The activation of a solid oxide fuel cell anode, a process that involves the reduction of the as-sintered nickel oxide (NiO)/yttria-stabilized zirconia (YSZ) composite to the electrochemically active Ni/YSZ state, is assessed using energy-filtered transmission electron microscopy images acquired in an H₂ atmosphere at elevated temperature in an environmental transmission electron microscope (ETEM). Quantitative measurements of both reaction kinetics (using oxygen K edge images) and evolution of thickness (using total-inelastic mean free path images) are obtained during NiO/YSZ reduction to Ni/YSZ in 1.3 mbar of H₂ up to 600 °C (Fig. 1) [1]. In addition, structural and crystallographic changes are monitored using bright-field (BF) imaging and selected area diffraction.

Measurements of the relative changes in thickness highlight the formation of voids within Ni particles to compensate the volume loss induced by oxygen removal. In regions not affected by diffraction effects, local measurements of volume shrinkage induced by NiO reduction to Ni agree with the theoretical prediction of -41% [2]. The sequence of oxygen maps allows the extraction of reaction kinetics localized at the pixel/nm scale and demonstrates the initiation of the reaction at grain boundaries with the YSZ phase. Density functional theory calculations suggest that this process may result from oxygen ion transfer from NiO to YSZ at these grain boundaries [3], which creates oxygen vacancies in the NiO phase and in turn triggers the reduction reaction [4]. The YSZ backbone remains stable throughout the reduction of the NiO phase at these temperatures.

While factors related to sample preparation, spatial drift and the presence of the high-energy electron beam must be considered, with care energy-filtered imaging in a gas atmosphere at elevated temperature has the ability to provide quantitative new insight into the activation of SOFC anodes with a spatial resolution in the nm range. Differences in reaction rate as a result of local features can be investigated in detail using the present methodology, paving the way for the development of detailed reaction/activation models.


Acknowledgement: The authors wish to thank U. Aschauer, A. Faes, F. Bobard, M. Cantoni, D. Laub, G. Lucas, D. Alexander, E. Oveisi, P. Stadelmann and the Swiss National Science Foundation.
Fig. 1: Reduction of NiO-YSZ in H₂ up to 600 °C. Selection of bright-field (BF), thickness maps (t/λ) and oxygen K edge (O K) images acquired at 300 °C, 428 °C and 604 °C. Depletion of oxygen in NiO occurs at NiO-YSZ grain boundaries (arrows at 428 °C). Measurements of volume shrinkage in regions A and B yield -40% and -42%, respectively.