3D MICROSTRUCTURAL EVOLUTION OF A SOLID OXIDE CELL DURING A REDOX CYCLE BY HIGH RESOLUTION PTYCHOGRAPHIC TOMOGRAPHY

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Summary: Tracking the 3D microstructural evolution of a solid oxide cell during operation is considered critical to understand the relationship between microstructure and performance. In this work, 3D ptychographic tomography is applied to SOC electrodes demonstrating unprecedented data quality and resolution. The effect of a redox cycle on a SOC anode is described in 3D analysing the tomograms of the same sample in its pristine, oxidized and reduced state.

1. INTRODUCTION

Solid oxide fuel cells (SOFC) and electrolysis cells (SOEC) convert chemical energy into electrical energy and vice-versa. While SOFC can efficiently produce electrical energy from a large variety of fuels, SOEC can store electricity as chemical fuels [1]. Therefore, solid oxide cells are expected to play an important role in the future energy landscape meeting the fluctuating demand of renewable sources through reversible operation. State-of-the-art SOC anode materials are porous cermet made of nickel and yttria-stabilized zirconia (YSZ) sintered together. SOC electrodes are expected to undergo several redox-cycle during their lifetime due to air leakages in the gas supply system or under condition of high fuel utilization. Microstructural changes due to nickel oxidation and reduction can lead to fading in performance or to complete cell failure. Therefore, it is crucial to understand the phenomena occurring within the microstructure during a redox cycle in order to guide the development of new redox robust SOC electrodes.

X-ray nano-tomography has been applied to SOC materials to study their degradation [2]. The non-destructive nature of X-ray tomography and the possibility to apply realistic sample environments, allow dynamic *ex-situ* or *in-situ* studies. Among other techniques, X-ray ptychography has demonstrated excellent sensitivity to mass density changes and the highest resolution among the X-ray imaging techniques [3].

In this work, for the first time, X-ray ptychographic tomography has been applied to SOC electrode to perform an “ex-situ” redox experiment in which the same sample is analyzed in its pristine, oxidized and reduced state.

2. EXPERIMENTAL METHOD

The nano-tomography experiment was performed at the X12SA (cSAXS) beamline at the Swiss Light Source, Paul Scherrer Institut, Switzerland. The ptychography procedure was carried out at 7.2 keV. The sample was obtained from a standard Ni-YSZ cell produced by type casting [4]. A thin slice (300 µm thick and 3 mm long) was carefully cut using a diamond saw and polished down to a pyramidal shape with a 60x60 μm square cross section at the top. The slice has been mounted on the sample holder using platinum paste and FIB-milled to a produce a cylindrical pillar of ~17 µm in cross section.

The field of view acquired was around 24 by 15 μm giving an object pixel size of 18.4 nm. For each dataset, 500 projections over an angular range of 180° were collected. The same sample was first analysed in its pristine state and subsequently imaged in its fully oxidized and reduced state.

The oxidation and reduction were performed in a custom-made tube furnace at 850°C with a flow rate of 5 l/h of

either air or a gas mixture of 4% H_2 in N_2 respectively. The heating time at maximum temperature was 3h for the oxidation and 1h for the reduction. The ramping rate was 10°C /min for both heating and cooling.
The raw data were segmented using a 3D (intensity vs intensity gradient) histogram thresholding while the datasets were registered through a rigid transformation computed by the iterative closest point algorithm. Only the points related to the YSZ were used in the procedure

3. RESULTS

Figure 1. presents the 3D evolution of the same volume before and after the redox cycle. The subset volume is obtained from the entire dataset in (e). Results show that, the original YSZ microstructure (a) presents several cracks after the redox cycle (b). Those cracks are mainly located at the grain boundaries, which are regions of stress intensification. This phenomenon is expected to affect the performance of the cell since it compromises the ionic conductivity and the electrode mechanical stability. Furthermore, the well-defined polyhedral shape of the nickel particle (c) evolves to a more rounded and fragmented structure (d). The evolution is driven by surface energy minimization and the expansion of the YSZ during oxidation. Finally, based on the information obtained from the tomograms, we are also able to propose a possible mechanism for the nickel oxidation in a real SOC electrode.

