ESRF	**Experiment title:** In-situ SXRD study of fuel cell model cathodes	**Experiment number**: HC902
Beamline: ID03	**Date of experiment**: from: 06.02.2014 to: 11.02.2014	**Date of report**: 26.02.2014
Shifts: 15	**Local contact(s)**: Jakub Drnec, Helena Isern	*Received at ESRF:*

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Report:

Solid oxide fuel cells (SOFCs) are regarded as a very promising technology to generate clean electrical energy by direct conversion from chemical energy [1]. Yttria-stabilized zirconia (YSZ) is a key material used in SOFCs where it acts as solid electrolyte for oxygen ions. The YSZ surface in addition plays a central role in the relevant reactions on SOFCs electrodes: it is involved in the adsorption and oxidation of hydrocarbons, the formation of H_2O and the oxidation of carbon monoxide at the anode side [1, 2]. At present the bottleneck for the efficiency of solid oxide fuel cells is the dissociation and incorporation of oxygen at the fuel cell cathode side, which requires high temperatures (above 1000 K). Oxygen incorporation is enhanced by the presence of perovskite-type oxides such as (La,Sr)MnO_3 and (La,Sr)(Co,Fe)$O_{3-\delta}$ on the cathode. At present, it is not clear if the triple phase boundary between oxygen, perovskite and YSZ plays the dominant role for the incorporation of oxygen or the surface of the perovskite electrodes. To shed light on these questions, electrochemistry experiments were performed at ID03 with a UHV chamber allowing for surface diffraction.

There were 4 samples placed on one sapphire substrate covered with silver paste. All 4 different electrode materials ($La_{0.8}Sr_{0.2}MnO_3$, $La_{0.6}Sr_{0.4}CoO_3$, Pt, Au) were deposited on YSZ (100) by Pulsed Laser Deposition (PLD) using circular shadow masks with diameters between 100-500μm (see Fig.1). Our electrochemistry setup (Fig.2) also allowed impedance spectra measurements of the electrodes directly at the beamline, which gives us information if the electrode we perform our measurements on is in working condition or not, and exact temperature of the sample surface. All the measurements were performed under controlled conditions: fixed oxygen pressure (200 mbar), fixed temperature (482°C on the sample surface) and variable potentials (within ±10.00V range). Anomalous SXRD data sets were collected slightly below Zr K edge (17.98 keV). The relatively small electrodes were aligned in the x-ray beam by their fluorescence signals, for which a detector mounted perpendicular to the beam. Data were collected both from regions underneath (interface) and far from the electrodes (free surface). The oxygen chemical potential was tuned has been tunable locally by applying a voltage to a micrometer sized tip, which had been brought into contact with the electrode from the top. The beam was focused in vertical direction to 5-10 μm by KB-optics and was around 50 μm in horizontal direction.

