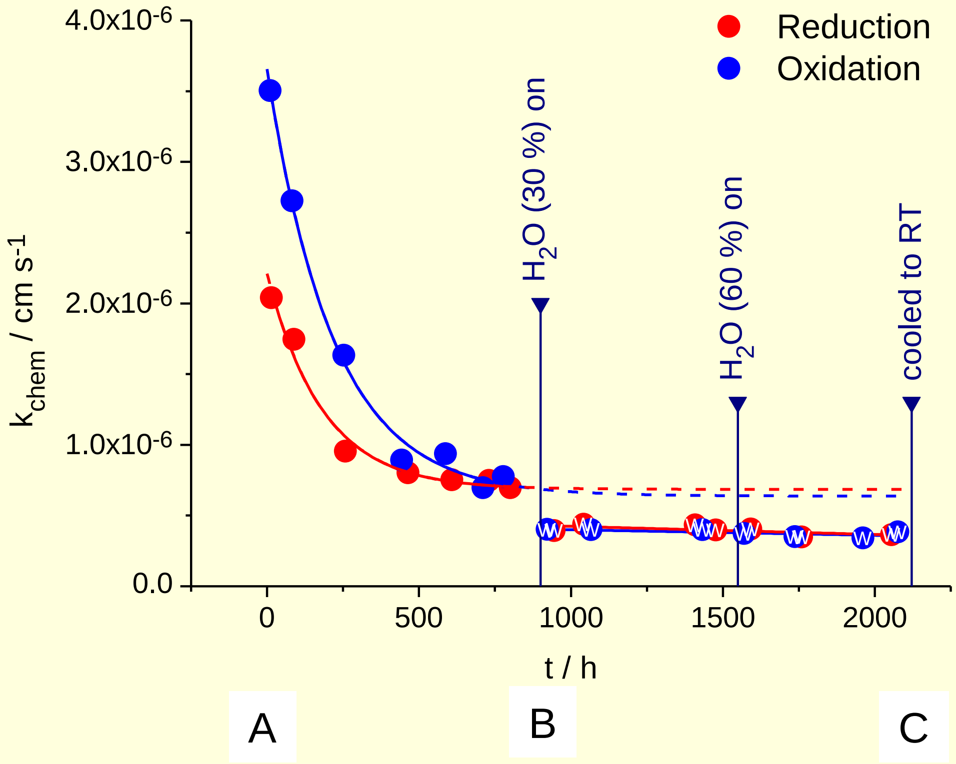
Long-term stability of the oxygen surface exchange of

- **$La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$**
- **$Nd_2NiO_{4+\delta}$**

in dry and humid O_2/Ar-atmospheres

$La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$

- Long term oxygen exchange kinetics of $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ in dry and wet atmospheres at 600°C



$La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ elemental depth profiles

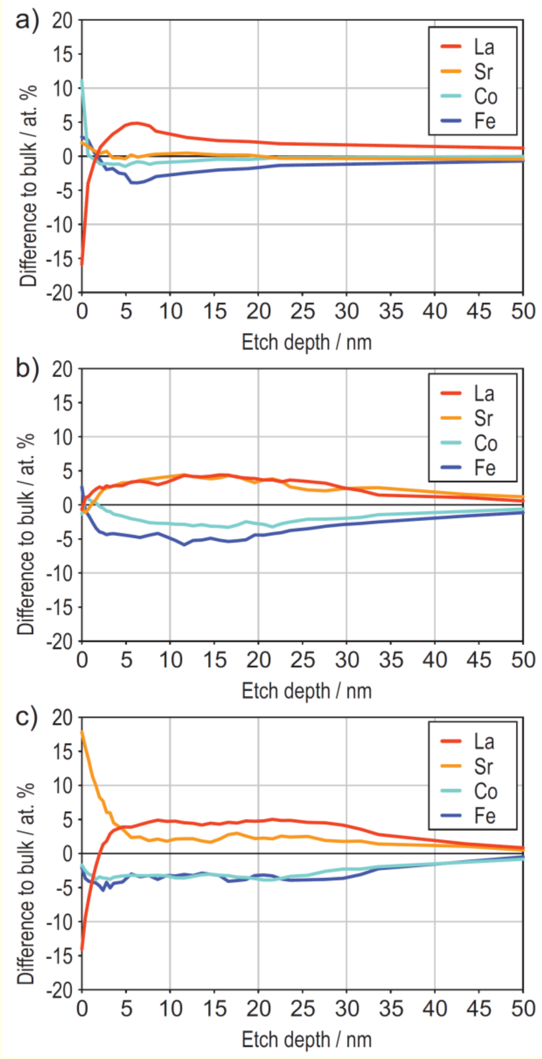
La, Sr, Co, Fe

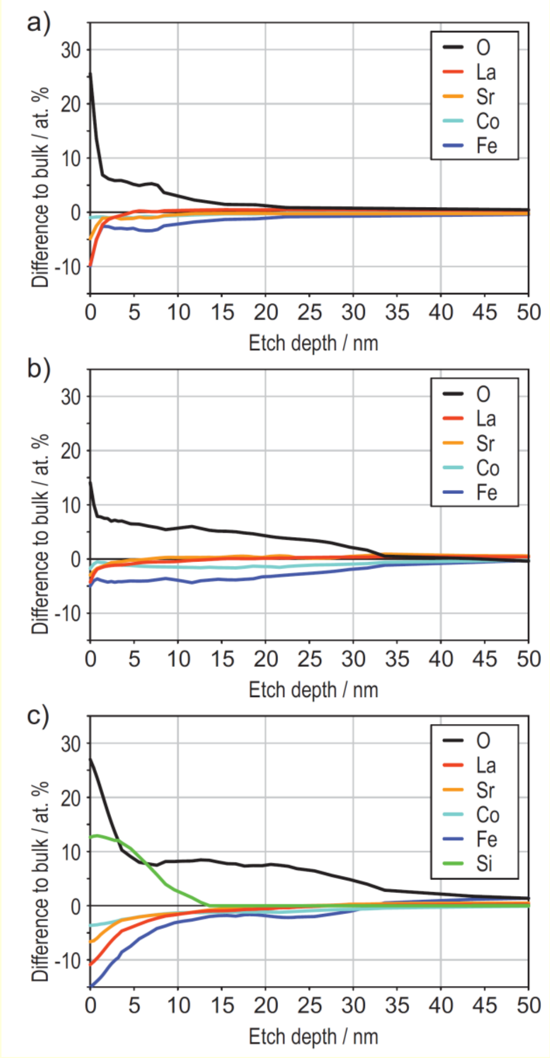
+ O and Si

fresh sample (A)

1000h
dry 1% O_2/Ar
atmosphere (B)

1000h dry + 1000h
humid 1% O_2/Ar-
atmosphere (C)



