**Changes in physical and mechanical properties of SOFC Ni-YSZ composites caused
by redox cycling**

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Abstract

Investigations of sequential cyclic reduction and oxidation (redox) of SOFC Ni-YSZ anode substrates are presented aimed at monitoring and understanding changes in critical physical and mechanical properties as a function of degree of oxidation at 800°C. The commonly observed expansion on oxidation, and its irreversibility on subsequent reduction, was confirmed, but was found to be greatly dependent on oxidation conditions, giving strains in the range 0.55-0.8 %. Nevertheless, redox cycling was accompanied by reversible changes in elastic modulus and no significant damage was detected in the YSZ network. Microstructure observations of oxidised Ni particles revealed formation of closed porosity of a similar magnitude to that observed in oxidised composites (ca. 5 %), suggesting that this is a major cause of the expansion on oxidation of the composite.

Introduction

Anode-supported Solid Oxide Fuel Cells (SOFCs) using Ni-based substrates (cermet composites) are susceptible to damage during fault conditions (e.g. interruption of the fuel supply, or too high a fuel utilisation at high overvoltage) as a result of dimensional changes of the cermet caused by the oxidation of Ni to NiO and cycles of reduction and oxidation (redox). Although there is considerable variability in results reported by different researchers, some trends are consistently observed in redox experiments with Ni-YSZ cermets. Upon initial reduction of the NiO-YSZ precursor there is negligible dimensional change, whereas the first complete oxidation (all Ni converted to NiO) is accompanied by a linear expansion strain of approximately 1 %. Successive redox cycles result in an accumulating expansion strain, revealing a non-reversible redox process for the cermet. This oxidation strain is recognised to be the critical parameter for driving damage (electrolyte cracking) in anode-supported cells (ASCs), which can take place for an oxidation strain as low as 0.1 % [1].

Nevertheless, the details of how the cermet expands with advancing oxidation and what controls this mechanism are not established. The relationship between degree of oxidation and composite expansion is of great interest for estimating how much oxidation the cell can accommodate before failure. Regarding the actual expansion mechanism, there is published work that suggests expansion is due to the agglomeration of metallic nickel [2, 3] and the formation of porosity upon oxidation [4, 5, 6], based mainly on qualitative SEM (scanning electron microscopy) observations. We present in this paper controlled oxidation studies of Ni particles and Ni cermet substrates in which changes in dimensions, porosity and elastic modulus were measured as a function of degree of oxidation.

While redox damage of the ASCs by electrolyte cracking is the expected failure mode, there is some controversy concerning the effect of redox on the integrity of the anode substrate itself. It has been reported in the literature that redox can cause microcracking or even catastrophic failure of the composite (see [1] and references therein). In the present work we assess damage to the composite from elastic modulus changes in combination with microstructural observations of the YSZ network.

Experimental

Samples

The Ni-based composite specimens were provided by Forschungszentrum Juelich in the form of NiO/YSZ composite plates with composition 56 wt % NiO / 44 wt % 8YSZ. The plates were pre-treated under the same conditions as would be used for co-sintering an electrolyte layer so that they were in the same state as they would be in a typical ASC. (The presence of the electrolyte and anode in the sintering of a production half-cell is not likely to affect the sintering of the substrate since the substrate has much greater thickness than the functional layers. After fabrication of a production half-cell the electrolyte would put the substrate under tension upon cooling down after sintering. Again, this is a small effect on the substrate, because of its greater thickness, and at operating temperature the substrate's residual stress is estimated to be only ~2 MPa [7]) Rectangular bars, of ca. 40×4×1.5 mm for the interrupted oxidation experiments, or 25×4×1.5 mm for the dilatometry measurements, were cut from the plates. Spherical Ni particles (Alpha Aesar, 5-15 micron, 99 % Ni) were used for the studies of individual particles. Samples of the porous YSZ network were prepared from the Ni-YSZ composites by completely dissolving the nickel using concentrated (16 molar) HNO₃.

