Many physical and chemical properties of ceria can be attributed to the tolerance of the fluorite structure to a high concentration of oxygen ion vacancies, which allows ceria to change oxidation states over a wide temperature range at low $P_{O_2}$. On ceria surface, oxygen vacancies can rapidly formed and re-oxidized, giving ceria an enhanced ability to release and store oxygen and to split $H_2O$ in catalytic reactors. In the bulk, oxygen vacancies are the predominant charge carriers, which makes ceria one of the most important oxygen ion conducting solid electrolytes in solid oxide fuel cells (SOFCs). Therefore, the abilities to monitor the oxygen vacancy number at the surface and in bulk at a given pressure, temperature, and gas environment are important and highly desirable to explore and create new ceria based materials and devices. By using ambient pressure photoelectron spectroscopy (AP-XPS) on a 50 nanometers thin ceria electrode [1], it has been shown that the electrochemically active region undergoes a pronounced Ce$^{4+}$ to Ce$^{3+}$ surface oxidation change during operation, suggesting that the surface reaction kinetics and lateral electron transport in thin ceria are co-rate limiting processes. Combining AP-XPS, micro X-ray absorption spectroscopy (micro-XAS) and X-ray microdiffraction (micro-XRD), we have investigated the water splitting process occurring at the ceria/gold interface of a 1 micron thick ceria SOEC cell, in situ. A shift of the cell parameters of ceria is observed under operation, in relation with the formation of oxygen vacancies. This is an evidence of a long-range process of ceria to change oxidation states over a wide temperature range to Ce$^{4+}$ to Ce$^{3+}$ surface oxidation change during operation, suggesting that the surface reaction kinetics and lateral electron transport in thin ceria are co-rate limiting processes.

Keywords: ceria, micro-XRD, solid oxide electrochemical cell

Polycrystalline ferroelectrics offer a cost-effective route to produce materials with enhanced dielectric and electro-mechanical coefficients. They are the backbone of many sensors, actuators, non-linear optics and power conversion devices. Understanding the microscopic mechanism of these functionalities is the key to the optimization and design of new materials with enhanced properties.

The existing techniques lack the capability to measure polarization-strain coupling. This presentation shows the novel efficient technique [1] which introduces time-resolved and resonant synchrotron X-ray diffraction to simultaneously measure the atomic displacements, lattice strain and macroscopic polarization in a polycrystalline ferroelectric under cyclic electric fields. The time-resolved X-ray diffraction implements a stroboscopic data acquisition strategy operating on the principle of a multi-channel analyser, and providing an ideal platform for the investigation of repetitive processes down to the nanosecond time scale [2]. X-ray diffraction measurements are combined with the polarization measurements (electric field-polarization hysteresis loop). Most significantly, the structural inversion in individual crystallites of ferroelectric ceramics was observed through the Friedel pair contrast. This is a significant methodological innovation: because the $h$-$k$ and $-h$-$k$ powder rings exactly overlap with one another, the conditions at which the violation of Friedel’s law can be observed using powder diffraction are very rare. These conditions can only be realized if: 1) a structure of individual powder grains can be actively inverted during the measurement and 2) the intensity of powder diffraction patterns is high enough to detect this small difference.

We demonstrate this approach using a high-energy (30 keV) X-ray beam on a material in which differentiating between multiple polarization reversal mechanisms remains a significant challenge: tetragonal $0.94\cdot BaTiO_3$-0.06$\cdot BiZn_{2/3}$Ti$_{1/3}$O$_5$ (BT-BZT) perovskite-based polycrystalline ferroelectrics. The approach offers significant opportunities for probing dynamics of intrinsic polarization using resonant X-ray scattering.

References:

Keywords: ferroelectrics, time-resolved X-ray diffraction, high-energy powder diffraction, in-situ measurements