Dimensional behavior of Ni-YSZ composites during redox cycling

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Published in:
Journal of The Electrochemical Society

Link to article, DOI:
10.1149/1.3046121

Publication date:
2009

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

Link back to DTU Orbit

Citation (APA):
The dimensional behavior of Ni–yttria-stabilized zirconia (YSZ) cermet during redox cycling was tested in dilatometry within the temperature range 600–1000°C. The effect of humidity on redox stability was investigated at intermediate and low temperatures. We show that both the sintering of nickel depending on temperature of the initial reduction and the operating conditions, and the temperature of reoxidation are very important for the size of the dimensional change. Cumulative redox strain (CRS) is shown to be correlated with temperature. Measured maximum CRS after three redox cycles varies within 0.25–3.2% d/L in dry gas and respective temperature range of 600–1000°C. A high degree of redox reversibility was reached at low temperature, however, reversibility is lost at elevated temperatures. We found that at 850°C, 6% steam and a very high $p_{H_2}/p_{H_2O}$ ratio is detrimental for redox stability, whereas at 600°C no negative effect was observed. Pre-reduction at 1100 instead of 800°C more than doubled redox strain on reoxidation at 800°C. For samples similarly pre-reduced at 1000°C, lowering the reoxidation temperature from 1000 to 750°C or below reduces the redox strain to less than half.

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The anode-supported solid oxide fuel cell (SOFC) concept based on Ni–yttria-stabilized zirconia (YSZ) anode materials is under intensive research and development. While new materials are being sought, e.g., fully ceramic anodes capable of operating at lower temperatures, the nickel-based ceramic–metal composite (cermet) anode is so far the reference to which the new anodes will be compared. So far no nickel-free anodes have been proven superior in long-term operation at technologically relevant sizes up to the stack and system level. In spite of this, some problems are associated with the Ni–YSZ electrode. The conductivity of a Ni–YSZ composite is known to degrade with time under operation at high temperature due to the growth of Ni grains, whereas the ceramic backbone remains largely unaltered.1,2 The sintering of the Ni network may result in performance degradation through loss of electrical conductivity of the anode support (current collection). It is known from catalysis with nanosized Ni on ceramic beds that both temperature and humidity (the $H_2O/H_2$ ratio) enhance Ni particle growth; the effect of steam arises from the formation and mobility of the Ni$_2$-OH species.3,4 The mobility also of micrometer-sized Ni embedded in the porous YSZ backbone is dependent on operation conditions and system logics. Insufficient sintering at high temperatures, e.g., Ni-based vs fully ceramic or metal-supported SOFC, or by defining safe operation regimes and system controls of a selected design or composition (knowledge of so-called external parameters and SOFC system logics). The reoxidation of the anode-supported cell can lead to (i) degradation and disruption of the anode support itself, or (ii) cracking of the electrolyte in a cell structure due to excessive macroscopic expansion of the anode support. Two requirements for a redox-improved anode-supported Ni–YSZ half-cell can be identified:

1. Based on mechanical modeling, the maximum allowable expansion of the anode support does not exceed 0.1–0.2% d/L.5-15 As larger expansions create tension forces that tend to crack the electrolyte, this cumulative strain level should not be exceeded. For development work, 0.1% maximum cumulative redox strain ($CRS_{max}$) is chosen as the target level.

2. During redox cycles the behavior of the composite should be reversible, that is, after the reoxidation cycle the bulk dimension should return to the original. An irreversible expansion will inevitably limit the number of allowable redox cycles and lead to violation of the first requirement.

This paper describes dimensional changes in Ni–YSZ composites under redox cycling in a wide range of operation conditions. We aim to address the “internal” processes of importance that take place in the composite. Part of the high-temperature data of the present paper have previously been published in Ref. 16.

