Measurements of local chemistry and structure in NiO/YSZ composites during reduction using energy-filtered environmental TEM

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Abstract

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 H\textsubscript{2} atmosphere in an environmental transmission electron microscope (ETEM). Quantitative measurements of both reaction kinetics (using oxygen K edge elemental and jump-ratio 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 H\textsubscript{2} up to 600 °C. Measurements of the relative changes in thickness highlight the formation of voids within Ni grains to compensate the volume loss induced by the removal of oxygen. Measurements of volume shrinkage induced by NiO reduction to Ni agree with the theoretical prediction of -41%. The sequences of oxygen K edge elemental and jump-ratio maps allow the extraction of reaction kinetics localized on the pixel/nm scale and demonstrate the initiation of the reaction at grain boundaries with the YSZ phase. Previous density functional theory calculations suggest that this process results from oxygen ion transfer from NiO to YSZ at these grain boundaries, which creates oxygen vacancies in the NiO phase and in turn triggers the reduction reaction of the NiO grain at the interface with YSZ.

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.
Introduction

Ni/YSZ composites are widely employed as anode structures in solid oxide fuel cells (SOFCs) [1]. 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, NiO particles are usually first co-sintered with YSZ and then reduced to Ni during the first operation of the cell. This anode activation process should ideally yield connected and intersecting networks of YSZ, Ni 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 [2].

1. Scientific Approach

The objective of this work is twofold; first to complement initial results that qualitatively address the activation of the Ni/YSZ cermet using environmental transmission electron microscopy (ETEM) [3] with a quantitative structural and chemical assessment of the process using energy-filtered TEM images (EFTEM) and second to demonstrate the advantages of such an analytical technique to capture spatially localized chemical and nanostructural information with the specimen held at elevated temperature in a gas atmosphere [4].

2. Experiments

Standard NiO/YSZ anodes were prepared for ETEM observations using a conventional focused ion beam (FIB) lift-out technique in a dual beam focused ion beam/scanning electron microscope (FIB/SEM) Zeiss NVision 40. 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 [2]. The microscope was operated at 300 kV at an electron dose rate of $10^3$ e$^-$ nm$^{-2}$ s$^{-1}$, which was constant throughout the entire experiment. H$_2$ was introduced in the column at a flow rate of 2 mlN min$^{-1}$, 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 bright-field (BF) TEM images (collection semi-angle of 6.8 mrad): one unfiltered image $I_t$, one zero-loss filtered image $I_0$ and three images $I_{\text{pre-edge} 1}$, $I_{\text{pre-edge} 2}$ and $I_{\text{post-edge}}$ 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 [5].

As shown in Fig. 1a, images $I_t$ and $I_0$ were used to construct a $t/\lambda$ thickness map (where $t$ is the specimen thickness in nm and $\lambda$ is the total inelastic mean free path, estimated here to be 127 nm for Ni and 155 nm for NiO at 300 kV and using a collection semi-angle of 6.8 mrad [6]). These images were then used to infer values of thickness (and thus volume) shrinkage of the sample due to oxygen removal induced by the reduction reaction.
Images $I_{\text{pre-edge 1}}$, $I_{\text{pre-edge 2}}$ and $I_{\text{post-edge}}$ were processed to obtain elemental maps of the oxygen K edge (532 eV) using the conventional three window method, whereby the two $I_{\text{pre-edge}}$ images were used to extrapolate a power law background that was subtracted from the $I_{\text{post-edge}}$ image that contains the oxygen K edge signal (Fig. 1b) [7]. Alternatively, the $I_{\text{post-edge}}$ images were divided by their corresponding $I_{\text{pre-edge 2}}$ images to yield jump-ratio maps of the O K edge (Fig. 1c) [7].

Fig.1: Positions of the slit (coloured in grey) to select parts the energy-loss spectrum to yield (a) $t/\lambda$ total inelastic mean free path images, which involves the division of the unfiltered image by a zero-loss filtered image, (b) O K edge elemental maps, whereby a power law background is obtained from two pre-edge images at the position of each pixel and then subtracted from the post-edge image to yield an image of the O K edge, (c) O K jump-ratio images, whereby the intensity in the post-edge image is divided by the intensity in the filtered image acquired just before the onset of the O K edge.

Experimental NiO and Ni references of O K elemental maps, O K jump-ratio images and $t/\lambda$ images were obtained 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).

