Quantifying the oxygen stoichiometry of Pr-doped ceria through X-ray diffraction

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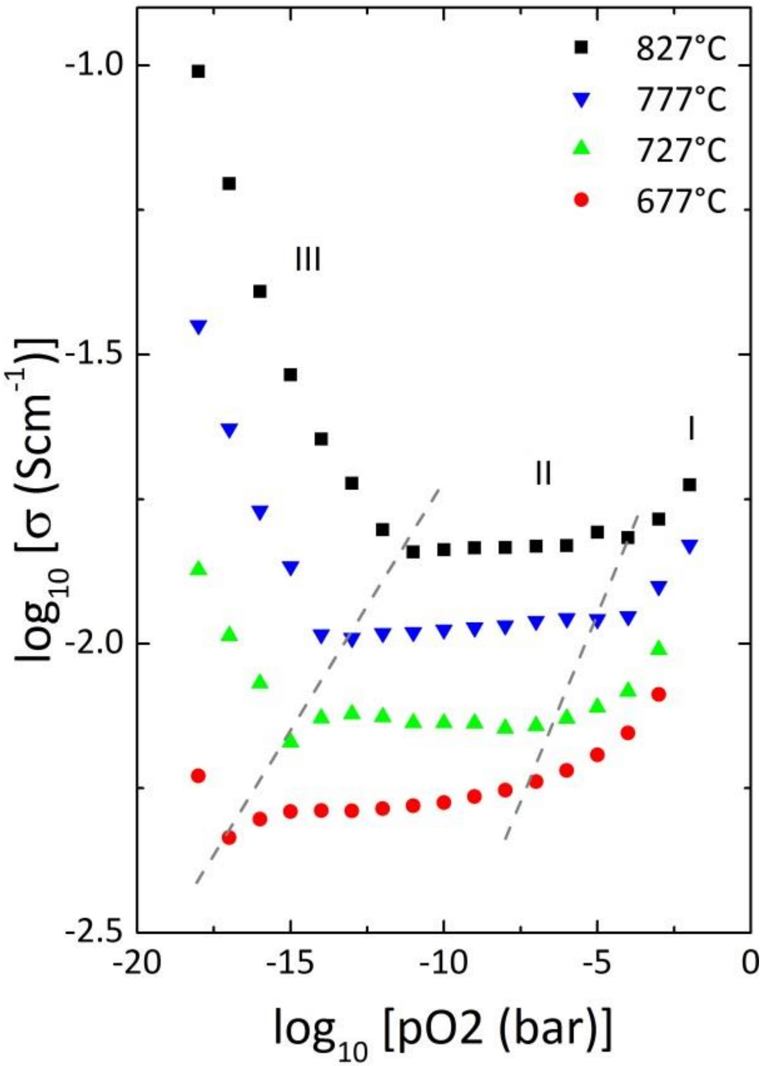
Institute for Energy- and Climate Research
IEK-1: Materials Synthesis and Processing

Outline

- **Background and Motivation**
- HT-XRD: oxygen stoichiometry and microstrain
- Impact of conductivity on cathode performance
- Summary

High Temperature Equilibrium Conductivity



HTEC of dense 20PCO ceramics

Region I:
MIEC ($[V_O^{**}]$, $[Pr_{Ce}']$)

Region II:
ionic plateau ($2[V_O^{**}] \approx [Pr_{Ce}'] = [Pr_{Ce}]$)

Region III:
Reduction of Ce (MIEC)

DC conductivity as expected for PCO[1,2]

[1]: Bishop *et* al., J. Mater. Res., Vol. 27, No. 15, Aug 14, 2012

[2]: Bishop *et* al., Phys. Chem. Chem. Phys., 2011, **13**, 10165–10173

PCO as a cathode material

Figure of merit: $L_C = D^*/k^q$

D^*: oxygen self-diffusion coefficient
k^q: oyxgen surface exchange coefficient

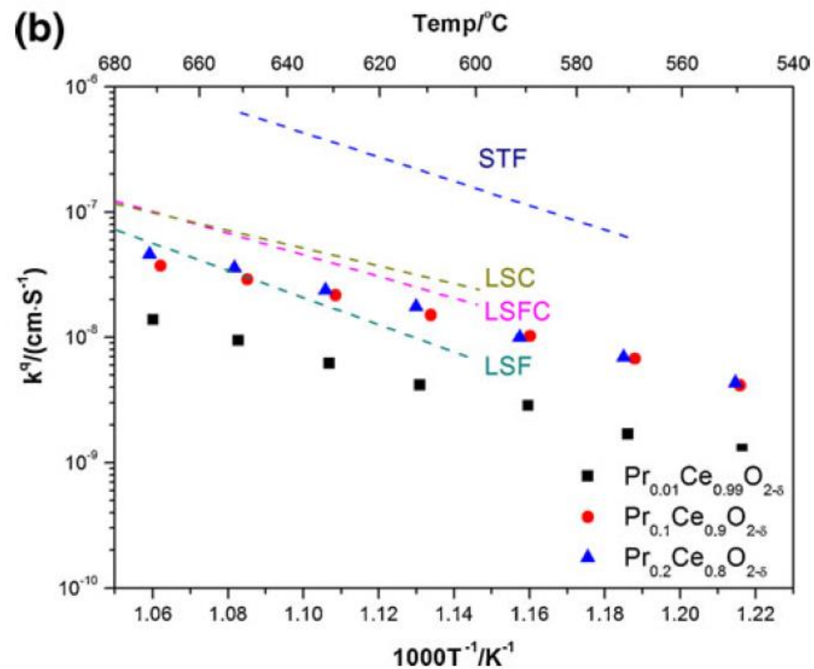
Model system suggests high k^q [1]