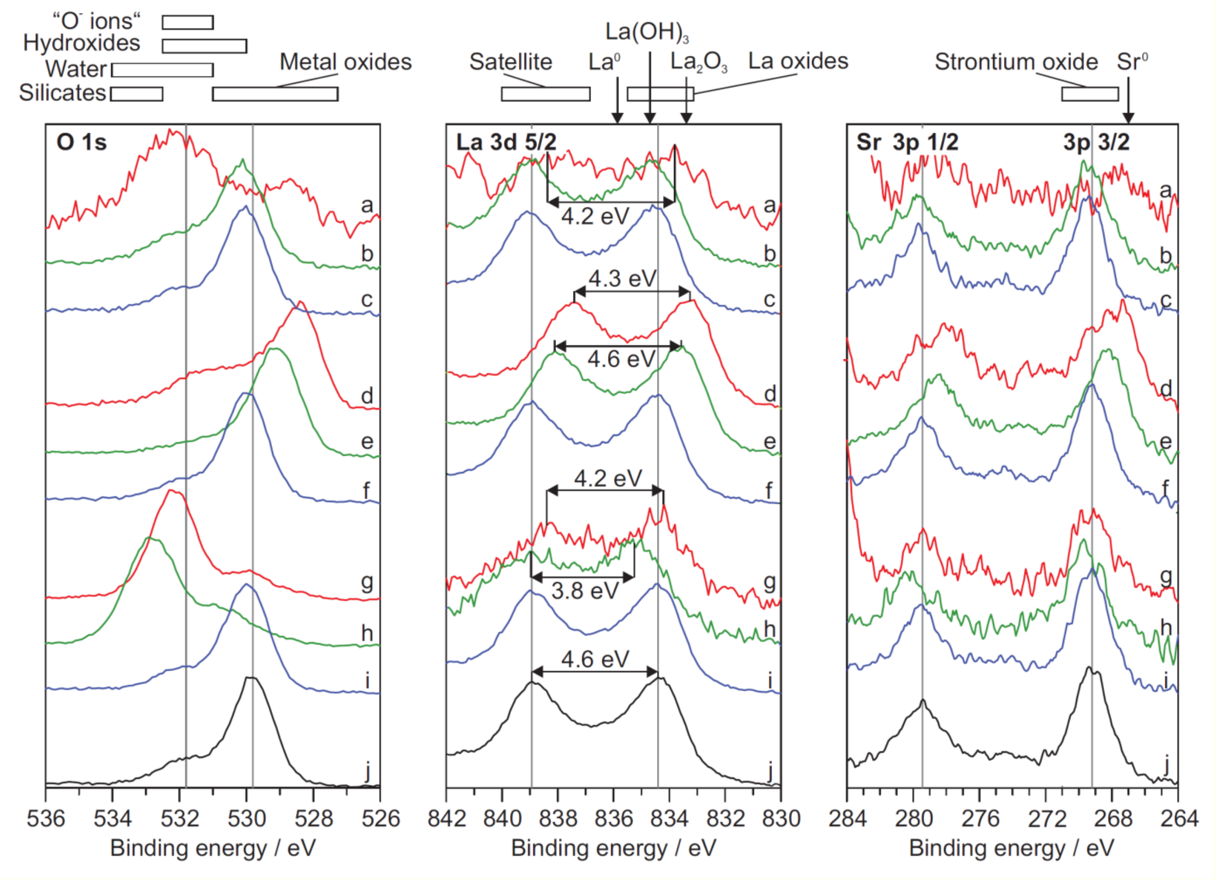


E. Bucher et al, Solid State Ionics, 191 (2011) 61-67

constant cation composition : ~ 50 nm.

$La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ core level spectra

O 1s, La 3d, Sr 3p



As prepared sample
a) 0 nm
b) 1 nm
c) 10 nm

After 1000 h in a dry atmosphere
d) 0 nm
e) 1 nm
f) 10 nm

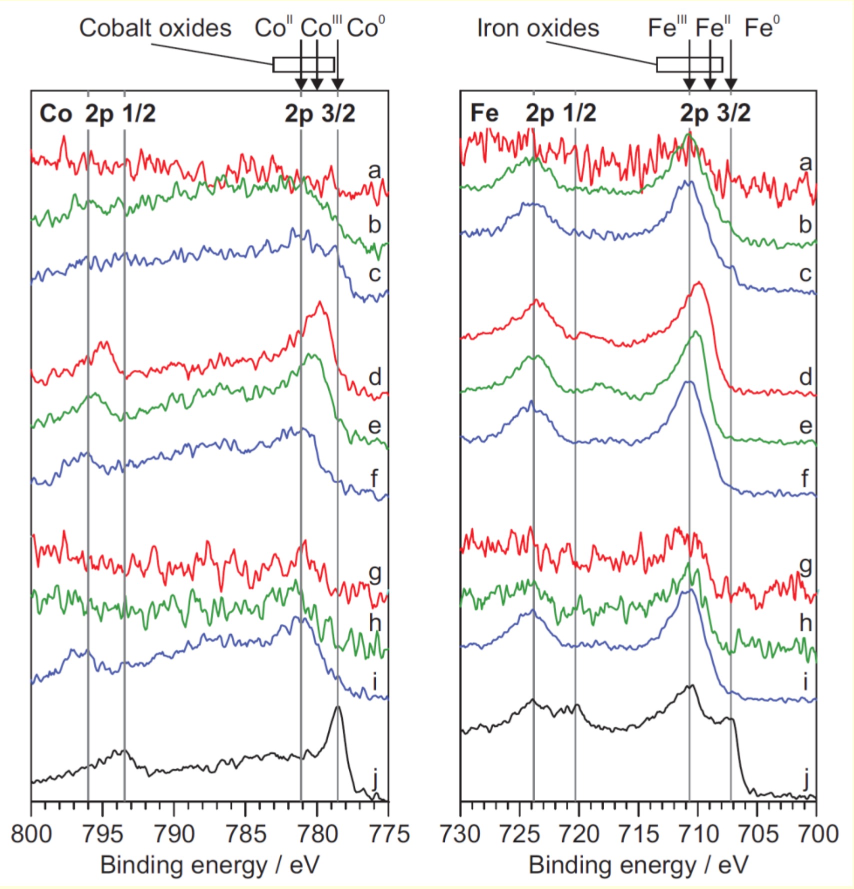
After additional 1000 h in a humid atmosphere
g) 0 nm
h) 1 nm
i) 10 nm

Bulk - reference
j) > 300 nm

XPS core level spectra of the O 1s, La 3d, Sr 3p peaks of the three different samples, obtained from immediate surface (0 nm), at etch depths of 1 nm and 10 nm, and from bulk (depth > 300 nm).