To analyse changes in thickness and chemistry induced by reduction of NiO to Ni, the Ni phase was segmented from the YSZ using an elemental map of the Ni L$_{2,3}$ edges acquired at room temperature before the reduction experiment (acquisition time of 40 s, slit width of 40 eV, pre-edge images at energy-loss onsets of 770 and 810 eV, post-edge image at an onset of 855 eV). This image was thresholded and binarized to obtain separate masks of the Ni and YSZ phases that could be applied to the thickness maps, O K edge elemental maps and O K edge jump-ratio images.

As the ceramic phase was found to be structurally and chemically stable at these temperature and hydrogen pressure conditions, the masked YSZ backbones in each thickness map, O K edge elemental map and O K edge jump-ratio image were used as invariant references to monitor intensity changes in the adjacent evolving Ni(O) phase. Each thickness map, O K edge elemental map or jump-ratio image was divided by the total number of counts in its YSZ phase to remove eventual intensity offsets and to yield images with comparable intensities. The thickness maps, O K edge elemental maps and O K edge jump-ratio images could then be analysed quantitatively on the pixel scale, which corresponded to an area of $\sim$6 x 6 nm$^2$, by comparing their intensity to that of their respective experimental NiO and Ni references.
3. Results & discussion

Fig. 2 shows a sequence of unfiltered BF TEM images acquired at different temperatures in 1.3 mbar of H2 during reduction up to 604 °C, alongside corresponding t/l and O K edge elemental maps (after normalization using the intensity in the YSZ backbone). An EEL reference spectrum of one NiO grain acquired at 30 °C is shown in the top-right corner. The first changes in NiO appear in the form of small voids at grain boundaries with the YSZ phase just below 350 °C (Fig. 2b), as already observed in previous work [3]. Density functional theory (DFT) calculations, which involved nudged elastic band (NEB) computations to determine the formation energy of an oxygen defect along the NiO/YSZ interface, indicated that O2- transfer from the NiO across the interface to vacancies in the YSZ may be energetically favourable [3]. This process creates oxygen vacancies in the NiO close to each interface and, as the Ni sites surrounding the vacancies dissociate H2 efficiently, the reduction reaction is triggered [8]. These voids are observed directly in the t/l image (Fig. 2b.2) and correspond to regions depleted in O, i.e. dark regions in the O elemental map (Fig. 2b.3). New porous regions appear closer to the centres of the NiO grains as the temperature increases to 428 °C (Fig. 2c). Voids are observed over the entire Ni grains at 460 °C, with larger voids appearing at the initial positions of some NiO/NiO grain boundaries (arrowheads in Fig. 2d). Intragranular voids become larger as the temperature increases to 604 °C (Fig. 2e). Images acquired 130 minutes after reaching 604 °C reveal a coarser reduced Ni structure (Fig. 2f). An EEL spectrum of one Ni grain acquired just before the set of data in Fig. 2f demonstrates full reduction (i.e. absence of O K edge, bottom-right inset in Fig. 2).

Fig. 3a shows the full sequence of O K edge elemental maps acquired during reduction up to 604 °C. In order to obtain statistically relevant information, Ni pixels that exhibit the same structural features (interfaces with YSZ or bulk material) are selected by masking the map accordingly. 9 different Ni regions are identified in the Ni elemental map. In each of these 9 Ni regions, the average intensity is measured in 4 different regions corresponding to the NiO/YSZ interfaces with YSZ. These average values obtained at different temperatures for different mask sizes are then normalized using the average values measured in the corresponding masked NiO and Ni reference images. As a result, the conversion fraction α of the reduction reaction (equivalent to the fraction of Ni) is obtained as a function of temperature in each masked region (Fig. 3b). Out of the 9 Ni regions identified in the micrographs, only regions 1 and 2 are entirely within the field of view. In the masks including only the Ni region close to the interfaces with YSZ (top mask), α is observed to gradually increase over a temperature range of 100 °C (348 °C to 444 °C). Alternatively, α measured in the entire Ni region (bottom mask) increases only by a few percent from 348 °C to 412 °C (interfacial reaction) and then quickly up to 90% between 412 °C and 444 °C. Free surface reduction occurs between 428 and 444 °C. Above 444 °C, α appears identical for the 4 different masks, demonstrating a homogeneous reaction of the Ni regions. A fraction of ~10% of NiO is left unreduced at the end of the heating ramp, which is consistent with previous in situ XRD and EELS experiments assessing the reduction of NiO particles [9]. While measurements of the reaction kinetics in regions 3 to 9 must be interpreted carefully since these do not contain entire NiO regions, similar trends are observed. The decrease in α measured at 556 °C is due to drift during acquisition (arrowheads in Fig. 3b). Bend contours (diffraction) may also induce an artificial decrease of α (arrows in Fig. 3b).