<u>Investigations on:</u>

PCO impregnated LSM-YSZ[2]

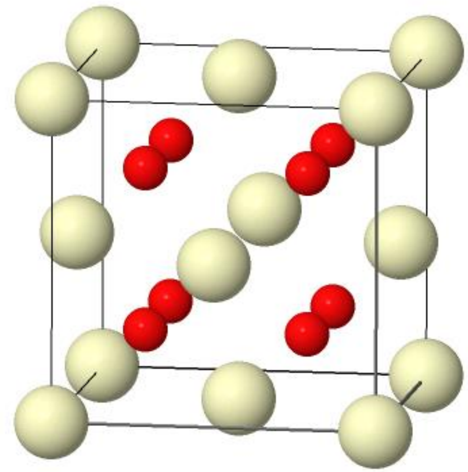
PCO interlayer for $LaNi_{0.6}Fe_{0.4}O_3$ [3]

PCO as an active material[4]



1: Chen *et* al., J. Electroceram. (2012) 28:62-69
2: Y. Ren, *et* al., *Journal of Materials Chemistry* **22** (2012) (48) 25042.
3: R. Chiba, *et* al., *Electrochemical and Solid-State Letters* **12** (2009) (5) B69.
4: R. Chiba, *et* al., *Solid State Ionics* **197** (2011) (1) 42.

Conductivity of $Pr_{1-x}Ce_xO_{2-\delta}$



Reduction

$$2\,Pr_{Ce}^{x} \rightarrow 2\,Pr_{Ce}^{'} + V_O^{**} + \tfrac{1}{2}O_2$$

Conductivity

$$\sigma_{tot} = \sum_i \sigma_i = \sum_i n_i q_i \mu_i$$

$$\sigma_{tot} = \sigma_{Pr} + \sigma_{ion} = [Pr_{Ce}^{'}] * |e| * \mu_{Pr} + [V_O^{**}] * 2|e| * \mu_V$$

Charge neutrality

$$2[V_O^{**}] \approx [Pr_{Ce}^{'}] + n$$

High pO_2

$$n \ll [Pr_{Ce}^{'}]$$

$$\mu_i = \frac{\mu_{0,i}}{T}\exp\left(-\frac{H_{m,i}}{kT}\right)$$

$$\sigma = [Pr_{Ce}^{'}] * e\left[\frac{\mu_{0,Pr}[Pr_{Ce}^{x}]}{T[Pr_{Ce}]}exp\left(-\frac{H_{m,Pr}}{kT}\right) + \frac{\mu_{0,V}}{T}exp\left(-\frac{H_{m,V}}{kT}\right)\right]$$

Bishop *et al.*, J. Mater. Res., Vol. 27, No. 15, Aug 14, 2012

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Synthesis

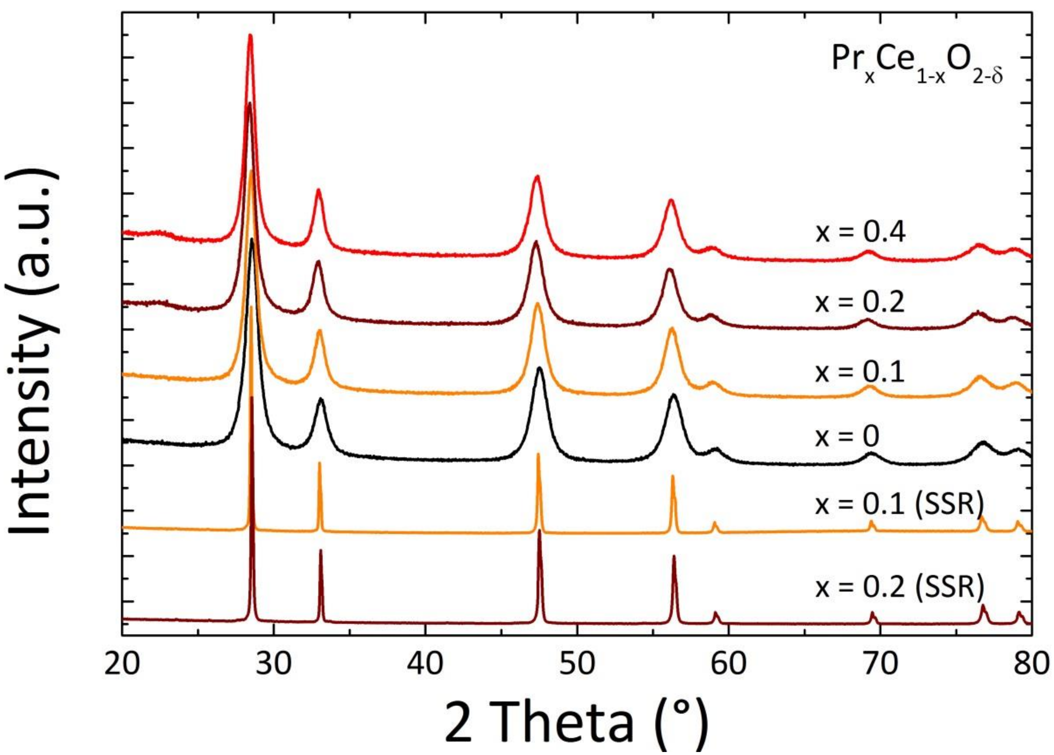
„Simplified Pechini" (Nanopowder)