$La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ core level spectra

Co 2p, Fe 2p



As prepared sample
a) 0 nm
b) 1 nm
c) 10 nm

After 1000 h in a dry atmosphere
d) 0 nm
e) 1 nm
f) 10 nm

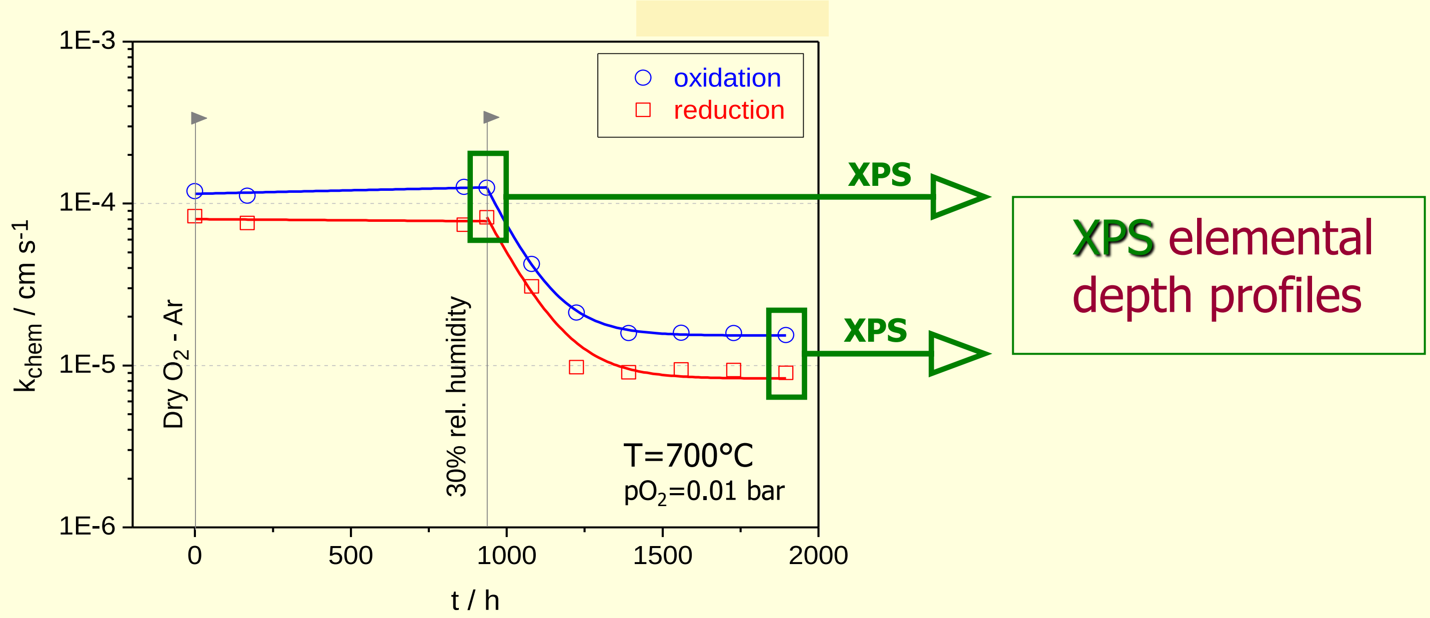
After additional 1000 h in a humid atmosphere
g) 0 nm
h) 1 nm
i) 10 nm

Bulk - reference
j) > 300 nm

XPS core level spectra of Co 2p and Fe 2p peaks of the three different samples, obtained from immediate surface (0 nm), at etch depths of 1 nm and 10 nm, and from bulk (depth > 300 nm).

$Nd_2NiO_{4+\delta}$

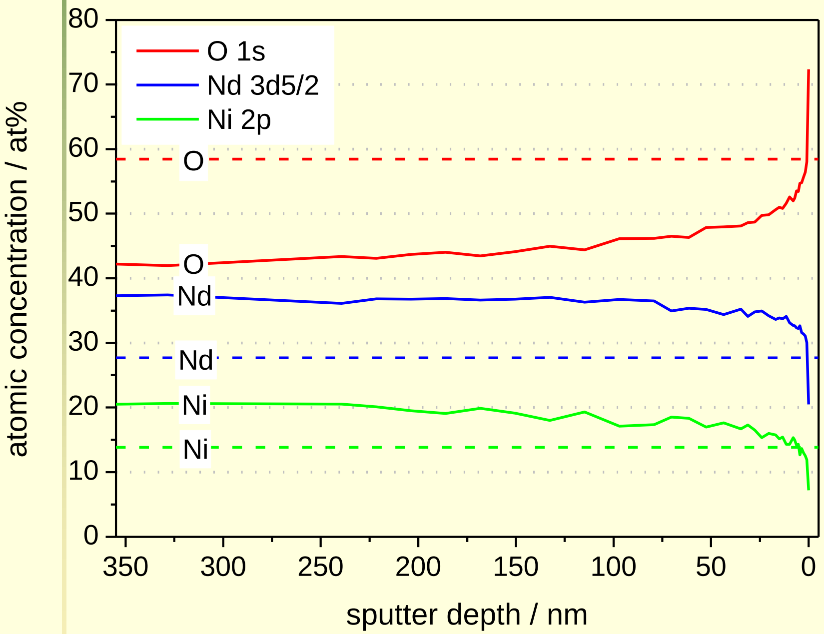
- **Long term stability of k_{chem} of $Nd_2NiO_{4+\delta}$ in dry + wet atmospheres (700°C)**

