Sulfur Poisoning of SOFC Anodes: Effect of Overpotential on Long-Term Degradation

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Published in:
Journal of The Electrochemical Society

Link to article, DOI:
10.1149/2.080406jes

Publication date:
2014

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

Link back to DTU Orbit

Citation (APA):

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Fuel flexibility is an attractive characteristic of solid oxide fuel cells (SOFC). They can for instance be fuelled with carbon containing fuels such as natural gas or fuels derived from biomass. A well-known drawback for the use of carbon containing fuels is the fact they contain varying amounts of sulfur, which poisons Ni-based SOFC anodes.1,8 Therefore, it is important to investigate the SOFC tolerance toward sulfur poisoning and how it is affected by operating parameters.

There are many studies concerning the initial, and mainly reversible, loss in performance occurring at SOFC anodes upon sulfur poisoning as a function of different operating conditions.4,5,9 Fewer results are reported on the long-term, and often irreversible, loss of performance due to sulfur poisoning.3,8,10 even though this will inevitably be of high importance for SOFC as an emerging energy conversion technology. In order to establish the acceptable limits for sulfur impurities in carbon containing fuels in order to avoid long-term, irreversible degradation,3,5,11 it is necessary to understand how the sulfur impurity tolerance correlate to operating parameters such as gas mixtures, temperature and current density, and indirectly to the cell overpotential.

It has been suggested that Ni-zirconia based SOFC anodes containing Sc are more tolerant toward H2S poisoning than Ni/YSZ based anodes.5,8 and in this work both short and long term tests were performed to investigate this hypothesis. Tests were mainly carried out at the same set of test conditions (e.g. temperature, current density, fuel) in order to compare Sc-Y co-doped (ScYSZ) and Y doped zirconia (YSZ) Ni cermet SOFC anodes. There are several studies showing the effect of H2S poisoning of Ni-YSZ based SOFC anodes as a function of parameters such as temperature, fuel gas composition and p(H2S) as summarized by Chen et al.3 However, such parameters (temperature, current density, fuel utilization etc.) are all externally set parameters and they do not necessarily impose identical conditions internally in the electrodes of different cells e.g. in terms of electrode overpotentials and current distributions. This work is a study of the long-term H2S poisoning effects on Ni-cermet SOFC anodes as a function of cell overpotential, rather than focusing on externally set parameters such as temperature, current density and gas compositions.

This work reports the results from long-term exposure to H2S containing CH4/H2O/H2 fuel mixtures at 850°C, with and without the presence of 2 ppm H2S, for 500 h of galvanostatic testing at different cell overpotentials. The degradation behavior is investigated via cell voltage curves, detailed analyzes of electrochemical impedance spectra and post-mortem SEM analyzes – qualitative and quantitative – of the anode from the different tests. Furthermore, correlations between the chosen cell overpotentials, measured long-term irreversible degradation behavior and resulting microstructural changes of the SOFC anodes are given.

Experimental

Cell specifications and test set-up.— The cells used for fuel cell testing in this study are anode supported full SOFC produced at the Department of Energy Conversion and Storage, Risø Campus, Technical University of Denmark.12–15 The cells have a 10–15 μm thick anode of Ni/YSZ cermet with a 300 μm thick Ni/YSZ support layer, a 10–15 μm thick YSZ electrolyte and a 15–20 μm thick LSM-YSZ composite cathode.15 The ratio between Ni and YSZ is 40/60 by volume both for the support layer and the active electrode layer. 8 mole percent Y2O3 stabilized zirconia (8YSZ) is used for the electrolyte and the active electrode layer. 3 mole percent Y2O3 stabilized zirconia is used for the support layer. The anode half cells (electrolyte, active anode and anode support layer) were produced via tape casting and lamination, followed by co-sintering of the half cell.15 The cells have an anode support layer thickness of ∼300 μm, an active anode layer thickness of 12 μm and porosities similar to those previously reported.16 All cells reported in this study originate from the same tape of anode half-cell. The composition of the LSM is (La0.85Sr0.15)0.995MnO3 and the ratio between LSA and YSZ in the composite electrode is LSA/YSZ = 50/50 by volume. The LSA/YSZ cathode and LSA contact layer were applied via screen printing. For the cell for the H2S free test, the LSA/YSZ cathode was substituted by a LSC/CGO based cathode and CGO barrier layer.20 The higher performing LSC/CGO cathode was chosen to ensure that the cathode overpotential would not be dominating at the very high current density that was necessary to apply for the H2S free test to reach anode overpotentials comparable with the H2S tests. From the sintered anode half-cell tape cells sized 5 × 5 cm2 are cut and 4 × 4 cm2 cathode was applied and sintered. Due to the set-up for cell testing, the cells have an active electrode area of 16 cm2. The set-up for cell testing, i.e. alumina housing, current collectors (Ni and Au foil), glass seals and Ni/YSZ and LSA based gas distributors, has been illustrated and described in detail elsewhere.21,22