Mechanical/Physical Properties Characterization

The characterization of the redox behaviour of the composites involved monitoring the linear strain, elastic modulus E , porosity and microstructure. Vernier callipers (10 μm resolution) and dilatometry (Netzsch 402E dilatometer, 0.01 μm resolution) were used for the strain measurements. The elastic modulus was measured by the impulse excitation of vibration technique [8] using the GrindoSonic MK5 instrument. Out of plane excitation was performed on samples supported by foam pads, while the signal was recorded with a microphone. The porosity measurements were performed with the aid of a Sartorius (CP 124 S) balance, based on the Archimedes principle and vacuum impregnation of water [9]. Thus values for the bulk density (which corresponds to the mass of unit volume of the porous composite), apparent solid density (i.e. the density of the solid phase including closed pores) and volume fraction of open porosity could be obtained. In the complete reduced (Ni-YSZ) and oxidised states (NiO-YSZ) values for the closed porosity were also deduced using theoretical true solid densities for the known composition of the cermet (reduced 7.10 g/cm^3 , oxidised 6.31 g/cm^3).

SEM (instrument: Jeol JSM 5610 LV) and focussed ion beam (FIB, instrument: FEI FIB200) techniques were used for observing the YSZ network and sectioning/imaging oxidised Ni (NiO) particles. The YSZ samples were coated with gold before being examined in the SEM.

Redox procedures

Reduction of the composites was carried out in a tube furnace with 10 % H_2/N_2 flowing at 50 ml/min and the following temperature programme: heating up to 650°C at 3

K/min – hold for 6 hours – heating up to 900°C at 3 K/min – hold for 10 hours – cooling down to RT at 3 K/min. A reduction experiment was also performed in situ in the dilatometer by heating up in N₂ to 900°C (10 K/min) and then introducing 5 % H₂/N₂ (50 ml/min) for 3 hours at 900°C.

Interrupted oxidation of the cermets was performed at 800°C (in a box furnace with ambient air) in steps. A step consisted of inserting the sample directly from RT (room temperature) into the furnace at 800°C, allowing it to oxidise for a few seconds or minutes, and then taking it out and letting it cool freely in air to RT. The degree of oxidation was determined after each step by the change in weight and dimensional changes were measured using Vernier callipers. Oxidation in the dilatometer was performed in flowing 50 ml/min air at 800°C after the sample was heated up in N₂ at 10 K/min. The nickel particles were oxidised in the box furnace at 800°C for 2 hours (full oxidation) or a few seconds or minutes (partial oxidation).

Results and Discussion

Redox of Anode Substrates

On initial reduction the bar specimens showed no detectable length changes when measured with the callipers, and only 0.017 % contraction in the dilatometer, in agreement with most other published work on similar composites [1]. Fig. 1 shows the relation between degree of oxidation and expansion strain of the anode substrates (interrupted oxidation). After the first complete oxidation the substrate had expanded to a total linear strain of 0.55 %, showing an almost linear relation between degree of oxidation and strain in the range of 20-90 % oxidation. However, in the first oxidation steps (up to 20 %) a slight contraction was recorded. After the first oxidation and

reduction cycle, re-oxidation of the composite showed a very similar trend to the first oxidation, except that there was a constant extra strain (ca. 0.1 %), resulting from the irreversibility of the first cycle. As a result, the total strain after the second complete oxidation was higher (0.63%) than after the first. (The slight vertical offset to the left of the re-oxidation points in Figs. 1, 3 and 5 was caused probably by some loss of material during handling the sample between the two redox cycles) This accumulation of oxidation strain with redox cycling is in accordance with published studies. Klemensø et al. [2] have suggested that it is the result of the sintering and rearrangement of the metal Ni particles in the YSZ network. The sample again showed a small initial contraction during the second oxidation. This kind of contraction was not observed however in the dilatometer oxidation (Fig. 2).

