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MS43-O4 Operando Study of Ceria Based Solid Oxide Electrochemical CellsCatherine Dejoie¹, Fabiano Bernardi², Yi Yu^{3,4}, Nobumichi Tamura¹, Martin Kunz², Matthew Marcus³, Chunjuan Zhang⁴, Bryan Eichhorn¹, Zhi Liu^{3,5}

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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 H₂O 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 Ce⁴⁺ to Ce³⁺ 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 and the reduction of ceria in the bulk. Comparison of the oxygen vacancy number extracted from micro-XRD and micro-XAS experiments shows that ceria is mainly under a crystalline form. Furthermore, the active region extends on the other side of the ceria/gold interface, which means that reduction also occurs on top of gold. Thus, the electron transport in ceria may not be rate limiting in a thicker ceria electrode [2]. Finally, we show that the phase diagram of deficient ceria (CeO_{2-x}, 0<x<0.2) is not valid anymore for such a non-equilibrium system. Such knowledge on structure and oxygen vacancy changes will be important in order to understand the ion transport and the degradation of electrodes in working electro-chemical cells (fuel cells and batteries).

[1] Zhang C., et al. *Nature Mater.* 2010, 9, 944. [2] Zhang, C. et al. *J. Am. Chem. Soc.* 2013, 135, 11572.

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

MS43-O5 Combined measurements of atomic displacements, lattice strain and macroscopic polarization in ferroelectricsSemën Gorfman¹, Hugh Simons², Hyeokmin Choe¹, Ullrich Pietsch¹, Michael Ziolkowski¹, Jacob Jones³

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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 discovery 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 hkl and -h-k-l 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-BaTiO₃-0.06-BiZn_{0.2}Ti_{0.8}O₃ (BT-BZT) perovskite-based polycrystalline ferroelectrics. The approach offers significant opportunities for probing dynamics of intrinsic polarization using resonant X-ray scattering.

[1] S. Gorfman, H. Simons, T. Iamsasri, S. Prasertpalichat, D.P. Cann, H. Choe, U. Pietsch, Y. Watier, J.L. Jones. *Scientific Reports*, 20829, (2016)

[2] S. Gorfman, H. Choe, V. V Shvartsman, M. Ziolkowski, M. Vogt, J. Strempler, T. Łukasiewicz, U. Pietsch, and J. Dec, *Phys. Rev. Lett.* 114, 097601 (2015)

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