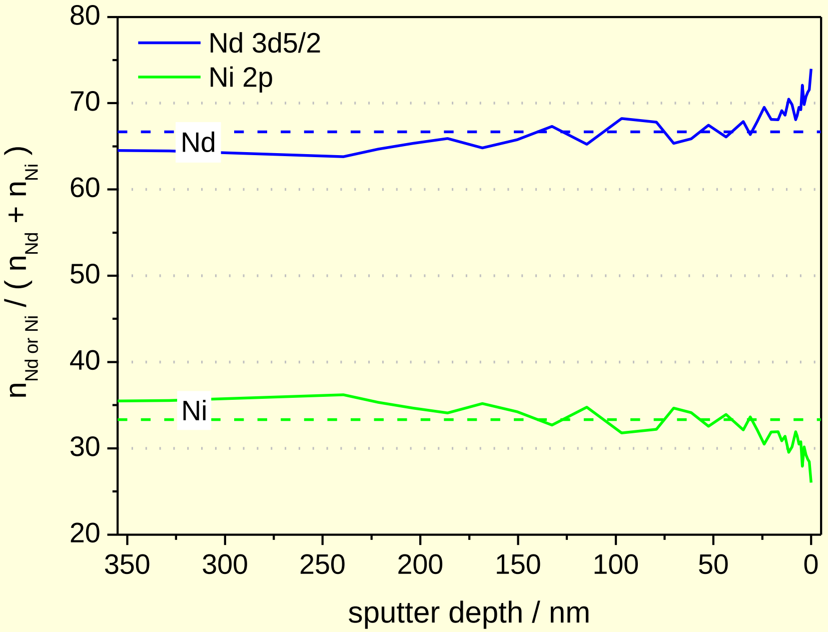


$Nd_2NiO_{4+\delta}$: XPS elemental depth profiles

$Nd_2NiO_{4+\delta}$ 1000h **dry atmosphere**

T = 700° C pO_2 = 0.01 bar

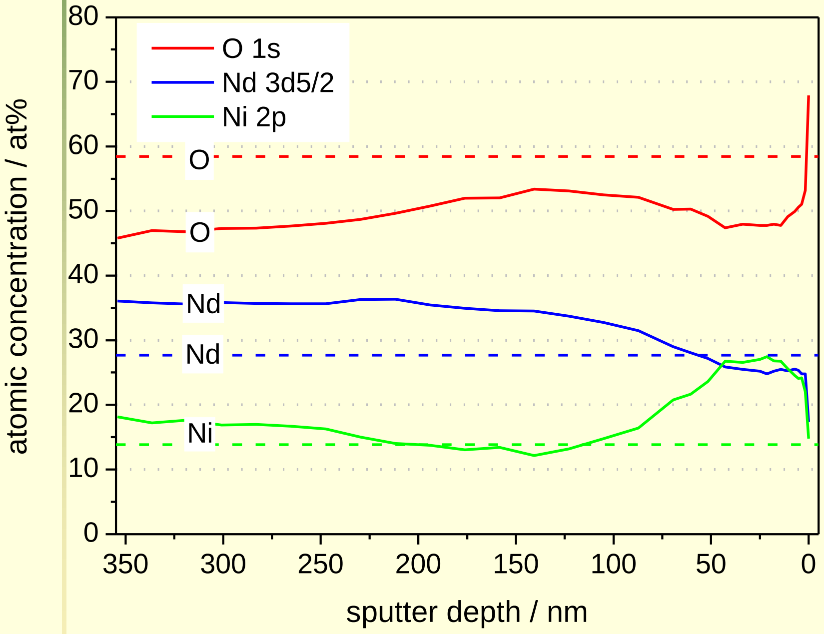


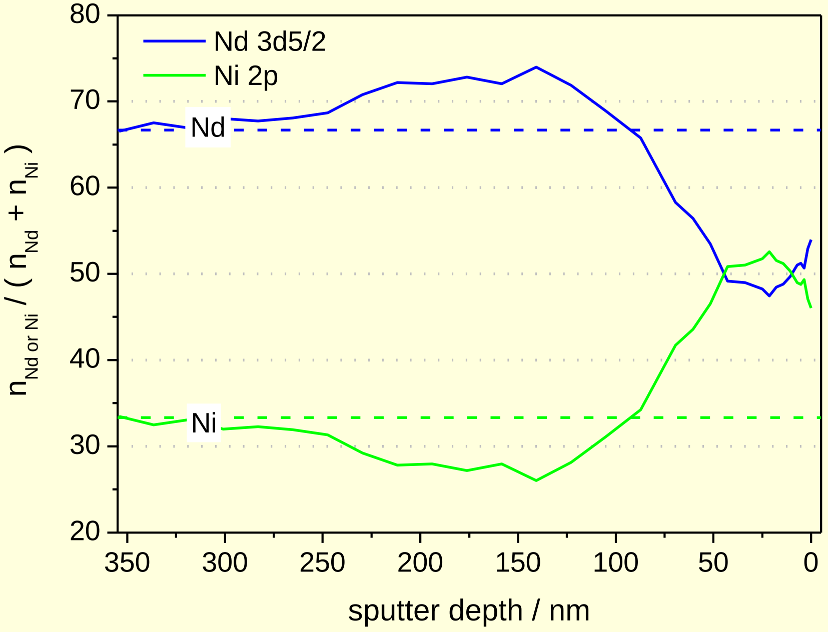


$Nd_2NiO_{4+\delta}$: XPS elemental depth profiles

$Nd_2NiO_{4+\delta}$ 1000h **dry** + 1000h **humid atmosphere**

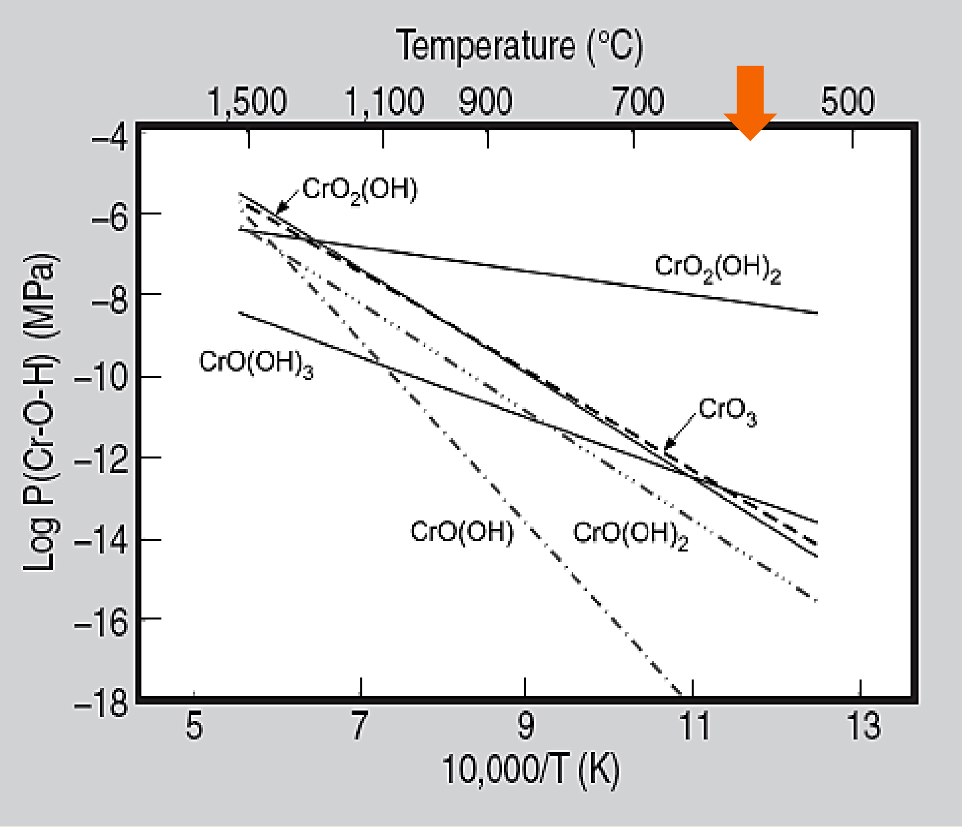
T = 700° C pO_2 = 0.01 bar





Gas phase equilibria

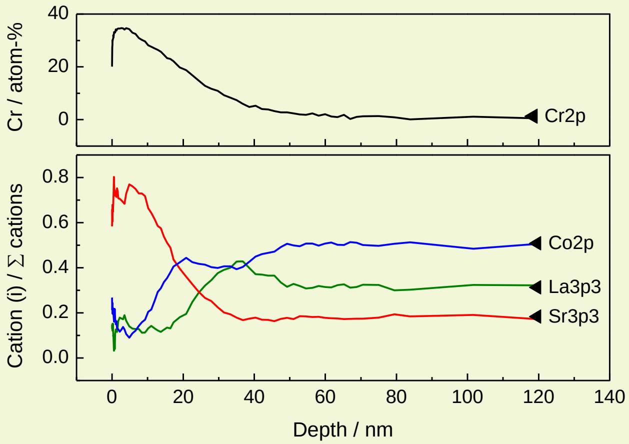
- Poisoning (degradation) is caused by reaction of the cathode with volatile species which are transported via the gas phase
- The predominating gas phase species depend on T, $p(O_2)$, $p(H_2O)$
- Under the present experimental conditions:
  - ½ $Cr_2O_3(s) + H_2O(g) + 3/4\ O_2(g) \rightarrow$ **$CrO_2(OH)_2(g)$**
  - ½ $Cr_2O_3(s) + 3/4\ O_2(g) \rightarrow CrO_3(g)$
  - $SiO_2(s) + 2\ H_2O(g) \rightarrow$ **$Si(OH)_4(g)$**