Test procedure and operating conditions.— The cells were heated (1°C/min) to 1000°C for sealing and the NiO was subsequently reduced. The description of the cell test start-up sequence can be...
found elsewhere. After initial characterization consisting of polarization curves and electrochemical impedance spectroscopy (EIS) at a series of different gas compositions fed to the anode and cathode, respectively, at 750 °C, 800 °C and 850 °C, the temperature was then fixed at 850 °C and the gas to the anode was changed to a CH₄/H₂O/H₂:30/60/10 gas mixture. For comparison with a previous study on similar cells, the total flow to the anode was set to 10 l/h (i.e. 3 l/h CH₄, 6 l/h H₂O and 1 l/h H₂ in the gas inlet tubing for the anode) for test at 1 A/cm² and for higher current densities the gas flows were scaled with the current density in order to keep the same fuel utilization i.e. a fuel utilization of 51%. The addition of H₂S to the fuel inlet gas will affect the reformate gas equilibrium as reported by Rasmussen and Hagen and upon addition of 2 ppm H₂S the CH₄ conversion degree will be decreased and a fuel utilization of approximately 70% can be expected at the chosen test conditions. OCV was checked before starting the test under current load. It was observed that complete internal reforming was obtained, since OCV values of ~988–992 mV correspond to the reformed equilibrium gas mixture of H₂/CO/H₂O/CO₂:65.6/15.5/15.6/3.2 (OCV_reo = 994 mV for full reforming at 850 °C, without leaks) before and after the long-term tests under current load. At these test conditions the carbon activity was calculated to be 0.04. After reaching the desired current density the cells were left at for 55 to 70 hours at constant conditions to observe possible change in cell performance prior to H₂S exposure. The cell voltages changed less than 4 mV during this period of cell testing. Hereafter; 2 ppm H₂S (by dilution of a 200 ppm H₂S in H₂) was added for approximately 500 h. Sulfur addition was then stopped and the cells were left to recover at a constant current load. For the H₂S-free test the anode gas composition was set to H₂/H₂O:80/20, which corresponds to the same inlet oxygen potential (pO₂) as that obtained via complete reforming of a CH₄/H₂O/H₂:30/60/10 mixture. This gives the same “driving force” at the gas inlet; however the anode polarization losses are different in reformate gas, but this gives a similar starting point in terms of “driving force” while avoiding possible impurities from the methane gas feed.

Analysis of cell test data.— Figure 1 provides a schematic of the cell voltage curve over time for these tests and illustrates the data used for evaluating the cell voltage changes. The voltage change from t1 to t2 is denoted, ΔV_{init}, and typically t2-t1 ~ 10–30 h. The maximum cell voltage loss, ΔV_{max}, is between t1 and t3, cell voltage recovery, ΔV_{recov}, is between t3 and t4. The irreversible cell voltage drop, ΔV_{irrev}, is thus ΔV_{max}−ΔV_{recov} i.e. the ΔV_{irrev} is calculated as the cell voltage measured under current load immediately prior to H₂S exposure minus the cell voltage after recovery after H₂S addition has been stopped but still operated under constant current load. To calculate the long-term degradation rates during long-term testing, the voltage change over the last 200 h of H₂S poisoning was used.

