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Published in:
CHEMICAL COMMUNICATIONS

Link to article, DOI:
10.1039/c3cc46682e

Publication date:
2014

Document Version
Publisher's PDF, also known as Version of record

Link back to DTU Orbit

Citation (APA):
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 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 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.2b The microscope was operated at 300 kV at an electron dose rate of 103 e− nm−2 s−1, which was constant throughout the entire experiment. H2 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 TEM images (collection semi-angle of 6.8 mrad): one unfiltered image I0, one filtered zero-loss image I0 and three images Ipre-edge 1, Ipre-edge 2 and I-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.4 Images I0 and I0 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 NiO4†). Images Ipre-edge 1, Ipre-edge 2 and I-post-edge were processed to obtain elemental maps of the oxygen K edge (532 eV) using the conventional three window method,4 whereby the two Ipre-edge images were used to extrapolate a power law background that was subtracted from the I-post-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

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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/l 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, 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 H₂ efficiently, the reduction reaction is triggered. 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/l map and the final fully reduced t/l image by multiplying the intensity in either the NiO or the Ni regions by lNiO and lNi, 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 l will also affect the results, the volume shrinkage resulting from NiO reduction to Ni measured in regions A and B in Fig. 1a.2 and f.2, were analysed. Although the accuracy of the estimation of l 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
describe the progress of the reaction as a function of temperature, as
Future work will involve the use of solid-state kinetic models to
masking the map accordingly. The mean intensity in these regions
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 NiO
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 NiO 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 due to the drift of the sample, 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 MEMS-
Based heating holders decreases thermally induced drift significa-
cantly 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 informa-
tion 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 quan-
titatively 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 \( E_m \) (an average energy-loss value) was used
for NiO (19.8 eV) to yield \( \Delta E \), the effective atomic number of Ni was
used to estimate \( \Delta E \) (25.2 eV) and in turn \( Z_{Ni} \) (see ch. 5 of ref. 4b).

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