E. Opila et al., JOM 58 (2006) 22.

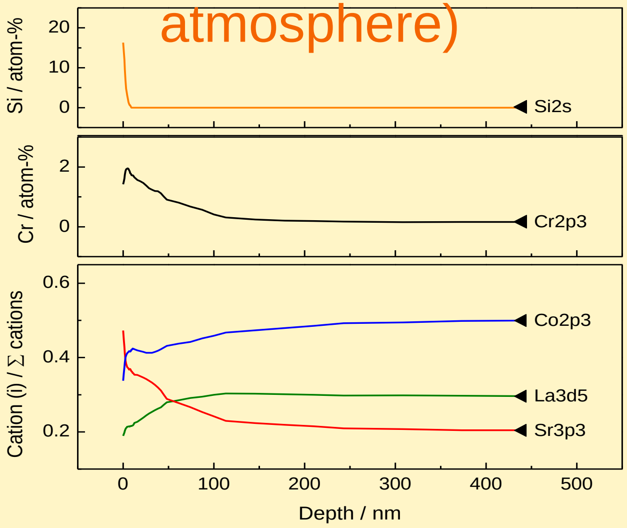
Comparison: Cr-layer vs. Cr-pellet

(La,Sr)$CoO_{3-\delta}$ 1000 h 600°C Cr-layer (dry atmosphere)



1. Cr present up to about 40 nm depth
2. **Sr-enrichment** up to 40 nm depth
3. Applied Cr-layer → higher Cr-content (<35 at-%)
4. Cr-content in 30 nm+**90 nm depth: 0.5 at-%**
5. No Si detected (dry atmosphere!)

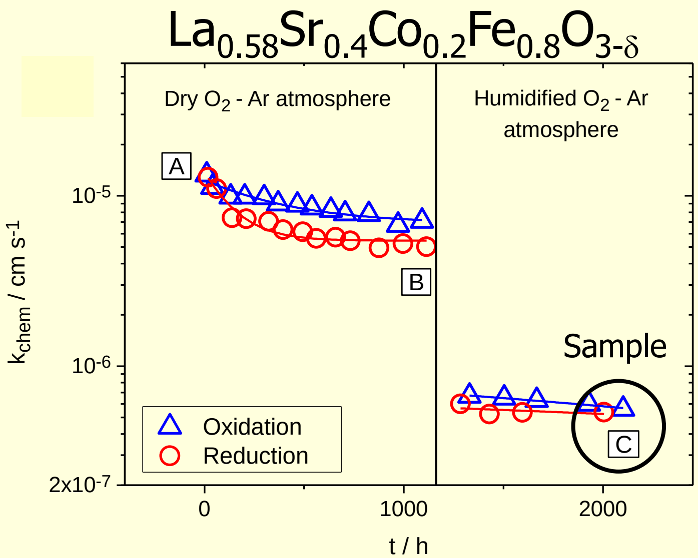
… with Cr-pellet (humid atmosphere)



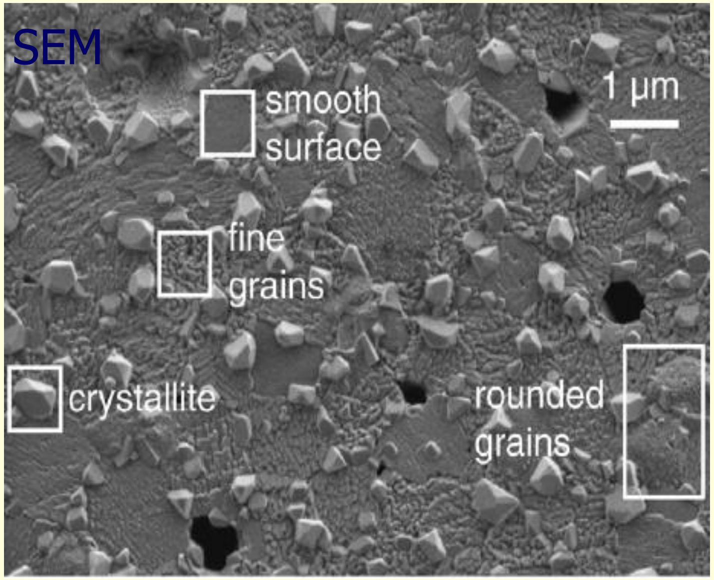
1. Cr present up to about 100 nm depth
2. **Sr-enrichment** up to 100 nm depth
3. External Cr-source → lower Cr-content (<2 at-%)
4. Cr-content in **90 nm depth: 0.5 at-%**
5. Thin zone of Si-poisoning (wet atmosphere!)

Scanning electron microscopy

k_{chem} in dry and humid atmosphere

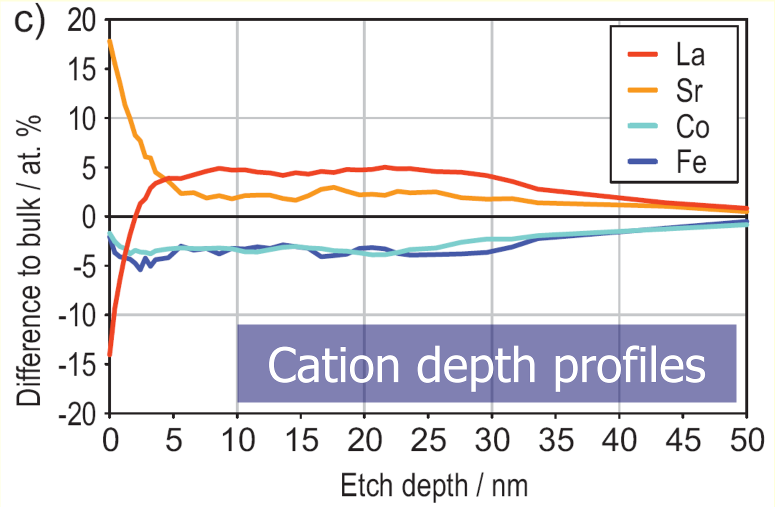


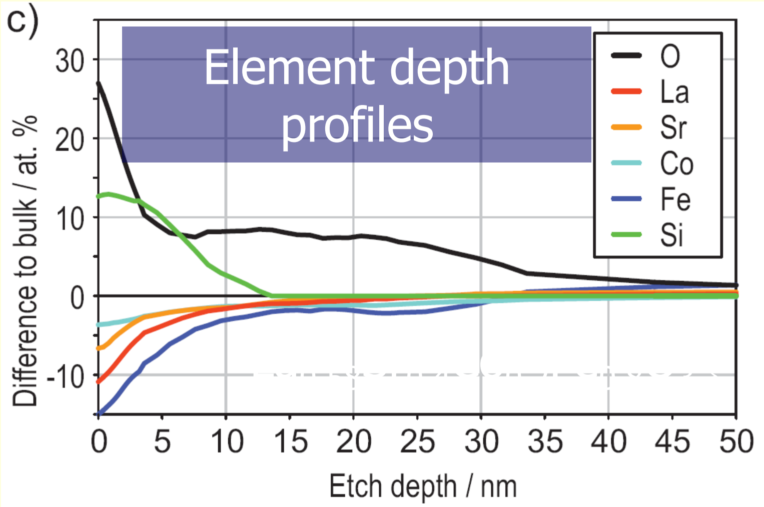
Information on surface topography (sample C)