$Pr(NO_3)_3 * 6\ H_20 + Ce(NO_3)_3 * 6\ H_20 \xrightarrow{500°C} Pr_{1-x}Ce_xO_{2-\delta}$

Dissolution, geling and combustion of nitrates

<u>Solid State Route</u>

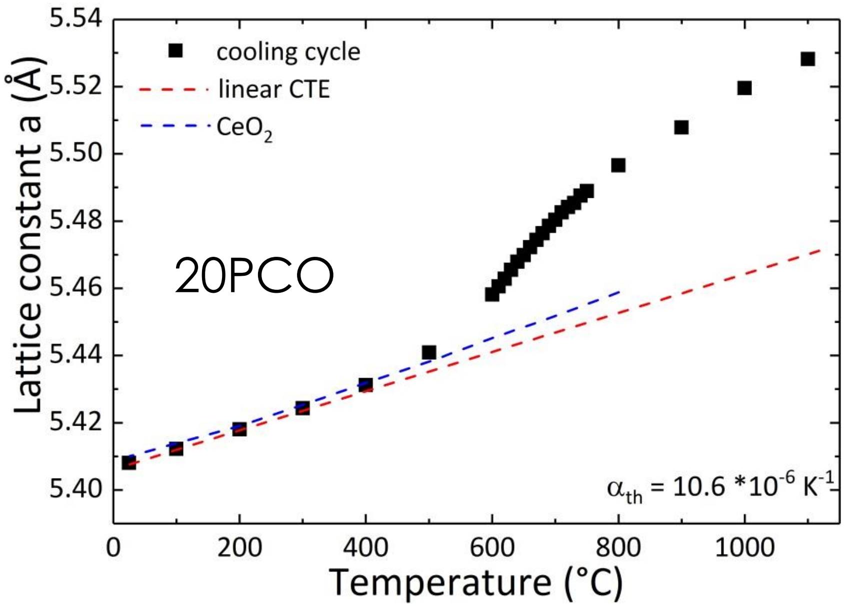
$Pr_6O_{11} + CeO_2 \xrightarrow{1400°C} Pr_{1-x}Ce_xO_{2-x/2}$

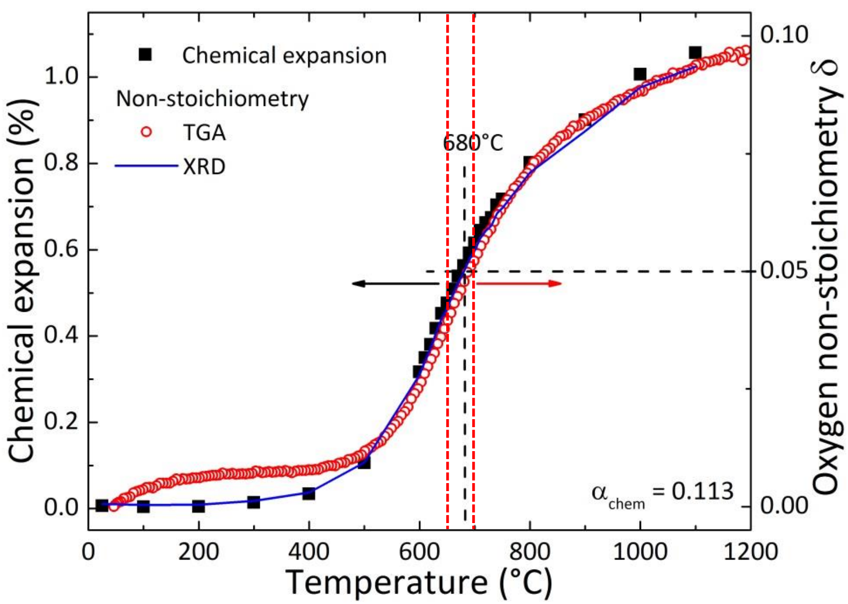


Line broadening:

- Crystallite size
- Microstrain (Δd_{hkl})