These artefacts induced by diffraction are limited when using O K edge jump-ratio images instead of 3-window elemental maps. However, jump-ratio involves a division that in turn results in pixels with intensities not related to chemistry (induced by drift and structural
changes during acquisition). These pixels are removed to infer reliable results. The reaction kinetics are extracted from O K edge jump-ratio images using the same procedure as for 3-window elemental maps and the results appear similar to these in Fig. 3b.

Fig. 2: (a-e) Selection of (1) bright-field TEM images and corresponding (2) \( \frac{t}{\lambda} \) and (3) oxygen K edge elemental 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 confirmed by EELS, bottom-right spectrum, the O K edge is absent). An EFTEM nickel map is shown as an inset in (a.1) to highlight the position of the NiO grains. Arrows indicate initiation of the reaction at the NiO/YSZ interfaces in (b) and at the free surface of NiO in (d), while arrowheads highlight pores at some Ni/Ni grain boundaries.
Figure 3: (a) O K edge elemental maps during reduction (after normalization using the intensity in the YSZ phase). For each Ni region identified in the Ni elemental map, the average intensity in 4 different masks starting at the YSZ interfaces, progressively selecting the entire Ni regions, was normalized using the NiO and Ni experimental references to yield in (b) the conversion fraction $\alpha$ of the reduction reaction as a function of temperature. The uncertainties in the measurement of $\alpha$ are obtained using the statistical deviation when the sample is unreduced (3σ), while the horizontal uncertainties are estimated to be ± 10 °C.
Fig. 4 shows the volume shrinkage induced by NiO reduction to Ni. The total intensity in the initial NiO phase in the $t/\lambda$ image acquired at 30 °C is multiplied by $\lambda_{\text{NiO}}$ and compared to the intensity in the reduced Ni regions in the $t/\lambda$ image acquired at 604 °C multiplied by $\lambda_{\text{Ni}}$. An overall volume shrinkage of -41.4% is measured here, which is consistent with theoretical predictions of -41.6% [10] and thus considered to be representative. The value of volume shrinkage measured in each Ni region labelled 1 to 9 in Fig. 4 is observed to vary from -36.2% to -45.6% due to diffraction contrast.

Fig. 4: Measurement of reduction-induced volume shrinkage. (a) Initial $t/\lambda$ image acquired at 30 °C (NiO/YSZ), (b) final reduced $t/\lambda$ image at 604 °C, 130 min after reaching 604 °C (Ni/YSZ, full reduction of sample confirmed by the EEL spectrum shown in Fig. 2), (c) Ni L$_{2,3}$ elemental map acquired at 30 °C before reduction to infer (d), a mask of the initial NiO phase, where 9 Ni regions are identified. This mask is used to segment images (a) and (b) to obtain (e) and (f), the NiO and Ni phase before and after reduction, respectively. From (e) and (f) and using the values of $\lambda$ calculated for NiO and Ni, the volume shrinkage induced by NiO reduction to Ni is measured independently in each Ni region (labeled 1 to 9 in d), while the overall volume shrinkage is measured to be -41.4%.
Changes in crystallography can also be assessed during reduction by acquiring selected area diffraction patterns. The results show that the Ni phase is mostly coherent with the initial NiO [3]. Moreover, Ni nanoparticles separated from the Ni bulk appear during reduction, probably as result of evaporation and redeposition of nickel hydroxide [11].

Different factors affect the acquisition and interpretation of reliable in situ data during reaction at elevated temperature. As only thin samples can be investigated using TEM, surface-related effects are amplified with respect to the processes that occur in the bulk. Sample preparation may also influence ETEM observations. For example, FIB-induced gallium implantation and surface amorphization effects on NiO reduction are not yet fully understood. Recently developed low-voltage argon ion milling systems with focused ion beams should remove such artefacts more efficiently. A comparison of unprocessed NiO powders and FIB-prepared NiO/YSZ samples that have the same chemistry may contribute to the understanding of sample preparation effects.

Thermal drift decreases the quality of energy-filtered images acquired over long exposure times. Although the use of a stainless steel grid instead of a conventional Cu grid to support the FIB sample reduced the overall drift, a low heating rate of 2 °C min⁻¹ was still required to acquire interpretable energy-filtered images and thus to capture the reaction. The recent introduction of heating holders based on microelectromechanical systems (MEMS) 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 [9,12]. While operating the microscope at a low electron dose can reduce these effects, a sufficient signal is still required to obtain statistically relevant data within the desired acquisition time. The acquisition of EFTEM images of core losses while the sample reacts is hence not suited to the study of fast processes. Moreover, this technique offers only limited flexibility in terms of pressure conditions and should ideally be related to other characterization techniques to bridge the gap with industrial applications such as SOFCs.