Fig.1 The sample

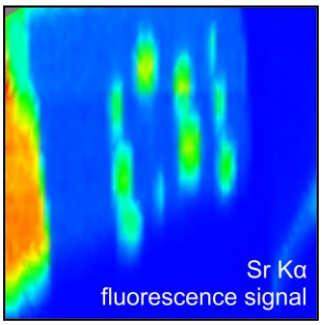

Fig.3. Mapping of the LSC sample

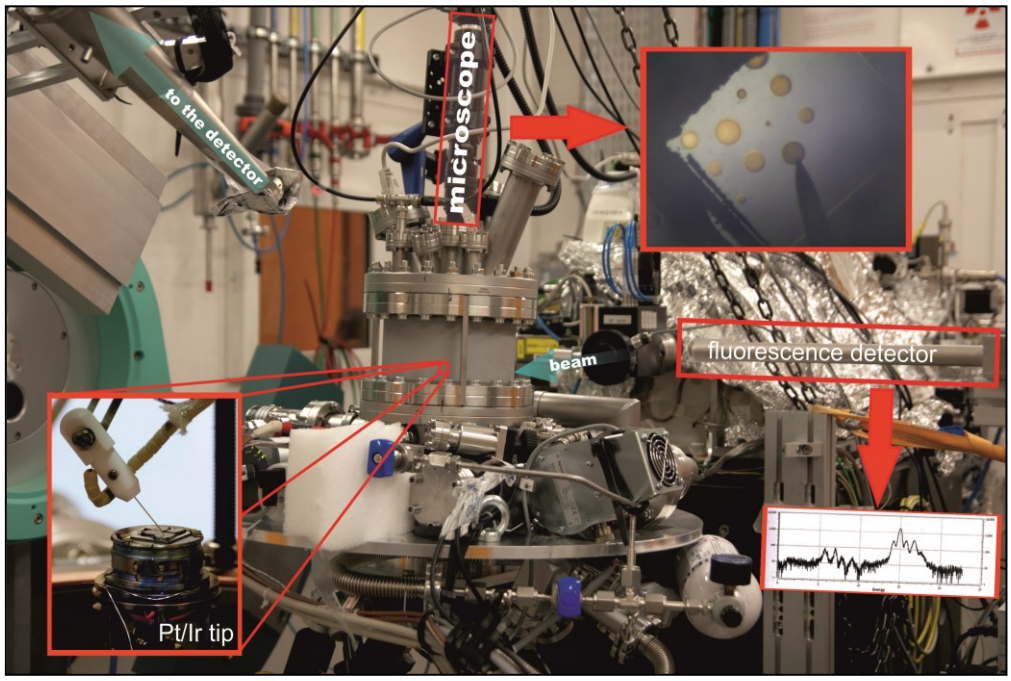

Fig.2. The Setup

Alignment of each of the crystals within the 2x2 mosaic turned out to be rather tedious and we were only able to measure sets of truncation rods for the LSC and LSM electrodes under different voltages. Acquired data still have to be analyzed but it is already clear that there measurable changes occur as shown in Fig.4 and Fig.5. Those measurements show the time-dependent intensity at the (1, 1, 1.5) point of the LSM electrode upon changing the voltage. In addition, we observed that the color of contacted LSC electrode had changed from light blue, which might indicate beam damage, to light brown, which usually corresponds to a normal working electrode. Also during CTR measurements at -10V the formation of a dendritic structure around the electrode was observed (Fig.6) and it was gone as soon as voltage was switched off. We were able to collect data sets from various electrodes and conditions which are presently being worked out.

Conclusion Our experiments show some very puzzling and exciting phenomena which should be studied in a forthcoming experiment.

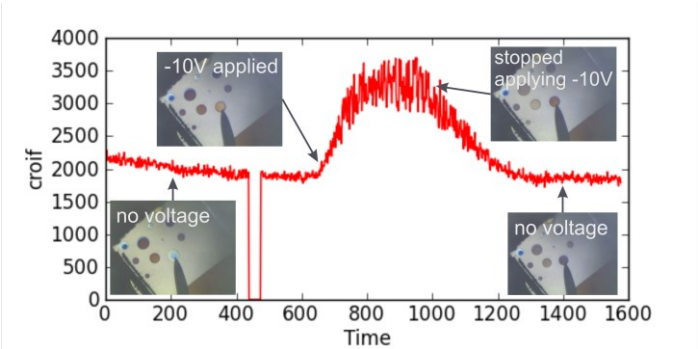

Fig.4. CTR signal and electrode color change over time while applying -10V

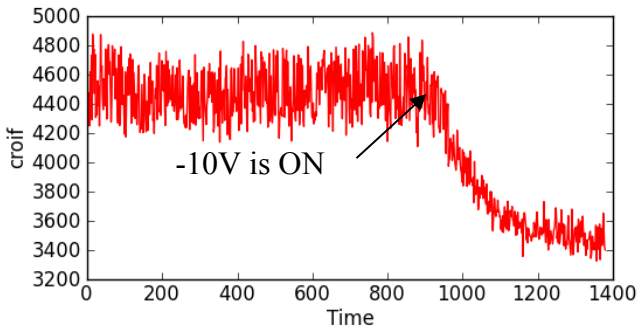

Fig.5. Time scan before and after -10V were applied for CTR measurements

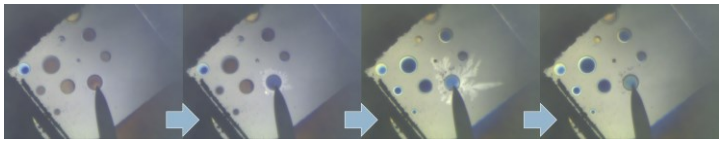

Fig.6. Dendrite formation during beam exposure and applied voltage.