Chemical expansion in air

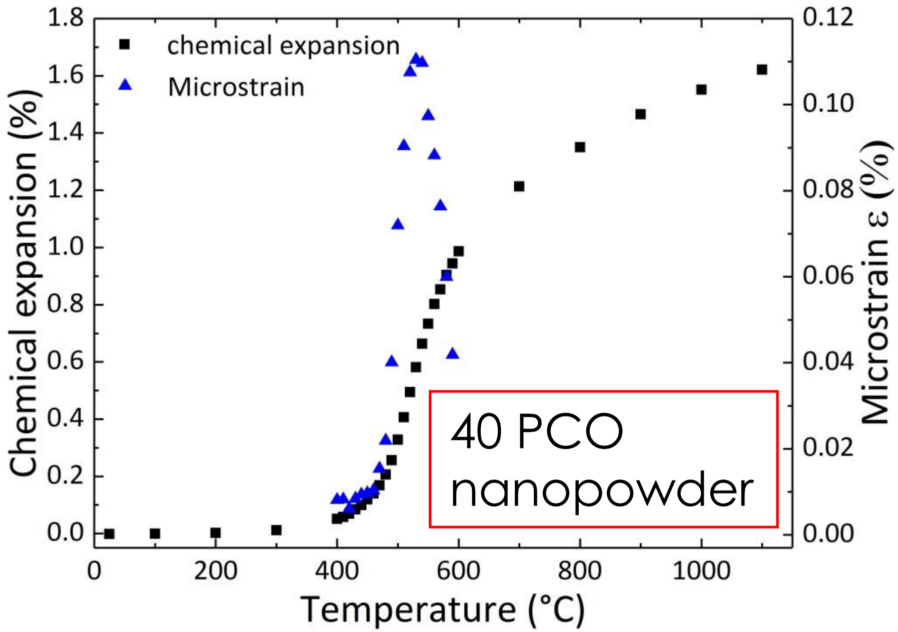


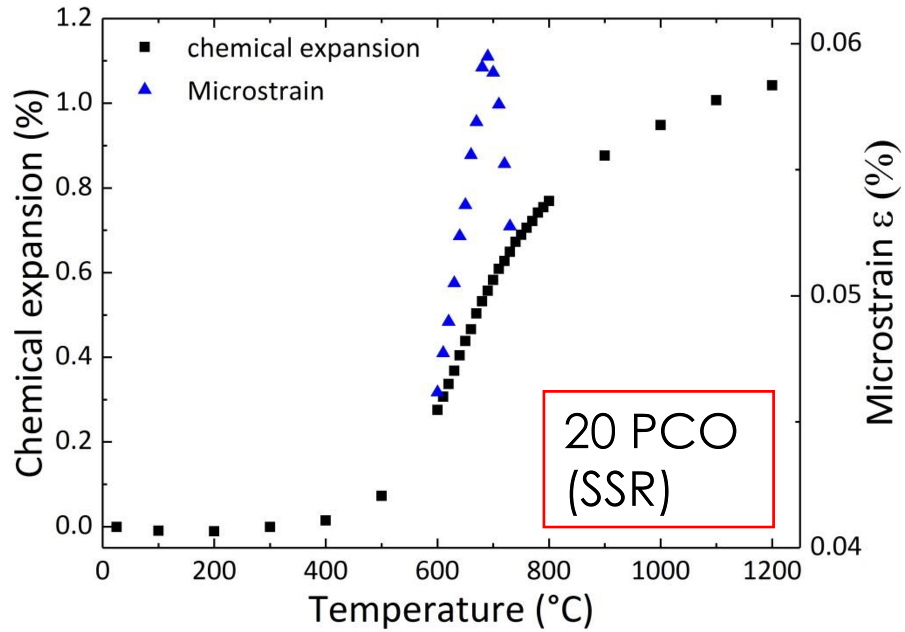


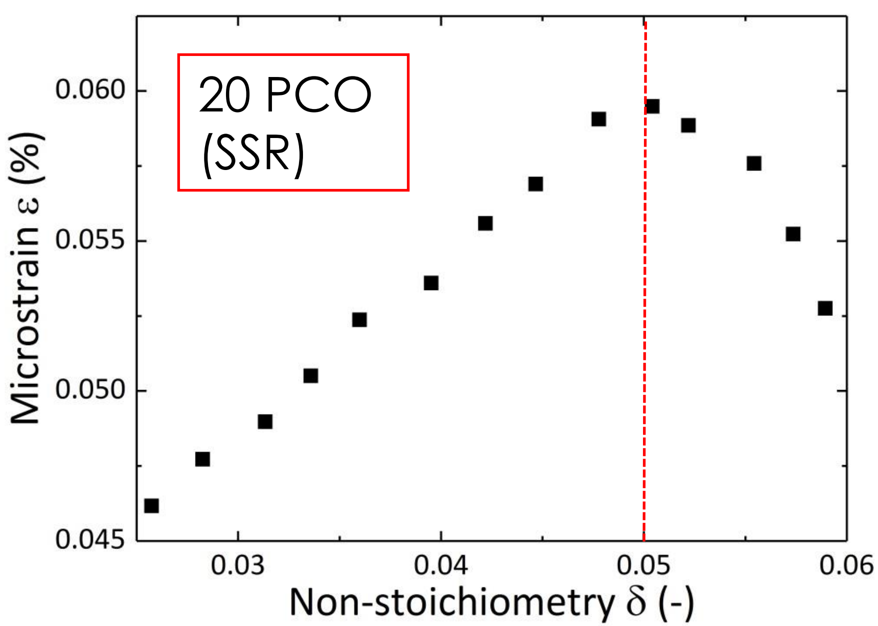
- Chemical expansion in air
- $\alpha_{tot} = \alpha_{thermal} + \alpha_{chem}$
- $\alpha_{thermal} = \frac{1}{a}\frac{da}{dT} = 10.6 * 10^{-6}\ K^{-1}$
- $\alpha_{chem} = \frac{da}{d\delta} = 0.113$
- $\delta = 0.05$ at ~680°C