While all of these effects must be considered, energy-filtered imaging in a gas atmosphere at elevated temperature still has the ability to provide quantitative new insights into both oxidation state and structure of the Ni/YSZ anode during activation. Indeed, these spatially- and temperature-resolved results obtained at the nm scale can be compared to both theoretical predictions (volume shrinkage, DFT calculations) and experimental results obtained at larger length scales using other techniques (thermogravimetry, in situ X-ray diffraction, etc.) to assess their reliability and develop detailed reduction/activation models of the Ni/YSZ anode. Combining this study, previous work and literature results, a qualitative description of the processes controlling the reduction of the NiO/YSZ composite to Ni/YSZ that are observed in the microscope can be developed (Fig. 5).

At the YSZ/NiO interface, DFT calculations have demonstrated that O²⁻ may transfer across the interface to fill oxygen vacancies that are inherent to the YSZ phase [3], leaving oxygen vacancies in NiO (Fig. 5a). Small voids appear in NiO at the interfaces with YSZ at ~332 °C (Fig. 5b). H₂ adsorption, dissociation and desorption as H₂O was demonstrated to be energetically favourable on YSZ, on which vacant sites are filled by externally provided oxygen atoms [14]. This process frees an oxygen vacancy in the YSZ, which can be filled by O²⁻ originating from NiO (process A in Fig. 5b, similar to [15]). As a result, an oxygen vacancy surrounded by Ni²⁺ is formed in NiO, which was shown to act as a preferential H₂ dissociation site, with adsorbed H then desorbing as H₂O [8] (process B in Fig. 5b). Once Ni domains of sufficient size have been formed through the processes A and B, the reaction is expected to proceed through the adsorption of H₂ directly on Ni and the transfer
of adsorbed H to the oxygen reactive sites at the Ni/NiO interfaces [16] (process C in Fig. 5b). The reaction front moves towards the centre of the NiO grain. Between 428 °C and 444 °C (Fig. 5c), a sufficient number of oxygen vacancies is present on the surface of the NiO grain to trigger direct reduction of the free surface (as process B shown in Fig. 5b). At the end of the experiment at 604 °C, irregular Ni structures that contain intragranular voids are observed, with voids expecting to disappear at higher temperatures and longer reaction times as the system minimizes its surface energy.

Fig. 5: Qualitative description of the reaction mechanism of the NiO/YSZ sample in the ETEM using an atomic model based on [13], showing in (a) the YSZ/NiO interface at the start of the reduction process at 332 °C, with an oxygen ion transferring from NiO to YSZ, a process leaving a vacancy in the NiO phase, (b) H₂ adsorbs, dissociates and reacts with the oxygen ion in YSZ transferred from NiO to form H₂O (process A [3,14,15]), with the oxygen vacancy left in the NiO phase acting as a preferential H₂ dissociation site, with adsorbed H then reacting with oxygen to form H₂O (process B [8]). Once Ni domains have nucleated at the interface, H₂ dissociates on metallic Ni and is transferred to the oxygen sites at the Ni/NiO interface (process C [16]). (c) At 428-444°C, a sufficient number of oxygen surface defects is present to trigger direct reduction of the free surface. (d) At 600 °C, the final structure contains large intragranular voids as the system minimizes its surface energy.
4. Conclusion

The acquisition of energy-filtered images during the reduction of a NiO/YSZ composite at different temperatures 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 phase during reaction up to 604 °C, 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 and correspond to theoretical predictions, temperature-resolved oxygen K edge elemental and jump-ratio images allow the extraction of reaction kinetics that are localized at the nm scale. Local differences in the reaction rate as a result of structural features can be investigated in detail using this methodology and support the development of Ni/YSZ reduction/activation models.

Acknowledgements

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)”), as well as from the European Union Seventh Framework Program under Grant Agreement 312483 – ESTEEM2 (Integrated Infrastructure Initiative – I3). The A.P. Møller and Chastine Mc-Kinney Møller Foundation is greatly acknowledged for its contribution toward the establishment of the Center for Electron Nanoscopy in the Technical University of Denmark. The authors wish to thank M. Cantoni, F. Bobard, D. Laub, G. Lucas, D.T.L. Alexander, E. Oveisi and P. Stadelmann.

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