Electrochemical impedance spectroscopy (EIS).— A Solartron 1255 frequency analyzer was used and impedance spectra (IS) were recorded from 96 kHz to 0.1 Hz with 12 points/decade. Analysis via distribution of relaxation times (DRT) at different test conditions (see Figure 1) was used to assist in the break-down of losses for the recorded IS. For quantitative analysis of the IS complex-non-linear-least-squares (CNLS) method was used to fit an equivalent circuit model to the data. For a quantitative break-down of losses via IS the equivalent circuit model depicted in Figure 1 was applied. This equivalent circuit is based on the work reported by Barfod et al.,24 and Kromp et al.,25 in which the electrochemical impedance response from the Ni/YSZ and LSM/YSZ electrodes have been approximated by two RQ-elements (Voigt-elements) each. The higher frequency impedance arc (RQ)_{high} at ~20–40 kHz has contributions from both electrodes and has previously been ascribed to the charged particle transfer. The lower frequency impedance arc (RQ)_{low} is attributed to Ni percolation in the Ni/YSZ cermet microstructure. Characteristic frequencies for the individual contributions to the IS can be found in the frequency decades sketched in Figure 1, with the summit frequency for (RQ)_{Ni-TPB} being slightly lower (~3 kHz) during testing under current load than at OCV. The software ZView 3.219 was used to CNLS fit a model to the experimental IS and in-house developed software RAVDAV² was used for DRT analysis of the IS.

SEM imaging and image analysis.— Pieces of a cross section length of ~1 cm of the tested cells were prepared for SEM investigations by vacuum embedding in epoxy (EpoFix from Struers) followed by grinding and polishing. A Zeiss Supra 35 FE-SEM (Field Emission Gun Scanning Electron Microscope) was used for imaging. SEM images obtained at 10 kV using the secondary electron detector and low-voltage SEM images were obtained at 0.9 kV using the in-lens detector. Low-voltage in-lens SEM imaging allows percolating and non-percolating Ni to be distinguished in the Ni/YSZ cermet microstructure, as described by Thydén et al.33 Image analysis by line-intercept-method²⁶ allowed the determination of the area fraction of percolating Ni and pores, using the in-house developed Matlab based software, ManSeg. For each sample, 15 recorded images at a magnification of 4 kX were used for the analyzes of percolating Ni and porosity; corresponding to analyzes of an anode/electrolyte interface of more than 1500 μm² for each cell.

Results and Discussion

Cell voltage curves as a function of time — degradation overview for sulfur testing.— Table I lists test acronyms, cell and test specifications, along with a summary of the test results in form of cell voltage changes.
Overview of cell and test specifications is given in Table I. \( \eta \) is the cell overpotential at start of \( \text{H}_2\text{S} \) exposure. \textit{YSZ-Hi-Spr} had a sprayed electrolyte and active anode while the rest of the cells have tape cast electrolyte and active anodes. “Low overpotential” tests are given in italic.

<table>
<thead>
<tr>
<th>Test acronym</th>
<th>Cell specifications</th>
<th>( i ) (A/cm(^2))</th>
<th>( \eta ) (mV)</th>
<th>( \Delta V_{\text{init}} ) (mV)</th>
<th>( \Delta V_{\text{max}} ) (mV)</th>
<th>Long-term degr. (mV/kh)</th>
<th>Long-term degr. (m2cm(^2)/kh)</th>
<th>( \Delta V_{\text{irrev.}} ) (mV)</th>
<th>( \Delta V_{\text{recov.}} ) (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>\textit{YSZ-Hi-Spr}</td>
<td>YSZ-based cell</td>
<td>1</td>
<td>320</td>
<td>100</td>
<td>216</td>
<td>225</td>
<td>225</td>
<td>105</td>
<td>111</td>
</tr>
<tr>
<td>\textit{ScYSZ-Low} (^1)</td>
<td>\textit{Sc}-\textit{Y} co-doped ZrO(_2)</td>
<td>1</td>
<td>237</td>
<td>61</td>
<td>85</td>
<td>0</td>
<td>0</td>
<td>75</td>
<td>10</td>
</tr>
<tr>
<td>\textit{YSZ-Low}</td>
<td>YSZ-based cell</td>
<td>1</td>
<td>209</td>
<td>93</td>
<td>109</td>
<td>10</td>
<td>10</td>
<td>102</td>
<td>7</td>
</tr>
<tr>
<td>\textit{YSZ-Hi}</td>
<td>YSZ-based cell</td>
<td>1.38</td>
<td>291</td>
<td>121</td>
<td>208</td>
<td>180</td>
<td>131</td>
<td>130</td>
<td>78</td>
</tr>
<tr>
<td>\textit{YSZ-no-S}</td>
<td>YSZ-based cell, LSC/CGO cathode and CGO barrier layer</td>
<td>1.88</td>
<td>360</td>
<td>-</td>
<td>-</td>
<td>15</td>
<td>8</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

