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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 set 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 of 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, O₂ should reduce at the cathode, while H₂ 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 N₂:H₂ in the ratio 20:1 under 15 mbar up to 750°C (N₂ was constantly used as a mixing gas for safety reasons due to the need of mixing O₂ and H₂ in the single-chamber configuration). The O₂ to H₂ ratio was then increased to trigger the operation of the cell. A small quantity of O₂ 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

https://doi.org/10.1017/S1431927622003658 Published online by Cambridge University Press
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 O2 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 O2-to-H2 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).
References:

[1] The authors acknowledge the French microscopy network METSA for funding and the consortium Lyon-St-Etienne de microscopie for ETEM access. The FIB preparation was performed at the facilities for analysis, characterization, testing and simulations (FACTS, Nanyang Technological University). Additional support was provided by the INSTANT project (France-Singapore MERLION program 2019-2021) and the start-up grant M4081924 at Nanyang Technological University.