Kuru et al., Solid State Ionics 193 (2011, 1-4)

Microstrain analysis







- Microstrain: Δd_{hkl}

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Conductivity of 20PCO in air

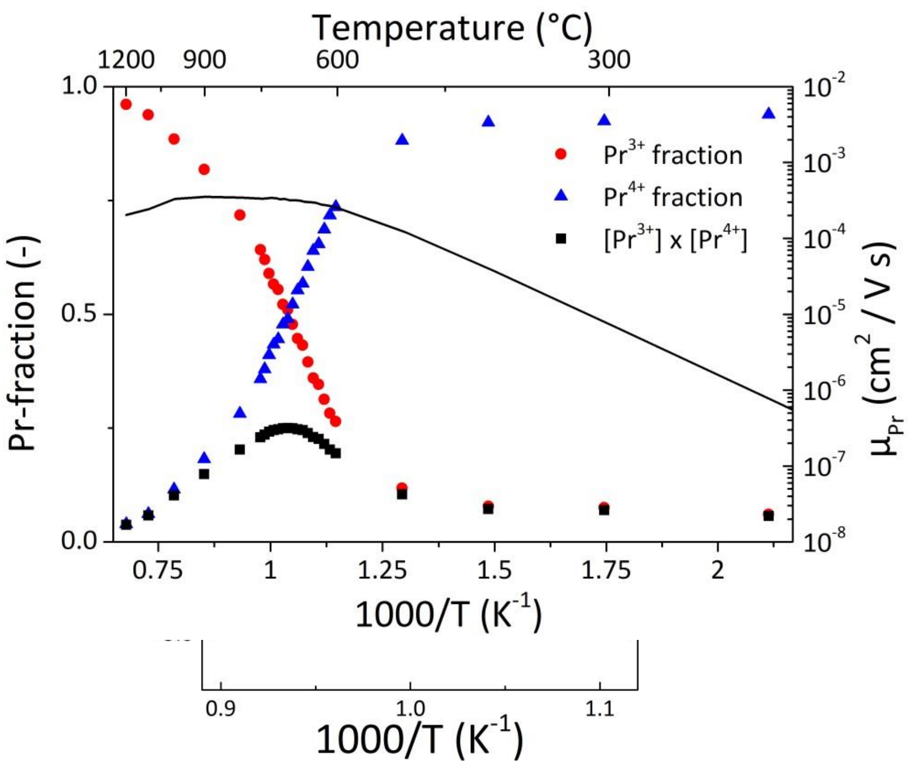
$$\sigma = [Pr'_{Ce}] * e \left[\frac{\mu_{0,Pr} [Pr^x_{Ce}]}{T[Pr_{Ce}]} exp\left(-\frac{H_{m,Pr}}{kT}\right) + \frac{\mu_{0,V}}{T} exp\left(-\frac{H_{m,V}}{kT}\right) \right]$$

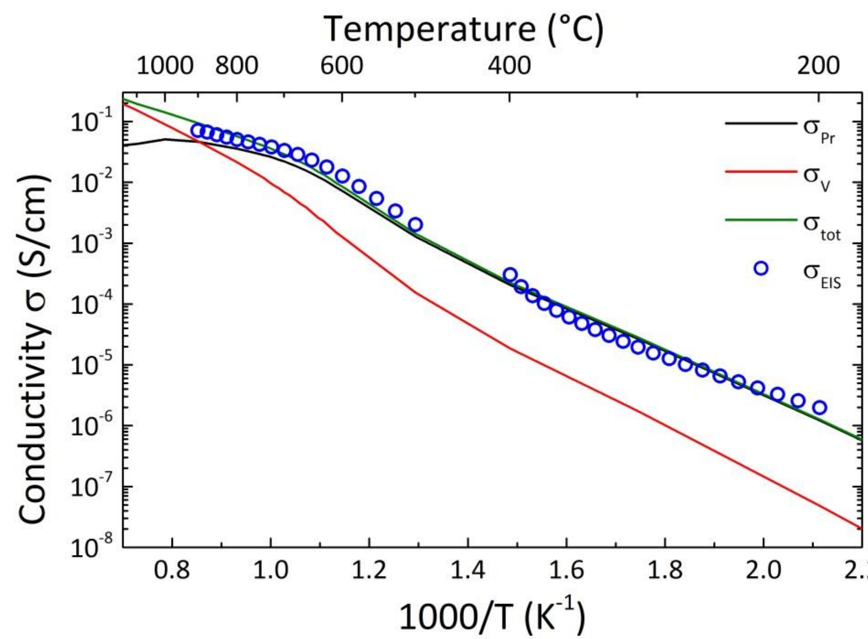
Ionic plateau ($pO_2 = 10^{-12}$ bar)