\(^1\)Test reported by Hagen et al.\(^5\) in which the tests where denoted “Ni,YSZ,LSM” and “Ni,ScYSZ,LSM”, respectively.

Table I. Overview of cell and test specifications and voltage changes. Description of the different voltage changes is sketched in Figure 1. Cell voltage curves as a function of time at 850 \( ^\circ \text{C} \). Figure 2.

Figure 2 shows the corresponding cell voltage curves as a function of time for the four \( \text{H}_2\text{S} \) poisoning tests and the \( \text{H}_2\text{S} \) free test. \textit{YSZ-Hi-Spr} and \textit{ScYSZ-Low} were previously reported by Hagen et al.,\(^5\) and are included here for comparison. In the article by Hagen et al. these tests were denoted “Ni,YSZ,LSM” and “Ni,ScYSZ,LSM”, respectively. The sulfur tests can be divided into two groups regarding long-term degradation behavior during \( \text{H}_2\text{S} \) exposure: Group I- tests with marginal long-term degradation (\textit{ScYSZ-Low} and \textit{YSZ-Low}); and group II- tests with significant, more or less linear, long-term degradation (\( \sim 131–276 \text{m2cm}^2/\text{kh} \), for \textit{YSZ-Hi-Spr} and \textit{YSZ-Hi}). This general trend regarding long-term degradation behavior can be related to one parameter, the cell overpotential (\( \eta \)) or perhaps more specifically the anode overpotential, which is low for group I and high for group II; while the cell compositions (YSZ vs. ScYSZ), microstructure i.e. anode porosity or specific current density obviously are less important parameters, when it comes to the long-term degradation behavior upon \( \text{H}_2\text{S} \) exposure. Parameters such as anode microstructures and current density can therefore be considered \textit{indirect} parameters when it comes to initiating the irreversible long-term degradation upon \( \text{H}_2\text{S} \) exposure as the eventually dictate the anode overpotential. As reported previously, a tape cast Ni/ScYSZ based cell showed similar high degradation rates for the long-term degradation as the Sc-free \textit{YSZ-Hi-Spr} and \textit{YSZ-Hi} (in this work) upon \( \text{H}_2\text{S} \) poisoning tested under similar conditions at high overpotential.\(^11\)

The irreversible cell voltage loss after stopping the \( \text{H}_2\text{S} \) poisoning and recovery (still under current load) is only \( \sim 7–10 \text{mV} \) for group I tests, while the high overpotential sulfur tests, i.e. group II tests, have irreversible cell voltage losses that are \( \sim 10 \) times larger (see Table I).

