

## Electron Energy-Loss Spectroscopy and Energy-Filtered TEM Imaging for the *in situ* Assessment of Reduction-Oxidation Reactions in Ni-Based Solid Oxide Fuel Cells

Q. Jeangros<sup>1,2</sup>, A.B. Aebbersold<sup>1</sup>, T.W. Hansen<sup>3</sup>, J.B. Wagner<sup>3</sup>, R.E. Dunin-Borkowski<sup>4</sup>, C. Hébert<sup>1</sup>, J. Van herle<sup>5</sup>, A. Hessler-Wyser<sup>1,2</sup>

<sup>1</sup> Interdisciplinary Centre for Electron Microscopy, Ecole Polytechnique Fédérale de Lausanne, Lausanne, Switzerland

<sup>2</sup> Photovoltaics and Thin Film Electronics Laboratory, Ecole Polytechnique Fédérale de Lausanne, Neuchâtel, Switzerland

<sup>3</sup> Center for Electron Nanoscopy, Technical University of Denmark Lyngby, Denmark

<sup>4</sup> Ernst Ruska-Centre for Microscopy and Spectroscopy with Electrons and Peter Grünberg Institute, Jülich Research Centre, Jülich, Germany

<sup>5</sup> Fuelmat group, Ecole Polytechnique Fédérale de Lausanne, Sion, Switzerland

Nickel/ceramic solid oxide fuel cell anodes exhibit dimensional instabilities when they are taken through reduction-oxidation cycles. When fuel is supplied on the anode side, the as-sintered nickel oxide phase (NiO) reduces to metallic Ni and then remains in this state during operation. However, several factors can then lead to accidental reoxidation of the Ni, which can rupture parts of the cell and degrade its performance.

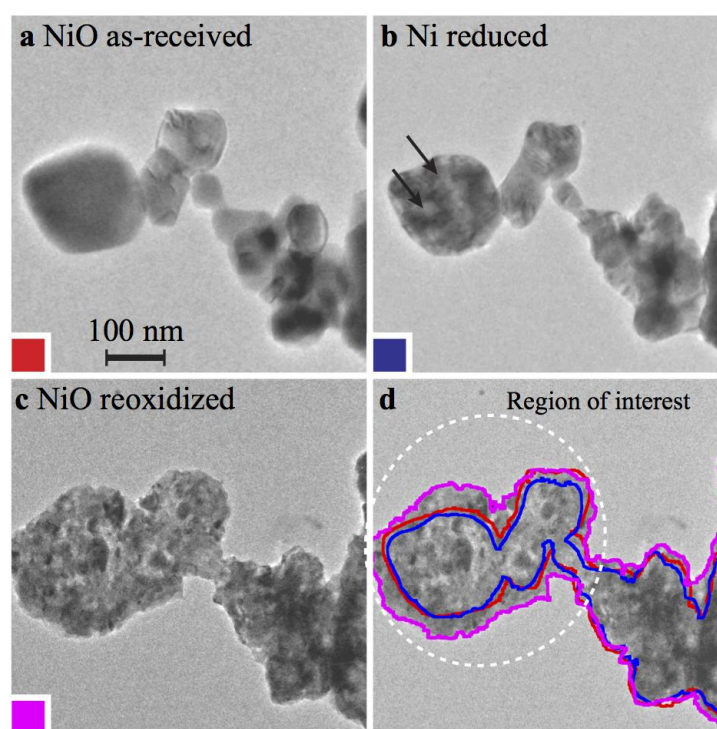
Here, we use environmental transmission electron microscopy (ETEM) to investigate the mechanisms that underlie the dimensional instability of Ni/yttria-stabilized zirconia (YSZ) anodes [1]. NiO particles and NiO/YSZ composites are reduced and reoxidized in an FEI Titan E-Cell 80-300ST ETEM in several mbar of H<sub>2</sub> and O<sub>2</sub>, respectively, up to 500-850 °C and at 300 kV. Images, diffraction patterns, electron energy-loss spectra (EELS) and energy-filtered TEM (EFTEM) images are acquired at constant temperature intervals during the reactions, in order to capture the changes in nanostructure, crystallography and chemistry *in situ* in the TEM. The reaction kinetics are retrieved either from changes in the shape of the Ni L<sub>2,3</sub> edge in EELS (for Ni(O) particles [2,3]) or, with nm resolution, from EFTEM images of the O K edge (for Ni(O)/YSZ composites [4]). For example, it is shown during NiO/YSZ reduction that, under certain assumptions, spatially-localized quantitative EFTEM data about chemistry could be combined with thickness measurements to provide three-dimensional insight into the evolution of the Ni(O)/YSZ anode while it reacts with H<sub>2</sub> at high temperature. The results are correlated with the observed microstructure and reaction mechanisms.

While surface nucleation of Ni domains, their growth and impingement are found to control the reduction of NiO particles to Ni, a different mechanism is observed in the presence of YSZ, with transfer of oxygen from NiO to oxygen vacancies in the YSZ ceramic triggering the reaction. Intra- and inter- granular voids form in both cases when oxygen is removed. At high temperature, the final Ni microstructure is observed to coarsen as it minimizes its surface energy, with percolation of the Ni phase influenced by the symmetry of its grain boundaries [5]. The reoxidation of Ni is controlled mainly by the outward diffusion of Ni ions through the grain boundaries of the growing NiO film. While some inward NiO growth occurs through the formation of oxide film cracks, the Ni<sup>2+</sup> outward diffusion process remains unbalanced and voids form in the NiO phase. These internal voids are responsible for the dimensional instability of the composite along with Ni coarsening at high temperature (Fig. 1). Several

parameters for improved performance and redox tolerance are then identified based on these results. [6]

#### References:

- [1] Q Jeangros, A Faes, JB Wagner *et al.*, *Acta Materialia* **58** (2010), p. 4578  
 [2] Q Jeangros, TW Hansen, JB Wagner *et al.*, *Journal of Materials Science* **48** (2012), p. 2893  
 [3] Q Jeangros, TW Hansen, JB Wagner *et al.*, *Acta Materialia* **67** (2014), p. 362  
 [4] Q Jeangros, TW Hansen, JB Wagner *et al.*, *Chemical Communications* **50** (2014), p. 1808  
 [5] Q Jeangros, AB Aebbersold, C Hébert *et al.*, *Acta Materialia* **103** (2016), p. 442  
 [6] Support is gratefully acknowledged from the Swiss National Science Foundation (project “IN Situ TEM study of reduction and oxidation of Ni(O)-ceramic composite (IN-SITE)”). The authors also wish to thank D. Laub, G. Lucas, D.T.L. Alexander, M. Cantoni, F. Bobard, E. Oveisi, P. Stadelmann, Z. Wuillemin and D. Montinaro.



**Figure 1.** TEM images showing (a) as-sintered NiO particles, (b) the same region after reduction (at 600 °C for 210 min in 1.3 mbar of H<sub>2</sub>) and (c) the same region after reoxidation (at 600 °C after heating from 250 °C at a rate of 4 °C min<sup>-1</sup> in 3.2 mbar of O<sub>2</sub>). In (d), the projected areas of (a–c) are superimposed onto the image shown in (c). Reduction results in a decreased in the projected area by -15% between (a) and (b) in the region of interest circled in (d), while oxidation results in an increase in the projected area by +65% between (b) and (c). The projected area of NiO increases by +40% between (a) and (c) after one redox cycle.