Measuring surface exchange characteristics of $Ce_{0.9}Gd_{0.1}O_2$ single crystals using Kelvin probe force microscopy

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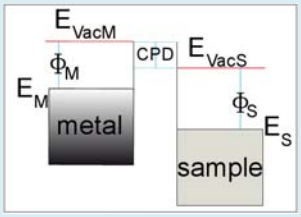
Doped ceria shows good oxide ion conductivity at intermediate temperatures and has already been proposed for a variety of different applications, especially in catalysis [1,2]. By polarizing doped ceria single crystals and mapping the reaction to the polarization with the help of Kelvin probe force microscopy (KPFM) information concerning the defect mobility and surface reactions of ceria in different atmospheres and at comparably low temperatures can be yielded [3,4]. This is valuable to improve ceria materials for the application at lower temperatures.

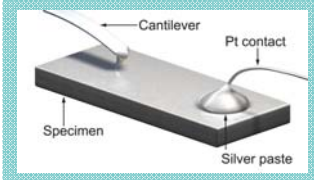
For the measurements, doped ceria single crystals with the composition $Ce_{0.9}Gd_{0.1}O_{2-\delta}$ (CGO10) produced by skull melting were used. Experiments were executed with an Agilent 5500 AFM, Asylum Cypher AFM and the CAHT-2 (controlled atmosphere, high temperature) scanning probe microscope by DME - Danish Micro Engineering [5]. Positive or negative biases were applied to the samples at different temperatures and atmospheres with AFM cantilever acting as a working electrode. Application time and bias voltage were changed.

KPFM

Measurement of the sample surface potential (SP) and information on work function. Information about the SP can be used to investigate changes in the defect chemistry of a material. All measurements were done with an Agilent 5500 AFM system.



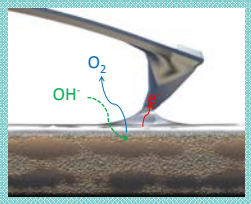
Measurement setup and prospects



Doped ceria is a mixed conductive material which can transport electrons and oxide ions. With application of voltage, vacancies can be generated and electrons can be pulled out or pushed into the material.

$$\frac{1}{2}O_2(g) + V_O^{\bullet\bullet} + 2e^- \rightleftharpoons O_O^x$$

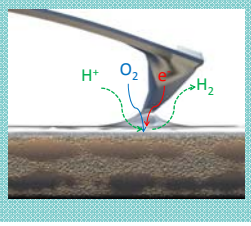
Interaction between sample, bias and adsorbed water



\+ Vacancies develop: electrons are pulled from the oxygen atoms in the crystal lattice
Possible reaction to decrease the potential:

$$2\,OH'_{ad} + V_O^{\bullet\bullet} \rightleftharpoons O_O^x + H_2O_{ad}$$

Filling vacancies with hydroxide ions



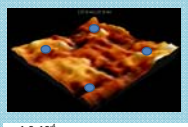
\- Electrons are pushed into material⟶ reduction of the electrolyte:

$$V_O^{\bullet\bullet} + 2e^- \rightleftarrows V_O^x$$

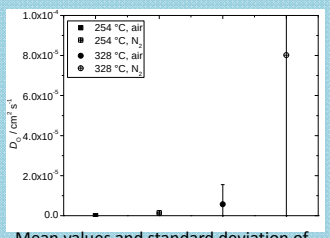
Possible reaction to decrease the potential:
1) Trapping of e^- at defect sites.
2) H^+ from hydrolysis reaction reacts with e^- to H_2.

Overall: change of defect concentration in both cases.

CAHT-2

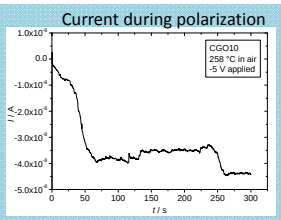


Single point measurements:
$T_{surface}$ = 254 °C and 328 °C
$T_{surface}$ < 254°C: no measureable current.