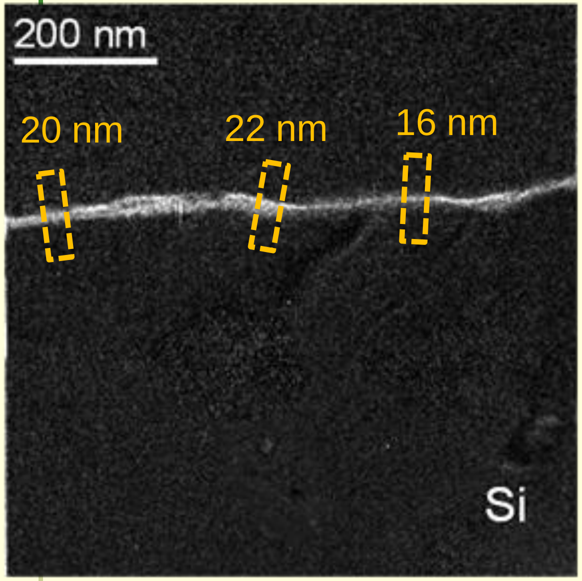
X-ray photoelectron spectroscopy

XPS → Average chemical composition of surface in the analyzed zone (around 500 µm)
after 1000h dry + 1000h humid 1% O_2/Ar-atmosphere



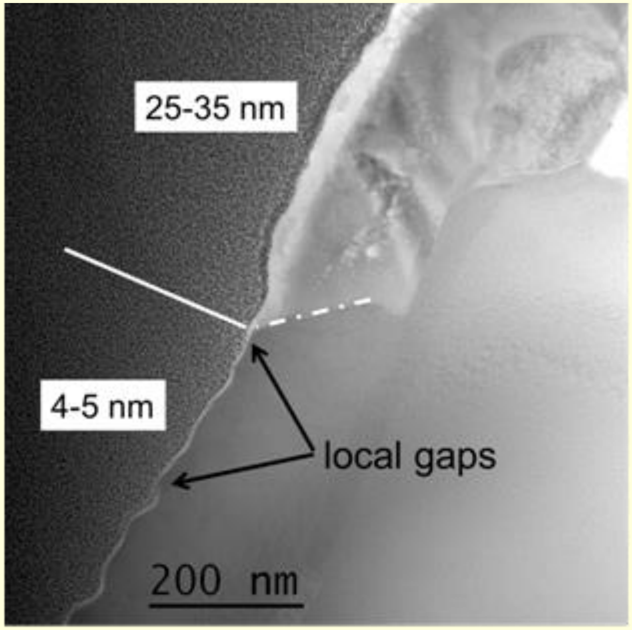


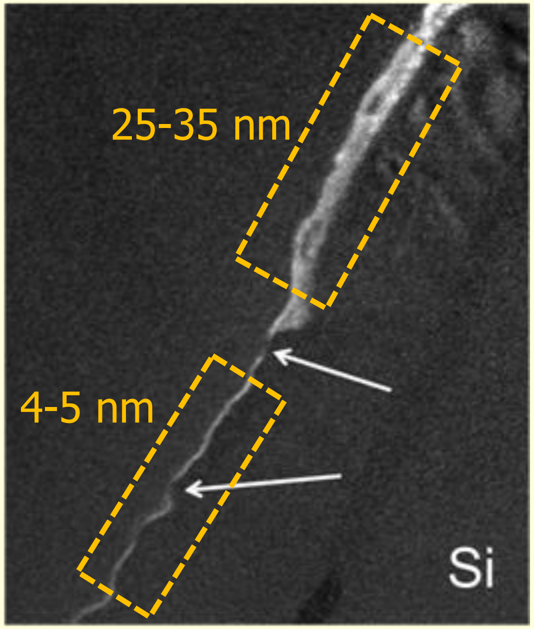
Silicon poisoning (EFTEM-SI)



- Energy-filtered TEM spectrum-imaging
- Si is present throughout the surface
- Thickness of the layer approx. 5-35 nm