**Experimental**

**Ceramic processing.**—The samples tested were manufactured from commercial NiO and YSZ powders using standard ceramic processing techniques and equipment. The solids composition of the samples was 53–56 wt % NiO and 44–47 wt % YSZ. The powders were ballmilled in ethanol-based slurries using dispersants and organic binders. The tested samples were similar to the anode supports...
of the state-of-the-art Risoe-TOFC\textsuperscript{17,18} cells.\textsuperscript{17,18} Two different slurries following the same processing route and parameters were tape-cast into green tapes, later referred to as A and B. Although the processing route of slurries A and B was the same, small differences in the resulting composites were possible due to, e.g., particle size distributions or sintering conditions. Slurry B was cast in two different thicknesses. After sintering at 1300–1400°C, the green tapes yielded resulting composites were possible due to, e.g., particle size distributions or sintering conditions. Slurry B was cast in two different thicknesses. After sintering at 1300–1400°C, the green tapes yielded

Dilatometer procedures.—A series of redox tests of the sintered cerments was carried out using a Netzsch 402 CD differential dilatometer equipped with a gas control unit capable of programmed mixing of up to three different gases. The heating rate used was 3–4°C/min. After a hold of about 1 h in air at the test temperature, the gas was switched to diluted hydrogen with a 20 min flush of N\textsubscript{2} in between. Furthermore, a p\textsubscript{O\textsubscript{2}} sensor running at a constant temperature was connected downstream in some of the tests to measure the oxygen partial pressure in the gas exiting the dilatometer. The p\textsubscript{O\textsubscript{2}} at the test temperature was calculated using the Nernst equation and hydrogen-steam reaction equilibrium constants at the test and sensor temperatures. Sibling samples of the thin Ni–YSZ cerments were exposed in dilatometry to reduction–oxidation cycles at temperatures between 600 and 1000°C. The gas change sequence is illustrated in Fig. 1, where the first reoxidation cycle at 850°C is marked; a change of gas was always preceded by a short N\textsubscript{2} flush. The redox cycling was in most tests carried out by varying between artificial air (20% O\textsubscript{2} and 80% N\textsubscript{2}) and dry diluted hydrogen (mixture of 9% H\textsubscript{2} and 91% N\textsubscript{2}), with the said flush of N\textsubscript{2} in between.

In real anode operation, water vapor will always be present. Humidity is believed to accelerate degradation due to sintering of nickel in microcomposites, possibly through changes in surface diffusivity of Ni on nickel grains\textsuperscript{19,20} this effect is also known from nanocalcination.\textsuperscript{3,4} Therefore, four test cases were run where the p\textsubscript{O\textsubscript{2}} was varied during the test by combining varying flows of diluted hydrogen and nitrogen with a small flow of air. Three tests were carried out isothermally at 850°C and the fourth one at 600°C. The gas change sequences in the four redox tests with humidity were implemented as follows. In the first test, the initial reduction and re-reductions after each redox cycle were carried out in dry 9% H\textsubscript{2}; at 850°C the oxygen partial pressure was typically p\textsubscript{O\textsubscript{2}} = 10\textsuperscript{-18}. The reoxidation sequences started by a 2 h humid gas flow of 6.51, and 46 mL/min of air, 9% H\textsubscript{2} diluted in N\textsubscript{2} and N\textsubscript{2}, respectively. The air flow of 6 mL/min equals an O\textsubscript{2} flow of 1.2 mL/min. The planned gas composition in this 2 h period was approximately 94.4% N\textsubscript{2}, 2.7% H\textsubscript{2}, 3.0% H\textsubscript{2}O, p\textsubscript{O\textsubscript{2}} = 6.5 × 10\textsuperscript{-18}, and a p\textsubscript{H\textsubscript{2}}/p\textsubscript{H\textsubscript{2}O} of 1.10. After 2 h under the humid conditions the gas was switched first to a mixture of 80% N\textsubscript{2} and 20% air (log\textsubscript{10}p\textsubscript{O\textsubscript{2}} = −1.4) for 2 h and then to dry air. In the remaining three tests the humidified or dry oxidizing conditions prevailed through the entire duration of the redox cycles, until terminated by a N\textsubscript{2} flush and re-reduction. In the second test, the ratio between 9% H\textsubscript{2} in N\textsubscript{2} and N\textsubscript{2} was varied between redox cycles by stepwise reducing the flow of diluted H\textsubscript{2} (e.g., 55 → 45 → 40 → 35 mL/min 9% H\textsubscript{2} diluted in N\textsubscript{2}), and respectively increasing flow of N\textsubscript{2} in order to keep the total gas flow at 100 mL/min the air flow was kept constant at 6 mL/min. The planned p\textsubscript{H\textsubscript{2}}/p\textsubscript{H\textsubscript{2}O} for the four flows of diluted H\textsubscript{2} are 1.0, 1.4, 1.9, and 2.9, respectively, and the p\textsubscript{O\textsubscript{2}} increases stepwise in successive redox cycles. The re-reductions were always carried out in dry, diluted 9% H\textsubscript{2}. In the third test, four redox cycles were implemented and the corresponding 9% H\textsubscript{2} flows in each of the cycles were 42, 38, 31, and 0 mL/min, with p\textsubscript{H\textsubscript{2}}/p\textsubscript{H\textsubscript{2}O} of 1.6, 2.2, 5.1, and undefined, respectively. For the fourth test, at 600°C, five redox cycles were implemented and the corresponding 9% H\textsubscript{2} flows in each of the cycles were 41, 40, 38, 36, and 31 mL/min and p\textsubscript{H\textsubscript{2}}/p\textsubscript{H\textsubscript{2}O} of 1.8, 1.9, 2.2, 2.9, and 5.1. At the test conditions, virtually all of the oxygen supplied will react with hydrogen to produce steam, and the planned p\textsubscript{H\textsubscript{2}}/p\textsubscript{H\textsubscript{2}O} was according to thermodynamic calculation between 3 and 3.4%. The tightness of the system and variations in actual gas flow give rise to uncertainty in humidity. For example, variation of 1 mL/min in the air flow from the nominal 6 mL/min corresponds to about ±0.7% points in p\textsubscript{H\textsubscript{2}}/p\textsubscript{H\textsubscript{2}O}. The actual gas composition that resulted during the experiments is discussed in the Results section.

