Measurements of local chemistry and structure in Ni(O)–YSZ composites during reduction using energy-filtered environmental TEM

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Energy-filtered transmission electron microscopy images are acquired during the reduction of a NiO–YSZ composite in H2 up to 600 °C. Temperature-resolved quantitative information about both chemistry and structure is extracted with nm spatial resolution from the data, paving the way for the development of detailed reduction models.

Nickel–yttria-stabilized zirconia (Ni-YSZ) composites are widely employed as anode structures in solid oxide fuel cells (SOFCs). In such applications, the anode operates at ~700–800 °C in a reducing atmosphere and acts as a fuel oxidation catalyst, a hydrocarbon reforming catalyst, a current collector and often as the mechanical supporting layer of the whole fuel cell. For ease of manufacturing, nickel oxide (NiO) particles are usually first co-sintered with YSZ and then reduced to Ni during the first operation of the cell, while the YSZ backbone remains chemically unchanged. This anode activation process should ideally yield connected and intersecting networks of Ni, NiO and voids, in order to guarantee high electrochemical efficiency. A full understanding of both chemical and structural changes induced by the reduction of NiO at the nanometre scale is therefore essential. Both aspects can be addressed at this length scale under gas reaction conditions and at elevated temperature using an environmental transmission electron microscope (ETEM) that is equipped with a post-column imaging filter. The objective of the present communication is twofold; first to complement initial results that qualitatively address the activation of the Ni–YSZ cermet with a quantitative structural and chemical assessment of the process using energy-filtered transmission electron microscopy (EFTEM) and second to demonstrate the feasibility of using such an analytical technique to capture spatially localized chemical and nanostructural information with the specimen held at high temperature in a gas atmosphere.

A standard NiO–YSZ anode was prepared for ETEM observations using a conventional focused ion beam (FIB) lift-out technique in a dual beam FIB/SEM Zeiss NVision 40 CrossBeam workstation. Reduction of the NiO–YSZ sample was performed in situ in a differentially pumped FEI Titan 80–300 ETEM equipped with a post-column imaging filter using a Gatan double tilt 652 heating holder. The microscope was operated at 300 kV at an electron dose rate of 107 e⁻¹ nm⁻² s⁻¹, which was constant throughout the entire experiment. H2 was introduced in the column at a flow rate of 2 ml/min, resulting in a pressure of 1.3 mbar around the sample. A temperature ramp with an overall rate of 2 °C min⁻¹ was used between 300 and 604 °C to study the evolution of the system as a function of temperature. The temperature was manually increased in steps of 16 °C over a duration of 2 minutes and then maintained constant for 6 minutes to perform structural and chemical measurements. Each acquisition sequence included the following bright-field TEM images (collection semi-angle of 6.8 mrad): one unfiltered image, one filtered zero-loss image and three images I₁, I₁₂ and I₁₂₃ at energy loss onsets of 472 eV, 502 eV and 532 eV, respectively (with a slit width of 30 eV and an acquisition time of 40 s). All of the recorded images were aligned by cross-correlation after filtering using a Sobel operator. Images I₁ and I₂ were used to construct a t/l thickness map where t is the thickness in nm and l is the total-inelastic mean free path, estimated here to be 127 nm for Ni and 155 nm for NiO. Images I₁₂ and I₁₂₃ were processed to obtain elemental maps of the oxygen K edge (532 eV) using the conventional three window method, whereby the two I₁₂ images were used to extrapolate a power law background that was subtracted from the I₁₂₃ image that contains the oxygen K edge signal. Oxygen t/l maps were initially acquired at 30 °C (NiO reference) and then at 604 °C, 130 min after the end of the ramp (Ni reference; full reduction of Ni regions confirmed using electron energy-loss spectroscopy, EELS). As the ceramic phase is structurally and chemically stable at these temperatures, the YSZ backbone in each oxygen and thickness map was used as an invariant reference to monitor intensity changes in the adjacent evolving Ni(O) phase. Each thickness/oxygen map was divided by the total number of counts in its YSZ phase to remove...
Fig. 1  (a–e) Selection of (1) bright-field TEM images and corresponding (2) $t/\lambda$ and (3) oxygen maps acquired during ramping at 2 °C min$^{-1}$ in 1.3 mbar of H$_2$. The images in (f) were acquired 130 minutes after reaching 604 °C (full reduction of Ni confirmed by EELS). An EFTEM nickel map is shown as an inset in a.1 to highlight the position of the Ni(O) grains as well as the region of interest investigated in Fig. 2 (also shown in a.3). The intensities of the regions that are labelled A and B in a.2 and f.2 were used to monitor reduction-induced thickness changes. Arrows indicate initiation of the reaction at the Ni(O)–YSZ interfaces in (b) and at the free surface of NiO in (d).

Ni grains and internal voids are observed to sinter at 604 °C. The acquisition of energy-filtered images allows quantitative thickness and chemical information to be determined. Volume changes induced by the complete reduction of NiO to Ni can be calculated directly using the initial unreacted $t/\lambda$ map and the final fully reduced $t/\lambda$ image by multiplying the intensity in either the NiO or the Ni regions by $\lambda_{NiO}$ and $\lambda_{Ni}$, respectively. As diffraction effects alter the overall intensity, regions that do not exhibit these contrast features, such as those labelled A and B in Fig. 1a.2 and f.2, were analysed. Although the accuracy of the estimation of $\lambda$ will also affect the results, the volume shrinkage resulting from NiO reduction to Ni measured in regions A and B is $-40\%$ and $-42\%$, respectively, which are close to the theoretical value of $-41.6\%$ and thus considered to be representative.

Fig. 2 shows a sequence of oxygen maps, which focuses on one Ni(O) grain surrounded by YSZ. The chemical information at the position of each pixel evolves as a function of temperature and time. In order to obtain statistically relevant information, Ni(O) pixels that exhibit the same structural
Future work will involve the use of solid-state kinetic models to evaluate and normalize using the corresponding mean values. Features (interfaces with YSZ or bulk material) were selected by evaluating and normalizing using the NiO and Ni experimental references to yield the fraction at 360 °C. The increase in the NiO fraction is due to the reaction. The recent introduction of MEMS-based heating holders decreases thermally induced drift significantly and thus allows the acquisition of reliable data during ramping at higher heating rates. However, the geometry of such a holder is not optimized for studies of FIB-prepared lamellae or low-voltage argon cleaning. Electron beam-induced artefacts must also be assessed in detail. While all of these effects must be considered, energy-filtered imaging in a gas atmosphere at high temperature still has the ability to provide quantitative new insights into solid-gas reactions with nm spatial resolution.

The acquisition of energy-filtered images during the reduction of a NiO–YSZ composite at different temperatures has allowed information to be obtained about both chemistry (using O K edge images) and structure (using total-inelastic mean free path images) with nm spatial resolution. The use of the YSZ backbone as an invariant reference throughout the experiment allowed the extraction of data about the evolution of the Ni(O) phase, which could be related quantitatively to NiO and Ni references. While relative changes in thickness provide information about the three-dimensional evolution of the system, oxygen maps allow the extraction of reaction kinetics localized at the nm scale. Local differences in the reaction rate as a result of structural and chemical features can be investigated in detail using this methodology.

Notes and references

† While a measured value of $F_{\text{Ni}}$ (an average energy-loss value) was used for NiO (19.8 eV) to yield $E_{\text{Ni}}$, the effective atomic number of Ni was used to estimate $F_{\text{Ni}}$ (25.2 eV) and in turn $E_{\text{Ni}}$ (see ch. 5 of ref. 4b).