Moreover, the different oxidation conditions produced different values of final expansion strain (Table 1). The interrupted and direct oxidation both took place in ambient air (no flow) implying that interruption of the oxidation process affects the expansion behaviour of the cermet. It seems that interruption of the early steps of oxidation causes the initial shrinkage and a final lower expansion on full oxidation (0.55 %) when compared to direct oxidation (0.65 %). The oxidation in the dilatometer on the other hand showed a distinctly higher expansion strain on full oxidation (0.8 %). The key feature in this experiment is that there was a flow of air for the oxidation in the dilatometer. Ettler et al. [10] have drawn attention to the effects that incident oxidising flows have on the kinetics and dimensional behaviour of Ni/YSZ cermets. The fact also that only in the dilatometry case did the strain measurement take place at high temperature suggests that room temperature measurements may not be as accurate and may also be compounded by the effects of additional internal stresses caused by the different thermal expansion coefficients of the constituent materials in the composites.

Nevertheless, in all cases an irreversible strain was observed after a complete oxidation/reduction cycle.

Young's modulus on the other hand exhibited a single linear dependence on degree of oxidation (Fig. 3) for both first oxidation and re-oxidation. As nickel oxidises and the solid volume increases, the porosity decreases and the elastic modulus of the composite increases. Its reversibility and repeatability implies that no significant damage occurs within the composite structure. No macroscopic cracking of any samples was observed, but some slight warping of the samples was evident after the intermediate steps of interrupted oxidation. After full oxidation however the samples appeared to be flat. Dissolution of the Ni from a piece (ca. $7 \times 4 \times 1.5$ mm) taken from the composite that had gone through two oxidation/reduction cycles revealed a coherent YSZ network structure (Fig. 4) that retained a rectangular bulk shape. Some minor localised cracking might have occurred, but if it did it was not clearly detectable by SEM and had no major effect on the mechanical integrity of the YSZ network. Although this is consistent with the observed elastic modulus behaviour, it is not what one would expect taking into account the cermet's oxidation strain. It is hard to explain how a brittle ceramic network can accommodate an elongation of 0.6 % without failing. It is possible that some degree of plastic deformation (creep) took place in the ceramic structure upon the increase in solid volume when the nickel was oxidised.

Monitoring of the evolution of porosity reveals that with increasing oxidation open porosity decreases and the overall bulk density increases in an approximately linear fashion (Fig. 5). However, the apparent solid density was observed to decrease to 5.73 g/cm^3 on complete oxidation, significantly lower than the 6.11 g/cm^3 value measured for the as-received NiO/YSZ composite. Hence, closed porosity forms on oxidation and in our case an increase of ca. 5 % in closed pore volume was estimated to have occurred

(Table 2). It is apparent from the values in Table 2 that a re-distribution of open and closed porosity takes place after the first reduction/oxidation cycle, but the relative porosity values remain practically unchanged after the second cycle.

There are two ways in which closed porosity can be forming. One is due to the redistribution and partial sintering of nickel grains in the reducing environment. The second is through the intrinsic properties of the nickel oxidation and reduction mechanisms at high temperatures. In order to clarify this, we conducted studies of the microstructural changes occurring during oxidation of nickel particles.

Oxidation of Ni particles

It has been established that Ni oxidation at $500^{\circ}\text{C} < T < 1000^{\circ}\text{C}$ is controlled by outward diffusion of Ni^{++} through the oxide scale [11], a process that should result in the formation of voids at the metal/oxide interface, or in the bulk of the metal if the metal/oxide interface is prevented from moving inwards. Although oxidation of nickel has been widely studied it is not very clear how porosity develops during oxidation, and especially for the case of the micron-size Ni particles/grains that are present in the cermets of interest. In experiments oxidising cylindrical nickel wires, Hales and Hill [12] showed that internal porosity developed in the nickel due to the inability of the circular metal/oxide interface to migrate inwards during oxidation. For a spherical geometry the problem of the oxide/metal interface recession and how contact can be maintained at that interface is a similar issue. If the interface cannot recess inwards then an outward Ni^{++} diffusion mechanism would be expected to create hollow shell oxide particles with internal void formation equal to the volume of initially present Ni. It has been found that when interface recession is prevented in bulk specimens (e.g. by impurities that pin the interface) inward oxygen permeation through fissures in the oxide occurs and two-

layered oxide scales form with the boundary between the layers coinciding with the original metal surface [13]. Recent studies show that very high purity nickel sheets develop just a simple oxide layer (outward diffusion of Ni^{++}) [14] and that the orientation of the Ni grains may also affect the oxide morphology [15].