In dilatometry, the push rod exerted a longitudinal force of 30 cN on the sample during the measurement, corresponding to about 0.8–1.8 kPa depending on the sample cross-sectional area. The total gas flow during the tests was 50 and 100 mL/min during the tests reported in the following subsections. After testing, both fracture surfaces and polished cross sections of several samples were examined in a JEOL low-vacuum scanning electron microscope (SEM) or Zeiss Supra field emission SEM. The accuracy of the differential dilatometer used is very good and the temperature control accurate within about 0.5°C. The biggest source of uncertainty in the results arises from possible sample-to-sample variations in, e.g., porosity. Such variations were, for example, observed between tapes A and B and they could arise from small differences between slurries or, e.g., slightly different sintering temperatures. However, in each subset of experiments where the dimensional response under different conditions is compared, the samples always stem from the same tape. Reproducibility of measurements using samples from the same tape and sintering batch was good.
Results

Unless otherwise stated in the sections that follow, the scales in all graphs have \( t = 0 \) when the initial reduction commences. The zero point on the relative \( \Delta L/\Delta L_0 \) scale corresponds to the hot state prior to the initial reduction; thermal expansion during heating has been deducted. The length change is calculated relative to the as-sintered cold sample length. For strain as a function of redox cycling we have used the term, the cumulative redox strain \( \text{CRS} \).

Initial reduction.— The dimensional response of the NiO–YSZ composite to reduction was investigated at temperatures from 600 to 1200 °C. Isothermal dilatometry was carried out for up to 48 h under a reducing atmosphere in order to study the dimensional changes. Upon the first reduction of the composite, clear differences in dimensional response were measured depending on reduction temperature, as displayed in Fig. 2 and tabulated in Table I (\( n = 0, \text{CRS}_{\text{reduced}} \)). The tested samples were from tape A.

Redox cycling in dry gas.— Results from the isothermal dilatometry are shown in Fig. 3. Three redox cycles were carried out isothermally at each temperature for samples from tape A. The expansion strains upon reoxidation strongly depend on conditions with varying degree of contraction back toward the initial length taking place upon the re-reductions. CRS as a function of redox cycles at the different isothermal temperatures is summarized in Table I, where \( \text{CRS}_{\text{max}} \) is the maximum strain measured during a redox cycle, and \( \text{CRS}_{\text{reduced}} \) is the measured strain at the end of the reducing step following that redox cycle.

