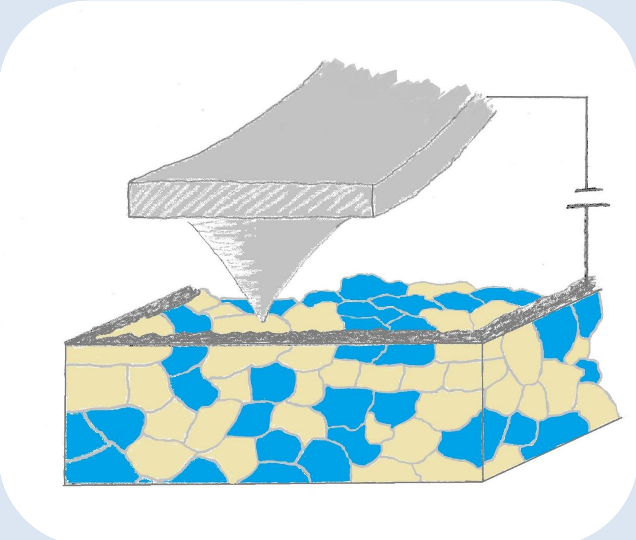
BATTERY CONFERENCE March 28-30, 2022

JÜLICH Forschungszentrum | HELMHOLTZ-INSTITUT MÜNSTER

Combined polarization-KPFM method to determine changes of the surface potential of ceria-spinel-based dual phase composites

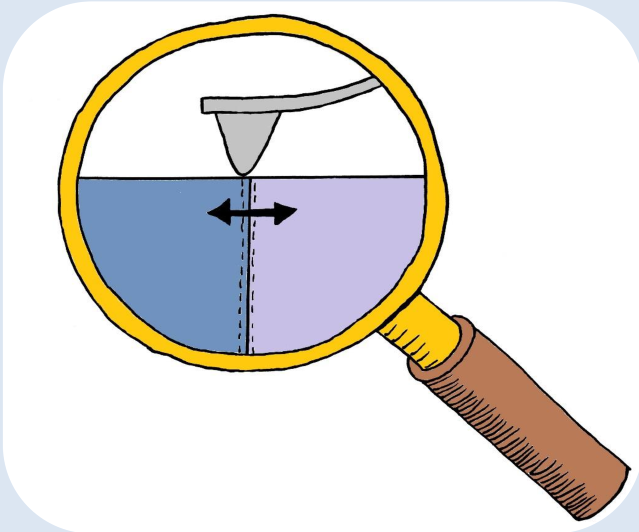
C. Schmidt, L. Fischer, K. Ran, J. Mayer, S. Baumann, K. Neuhaus

What is Kelvin Probe Force Microscopy?



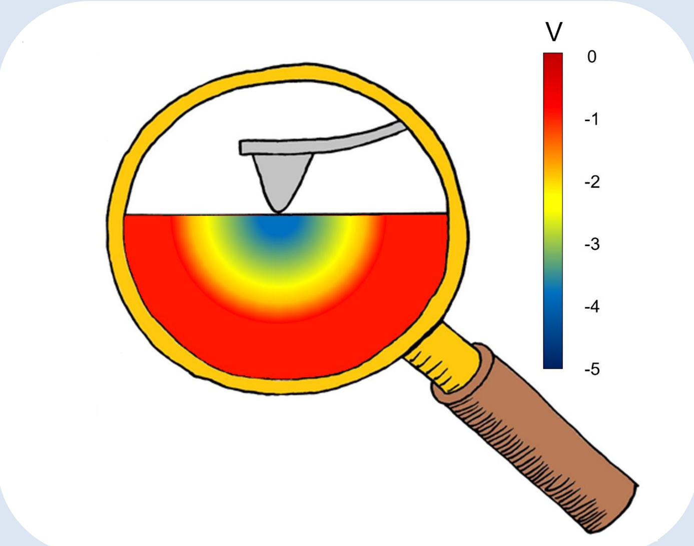
Kelvin Probe Force Microscopy (KPFM) is an atomic force microscopy based analysis technique, which allows for imaging of the local surface potential distribution and has a resolution in the nm range. A Pt coated AFM tip is used as probe. The surface potential φ_{SP} is sensitive to local changes of the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

