MAPPING OF THE OXYGEN VACANCY DISTRIBUTION IN PbZr\textsubscript{1-x}Ti\textsubscript{x}O\textsubscript{3} – THE INFLUENCE OF FIELD, ELECTRODES, TEMPERATURE AND TIME

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Introduction
Oxygen vacancies can play an important role in fatigue and resistance degradation of electroceramics. For example, under external or internal fields an accumulation of oxygen vacancies at interfaces and domain walls could be observed in PbZr\textsubscript{1-x}Ti\textsubscript{x}O\textsubscript{3} (PZT) based ceramics and other perovskite-type titanates such as SrTiO\textsubscript{3}, BaTiO\textsubscript{3} [1,2]. To improve the performance of PZT based applications, a detailed understanding of field-driven degradation phenomena and their defect chemical background is essential. The aim of our study is thus to investigate the influence of electric field, electrodes, temperature and degradation time on the distribution of oxygen vacancies in PZT.

Experiments
High electric fields were applied to either Cu or Pt electrodes on donor doped PZT. During such a DC polarization, the sample was exposed to an oxygen tracer-rich ambient (\textsuperscript{18}O\textsubscript{2}, 200mbar), either for the entire time or for certain shorter time intervals. Subsequent time-of-flight-secondary ion mass spectrometry (ToF-SIMS) was used to analyze the tracer diffusion process. Operating ToF-SIMS in “Collimated Burst Alignment” (CBA) mode provides high spatial resolution in addition to an accurate determination of the local oxygen isotopic fraction [3]. Since the resulting oxygen tracer diffusion coefficient depends on the vacancy concentration, a detailed mapping of the oxygen vacancy distribution became possible. \textsuperscript{18}O depth profiles in anode- and cathode-near diffusion zones or non-stressed areas without applied field allowed monitoring of the oxygen vacancy redistribution under high fields.

Results and Discussion
The cumulative \textsuperscript{18}O fraction in Fig. 1 shows a typical oxygen tracer distribution after DC-degradation. An electric field of 1kV/mm\textsuperscript{-1} was applied to Cu inner electrodes in tracer ambient for the entire degradation time of 4h. Compared to tracer diffusion without electric field, a higher \textsuperscript{18}O fraction was observed in both anode- and cathode-near regions (see Fig. 2). A significantly enhanced \textsuperscript{18}O fraction in the cathode-near diffusion zone indicates a field-driven oxygen vacancy accumulation at a partly or completely blocking cathode. The slightly higher tracer fraction in the anode-near area indicates oxygen evolution.

Fig. 1. Mapping of oxygen tracer ions after DC-degradation. Bright color indicates high concentration.

Fig. 2. \textsuperscript{18}O depth profiles obtained in reference, anode- and cathode-near regions.

Many additional measurements revealed information on the time, temperature, electrode and field dependence of the vacancy distribution.

Conclusions
Mapping of oxygen tracer ions and thus indirectly of the oxygen vacancy distribution indicates a field-driven stoichiometry polarization in PZT under field load. Spatially resolved ToF-SIMS analysis gives detailed information on local grain and grain boundary diffusion coefficients and their dependence on several experimental parameters.

References