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Microstructural investigations of blackening in YSZ sensors for hydrogen coulometry

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Summary:
A detailed microstructural analysis of a coulometric hydrogen sensor after operation at high electrical load is presented. The sensor is based on YSZ ceramic tube with outer and inner electrodes. Oxygen diffusion at grain boundaries under chemical and electrical potential leads to color changes (blackening), crack formation at the grain boundaries and phase transitions in the YSZ ceramic from cubic to monocline. These findings can explain an irreversible degradation mechanism of the solid electrolyte sensor.

Keywords: hydrogen sensor; Yttria-stabilized zirconia (YSZ), coulometry, gas chromatography, trace gas analysis

Background, Motivation and Objective

Using hydrogen produced by green electricity helps to satisfy the demand for fuel without using non-renewable fossil sources. The key component for producing hydrogen by electricity is the electrolyzer splitting water into hydrogen and oxygen. To ensure the safety during the production and storage of hydrogen gas sensors are mandatory. For the electrolyzer, hydrogen sensors must have a sensitivity of 100 Vol.-ppm up to a concentration of 4 Vol.-% hydrogen at pressures up to 30 bar and temperatures up to 90 °C. Coulometric solid electrolyte sensors for hydrogen are sufficient for these operation conditions and provide the required sensitivity. To suppress the cross sensitivity against other gases the substances can be separated in advance by gas chromatography. Such sensors have to sustain under harsh environment and high electrical fields causing degradation of the sensor materials and limiting the life time. This study focusses on the solid electrolyte YSZ in the coulometric measurement cell and its structural changes during extreme load conditions.

Description of the Methods

For the experiments a coulometric sensor was used based on a commercial sensor set up (Zirox GmbH). The main component is a YSZ ceramic gas-tight tube (Friatec, 8 mol% Y) inside a furnace with two pairs of Pt (99,99% pure) electrodes. One pair is used for the measurement and the other one as a reference. The YSZ tube is used to transport oxygen and to measure the difference of the chemical potential between inside and outside the tube. The microstructure of the ceramic was determined by electron microscopy (SEM Zeiss Supra, TEM FEI Titan) combined with diffraction and analytical methods (Trident EBSD-EDX, EDAX). Additional structural information was obtained by Raman spectroscopy.

Results

The electrical load experiments started with oxygen transport from outside air to a reforming gas (50 Vol.-ppm H_2 in N_2) inside the tube for 60 s at 750 °C. The transport was forced by a voltage of 11 V and the current was limited to 0.6 A. During the conditioning the tube was damaged by elevated local current densities and developed several micro cracks which enable remarkable oxygen gas diffusion through the tube wall. After conditioning the voltage at the electrodes was reversed automatically to establish a low oxygen partial pressure inside the tube. Due to the unnoticed gas leakage, a high pumping current was established for more than 60 min. The structural changes caused by this experiment were investigated in detail.

3.1. Blackening

In reduction atmosphere the color of the YSZ changes from opaque to black known as blackening-effect [1]. The blackening is a local phenomenon and could indicate the sites of the morphological and electrical failure of the sensor. Microstructural investigations were performed at sites of visible blackening (Fig.3). The localized areas were separated by sawing to get cross sections of the YSZ tube. Blackening could be observed at the electrodes of the inner tube part. In addition, at some positions the blackening reaches the outer surface of the tube indicating possible sites for gas leakage and electrical shorts (Fig.1).

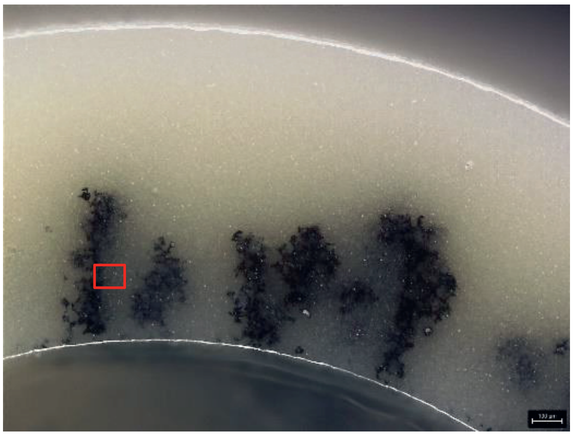

Fig. 1 Light microscope image of mechanical cross section of the YSZ tube. Blackening is visible in the YSZ ceramic starting at inner surface.

3.2. Microstructural characterization

Different analysis methods were applied to correlate the blackening with changes in the microstructure of the YSZ. To determine the grain structure back scatter electron (BSE) imaging was applied to identify the different phases of the ceramic (Fig.2). In comparison to unaffected areas void formations and cracks at the grain boundaries could be found in the blackening areas. EBSD (Fig.4) and EDX analysis reveal hexagonal Alumina structure of the darker precipitates seen in the BSE images. Raman measurements indicate additional monoclinic Zirconia at the blackening areas.

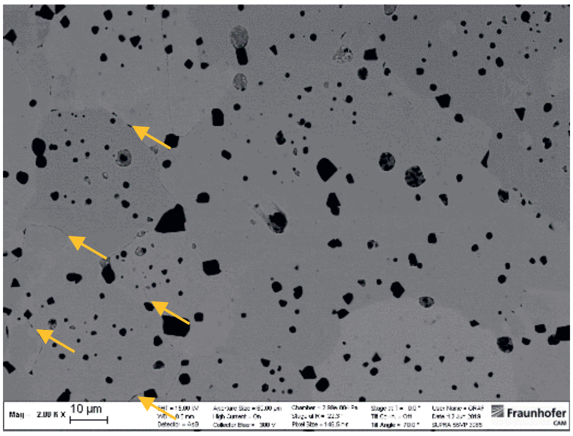

Fig. 2 BSE image of the cross section with grain structure and Al_2O_3 inclusions. Cracks and voids have formed (left side) at the grain boundaries in the black regions.

References

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Acknowledgments

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Illustrations, Graphs, and Photographs

A.

B.

Fig. 3. **A.** Overview of the YSZ tube with electrodes. **B.** Part of the ceramic tube with inside illumination at the electrode position. Blackening inside the tube is visible.

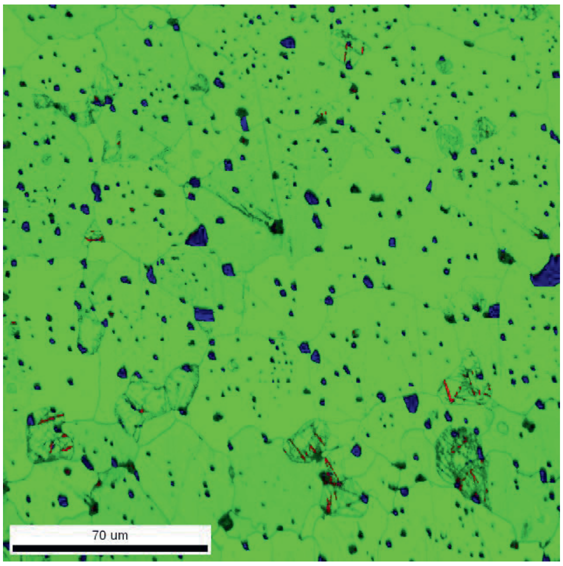

Fig. 4 EBSD phase and quality image of the cross section with grain structure and Al_2O_3 (blue) inclusions as well as YSZ (green).