References

[1] B. Shri Prakash, S. Senthil Kumar, S. T. Aruna, *Renew. Sustain. Energy Rev.* **2014**, *36*, 149

[2] J. Villanova, J. Laurencin, P. Clotens , B. Bleuet , G. Delette, H. Suhonen, F. Useeglio-Viretta, *J. Power Sources* **2013**, *243*, 841 [3]

[3] M. Holler, A. Diaz, M. Guizar-Sicairos, P. Karvinen, E. Färm, E. Härkönen, M. Ritala, A. Menzel, J. Raabe, O. Bunk, *Sci. Rep.* **2014**, *4*

[4] S. L. Ebbehøj, T. Ramos, M. Mogensen, *ECS Trans.* **2012**, *45*, 363

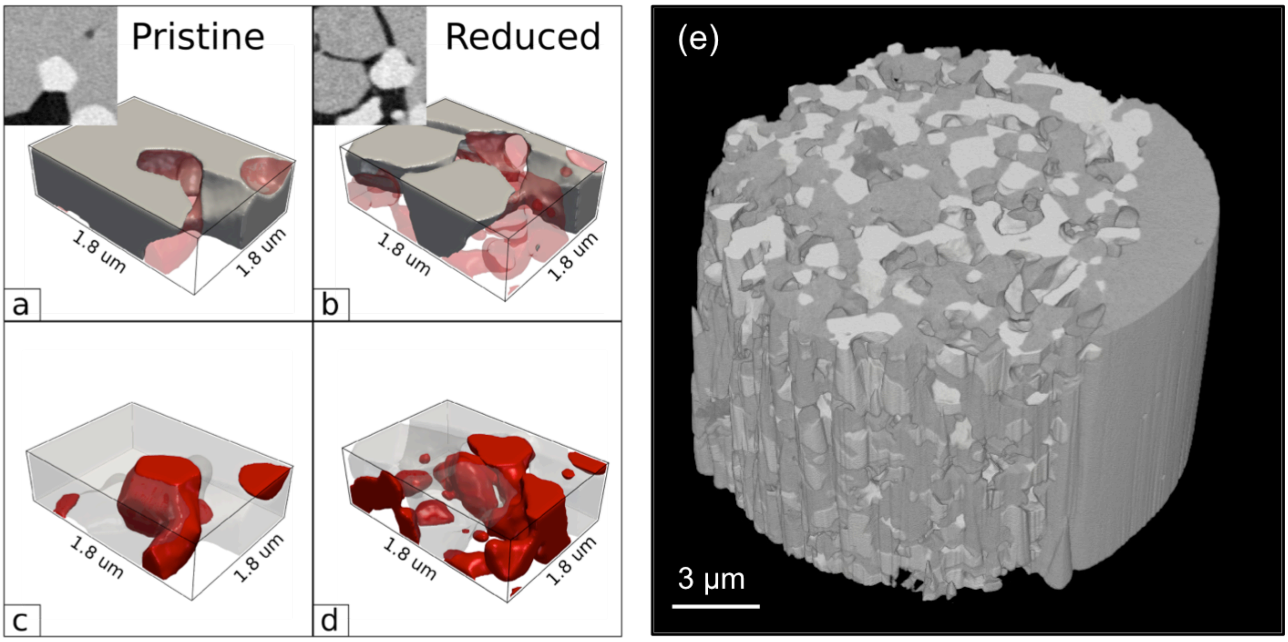

Figure 1. Subset volume of the entire dataset before and after the redox cycle. (a) YSZ structure in its pristine state and after the redox cycle (b). Nickel particle before (c) and after reduction (d). (e) 3D volume rendering of the entire dataset acquired.