Cell voltage as a function of time – sulfur free test.— Figure 2 also includes the cell voltage curve for the high overpotential test with no \( \text{H}_2\text{S} \) added i.e. the \textit{YSZ-no-S} test. The cell used for the \textit{YSZ-no-S} has anode half-cell identical to the cells used for the \textit{YSZ-high} and \textit{YSZ-low} tests. To reach a similar high overpotential in the \( \text{H}_2\text{S} \) free test, the current density was increased to 1.88 A/cm\(^2\) for \textit{YSZ-no-S} (\( t = 0 \) h in Figure 2). Due to \( \text{H}_2 \) flow limitations of the used test rig the current density could not be increased further while keeping the gas mixtures and fuel utilization equivalent to previous tests. The cell overpotential for \textit{YSZ-no-S} was therefore increased further by decreasing the temperature by 30 \( ^\circ \text{C} \) and subsequently three times by 10 \( ^\circ \text{C} \). The \( \text{H}_2\text{S} \)-free test, \textit{YSZ-no-S}, had a degradation rate of only 15 mV/kh (8 m2cm\(^2\)/kh) for the last 200 h of testing, while the equivalent cell of test \textit{YSZ-Hi} degraded 180 mV/kh (131 m2cm\(^2\)/kh) during the last 200 h of \( \text{H}_2\text{S} \) poisoning. This strongly indicates that the observed irreversible degradation for the high overpotential tests \textit{YSZ-Hi-Spr} and \textit{YSZ-Hi} and for the \textit{ScYSZ-Hi} reported previously\(^11\) must be closely related to the presence of \( \text{H}_2\text{S} \), even at such relatively low concentrations of 2 ppm. The significantly lower long-term degradation rate for the \textit{YSZ-no-S} compared to \textit{YSZ-Hi} could simply be an effect of changing to \( \text{H}_2\text{O} \) fuel instead of \( \text{CH}_4\text{H}_2\text{O} \) fuel, as used for the \textit{YSZ-Hi} and thereby not solely related to the absence of \( \text{H}_2\text{S} \). However, this is not likely when considering the long-term degradation results for non-\( \text{H}_2\text{S} \) tests at high current and high overpotential at
850 °C reported previously by Hagen et al.13 In this work Hagen and co-workers reported degradation rates in the order of 10–20 mV/kh (∼10 μm/V) for long-term H2S-free tests operated at 850 °C also applying methane containing fuels (internal reforming conditions) for 1500 h at high current densities giving rise to cell overpotentials of ∼300–400 mV. To summarize, the long-term degradation rate for the high overpotential test YSZ-no-S (anode half cell identical to the cells used for the YSZ-Hi and YSZ-Low tests, but anode gas compositions) and for the previously reported high overpotential sulfur-free test reported by Hagen et al. (internal methane reforming gas conditions) are similar and both in the range of 10–20 mV/kh, while the long-term degradation rate for YSZ-Hi is significantly different as it is a factor of 10 times larger.

The subsequent analyzes of the process specific impedance contributions and postmortem SEM analyzes were divided into three: 1) Low cell overpotential H2S cell test, 2) high cell overpotential H2S test, and 3) high cell overpotential H2S-free cell test.

**Low overpotential H2S test – EIS.**— Figure 3 shows the IS recorded at t1, t2, t3 and t4 for the low overpotential test YSZ-Low where a current density of 1 A/cm² was applied. Table II gives an overview of the resistances determined by CNLS fitting of the equivalent circuit model depicted in Figure 1 to the measured impedance data. Only negligible variation of the ohmic resistance was observed during the entire test. Upon start of H2S addition the impedance response in the frequency range 1–3 kHz increases significantly corresponding to an increase in the resistance associated with the charge transfer reaction at the TPB in the anode, RNi-TPB, denoted “Anode electrochem” in Figure 1. RNi-TPB increases by a factor of 8 within ~24 h of H2S exposure. However, during the subsequent 480 h of testing with an exposure of 2 ppm H2S to the anode, RNi-TPB remains constant. When H2S addition was stopped and the cell was left to recover (still under current load) RNi-TPB decreased almost to the pre-H2S exposure value. Furthermore, a small increase in the impedance at high frequency (20–40 kHz) is observed over these 500 h of H2S poisoning, corresponding to an increase in Rhigh.

In the work by Hagen et al.13 it was discussed whether the increased long-term stability for ScYSZ-Low compared to YSZ-Hi-Spray H2S-poisoning could be an effect of the scandia-doping, which will lead to increasing ionic conductivity compared to the YSZ-based cells and changes in the wettability and bonding of Ni on the ceramic backbone.34,35 The results in this work are remarkable as the Ni/YSZ-based (i.e. Sc-free) cell used for YSZ-Low, seems equally long-term stable during H2S poisoning when compared to the Ni/ScYSZ-based cell in the ScYSZ-Low test when the two cells are tested at similar low overpotential.