Distinguishing phases in a composite



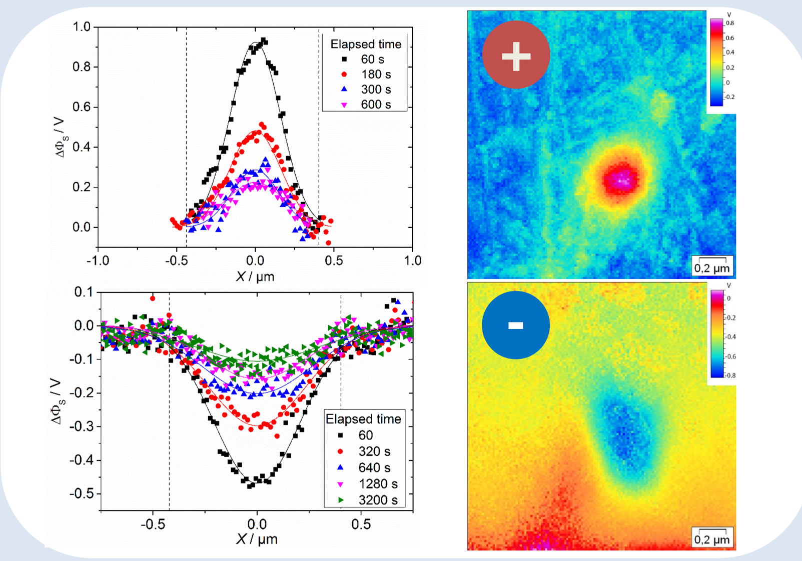
The dual-phase oxygen permeation membrane in this study consists of a good electron conductor and a good oxygen ion conductor. As the surface potential is directly related to the local Fermi niveau, both materials are easily distinguishable because the spinel phase has a low and the ceria phase a high surface potential.

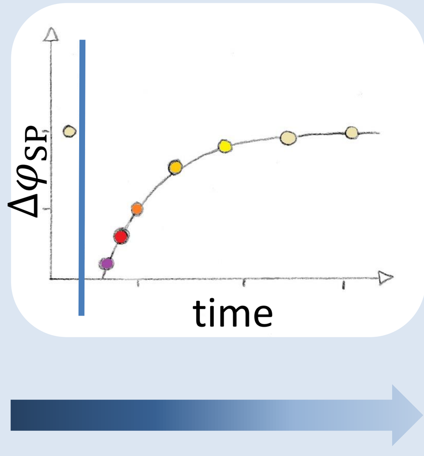
Polarization-KPFM method



The AFM tip is used as an electron-conductive nanoscale electrode to apply a constant voltage pulse to the sample. In a subsequent mapping experiment, the AFM tip is used as Kelvin probe to scan the locally changed surface potential distribution until the original state is reached again.