Fig. 6 shows SEM pictures of the almost spherical Ni particles and their appearance after full oxidation to NiO particles. The surface of the oxidised particles has changed significantly to show a more textured outer surface. Generally this surface appearance is taken to signify porosity extending below the surface, what is commonly described as ‘sponge’-like texture [4, 5]. When the same samples were imaged using the secondary electrons generated by the scanned primary ion beam in the FIB microscope, a similar texture was revealed, but less pronounced (Fig. 7a). However, when sputtered ions were used to form the image in the FIB microscope, Fig. 7b, the surface texture of the fully oxidised NiO particles appears much smoother. This surface morphology is more aptly described as dimpled rather than porous. Sputtered ions originate from the top surface layers only, that is, they are of sub-nano-meter origin and have an energy range that is at least an order of magnitude greater than secondary electrons generated in the SEM. Both of these fundamental aspects mean that the ion image shows the surface topography with less enhancement of edges and thin features.

To investigate the subsurface porosity of the oxidised particles we have exploited the ability to control the FIB ion beam current over four orders of magnitude. Localised scanning of the FIB beam at high currents in the nano-amp range sputters the Ni and NiO at a sufficient rate to form a cross-section in-situ through a particle. Subsequently, the section is imaged with the same ion beam on tilting the particle through 45° , but at the much lower ion current of approximately 50 pA. Images of such cross sections are shown in Fig. 8. There are structure changes both in terms of grain morphology and porosity as a

result of oxidation. From a completely dense Ni particle, a NiO particle containing some porosity is formed on complete oxidation. However, a hollow core is not formed.

In order to monitor the porosity changes as oxidation advances, Ni particles were exposed to oxidising conditions for time periods ranging from 30 seconds to 5 minutes, and then sectioned and observed in the FIB microscope (Fig. 9). With the exception of Fig. 9b, it can be observed that as oxidation proceeds grain growth and formation of porosity take place. The particle of Fig. 9b is significantly smaller than the rest of the batch and this probably resulted in a higher degree of oxidation than intended. After 5 min of oxidation, and using secondary ion imaging, the oxide scale around the particle is clearly visible (Fig. 9f). Pores are present both in the scale and the metal. A comparison of the fully (Fig. 8b) and partially (Fig. 9) oxidised particles shows that partial oxidation can be characterised by higher porosity formation than full oxidation, implying a complex oxidation mechanism. While outward Ni diffusion may dominate at the early oxidation stages it is apparent that inward oxygen transport is also involved, given that the oxide/metal interface cannot recess in our spherical geometry.

The above observations show that the oxidation process of small particles does lead to some small amount of closed porosity, but not nearly as large an amount as observed on oxidation of wires. Thus the “swelling” on oxidation is much smaller than would be expected if hollow oxide particles had been formed. Werber [16] has suggested that the presence of porosity in the initial Ni particles has an adverse effect on the oxidation “swelling”. However, this cannot account for the present observations, as the Ni particles were originally fully dense. Nevertheless, even the small amount of porosity observed in the FIB images can easily account for the ca. 5 % increase in closed porosity measured for the oxidation of the cermet. Although this closed porosity formed by the oxidation mechanism can account for the swelling of the cermet, additional contributions from

sintering of metallic Ni cannot be excluded, and it is likely that a combination of the two – nickel sintering and intrinsic oxidation properties – is involved.

Conclusions

Investigations on Ni-YSZ composites used in state-of-the-art SOFCs were performed involving monitoring changes in critical physical (dimensions and porosity) and mechanical (Young's modulus) properties upon redox cycling at 800°C. A correlation between degree of oxidation and changes in these properties was established using interrupted oxidation.