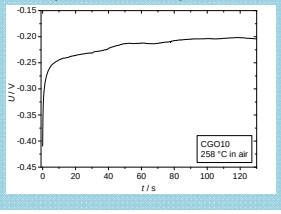


Mean values and standard deviation of diffusion coefficient calculated from relaxation measurements.

Current during polarization

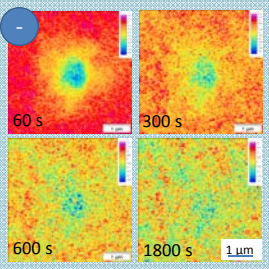


Open circuit after polarization

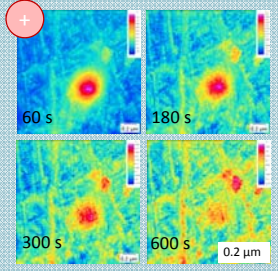


Results after charge application: acceptor doped single crystals

-5 V, 300 s , measurement on $Ce_{0.9}Gd_{0.1}O_2$

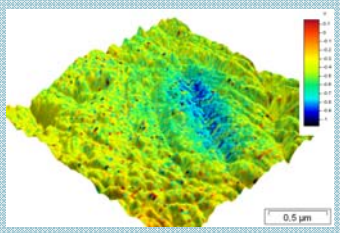


+5 V, 300 s measurement on $Ce_{0.8}Y_{0.2}O_2$

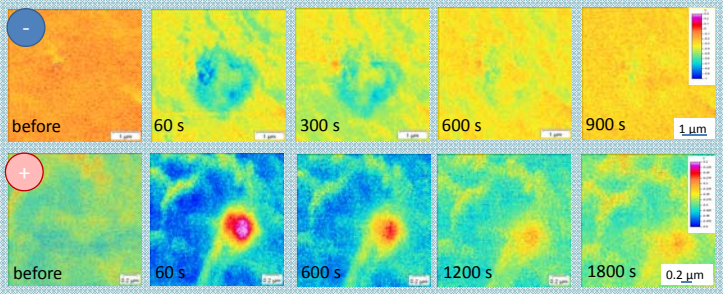


- Single crystals = comparable behavior to thin films, measured by Lee et al. [3]
- Negative polarization = longer visibility
- Polarization effect follows topography
- Effects discharge faster than for thin films
  Reason = no grain boundaries?
- Polarization effects on 10 mol% acceptor doped sample less intensive than for 20 mol% acceptor doped sample

Polarization effect follows features of the topography (height difference in the range of 30 nm). CYO, -3 V, 300 s application time.



Effect of temperature (T_{sample} = 50 °C) on CGO10



±5 V, 300 s , measurement on $Ce_{0.9}Gd_{0.1}O_2$

- Diameter of effect of negative polarization is much larger
- Negative effect decays faster
- Positive effect is more or less circular while negative effect always has an area of lower intensity in the middle

Different behavior after polarization reveals different transport mechanisms.

Conclusion:
By locally changing the electron concentration, the local concentration of oxygen vacancies in the sample is varied, giving valuable information about the surface exchange processes during oxygen uptake or exsolution from the crystal structure.

During single point measurements, electrochemical data about the defect mobility were collected. Here, no sensible values were measureable below a temperature of 250 °C. The disappearance of the defect gradients after bias application was subsequently mapped using KPFM. An effect was measurable reproducibly even at room temperature, making KPFM a versatile tool to further investigate surface exchange of ceria, e.g. for catalyst application.

Literature:
[1] V.V. Kharton et al. **2001** *J. Mat. Sci. 36*, 1105
[2] A. Trovarelli **1996** *Catal. Rev: Sci. Eng. 38*, 439
[3] W. Lee et al. **2009** *Nanotechnology 20*, 1
[4] H.J. Avila-Paredes et al. **2010** *J. Mat. Chem.* 20, 10110
[5] K.V. Hansen et al. **2013** *Rev.Sci. Instrum. 84*, 073701

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