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Benefits of Nanoscale Operando Experiments in Environmental Transmission Electron Microscopy for Solid Oxide Fuel Cell Devices

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Solid oxide fuel cells (SOFC) are a class of solid-state electrochemical conversion devices that produce electricity directly by oxidizing a fuel gas. They consist in an anode-cathode duet separated by a solid electrolyte, i.e., a material conducting oxygen ions. The anode is fed with hydrogen or other fuels whereas the cathode is in contact with air, meaning oxygen. Overall, a SOFC operates thanks to the combined action of two external stimuli: a gaseous environment and temperature. Owing to the recent advances in *in situ* and *operando* transmission electron microscopy (TEM), we have set up an experiment to operate a SOFC inside an environmental TEM to identify how the device microstructure determines its electrical properties. To do so, an elementary anode-electrolyte-cathode sandwich was prepared by focused ion beam (FIB) and mounted on a heating and biasing microelectromechanical (MEMS)-based specimen holder (DENSsolutions) and inserted in an Environmental TEM (FEI Titan ETEM), as shown in Fig. 1.

Standard SOFC materials were investigated: the cathode was strontium-doped lanthanum manganite (LSM) co-sintered with yttria-stabilized zirconia (YSZ), the electrolyte was YSZ, and the anode a cermet of NiO co-sintered with YSZ. NiO was first reduced to Ni, leaving pores in the structure due to the volume loss and hence enabling the penetration of the fuel to the triple phase boundaries Ni/YSZ/porosity at the anode side. For practical reasons, we used a single chamber configuration to trigger the operation the cell: the anode and cathode were exposed simultaneously to the oxidant and reducing gases. Due to a difference in the catalytic activity between the electrodes, O_2 should reduce at the cathode, while H_2 should oxidize at the anode, thus leading to a voltage difference between the two terminals.

The reduction of NiO was first performed under a forming gas N_2:H_2 in the ratio 20:1 under 15 mbar up to 750°C (N_2 was constantly used as a mixing gas for safety reasons due to the need of mixing O_2 and H_2 in the single-chamber configuration). The O_2 to H_2 ratio was then increased to trigger the operation of the cell. A small quantity of O_2 was introduced into the microscope, leading to a total pressure of about 16 mbar at 600°C. At this point, the variation of voltage between the anode and cathode was

correlated to the gas composition and the anode microstructure (see Fig. 2). The latter was analyzed by means of conventional and high-resolution imaging, diffraction, and EELS (electron energy-loss spectroscopy). The system was cycled several times by decreasing and re-increasing the O_2 concentration in the gas flow, and correlations between microstructure, gas composition, and cell voltage were established, as it will be discussed at the conference. Results were further confirmed by macroscopic *ex situ* tests in an oven using the same materials.

The operation of a SOFC in a single chamber configuration was demonstrated using *operando* ETEM. Such *operando* experiments open numerous perspectives to investigate the root cause of failure pathways affecting SOFCs, like poisoning of active sites or coarsening of the Ni catalyst [1].

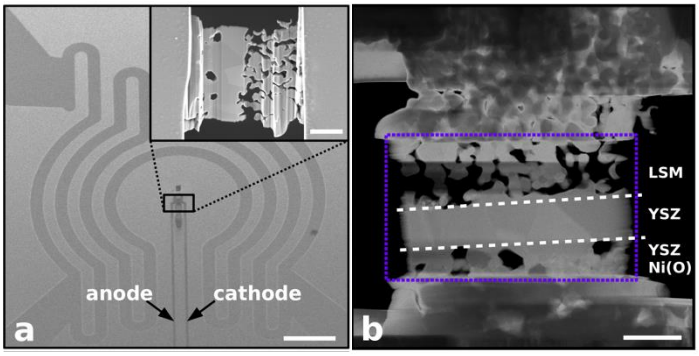

Figure 1. SOFC on MEMS chip. a) Secondary electrons SEM image of a biasing and annealing MEMS chip (DENSsolutions) for operando TEM, where the anode and cathode of the SOFC lamella (inset) are electrically connected to the biasing electrodes of the chip. Scale bar: 50 µm. b) STEM ADF of the electrically connected SOFC sample. Scale bar: 2 µm.

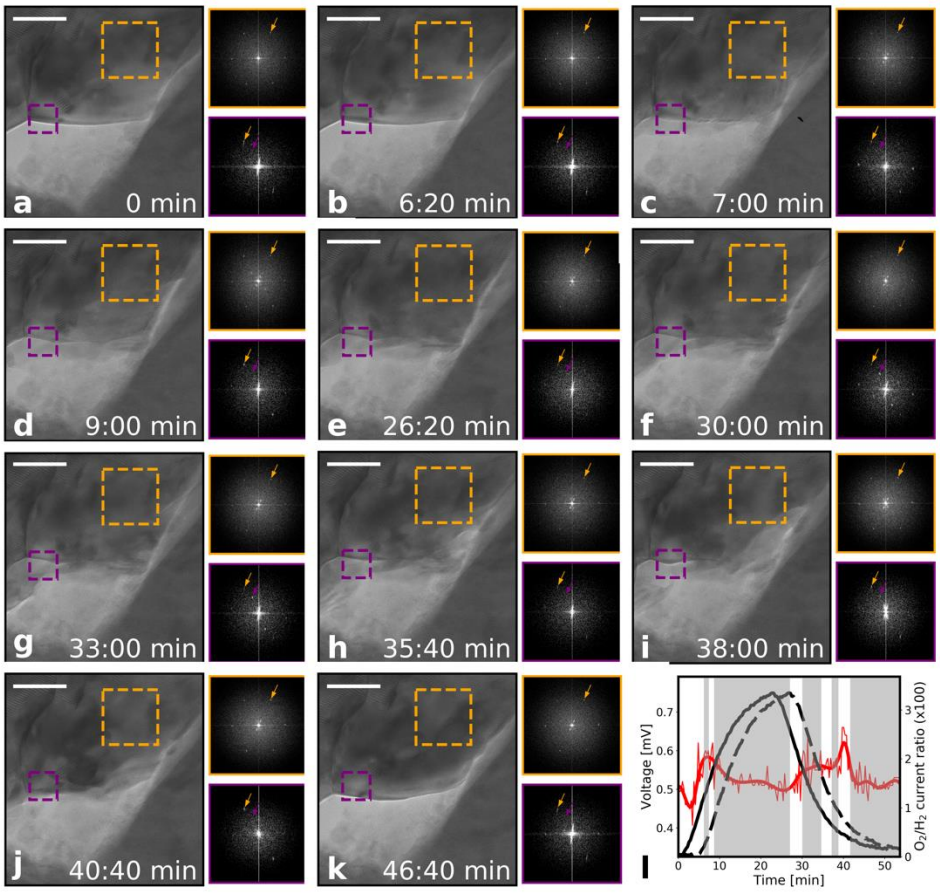

Figure 2. Operando ETEM experiments. a-k) Bright field TEM around the edge of a Ni grain at the critical steps of the reoxidation and reduction processes. The time corresponds to the white/grey areas in i). Scale bars: 20 nm. i) RGA O_2-to-H_2 ratio (raw data, black full line, and shifted forward in time by 180 seconds, black dashed line), and voltage measured between the anode and cathode (raw and Gaussian-filtered data, red lines).

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