Initial reduction of the NiO-YSZ composite resulted in negligible shrinkage whereas subsequent interrupted oxidation exhibited a total linear expansion of ca. 0.55 %, following a close to linear relation with degree of oxidation. However the oxidation expansion was shown to depend on the oxidation procedure (interruption of oxidation, measurement temperature, or air flow) giving values as high as 0.8 %. It was established that the oxidation strain is not reversible and residual strain of ca. 0.1 % remains after the first oxidation/reduction cycle and adds on to the second. However, the oxidation expansion did not have a detectable effect on the integrity of the composite. The changes in elastic modulus of the composite were reversible and a coherent YSZ network structure was revealed after two redox cycles. Finally, measurement of porosity changes showed that closed porosity forms on oxidation and this was estimated to be of the order of 5 % of the volume of the composite. Sectioning of partially oxidised spherical Ni particles using FIB techniques revealed formation of closed pores, which can account for increase in closed porosity and the expansion of the composite on oxidation.

It is clear that expansion of the Ni-YSZ composite on oxidation, which is the critical parameter for cell failure, is closely related to microstructural changes of the Ni particles

during oxidation. It is shown in this paper that formation of closed porosity in the NiO particles due to intrinsic features of the oxidation mechanism makes a key contribution to the oxidation expansion of Ni cermet anodes and anode supports.

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Figure Captions

Fig. 1 Expansion strain of anode substrates as a function of degree of oxidation. Error bars indicate the uncertainty introduced by the dimensional measurements.

Fig. 2 Dilatometry of anode substrate oxidation with inset on the right magnifying the region in which oxidation is taking place.

Fig. 3 Elastic modulus E of anode substrates as a function of degree of oxidation.

Fig. 4 Fracture surface of the YSZ network after two redox cycles and dissolution of nickel.

Fig. 5 Bulk density, apparent solid density and open porosity of anode substrates as a function of degree of oxidation.

Fig. 6 SEM of a) as received Ni and b) fully oxidised Ni (NiO) particles. The secondary electron images were recorded using a beam energy of 20 keV.

Fig. 7 FIB microscope images of fully oxidised Ni particles using (a) secondary electrons and (b) positively-charged secondary ions.

Fig. 8 FIB cross-section secondary electron images of (a) as received Ni and (b) fully oxidised Ni (NiO) particles.

Fig. 9 FIB cross-section secondary electron images of Ni particles oxidised at 800°C for (a) 30 sec, (b) 60 sec, (c) 90 sec, (d) 180 sec and (e) 300 sec. Image (f) is the same particle as in (e) but obtained using the secondary ion signal.

Tables

Table 1 Linear expansion strain of composites after total oxidation for different methods of oxidation

	interrupted oxidation (ambient air)	direct oxidation (ambient air)	dilatometry oxidation (air flow)
oxidation strain (%)	0.55 ± 0.03	0.65 ± 0.03	0.80 ± 0.01

Table 2 Properties of the composites after different successive stages of reduction and oxidation. (E elastic modulus, ρ_b bulk density, ρ_{as} apparent solid density, Pa open porosity and Ps closed porosity.)

	strain (± 0.03 , %)	E (± 1.3 , Gpa)	ρ_b (± 0.05 , g/cm ³)	ρ_{as} (± 0.05 , g/cm ³)	Pa (± 0.3 , %)	Ps (± 0.3 , %)
as-received	-	79	4.65	6.11	23.9	2.5
reduced	0.00	32	4.02	6.90	41.8	1.6
oxidized	0.55	74	4.57	5.73	20.3	7.3
re-reduced	0.14	31	4.04	6.87	41.2	1.9
re-oxidized	0.63	72	4.55	5.72	20.4	7.4

15kV

X9,000

2µm

12 20 SEI

20kV

X5,000

5 μ m

16 17 SEI

20kV

X3,500

5 μ m

16 17 SEI

pA 49.0	Mag 10.0 kX	Det CDM-E	FWD 17.0	Tilt 0.0°	Scan H 6.34 s	5 μ m
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pA 49.0	Mag 25.0 kX	Det CDM-I	FWD 17.0	Tilt 0.0°	Scan H 11.77 s	2 μ m
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— 2 μm

a

b

c

d

e

f