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

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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.2b The microscope was operated at 300 kV at an electron dose rate of 107 e− nm−2 s−1, which was constant throughout the entire experiment. H2 was introduced in the column at a flow rate of 2 mlmin−1, 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 brightfield TEM images (collection semi-angle of 6.8 mrad): one unfiltered image, one filtered zero-loss image I0 and three images Ipre-edge 1, Ipre-edge 2 and Ipost-edge 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.4a Images I0, Ipre-edge and Ipost-edge were used to construct a t/λ thickness map (where t is the thickness in nm and λ is the total-inelastic mean free path, estimated here to be 127 nm for Ni and 155 nm for NiO4b). Images Ipre-edge 1, Ipre-edge 2 and Ipost-edge were processed to obtain elemental maps of the oxygen K edge (532 eV) using the conventional three window method,4b whereby the two Ipre-edge images were used to extrapolate a power law background that was subtracted from the Ipost-edge image that contains the oxygen K edge signal. Oxygen and t/λ 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
intensity offsets and to yield thickness/oxygen maps with comparable intensities. The results could then be analysed quantitatively, by comparing them to the experimental NiO and Ni references.

Fig. 1 shows a sequence of unfiltered bright-field TEM images acquired at different temperatures, alongside corresponding \( t/\lambda \) and oxygen maps (after normalization using the total intensity in the YSZ backbone). The first changes in NiO are observed at grain boundaries with the YSZ phase just below 350°C, as in preliminary observations,\(^a\) presumably as a result of oxygen ion transfer from the NiO to the YSZ. This process creates oxygen vacancies in the NiO close to each interface, and as these sites dissociate H\(_2\) efficiently, the reduction reaction is triggered.\(^b\) Oxygen depletion in the Ni(O) regions close to the YSZ phase is observed directly in the oxygen maps, while the thickness maps demonstrate void formation in the Ni(O) regions at the interfaces, in order to compensate the volume shrinkage that takes place during reduction (see arrows in Fig. 1b). The reaction fronts proceed towards the centres of the Ni(O) grains up to a temperature of at least 428°C. At higher temperatures, the free surface of the Ni(O) grains reduces directly (see arrows in Fig. 1d).

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 \( \lambda_{\text{NiO}} \) and \( \lambda_{\text{Ni}} \), 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 \(-41.6\%\)\(^b\) 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
describe the progress of the reaction as a function of temperature, as future work will involve the use of solid-state kinetic models to yield the reaction kinetics, obtained from the NiO and Ni references to yield the fraction of NiO as a function of temperature. The increase in the NiO fraction at 360°C is induced by bend contours (diffraction), while the peak at 556°C is due to drift during acquisition.

Arrows mark the initiation of reduction at the NiO interfaces with YSZ and then at the NiO free surface. The mean intensity in 4 different masks starting at the YSZ interfaces, progressively selecting the entire Ni(O) grain, was normalized using the NiO and Ni experimental references to yield the fraction of NiO as a function of temperature. The increase in the NiO fraction at 360°C is induced by bend contours (diffraction), while the peak at 556°C is due to drift during acquisition.

Fig. 2 Sequence of oxygen maps showing the evolution of one Ni(O) grain during reduction (see Fig. 1a for the position of the chosen grain). Arrows mark the initiation of reduction at the NiO interfaces with YSZ and then at the NiO free surface. The mean intensity in 4 different masks starting at the YSZ interfaces, progressively selecting the entire Ni(O) grain, was normalized using the NiO and Ni experimental references to yield the fraction of NiO as a function of temperature. The increase in the NiO fraction at 360°C is induced by bend contours (diffraction), while the peak at 556°C is due to drift during acquisition.

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