$H_{m,V} = 0.83$ eV
$\mu_{0,V} = 327$ cm²/Vs

$\sigma_{Pr} = \sigma_{tot} - \sigma_{ion}$

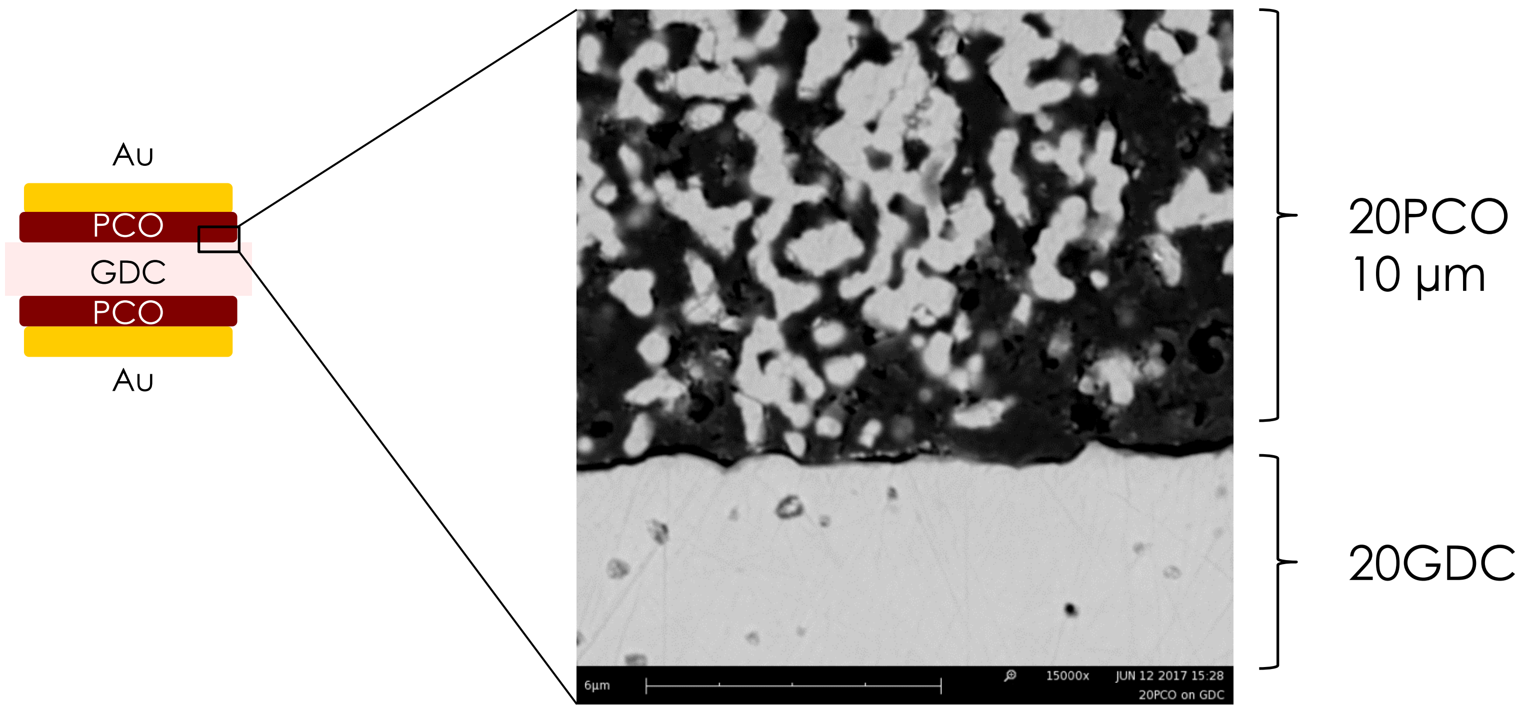
$H_{m,Pr} = 0.72$ eV
$\mu_{0,Pr} = 589$ cm²/Vs





