



# Environmental TEM study of the dynamic nanoscaled morphology of NiO/YSZ during reduction

Søren Bredmose Simonsen<sup>a,\*</sup>, Karsten Agersted<sup>a</sup>, Karin Vels Hansen<sup>a</sup>, Torben Jacobsen<sup>a</sup>, Jakob Birkedal Wagner<sup>b</sup>, Thomas Willum Hansen<sup>b</sup>, Luise Theil Kuhn<sup>a</sup>

<sup>a</sup> Department of Energy Conversion and Storage, Technical University of Denmark, DK-4000 Roskilde, Denmark

<sup>b</sup> Center for Electron Nanoscopy, Technical University of Denmark, DK-2800 Kgs. Lyngby, Denmark

## ARTICLE INFO

### Article history:

Received 16 June 2014

Received in revised form 2 October 2014

Accepted 15 October 2014

Available online 30 October 2014

### Keywords:

Nickel oxide reduction

NiO

YSZ

SOFC

SOEC

In situ TEM

ETEM

Autocatalysis

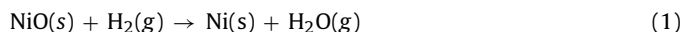
## ABSTRACT

The reduction of a metal oxide is often a critical preparation step for activating catalytic behaviour. This study addresses the reduction process of NiO in pure form and in a composite of NiO/yttria-stabilized zirconia (YSZ) in hydrogen relevant for solid oxide electrochemical cells by comparing results from environmental transmission electron microscopy (ETEM) with thermogravimetric analysis (TGA). The temperature dependent reduction profiles obtained from TGA confirm an inhibitive effect from YSZ on the NiO reduction. The ETEM images show the growth of Ni in decaying NiO and reveal the nanoscale morphological changes such as pore formation in NiO above 280 °C and densification and collapse of the pore structures above 400 °C. The accelerated Ni front in NiO illustrates the autocatalysis of the reaction. A rapid temperature ramping from room temperature to 780 °C in hydrogen in 1 second resulted in immediate morphological changes at the nanoscale from dense NiO to dense Ni. The analysis suggests that the inhibitive effect of YSZ on the NiO reduction reaction is not due to a direct local interaction between YSZ and NiO, but instead due to gas and/or mass transport limitations.

© 2014 Elsevier B.V. All rights reserved.

## 1. Introduction

The reduction of metal oxides is a typical step in the preparation of the active metal surfaces for various catalyst systems. Conditions of the reduction process, such as temperature, reduction time, gas composition, gas flow and pressure, are important for optimizing the catalyst performance [1,2]. Understanding the metal oxide reduction process is therefore important in order to be able to optimize the catalyst activity. The reduction of nickel-based catalysts used for e.g. oxidation [3], methanation [4] and ammonia decomposition [5] has been extensively studied [2,6–16]. The reduction of NiO with H<sub>2</sub> occurs without any intermediate phase [8] and can be described by the relatively simple formula:



The loss of oxygen during reduction leads to a volume decrease by 41% resulting in a restructuring of the overall morphology of the solid and can lead to pore formation in the Ni [17–19]. A delay in the reduction onset, a so-called incubation or induction period is

reported, which decreases with reaction temperature [6,8,10,12] and increasing number of defects on the NiO surface [10]. It has been suggested that dissociative adsorption of hydrogen, which is a necessary initiation step for the NiO reduction, preferentially takes place at NiO surface oxygen vacancies [8,10]. The reduced Ni surface will act as a catalyst for dissociative H<sub>2</sub> adsorption and it has been suggested that the reduction of NiO will be autocatalytically accelerated in the vicinity of a Ni surface [6]. On the contrary, the produced H<sub>2</sub>O influences the reaction rate negatively, possibly by poisoning of the active sites for H<sub>2</sub> adsorption [6,18]. In addition it has been reported that the reaction rate scales with the H<sub>2</sub> pressure [8,10,17].