A SEM backscattered electron image (BEI) from a polished cross section of the as-sintered NiO–YSZ composite is shown in Fig. 4. YSZ appears light gray, NiO is dark gray, and porosity is black. BEI images from polished cross sections after reduction for 48 h at 600 °C are shown in Fig. 5A and after three redox cycles in Fig. 5B; now there is no contrast between metallic Ni and YSZ due to a similar electron backscatter coefficient. For comparison, the polished surfaces after reduction for 13 h and three times redox cycling at 1000 °C are displayed in Fig. 6A and B, respectively. Porosity of the reduced samples has increased compared to the as-sintered state due to Ni reduction. The microstructure after low-temperature reduc-

![Figure 2](image1.png)

**Figure 2.** (Color online) Relative sample length change from the hot as-sintered state of NiO–YSZ composites as a function of time during isothermal reduction at different temperatures in dry 9% H\(_2\) diluted in N\(_2\). The reduction commences at \( t = 0 \).

![Figure 3](image2.png)

**Figure 3.** (Color online) Relative length change of Ni–YSZ composites as a function of time during three isothermal reoxidation cycles under dry conditions at different temperatures. The initial reduction takes place at \( t = 0 \), and the \( \Delta L \) scale shows relative length change from the hot as-sintered state prior to the initial reduction.

![Figure 4](image3.png)

**Figure 4.** Backscattered electron image in SEM of a polished cross section of the as-sintered NiO–YSZ composite.

<table>
<thead>
<tr>
<th>Test case</th>
<th>( n ) of redox cycle</th>
<th>( \text{CRS}_{\text{max}} )</th>
<th>( \text{CRS}_{\text{reduced}} )</th>
<th>DRR</th>
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<td></td>
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<td>—</td>
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<td>0.00</td>
<td>—</td>
</tr>
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<td>—</td>
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<td>-0.01</td>
<td>—</td>
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<td>0.63</td>
<td>0.34</td>
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<td>2.36</td>
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duction has caused remarkably less growth of Ni grains than after high-temperature reduction, as can be observed by comparing Fig. 5A and 6A, where Fig. 5A clearly shows a finer microstructure. Redox cycling three times at 600°C shows further refinement of the microstructure. The third reoxidation time during redox cycling at 600°C was 5 h and the subsequent re-reduction 3 h (Fig. 3). As will be evident from an upcoming paper on thermal analysis and also as reported in Ref. 8, these times were possibly insufficient for full oxidation or reduction. Figure 5B also shows creation of some new intragranular porosity in the Ni phase. This effect was also reported by, e.g., Sarantaridis and is known from high-temperature oxidation of nickel. After tests at 1000°C, the cermet shows increased grain and pore size after reduction (Fig. 6A). Microstructural damage and loss of contact between grains due to redox cycling can be observed in Fig. 6B; the sample was also macroscopically cracked.

Variation in $p_{O_2}$, $p_{H_2}$, and $p_{H_2O}$.— Three tests were executed at 850°C and a fourth one at 600°C to examine the effect of humidity and $p_{O_2}$ on the dimensional redox behavior of Ni–YSZ cerments. The three tests at 850°C were done with samples from tape A and the test at 600°C using a sample from tape B. Figures 7-10 show the results from the isothermal dilatometry, where the measured oxygen partial pressures at the test temperature are given by the dashed lines. Results from the first test are shown in Fig. 7. The gas changes are illustrated by the vertical dashed lines separating the following steps: the time prior to I pertains to reduction in dry 9% $H_2$, followed by (I) humid reducing-oxidizing (air + $N_2$ + $H_2$); (II) air + $N_2$; (III) air; and (IV) humid oxidizing (air + $N_2$ + $H_2$). After IV the sample was re-reduced. When humidity is introduced during the initial 2 h of the redox cycle (part I), the relative expansion upon subsequent reoxidation increases clearly from the dry air case (shown in Fig. 3; see Table I). During this 2 h period there is little bulk expansion in the sample although the $p_{O_2}$ rises to $\sim 2 \times 10^{-4}$, which is above the oxidation threshold and much more than what was predicted using the nominal input gas flows, $p_{O_2} = 7 \times 10^{-18}$.