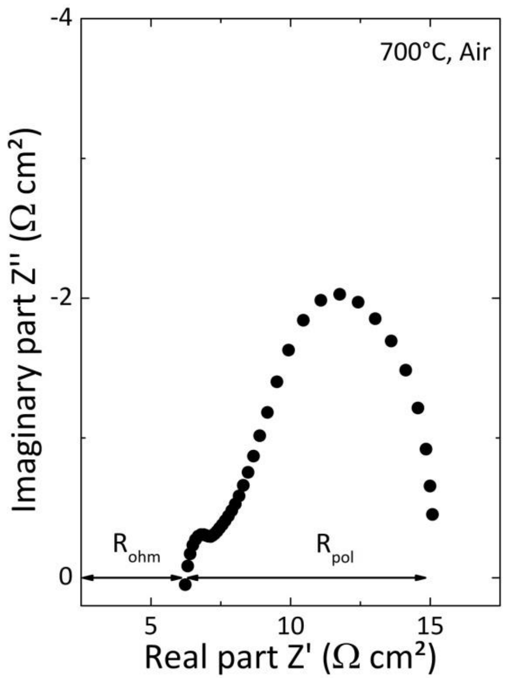
Sample preparation

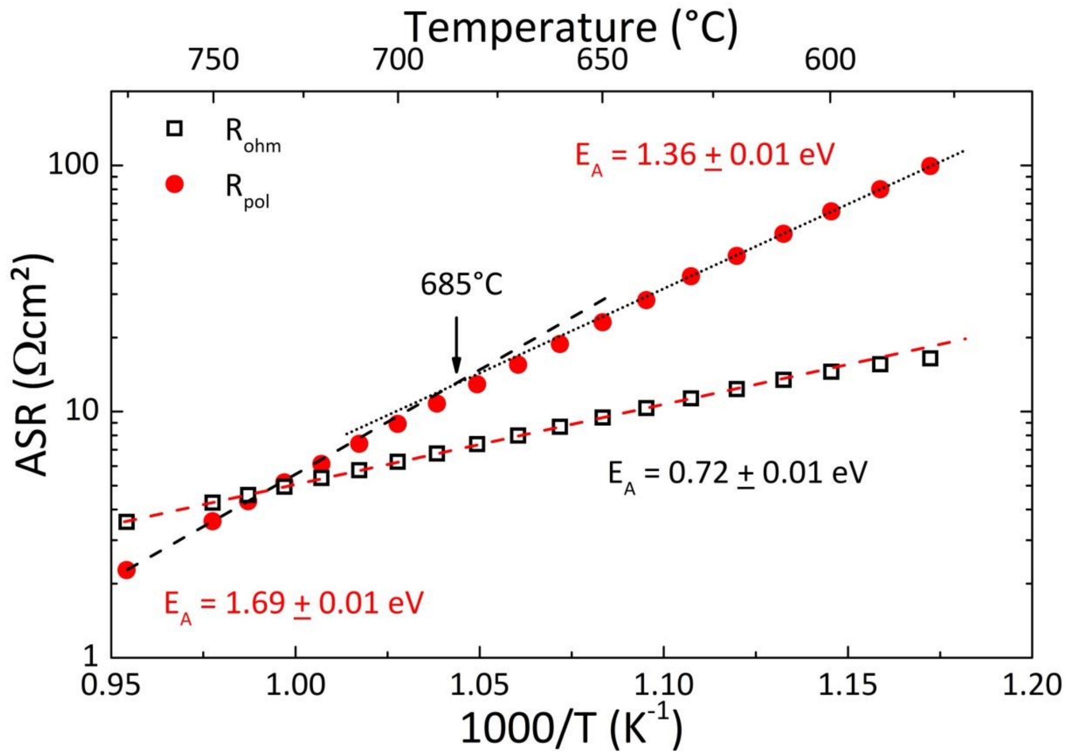
Screen printed samples on 1 mm 20GDC pellet



Cathode sintering at 1300°C

Electrochemical impedance spectroscopy





<u>Assumptions:</u>

R_{ohm} = ionic resistance of electrolyte

R_{pol} = oxygen surface exchange resistance of electrode

Summary

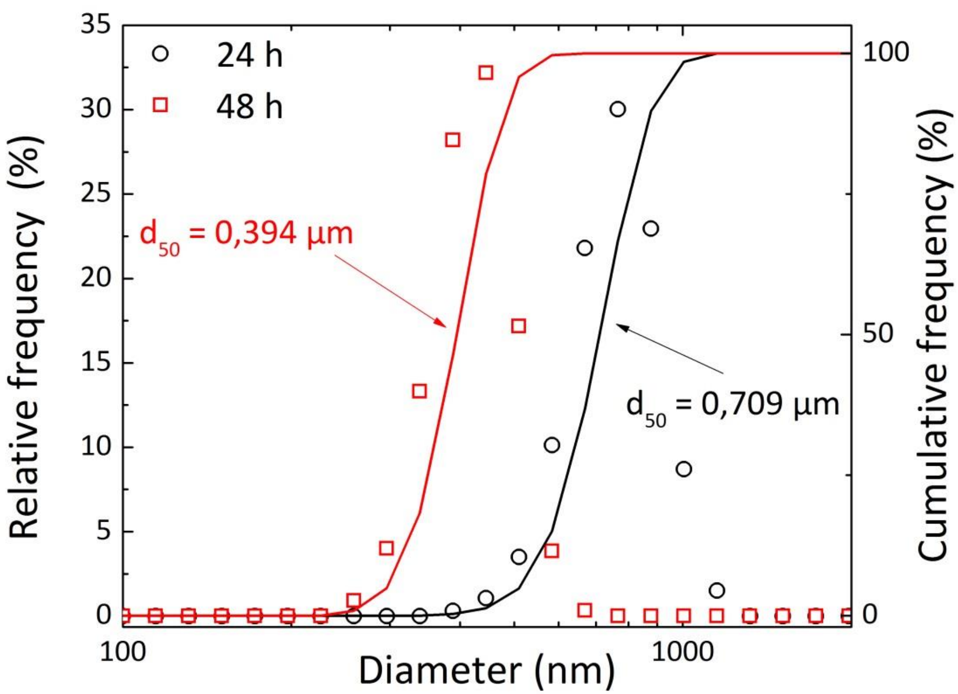
- Conductivity of 20PCO sensitive to Pr-valence state
- Mixed valence of Pr induces microstrain – maximum at $[Pr^{3+}] = [Pr^{4+}]$
- Polaron mobility has maximum at $\delta = 0.05$ – 680°C for 20PCO in air
- Polaron mobility influences polarization resistance R_{pol}
- Activation energy of 20PCO cathodes increases with T
- Chemical expansion a problem for processing

Thank you for your attention!