- Thinner and thicker regions coexist



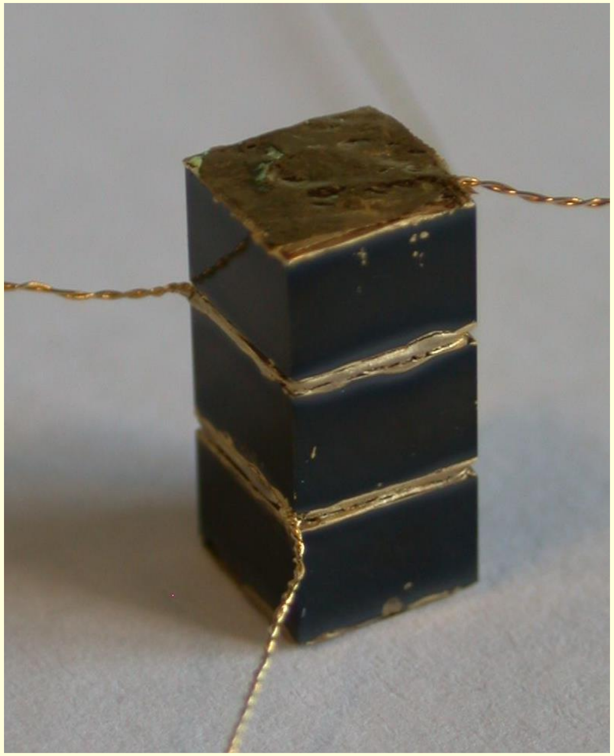


E. Bucher, C. Gspan, F. Hofer, W. Sitte, Solid State Ioncis, 230 (2013) 7–11

Ag activated oxygen exchange of $La_2NiO_{4+\delta}$

Ag-activated oxygen exchange of $La_2NiO_{4+\delta}$

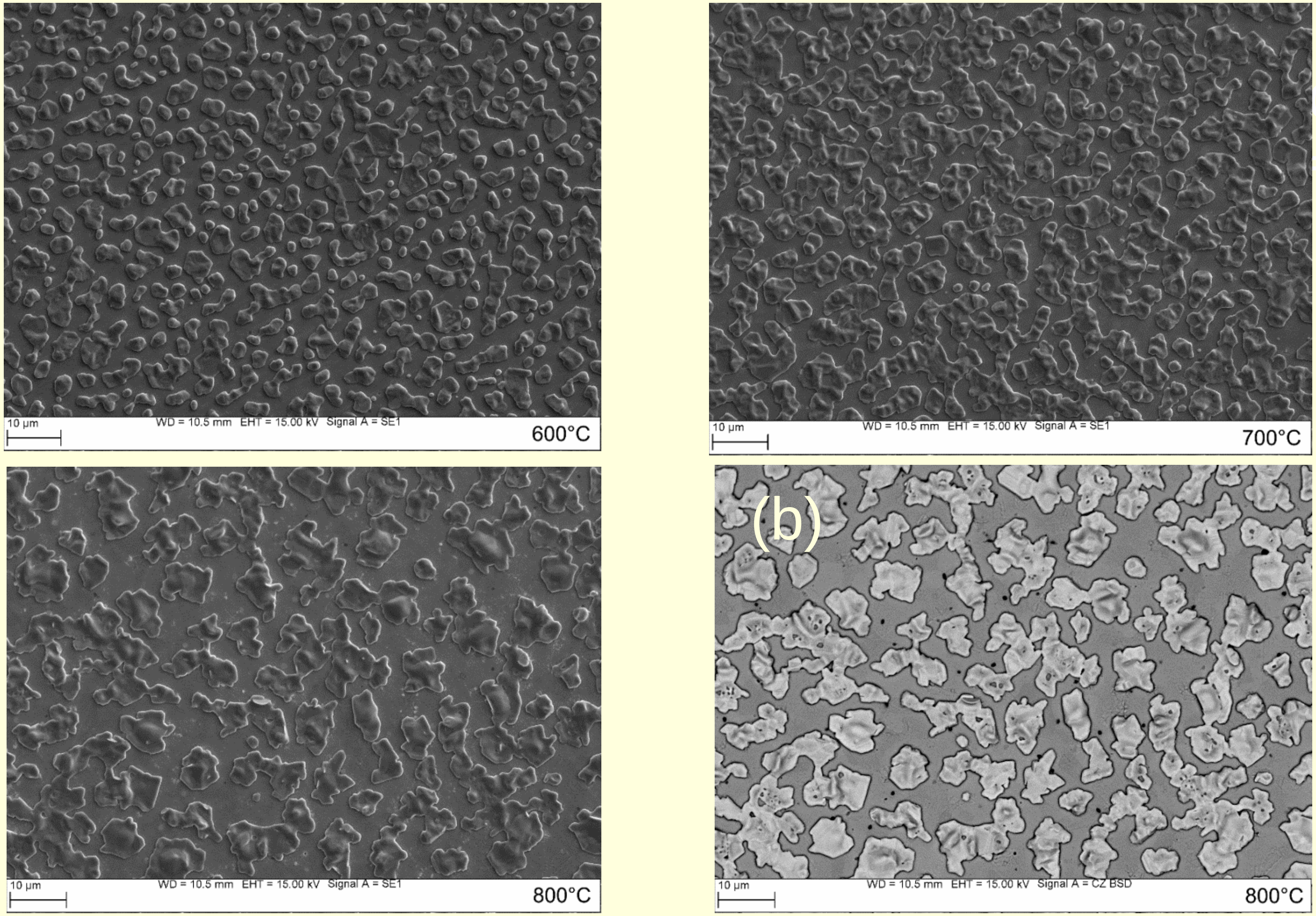
- Problem
  - Surface limited oxygen exchange of $La_2NiO_{4+\delta}$
  - even large samples 6 x 6 mm do not allow the determination of D_{chem}



Ag-activated oxygen exchange of $La_2NiO_{4+\delta}$

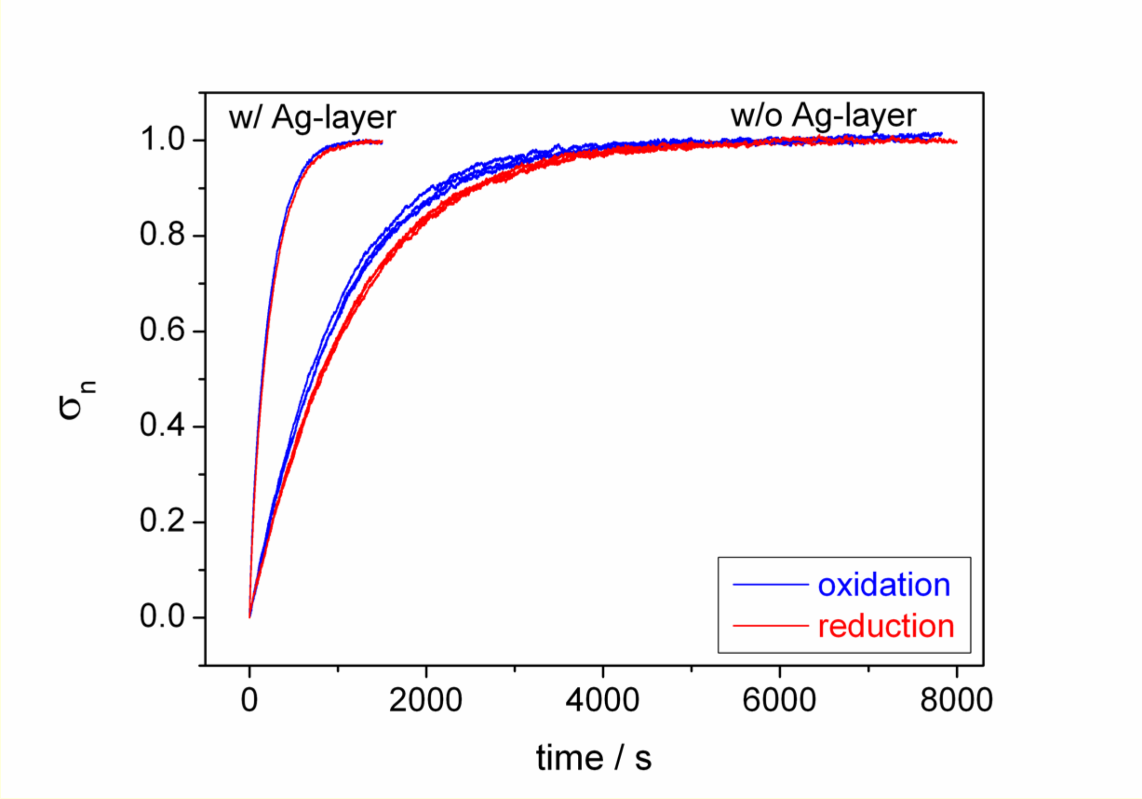
- Solution
  - $La_2NiO_{4+\delta}$ is covered by a 200 nm-thick Ag-layer
  - gold plated at the ends
  - enhanced oxygen exchange: D_{chem} can be determined with usual sample sizes

Ag-activated oxygen exchange of $La_2NiO_{4+\delta}$



(a) SEM-pictures of a silver film on $La_2NiO_{4+\delta}$ after annealing for 24 hours at 600, 700 and 800°C. (b) Backscatter image

