Numerical Simulation of Transport Processes in Mixed Ionic/ Electronic Conductors in the Mesoscopic Scale

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We report on the numerical simulation of diffusion and charge transport in mixed ionic/ electronic conductors based on a continuous medium approach. The utilized model allows calculating thermodynamic and kinetic processes in the bulk and at grain boundaries of mixed conductors even for significant changes in the defect concentrations and under large potential gradients. The model also includes the derivation of experimentally accessible parameters such as tracer diffusion profiles and of electrical quantities such as dc conductivity or complex impedance spectra.

The excellent applicability of the proposed model for diffusion processes is demonstrated on the re-oxidation of donor-doped $SrTiO_3$ (STO) in combination with ^{18}O tracer diffusion experiments [1]. The experimental observation of anomalous ^{18}O tracer diffusion profiles for oxygen pre-annealed STO single crystals can be explained in detail by an enrichment of oxygen vacancies towards the surface. The heterogeneous distribution of oxygen defects is found to originate from a negative internal electric field, which is formed by the ambipolar diffusion of the majority defects electrons and strontium vacancies. The influence of several experimental parameters on the tracer profile could be predicted by simulations semi-quantitatively.

A numerical estimation of the ac ionic conductivity in Y-doped CeO_2 ceramics under dc voltage bias is performed as an example of a charge transport process. A back-to-back Schottky barrier model is used to introduce a grain boundary in the simulation. The experimentally determined shrinking of the grain boundary semi-circle in the Cole-Cole diagram upon applying a dc bias voltage can be well reproduced by the simulation. Here, we find a bias dependent asymmetric space charge distribution adjacent to the grain boundary, which is accompanied by an increase of the oxygen vacancy concentration in the vicinity of the interface. Hence, the grain boundary conductivity increases in agreement with the experiment. The flattening of the grain-boundary semi-circle, in an equivalent circuit commonly described by a constant phase shift element, is also observed in the simulation.

[1] R. Meyer, R. Waser, J. Helmbold, G. Borchardt, Phys. Rev. Lett. 90 105901/ 1-4