**High overpotential H2S test – EIS.**— Figure 4 shows the IS recorded at t1, t2, t3 and t4 for the high overpotential test YSZ-Hi i.e. a cell similar to the one used in YSZ-Low test but now applying a current density of 1.38 A/cm². Table III gives an overview of the resistances obtained from CNLS fitting the IS in Figure 4 based on CNLS fit to the experimental data applying the equivalent circuit model depicted in Figure 1. From the results in Table III it can be seen that the high overpotential test, YSZ-Hi, basically exhibits the same trend regarding RNi-TPB, as observed for the low overpotential test, YSZ-Low. The striking difference between this high overpotential test (YSZ-Hi) and the previous low overpotential test (YSZ-Low) is that the ohmic

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**Table II.** Results from CNLS fitting of IS shown in Figure 3 for YSZ-Low i.e. low overpotential test H2S-test. The equivalent circuit model applied for fitting is sketched in Figure 1. Estimated uncertainty for calculated resistances is ∼4 mΩcm².

<table>
<thead>
<tr>
<th>Time</th>
<th>( R_n ) (mΩcm²)</th>
<th>( R_{high} ) (mΩcm²)</th>
<th>( R_{Ni-TPB} ) (mΩcm²)</th>
<th>( R_{LSM,low} ) (mΩcm²)</th>
<th>( R_{Diff} ) (mΩcm²)</th>
<th>( R_{Conv} ) (mΩcm²)</th>
<th>( R_{Reform} ) (mΩcm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before H2S (t1)</td>
<td>23</td>
<td>55</td>
<td>6</td>
<td>28</td>
<td>22</td>
<td>34</td>
<td>15</td>
</tr>
<tr>
<td>Inlet point (t2)</td>
<td>23</td>
<td>50</td>
<td>48</td>
<td>44</td>
<td>19</td>
<td>34</td>
<td>6</td>
</tr>
<tr>
<td>498 h H2S (t3)</td>
<td>26</td>
<td>62</td>
<td>45</td>
<td>40</td>
<td>18</td>
<td>37</td>
<td>6</td>
</tr>
<tr>
<td>Recovery (t4)</td>
<td>27</td>
<td>58</td>
<td>12</td>
<td>19</td>
<td>22</td>
<td>28</td>
<td>13</td>
</tr>
</tbody>
</table>
resistance ($R_r$) and the high frequency contribution to the polarization resistance ($R_{high}$) increase over the entire sulfur poisoning test period for YSZ-Hi and did not recover after stopping the H$_2$S addition i.e. YSZ-Hi experiences an irreversible loss of performance.

Analyses of the four IS recorded for YSZ-Hi-Spr at $t_1$, $t_2$, $t_3$ and $t_4$ (IS shown by Hagen et al.)$^5$ show the same trends as the results given in Table III for YSZ-High (Table II in)$.^3$ That is; $R_r$ and $R_{high}$ increase (irreversibly) during the long-term H$_2$S exposure.

Using the results from CNLS fitting of IS (Table II and Table III) one can estimate the anode overpotentials (see Supplementary Material) during testing with H$_2$S-exposure. At the inflection point ($t_2$) the anode overpotential can be estimated to be $\sim 132$ mV for YSZ-Low which does not initiate significant long-term irreversible degradation; whereas the anode overpotential at $t_2$ for YSZ-Hi can be estimated to be $\sim 221$ mV which evidently entail significant long-term irreversible degradation.

Comparison of YSZ-Low and YSZ-Hi illustrates that by “pushing” the otherwise high performing and sulfur tolerant tape cast laminat Ni/YSZ anode half-cell (YSZ-Low) to a higher overpotential, and especially higher anode overpotential (YSZ-Hi), the cell can be forced to a largely irreversible "degradation-regime", where an almost linear increase (irreversibly) during the long-term H$_2$S exposure.