Figure 5. Polished SEM micrograph of the Ni–YSZ cermet reduced at 600°C (A) and the same material redox cycled three times at 600°C (B).

Figure 6. Polished SEM micrograph of Ni–YSZ cermet reduced at 1000°C (A) and the same material redox cycled three times at 1000°C (B).

Figure 7. (Color online) Measured relative length change of a Ni–YSZ cermet and $p_{O_2}$ of the atmosphere as a function of time. Redox cycling is carried out isothermally at 850°C with 6% steam introduced for 2 h (part I) prior to each reoxidation in dry air (parts II–III). The initial reduction commences at $t = 0$, and the $DL$ scale shows relative length change from the hot as-sintered state prior to the initial reduction.
Based on the measured $p_{O_2}$, the gas composition during the 2 h period is $p_{H_2O} = 0.067$, $p_{H_2} = 1.3 \times 10^{-8}$, $p_{N_2} = 0.93$, $p_{O_2} = 1.5 \times 10^{-4}$, and $p_{H_2O}/p_{H_2} = 5.29 \times 10^6$.

The second test run with varying $P_{O_2}$ levels is shown in Fig. 8. The final strain levels were not reached in the test shown in Fig. 8, as the gas was switched back to reducing before stabilization at $t = 3600$ min, and the sample bent upon the second reoxidation, about $t = 4100$ min. The spike in $P_{O_2}$ at $t = 2300$ min is probably due to a transient in actual gas flow that was too short to initiate cermet expansion. The third test, shown in Fig. 9, was comprised of four redox cycles isothermally at 850°C using a thicker laminated sample. The maximum redox strain after three redox cycles in humid gas was 3.5%. Another redox cycle in dry air was started at $t = 14000$ min, and this increased $CRS_{max}$ to 3.6%. Figure 10 displays results from the humid redox cycling test carried out at 600°C. The maximum redox strain is about 0.21% $dL/L$, which is close to what was measured during redox cycling in dry gas at the same temperature (0.19% after the first and 0.25% after the third reoxidation).

Effect of the initial reduction temperature.—The effect of temperature during the initial reduction on redox stability was investigated by reducing two cermets from tape A at two different temperatures. One sample (case 1) was reduced 4.5 h at 1100°C, taken down in temperature to 800°C for 25 h before the reoxidation. The other sample (case 2) was reduced 5.5 h at 800°C. After the initial reduction, both cermets were reoxidized at 800°C. By testing two sibling samples in this way the difference in redox strain can be ascribed to different Ni–YSZ microstructures due to sintering of nickel during operation under reducing conditions. The results of the tests are shown in Fig. 11. The $dL/L_o = 0$ point for case 1 is prior to the reoxidation, and for case 2 before the initial reduction; the initial difference when reoxidation commences is about 0.01. The time scales were shifted so that the reoxidation takes place simultaneously; for case 2 the initial sample reduction occurs from $t = 0$, for case 1 during negative time (not shown). The maximum redox strain from the first redox cycle is 0.27% $dL/L_o$ for reduction at 800°C (the entire redox curve is shown in Fig. 3). In case 1 the measured bulk expansion upon reoxidation at 800°C is about double, 0.59%. The decrease of the $dL/L$ curve at $t = 1400$ min and after is due to rereduction of the samples.

Effect of the reoxidation temperature.—The effect of the reoxidation temperature on redox stability was investigated by reducing Ni–YSZ samples 3 h at 1000°C and exposing them to air at different temperatures. The chosen reoxidation temperatures were 1000, 850, 750, and 600°C; after the initial reduction the samples were cooled to the reoxidation temperature. The samples were additionally stabilized for 1 h at the reoxidation temperature before the reoxidation. Samples prepared from tape B were used, though the sample tested at 850°C was thicker and sintered in a batch different from the other samples. When the initial reduction treatment of the samples was the same, the differences in redox strain response are in
this set of experiments mainly\(^4\) related to differences in the thermomechanical behavior of the composites during the oxidation phase, including also possible effects from reaction kinetics depending on the temperature. Results from the cyclic redox dilatometry experiments with different reoxidation temperatures are given in Fig. 12. The time scale has been shifted so that the reoxidations commence at \(t = 0\); thus, the initial reduction (not shown) takes place during negative time. The \(dL\) axis has been shifted to \(dL/L_0 = 0\) in reduced state at each temperature before the reoxidation. The maximum strains upon the reoxidation at different temperatures are given in Table II.

