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

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Dual phase composites, consisting of doped ceria as oxygen conductive phase and an iron-cobalt-based spinel ($Fe_{3-x}Co_xO_4$) as electron conductive phase can be used as oxygen permeation membranes working at high temperatures above 800 °C [1-3].

The defect chemistry of these materials is well analyzed for temperatures between 600-1200 °C, whereas for other applications, for example in membrane reactors to enable partial oxidation, lower temperature is needed. Especially ceria-based composites hold great promise for low-temperature applications due to their very high oxide ion conductivity at comparably moderate temperatures. Yet, for a better understanding of low temperature charge transport, further investigation is required.

In this study we used composites of ceria, doped with Gd or Sm and FeCo₂O₄ or its iron-rich counterpart Fe₂CoO₄. We apply Atomic Force Microscopy (AFM) to determine the local surface potential [4, 5], which is a sensitive indicator for local changes of the defect chemistry.

By using a platin coated AFM tip as an electron conducting nano-electrode, a constant voltage pulse was applied to a certain point at the sample surface to induce a local polarization with distinctly changed redox state and defect concentrations. Straight afterwards, a Kelvin Probe Force Microscopy (KPFM) measurement was followed, where the AFM tip was used as Kelvin probe to scan the locally changed surface potential distribution at the sample surface. On this way the relaxation process was mapped until the original state was reached again.

This measurement setup allows us to observe local surface potential distribution, lateral extent of the gradient, variations of the shape of the gradient and changes in the potential distribution at grain boundaries [6, 7]. We are also able to determine room temperature diffusion coefficients. This type of measurement can also be used in the research of composites utilized in batteries.

Literature:

- 1. Ramasamy, M.; Baumann, S.; Palisaitis, J.; Schulze-Küppers, F.; Balaguer, M.; Kim, D.; Meulenberg, W. A.; Mayer, J.; Bhave, R.; Guillon, O. *J Amer Ceram Soc* **2016**, *99* (1), 349-355.
- 2. Ramasamy, M.; Persoon, E. S.; Baumann, S.; Schroeder, M.; Schulze-Küppers, F.; Görtz, D.; Bhave, R.; Bram, M.; Meulenberg, W. A. *Journal of membrane science* **2017**, *544*, 278-286.
- 3. Lin, Y.; Fang, S.; Su, D.; Brinkman, K. S.; Chen, F. Nature Comm **2015**, 6 (1), 1-9.
- 4. Örnek, C.; Leygraf, C.; Pan, J. Corr Eng Sci Tech 2019, 54 (3), 185-198.
- 5. Melitz, W.; Shen, J.; Kummel, A. C.; Lee, S. Surf Sci Rep **2011**, 66 (1), 1-27.
- 6. Neuhaus, K.; Schulze-Küppers, F.; Baumann, S.; Ulbrich, G.; Lerch, M.; Wiemhöfer, H.-D. *Solid State Ionics* **2016**, *288*, 325-330.
- 7. Lee, W.; Lee, M.; Kim, Y.-B.; Prinz, F. B. *Nanotechnology* **2009**, *20* (44), 445706.