Post-mortem analysis of the anode layers.— Figure 6 shows representative low voltage in-lens SEM images of the anode/electrolyte interface for cells from the YSZ-Low, YSZ-Hi, and YSZ-no-S tests, where percolating Ni particles appear bright.$^3$ From the images in Figure 6 it is evident that the percolating Ni network for the YSZ-Low and YSZ-no-S looks similar, and with an acceptable fraction of percolating Ni in both the cermet anodes and support layers, when compared to non-tested reference cells.$^8,36$ In contrast, for the anode from the YSZ-Hi test there is a significant lack of percolating Ni in the 2–4 microns closest to the electrolyte, whereas the percolating Ni network in the region further away from the anode/electrolyte interface seems unaltered when compared to the anodes from the YSZ-low and YSZ-no-S. These observations are in accordance with the observations made by Hagen et al. for cell from the YSZ-Hi-Spr test.$^5$

Quantification of the percolating Ni network, i.e. area fraction and number of percolating Ni particles/100 μm grid line, was obtained from the in-lens low voltage SEM images. When obtaining quantitative data for the area fraction of percolating Ni from the low voltage in-lens SEM images such as those given in Figure 6, attention should be paid to two issues associated with this type of measurement; 1) the percolation images do not take into account percolation through pathways in the part of the sample that has been polished away and 2) it has been reported that a slight over-estimate of the Ni fraction will occur due to charging effects as described and quantified elsewhere.$^37$ This means that the accuracy of the measurements is likely to be influenced by a small systematic (overestimation) error, but precision of the measurement is high due to the same reproducible methodology being applied to all samples. The measured fraction of percolating

High overpotential H$_2$S-free test —EIS.— Due to the nature of the test sequence for the YSZ-no-S test it is not possible to show IS at times corresponding to $t_1$, $t_2$, $t_3$ and $t_4$ as given in Figure 3 and Figure 4 for YSZ-low and YSZ-Hi, respectively. Figure 3 shows the first and the last IS recorded for this last part of the YSZ-no-S test i.e. at $t = 675$ h and $t = 900$ h in Figure 2. This verifies that the stable cell voltage over the last approximately 225 h at constant test conditions for the YSZ-no-S is due to cell stability and not due to counteracting resistance changes within the cell. The LSC/CGO cathode will give rise to an impedance response with a summit frequency $\sim 100$ Hz.$^{20}$ The IS in Figure 5 shows the stability of $R_r$ and the high frequency part of $R_p$, ($R_{high}$), in contrast to the development of the impedance observed from $t_2$ to $t_3$ for the YSZ-Hi test (Figure 4).

![Figure 5](image)

**Figure 5.** IS recorded for the YSZ-no-S test in the last test period i.e. corresponding to $t = 675$ h and $t = 900$ h in Figure 2 at constant test conditions i.e. 1.88 A/cm$^2$, 790°C, inlet anode gas composition $p$(H$_2$)/$p$(H$_2$O) = 0.8/0.2, air to the cathode.
Representative SEM images at an acceleration voltage of 10 kV for polished cross-sections of anode/electrolyte interfaces for the tested cells from (a) YSZ-Low test, (b) YSZ-Hi test and (c) YSZ-no-S test. Circles indicate large porosities in the innermost few microns of the cell from the electrolyte interface.

Ni given in Table IV should thus be valid for a comparative study between the different tests in this work since the unknown accuracy error is expected to be the same for all samples. However the measured fraction of percolating Ni given in Table IV is not necessarily directly comparable with similar numbers for the fraction of percolating Ni given in literature. In this perspective the number of percolating Ni particles (or Ni agglomerate) per 100 \( \mu m \) grid line – instead of the area fraction - is a valuable and simple parameter for comparison with other studies.

Table IV gives a summary of the quantitative analysis of the area fraction of percolating Ni and the number of percolating Ni particles/100 \( \mu m \) grid line for anodes from the three tests, YSZ-Low, YSZ-Hi and YSZ-no-S near the anode/electrolyte interface and near the anode/anode support interface. Clearly, the YSZ-Hi cell has much lower number of percolating Ni particles in the inner most 2–4 \( \mu m \) of the anode.