**Data analysis.**—We have used a systematic approach based on selected points directly derived from the isothermal dilatometry data in accordance with the practice used in Ref. 7 and 16. The CRS is tabulated for the following steps (see Fig. 1):

0. Initial relative length when the sample is kept isothermally in oxidized state (\(dL/L_0 = 0\)).
1. Relative sample length shortly after reduction.
2. Relative sample length after a hold (here \(12–18\) h) under reducing conditions.
3. Maximum relative sample length after the first reoxidation.
4. Relaxed relative sample length at the end of the reoxidation step.
5. Relative sample length after the fast shrinkage of the sample upon the second reduction.
6. Relative sample length after a second reduction stabilization period.
7. Further numbers in the same manner for each point of interest in the \(dL\) curve up to three redox cycles.

We further define the parameter degree of redox reversibility (DRR) describing the strain reversibility during the redox cycles. DRR is based on the following quantities (Fig. 1): \(a =\) shrinkage of a sample in an oxidized state upon reduction (from the \(CRS_{\text{max}}\) during the preceding oxidized state or redox cycle), and \(b =\) maximum expansion of a reduced sample upon reoxidation. The parameter DRR is defined as \(DRR = a/b\) and describes the fraction of the reoxidation expansion that is recovered upon re-reduction; thus, a value of unity

\(^4\) The partial reservation in the form of the word “mainly” stems from the fact that the four samples here were not pure siblings. Although from the same slurry, the sample tested at \(850\) °C was from a thicker tape and sintered in another batch. Minor differences could arise from, e.g., small differences in sintering temperature, or structurally from tape thickness.
age of NiO to Ni during reduction exposes a new YSZ surface which can be active for sintering and thus, the sample shrinks due to sintering of the ceramic backbone when the temperature is high enough, in this case above 1000°C. The low-temperature contraction of the composite can hardly arise from residual stresses in the composite due to the difference in the coefficient of thermal expansion (CTE) of NiO and YSZ. The CTE is 1.41 × 10⁻⁶ K⁻¹ for NiO and 1.03 × 10⁻⁶ K⁻¹ for YSZ, and there is an internal stress controlling the YSZ network after cooldown from high-temperature sintering down to room temperature due to internal stress (depending on, e.g., the cooling rate). How fast the stress is relaxed is a function of time and temperature, but it is hardly possible that this stress would have relaxed and turned into a tensile force on the YSZ during the heat-up to 600°C prior to the initial reduction. Thus, we do not consider the relaxation of the internal thermal stress to be a plausible origin of the low-temperature contraction upon reduction.

The dimensional behavior on isothermal redox cycling was investigated under varying temperature and humidity conditions as summarized in Table I. From the reported redox cycling dilatometry, a clear dependency on temperature can be noted. The durations of the reduction-oxidation treatments were long enough at each step to either completely reduce or oxidize the samples. Even if the step durations between the different isothermal temperatures differ, we consider them valid for comparing the behavior between different isotherm temperatures. In other words, we think that the effect of the redox conditions is greater than that of the step durations. Increasing the temperature impairs redox stability by fast takeoff of the CRS far beyond the target level of maximum CRS = 0.1% set for the anode-supported SOFC (based on work reported in Ref. 13-15). However, not even at the lowest temperature tested does the tested material reach the target level. Second, when about 6% humidity is introduced during 2 h prior to each dry air redox cycle by mixing air, N₂, and H₂, the cumulative expansion after three redox cycles at 850°C increased almost 80% (from 1.55 to 2.78%, Table I). This is in qualitative agreement with literature suggesting enhancement of Ni sintering with humidity in microcomposites.⁶,²⁸ Sehested et al. examined the sintering of Ni nanocatalysts on A₁₂O₃ support at 550°C and reports increased Ni particle growth with increasing pO₂/pH₂ ratio. He explains the increase in Ni sintering in the presence of humidity through the improved surface diffusivity of the Ni₇–OH species formed. It could thus be argued that the formation of the nickel hydroxide is favored by the increasing pO₂/pH₂ ratio.³⁴ If all the redox cycles are performed at 850°C in humid gas (log[pO₂] between ~2.8 and ~2.3), redox expansion on the third reoxidation is slightly more than was measured at 1000°C and dry conditions. The pO₂/pH₂ ratios during all the experiments with humid gas were very high. For the steam–oxygen–hydrogen balance the situation is actually close to an operating cell with fully utilized fuel when the oxygen and hydrogen react close to stoichiometric ratios to produce H₂O. In our interpretation the increase in the redox strain observed at 850°C and humid conditions is a result of increased Ni sintering due to the presence of steam. The fact that at 600°C no such effect with humidity could be discerned suggests that the effect from steam is insufficient at that temperature to activate significant Ni sintering in the microcomposite studied.

