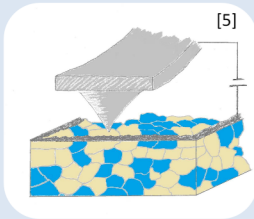JÜLICH Forschungszentrum | HELMHOLTZ-INSTITUT MÜNSTER

Measuring Chemical Diffusion Coefficients of Acceptor Doped Ceria at Room Temperature Using a Combined Polarization-KPFM Method

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## What is Kelvin Probe Force Microscopy?

[5]

Kelvin Probe Force Microscopy (KPFM) is an atomic force microscopy based analysis technique, which allows for imaging of the local surface potential distribution. A Pt coated AFM tip is used as probe. The surface potential φ_{SP} is sensitive to local changes of the defect chemistry and KPFM has a resolution in the nm and mV range.

Effect of polarization

[1]

Setup and local voltage drop
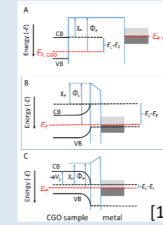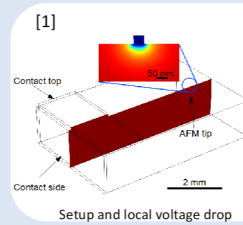
A) Initial state of the CSO sample and the tip without contact

B) Tip polarized positively

C) Tip polarized negatively

[1]
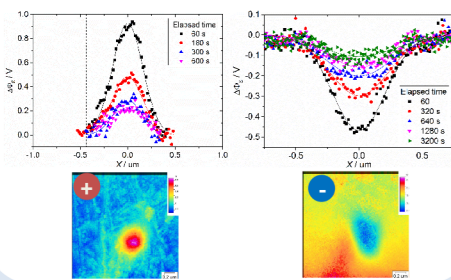
Determining diffusion coefficients

1) Mapping the pristine surface potential of a sample.
2) Polarization with a certain potential over a defined amount of time.
3) Mapping of the time-dependent decay of the introduced surface potential gradient.

τ_{fit} [5]
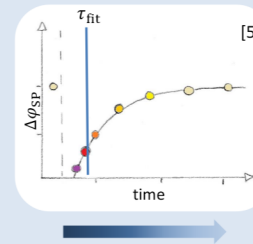
The time constant τ_{fit} can be determined from exponential fit of the data.

Chemical diffusion coefficients can then be calculated according to

$$D^{\delta} = \frac{L^2}{\pi^2 \cdot \tau_{fit}}$$

Effect of dopant concentration and redox-active dopants

$$Gd_2O_3 \xrightarrow{CeO_2} 2Gd'_{Ce} + V_O^{\circ\circ} + 3O_O^x$$

$$2[V_O^{\circ\circ}] + [h^\circ] \approx [A'_{Ce}] + [e']$$
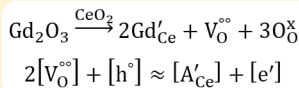
Dopant concentration in ceria is directly related to oxygen vacancy concentration $[V_O^{\circ\circ}]$.

[3]
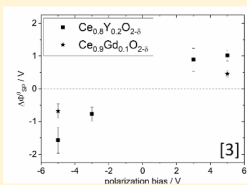
Sample with 20 mol% trivalent dopant showed SP gradient after polarization with ±3 V for 300 s, sample with 10 mol% trivalent dopant only showed evaluable results after polarization with ±5 V for 300 s (shown: SP change 60 s after end of polarization in single crystals).
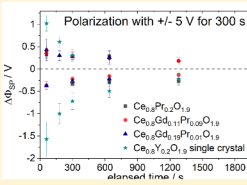
Effect of redox active dopant concetration (Pr^{4+}/Pr^{3+}) has less effect than existence of grain boundaries: Figure shows polished pellets with variable co-doping with Gd+Pr=20 mol% and 20 mol% Y-doped single crystal.

Effect of grain boundaries

[3]
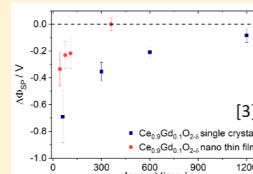
Single crystal with 10 mol% Gd doping shows a much smaller SP change than nanocrystalline thin film with same dopant concentration.

Comparing nanocrystalline and epitactic thin films, the nanocrystalline films show higher chemical diffusion coefficient. Kinetics for oxygen release is faster then for oxygen uptake to regain equilibrium with air.

Material	Experiment	τ_{fit} / s	L / nm	D^{δ} / cm^2 s^{-1}	[4]
$Ce_{0.9}Gd_{0.1}O_{1.95}$ nanocrystalline thin film	- 5 V for 300 s	132	200	$3.07 \cdot 10^{-13}$	
$Ce_{0.9}Gd_{0.1}O_{1.95}$ nanocrystalline thin film	+ 5 V for 300 s	186	200	$2.18 \cdot 10^{-13}$	
$Ce_{0.9}Gd_{0.1}O_{1.95}$ epitactic thin film	-3 V for 300 s	310	200	$1.27 \cdot 10^{-13}$	
$Ce_{0.9}Gd_{0.1}O_{1.95}$ epitactic thin film	+3 V for 300 s	479	200	$8.74 \cdot 10^{-14}$	

Conclusion

A combined method of polarization and measuring the relaxation process using Kelvin Probe Force microscopy has been shown to yield resonable results at room temperature, where doped ceria materials normally cannot be assessed due to their low charge carrier mobility below 400 °C.

The experimental approach can be adapted to different materials, e.g. it can also be used for battery materials. In addition, the method can be used to reliably determine diffusion coefficients of a single phase in a multi-component system.

Literature on this method:
[1] K. Neuhaus, K. Vels Hansen, M. Bernemann et al. **(2016)** J. Electrochem. Soc. 163 (14) H1179-H1185
[2] K. Neuhaus, F. Schulze-Küppers, S. Baumann et al. **(2016)** Solid State Ionics 288, 325-330
[3] K. Neuhaus **(2018)** in: Microscopy Science: Last Approaches on Educational Programs and Applied Research, Publisher: Formatex Research Center
[4] K. Neuhaus, G. Gregori, J. Maier **(2018)** ECS J Solid State Sci. Technol. 7 (8) P362-P368
[5] K. Neuhaus, C. Schmidt, L. Fischer, W.A. Meulenberg, K. Ran, J. Mayer, S. Baumann **(2021)** Beilstein J Nano 12(1):1380-1391

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