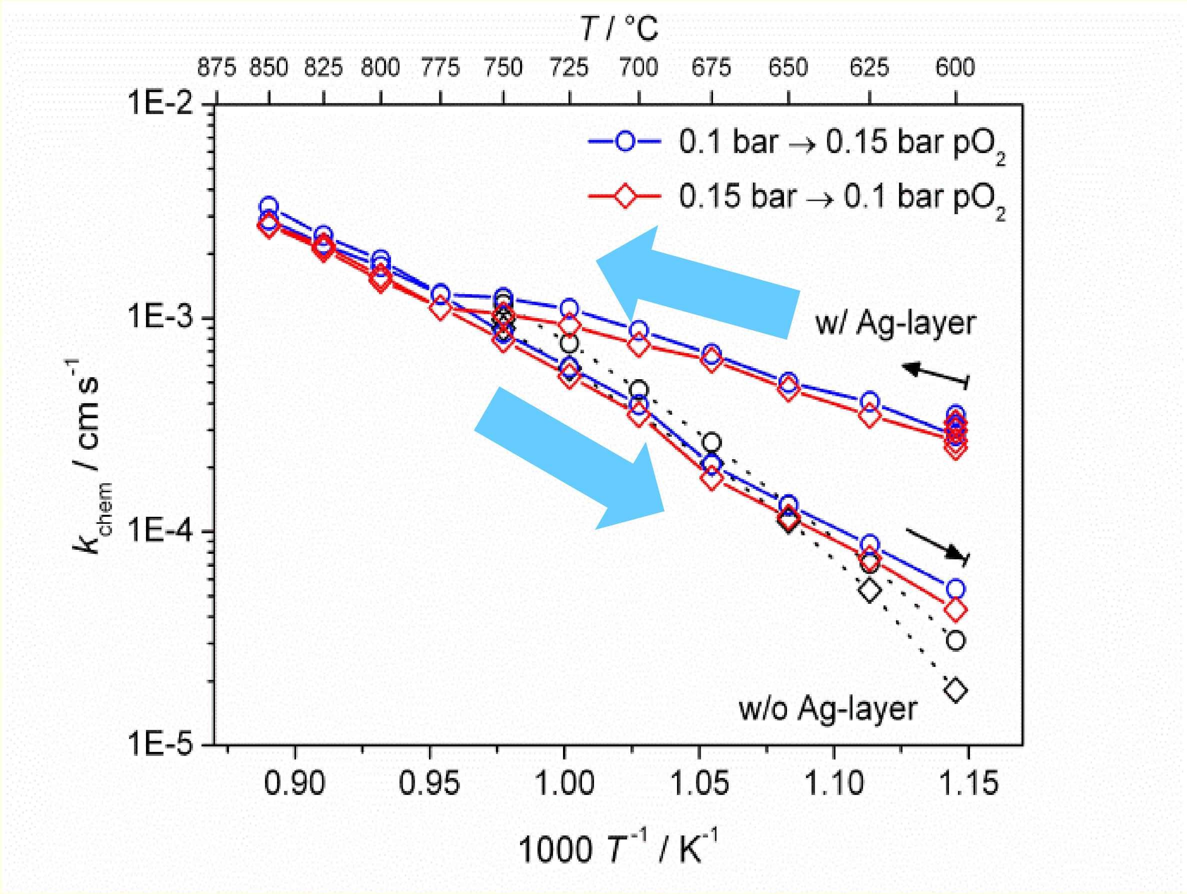
Ag-activated oxygen exchange of $La_2NiO_{4+\delta}$



700°C
pO_2=0.01 bar

Conductivity relaxation curves of $La_2NiO_{4+\delta}$ with and without a surface layer of silver.

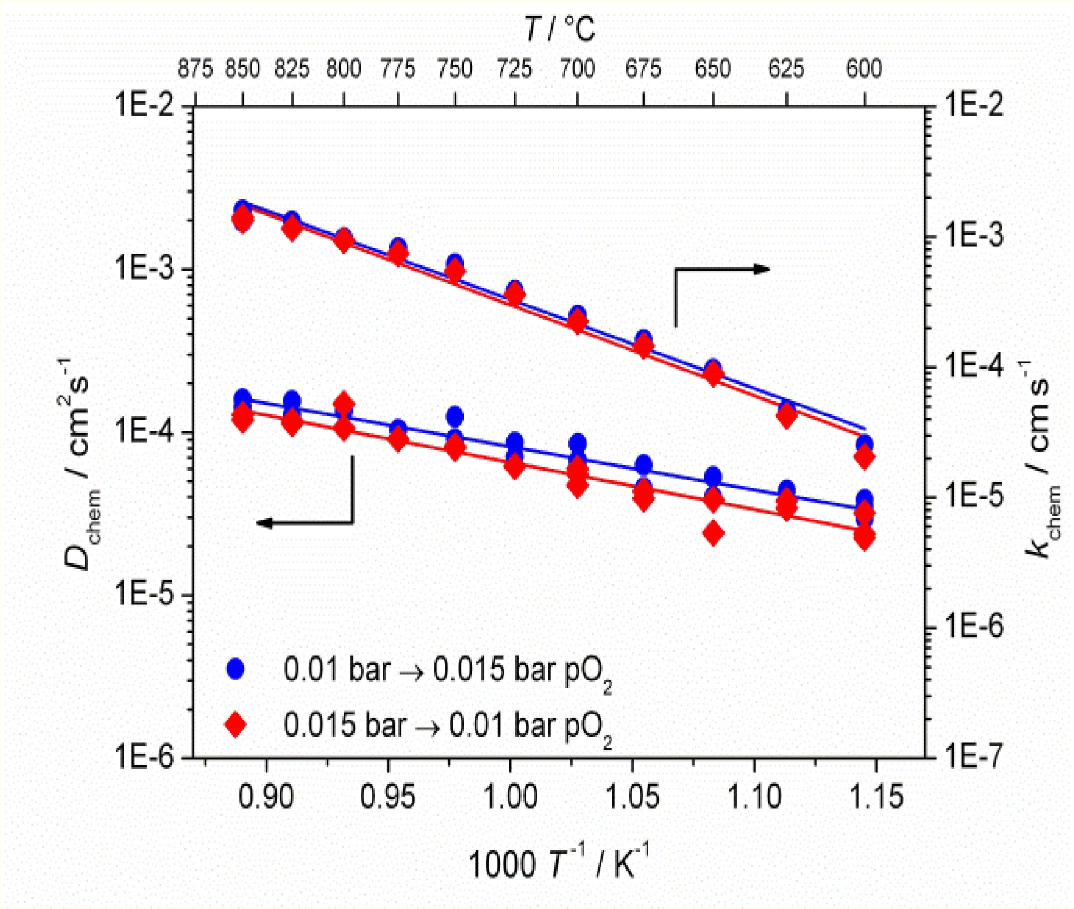
Ag-activated oxygen exchange of $La_2NiO_{4+\delta}$



Effect of a 200nm Ag layer on k_{chem} of $La_2NiO_{4+\delta}$ at pO_2 =0.1 bar.

A. Egger, W. Sitte, Solid State Ionics 258 (2014) 30–37

Ag-activated oxygen exchange of $La_2NiO_{4+\delta}$



Arrhenius plot of D_{chem} and k_{chem} of oxygen for $La_2NiO_{4+\delta}$ at pO_2 =0.01 bar.

Conclusions

- **Long time investigations (1-2 kh)** → necessary to investigate signifcant changes of the oxygen exchange kinetics of **complex oxides** in dry or humid O_2/Ar-atmospheres.
- k_{chem} of **Sr-containing SOFC cathodes** → more severely affected in dry and humid atmospheres than Sr-free alternatives.
- **XPS and elemental depth profiles, HRTEM investigations** → insight into the origin of the degradation in the range 0-50 nm.
- **Humid atmospheres** → strongly enhance transport of Si and Cr via the gas phase in the presence of a Si- or Cr-source, even at temperatures as low as 600°C.
- **Surface limited oxygen exchange:** increase of k_{chem} by deposition of a thin layer of catalytically active nanocrystalline Ag.