From calculations using the thermodynamic code FACTSAGE, the oxidation–reduction equilibrium between Ni/NiO is roughly at pO₂ = 6 × 10⁻⁸ to 10⁻¹⁰, and 5 × 10⁻¹¹ at temperatures of 600, 850, and 1000°C, respectively. In practice, the kinetics of the oxidation–reduction process depends, besides on the pO₂, on the molar flow of oxygen per mole of nickel in the sample, arriving at the metallic surface where the oxidation reaction takes place. In the redox tests in dry air, the incoming pO₂ is 0.2 and the theoretical redox times, if all oxygen supplied would be consumed in oxidizing nickel, are about 1–3 min. In humid or wet conditions this situation changes drastically, because the measured pO₂ is then about 10⁻²–10⁻⁴ and furthermore, the oxidation reaction is likely to also involve intermediate species such as the Ni₁–OH. As a result, some-
stress deduction during the reoxidation phase. The DRR is thought to be connected with the amount of micro- and macrodamage as well as creep in the YSZ. Once the ceramic YSZ backbone is fractured due to excessive stress caused by the reoxidation strain, its capability to return to the original dimension is degraded. The very small values of DRR at 1000°C suggest that fractures in the YSZ network have occurred to accommodate the oxidation strain.

Conclusions

Ni–YSZ cermets of the type used for SOFC were tested in redox cycling dilatometry under a wide range of operation conditions. The main parameters that were varied were temperature and humidity. Dependencies of the dimensional behavior of the cermet were obtained both during reduction and reoxidation.

Upon initial reduction at low temperatures (600°C), a contraction of about 0.08% and recovery toward the initial length was observed. At intermediate temperatures (800–850°C), little or no dimensional change was measured upon reduction. Upon reduction at high temperature (1000°C), bulk shrinkage of 0.05% after was measured; at still higher temperatures the cermet shows marked shrinkage upon reduction.

Cumulative redox strain after three redox cycles in dry conditions increases from 0.25 to 3.2% dL/L0, when the isothermal redox cycling temperature is lifted from 600 to 1000°C. Humidity deteriorates redox stability at high temperatures (roughly 850°C or above); CRS after three redox cycles under 6% steam and a very high PO2/P2O5 ratio was in one case slightly less and in another case in excess of the CRS from dry redox cycling at 1000°C. No effect on redox strain by humidity was observed at 600°C. The degree of reversibility of the redox strain decreases with increasing temperature and at 850°C in the presence of humidity. The rate of dimensional change during oxidation decreased when PO2 during the oxidation phase decreased.

It was found that Ni sintering deteriorates redox stability by increasing redox strain on reoxidation. Of two similar samples, one was reduced 5.5 h at 800°C and the second one 4.5 h at 1100°C. The sample reduced at 1100°C showed about twice the amount of redox strain when reoxidized at 800°C.

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Acknowledgments

The authors acknowledge support from the staff at the pre-pilot laboratory and thermal analysis at Risø. M. Pihlatie was financially supported by the Marie Curie Intra-European Fellowship, contract no. MEIF-CT-2005-023882, as part of the European Commission’s 6th framework program. Other authors were supported by Energinet.dk under project no. PSO 2007-1-7124 Solid Oxide Fuel Cell Research and Development.

Riso National Laboratory assisted in meeting the publication costs of this article.

References