Preparation of screen printing pastes

Grain size is very important for properties of ceramic

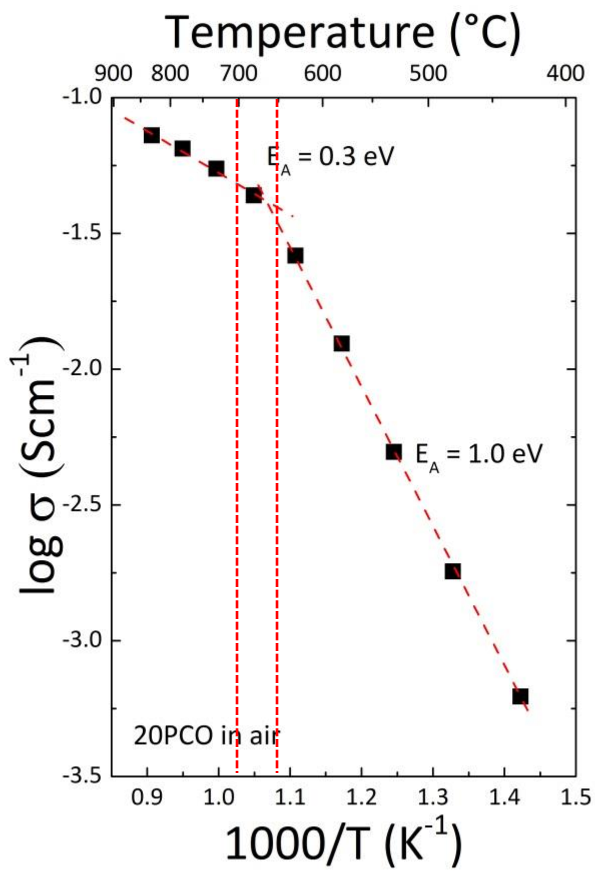
Control of particle size via ball-milling for solid state powders



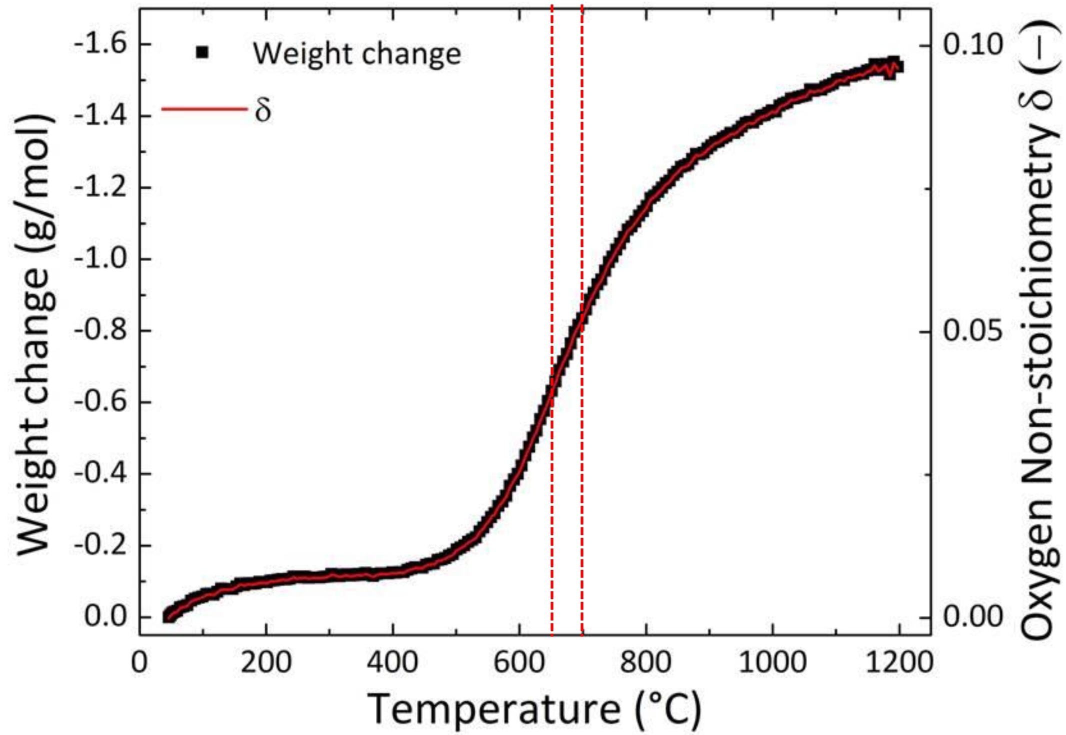
Screen printing pastes: powders in terpineol mixing the pre-suspension with ethylcellulose solved in terpineol.
Layers were printed on 150 µm 8YSZ foils (Kerafol), using a circular geometry with Ø = 12 mm for PCO and Ø = 10 mm for LSCF. Symmetric and asymmetric cells were prepared for EIS and microscopy.

PCO in air

<u>4-point conductivity</u>



<u>Thermogravimetry</u>



- Change in E_A
- Temperature interval close to $\delta = 0.05$