Ni catalysts are often integrated into an oxide matrix and for such systems the reduction of Ni oxide can be slower than for the pure NiO [7,12]. An important example is the porous composite of Ni and yttria-stabilized zirconia (YSZ), which is the state-of-the-art anode in commercial solid oxide fuel cells (SOFC) and cathode in solid oxide electrolysis cells (SOEC) [11–16]. In these electrochemical cells Ni simultaneously acts as an electron conductor and catalyst for splitting the adsorbed reactive gases, while YSZ acts as an oxygen ion conductor. The porous Ni/YSZ is typically prepared from powder mixtures of NiO and YSZ [13,14,16], sintered into a dense structure and finally reduced during start-up of the

\* Corresponding author. Tel.: +45 20 12 06 11.  
E-mail address: [sobrs@dtu.dk](mailto:sobrs@dtu.dk) (S.B. Simonsen).

SOFCs/SOECs, typically around 800 °C [13,15,16]. The overall performance of SOFCs/SOECs depends on the initial reduction step and the related morphology [12,20] and several studies have focused on the reduction of NiO in mixtures with YSZ [12,15,16,19,20]. It is reported that YSZ inhibits the reduction of NiO [11,12,16], but the reason for the inhibitive effect of YSZ is not clear. Linear kinetics in the reduction of dense NiO/YSZ samples at temperatures below 700 °C suggests that the reaction is interface controlled and therefore not limited by gas transport in the produced porous Ni [13,16,18]. On the other hand, YSZ has been suggested to act as transport barrier for the reaction front inside the NiO/YSZ matrix [12]. Increasing sintering temperatures leads to a stronger inhibitive effect of YSZ, and the effect has therefore previously been explained by formation of NiO crystallites incorporated in YSZ and formation of a metastable solid solution of NiO in YSZ [16]. It has also been suggested that the reduction rate at the NiO–YSZ interfaces is relatively low due to a NiO–YSZ chemical interaction [16] or due to a slow Ni nucleation [12].

Techniques, such as thermogravimetric analysis (TGA) [12,14], thermomechanical analysis (TMA) [14], temperature programmed reduction (TPR) [11], X-ray diffraction (XRD) [10,11,15], X-ray photoelectron spectroscopy (XPS) [8,10] and Auger spectroscopy [8,10] have given significant insight into the NiO reduction process. In addition, local information has been obtained using post mortem electron microscopy [12–14,17,18]. However, nanoscale dynamics, such as initiation of the reduction, crystal growth/decay or morphological changes of NiO and Ni during reduction can only be indirectly probed with these techniques. It can also be difficult to separate the different structural parameters that simultaneously influence the reduction process, such as local composition, particles sizes, mobility of the solids and pathways for gas transport in the samples [17,18]. ETEM offers a localized study with atomic resolution in a gas environment at elevated temperatures [21–24]. ETEM has been used to study the NiO reduction reaction at the nanoscale [19,25–28] and has given insight into e.g. the mobile species (Ni-atoms [25] or O-atoms [19]) and the initial Ni formation at the NiO surfaces [24].

The present work is a comparative study of the reduction of pure NiO and NiO/YSZ with (a) TGA to describe the overall temperature dependency of the reaction for macroscopic samples and with (b) ETEM to probe the sample at the nanoscale during exposure to H<sub>2</sub> at elevated temperatures. The goal of the study is firstly to address the apparent inhibitive influence from YSZ on the NiO reduction and secondly to describe the morphological changes of the NiO/YSZ during reduction at different temperature ramping rates for temperatures up to 780 °C.

## 2. Experimental

### 2.1. Catalyst preparation

An SOFC anode (SOEC cathode) consisting of 56 wt.% NiO and 44 wt.% YSZ with 8 mol% yttria was prepared by tape casting from mixed powder of NiO (Novamet Specialty Products Corp.) and YSZ (Tosoh Corporation) as described in detail in reference [29]. A reference sample was prepared by tape casting the pure YSZ. An additional reference sample was prepared by die pressing a pellet from the pure NiO powder. All of these samples were sintered in air at 1350 °C for 3 h. In one experiment the dense NiO/YSZ sample was used without further preparations, but for other experiments the samples were ground into a fine powder in a mortar. In addition, the raw NiO powder was used as a non-sintered reference sample.