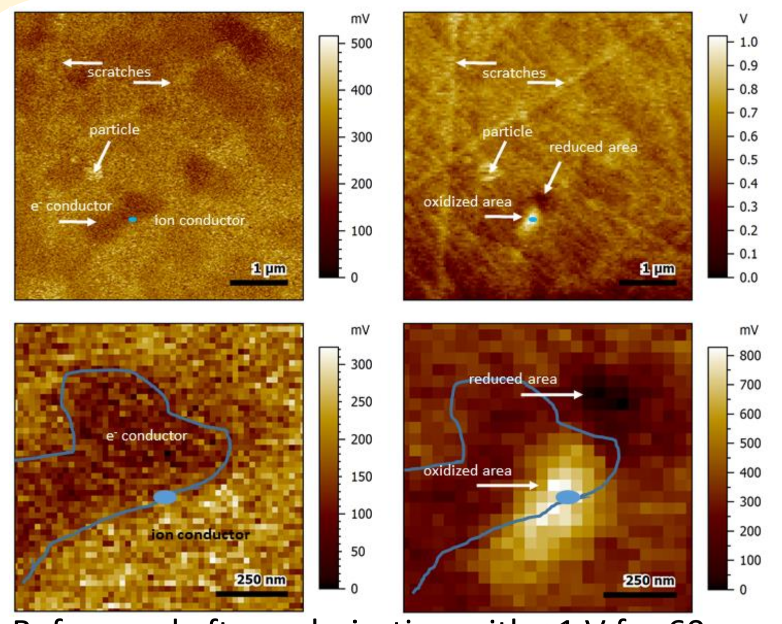
Determining diffusion coefficients





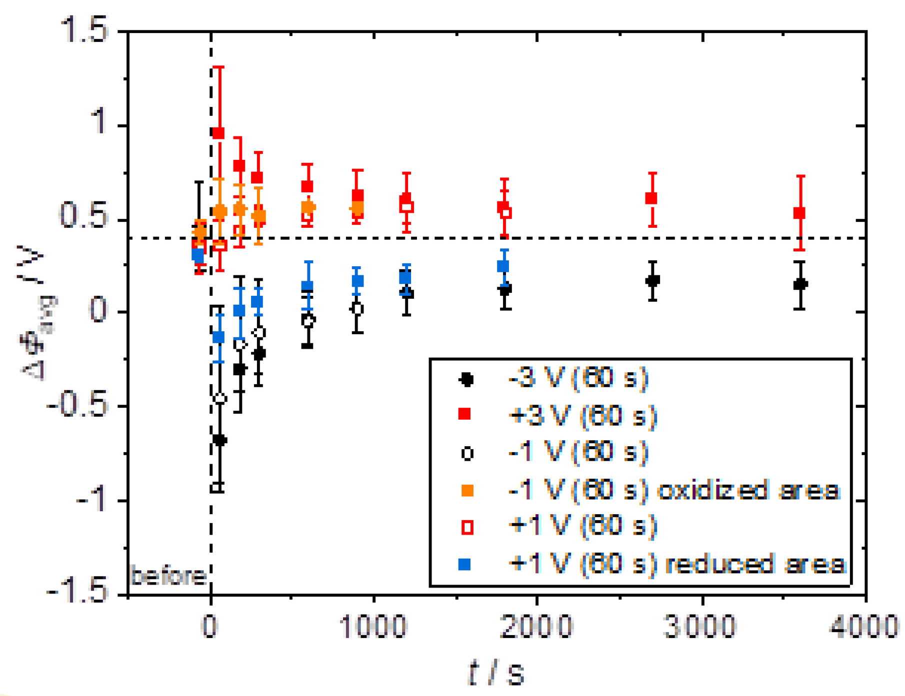
Time constant τ_{fit} can be determined from exponential fit of the data. Diffusion coefficients can be calculated according to $D^{\delta} = \frac{L^2}{\pi^2 \cdot \tau_{fit}}$

Results for 60 wt% $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ + 40 wt% $FeCo_2O_4$ (CSO-FC2O)



Before and after polarization with +1 V for 60 s. Blue dot illustrates contact area.

If the polarization with +/-1 V was performed in direct vicinity of the electron conductive spinel phase, in several cases, an additional affected area near the contact zone was identfied, which showed a local oxidation when a negative bias had been applied and vice versa.
This did not occur when higher voltages (+/-3 V) were applied.



Relaxation process for positively polarized areas and for oxidized areas after polarization with -1 V do not follow exponential rule. Relaxation process after polarization with +/- 3 V and of reduced area after polarization with +1 V can be used for calculation of diffusion coefficients.

Material	Experiment	τ_{fit} / s	L / nm	D^{δ} / cm² s⁻¹
$Ce_{0.9}Gd_{0.1}O_{1.95}$ thin film*	- 5 V for 300 s	132	200	$3.07 \cdot 10^{-13}$
$Ce_{0.9}Gd_{0.1}O_{1.95}$ thin film *	+ 5 V for 300 s	186	200	$2.18 \cdot 10^{-13}$
CSO-FC2O	-3 V for 60 s	274	300	$3 \cdot 10^{-13}$
CSO-FC2O	+3 V for 60 s	202	300	$5 \cdot 10^{-13}$
CSO-FC2O	-1 V for 60 s	200	200	$2 \cdot 10^{-13}$
CSO-FC2O (reduced area)	+1 V for 60 s	116	200	$4 \cdot 10^{-13}$

* Nanocrystalline thin film samples. K. Neuhaus, G. Gregori, J. Maier (2018) ECS J Solid State Sci Technol 7 (8) P362-P368

Implementation to Battery material investigation

The polarization-KPFM method presents an opportunity to investigate transport properties in a focused area like single particles in a hybrid electrolyte or in a composite cathode material.
On this way, local concentration polarizations and selective diffusion coefficients can be obtained.
The Informations can be used to clarify the pathway of lithium ions throught hybrid materials in battery components.

Conclusion

Measuring the diffusion coefficient of the ceria phase in a dual-phase material is possible by using a combined polarization-KPFM method. Results are comparable to data for ceria thin films with a similar dopant concentration. In the future, this technique can be used to answer important questions for the transport processes in hybrid materials for lithium ion batteries.

Check out our publications on this topic:

K. Neuhaus, K. Vels Hansen, M. Bernemann et al. **(2016)** J. Electrochem. Soc. 163 (14) H1179-H1185

K. Neuhaus, F. Schulze-Küppers, S. Baumann et al. **(2016)** Solid State Ionics 288, 325-330

K. Neuhaus, G. Gregori, J. Maier **(2018)** ECS J Solid State Sci. Technol. 7 (8) P362-P368

K.Neuhaus, C. Schmidt, L. Fischer, W.A. Meulenberg, K. Ran, J. Mayer, S. Baumann **(2021)** Beilstein J. Nanotechnol. *12* 1380-1391

ch.schmidt@fz-juelich.de