### 2.2. Catalyst characterization

TGA was performed on all samples on a Netzsch STA 409CD Thermobalance. The powder samples were spread out on the surface of a wok-type sample holder mounted vertically in the test chamber. 50 mg of YSZ and NiO/YSZ powder was used. 30 mg of the pure NiO powder was used, to assure a similar amount of NiO was used in both sample types. In addition to the powder samples, a piece of 30 mg of the sintered dense NiO/YSZ sample was placed in a flat holder with a diameter of 17 mm (Netzsch 445.240). The TGA experiments were performed in a flow of 50 Nml/min 9% H<sub>2</sub>/N<sub>2</sub> (Air Liquide: H4.6; N6.0). The temperature was initially ramped from room temperature to 150 °C at 10 °C/min and held at this temperature for 2 h to dry the samples prior to the actual reduction experiment. The reduction experiment was performed by ramping the temperature to 1200 °C at 1 °C/min.

Using a JEOL 3000F equipped with a 300 kV FEG, a scanning unit (STEM) and a high-angle annular dark-field (HAADF) detector, ex situ STEM of the NiO/YSZ powder was carried out to determine the spatial distribution of the different elements in the sample at the nanoscale. Energy-dispersive X-ray spectroscopy (EDS) was carried out for compositional analysis by using an Oxford Instruments detector with an ultra-thin window. The analysis was performed using the Inca software. The ground powder was dispersed in ethanol and a droplet of the suspension was placed on a standard TEM copper grid.

The ETEM experiments were performed using a Titan 80-300 (FEI) electron microscope equipped with a differentially pumped environmental cell [30]. The microscope was operated with a primary electron energy of 300 keV. In the electron microscope, the powder samples were exposed to 2 mbar H<sub>2</sub> (AGA 6.0). The powder samples were ground with ethanol and droplets of the suspension were deposited on the surface of MEMS thermal E-chips (Protechips Inc.) and the samples were allowed to dry in air at room temperature before inserting the TEM holder. The chips used for the experiments were either with or without a carbon support. The chips were mounted in an Aduro 300 heating holder (Protechips Inc.) facilitating the heating of the samples in the gaseous environment. The temperature calibration of the heating holder is described in detail in the Supplementary materials Appendix A.

### 2.3. Critical remarks on the ETEM analysis

Before performing the actual reduction experiments it is necessary to determine whether artefacts are induced by the electron beam. Indeed it has been reported that NiO can be reduced by a focused 100 kV electron probe in vacuum [9]. The NiO/YSZ sample was exposed to 2 mbar H<sub>2</sub> and a constant exposure to the electron beam with a beam current density of ca. 600 e<sup>-</sup>/nm<sup>2</sup> s for 30 min at room temperature. No structural changes of the NiO/YSZ were observed after this treatment, except that a layer of amorphous carbon builds up on the sample surface. The actual reduction experiments were performed at approximately the same beam current density, but with a lower total dose since the electron beam was blanked between image acquisitions. For the longest experiment the estimated total electron beam exposure was 15 min. In addition, comparison of areas followed over time with previously unexposed areas showed no characteristic structural differences. It is therefore unlikely that the dominating structural changes of the samples during the reduction experiments are due to the electron beam.

Since the TEM images are two-dimensional projections of the three-dimensional sample, the TEM image analysis can be challenging. For the present powder samples, it is easier to observe the initiation of the reduction process in thin regions and at the edges of the particles than at thicker regions and at surfaces normal to the electron beam. Also, overlapping NiO and YSZ grains with

Download English Version:

<https://daneshyari.com/en/article/39404>

Download Persian Version:

<https://daneshyari.com/article/39404>

[Daneshyari.com](https://daneshyari.com)