When viewing the low voltage in-lens SEM images of the cell from the YSZ-Hi test, the changes in the microstructure correspond to “extending” the dense YSZ electrolyte by 2–4 \( \mu m \) with an extra porous YSZ layer. These observations fit well with the irreversible \( R_e \) increase observed in the IS in Table IV for YSZ-Hi during the long-term degradation. Furthermore, it is hypothesized that the thickness of this percolating Ni depleted layer will increase with increasing time test, at conditions where irreversible long-term degradation dominates (\( t2 \) to \( t3 \) Figure 1 and Figure 2). This in turn implies 1) that for two identical microstructures the long-term degradation rate for cells with a better ion-conductor such as ScYSZ as anode skeleton can be expected to be lower, when compared to a YSZ-based cell and 2) for electrolyte supported cells a “sudden death” of the anode, e.g. as observed by Sasaki and co-workers, can be expected when the depleted layer thickness equals the total thickness of the anode.

The loss of percolating Ni network, both in terms of area fraction and number of percolating Ni particles, in the innermost few microns of the anode for the YSZ-Hi cell (Figure 6b), can be caused by several different phenomena: 1) buildup of impurities in between Ni particles, 2) nano-scale Ni morphology changes 3) evaporation as Ni-hydroxide species41 and 4) diffusion of Ni).41,42 In case 1 and 2 the Ni will still be present more or less in its original position in the anode structure however it will not be electrochemically active. In case 3 and 4 there will be a decrease in the total Ni area fraction and this must be accompanied by an increase in the pore phase fraction. Therefore, investigation of the pore phase in the innermost part of the anode layers can provide an indirect measure of decreased Ni fraction and avoids the challenges and uncertainties related to automated segmentation and quantification of the Ni and YSZ phases from higher voltage SEM images.43,44

Figure 7 shows representative SEM images of the anode/electrolyte interface for the cells used in YSZ-Low, YSZ-Hi and YSZ-no-S tests. It
Table V. Quantification of porosities in the anodes for long-term tested cells. “Anode(electrolyte)” refers to the anodes approximately 0.5–1 μm from the electrolyte interface. Reference cell refers to a reduced, but not long-term tested cell previously reported.18

<table>
<thead>
<tr>
<th>Test</th>
<th>Pore fraction Anode(electrolyte)</th>
<th>No of pores/100 μm Anode(electrolyte)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference cell*</td>
<td>0.14</td>
<td>30.6</td>
</tr>
<tr>
<td>YSZ-Low</td>
<td>0.15 ± 0.03</td>
<td>27.1 ± 3.1</td>
</tr>
<tr>
<td>YSZ-High</td>
<td>0.29 ± 0.04</td>
<td>30.6 ± 3.5</td>
</tr>
<tr>
<td>YSZ-No-S</td>
<td>0.18 ± 0.02</td>
<td>31.7 ± 3.8</td>
</tr>
</tbody>
</table>

*Data from Hauch et al.18

can be observed that the anode from the YSZ-Hi test has a significant number of larger pores close to the anode/electrolyte interface, if compared to the anodes from YSZ-low and YSZ-no-S test. These are indicated by the circles in Figure 7b. The porosity change is mainly caused by some larger pores within the 2–4 μm of the anode layer closest to the electrolyte.

Table V gives a summary of the quantification of pore area fraction and number of pores on a grid line 0.5–1 μm from the anode/electrolyte interface. From Table V it is evident that the number of pores is similar for the investigated anodes, but the pore area fraction is significantly increased for the anode from the YSZ-Hi test.

Table V . Quantification of porosities in the anodes for long-term tested cells. “Anode(electrolyte)” refers to the anodes approximately 0.5–1 μm from the electrolyte interface. Reference cell refers to a reduced, but not long-term tested cell previously reported.18

To summarize, the SEM results show that the irreversible long-term degradation has led to significant structural changes even on the micrometer scale. The migration of Ni from the anode/electrolyte interface excludes the possibility of “re-activation” of the Ni catalyst as it is no longer present in the required positions in the anode. Furthermore, the corresponding increase in the fraction of porosity in the anode/electrolyte interface will inevitably change the mechanical properties of this interface.

Figure 8 shows higher magnification SEM images of the part of the anode closest to the electrolyte for the YSZ-Hi test. The features observed in Figure 8 can be found in numerous places in the anode/electrolyte interface region of the cell from the YSZ-Hi test. The curvature and size of the right side of the pore seems to indicate an empty space left over by a now missing Ni particle as the “rounded” shape of the pore is different from the more “fractured” pores formed by the YSZ grains. The higher magnification SEM image (Figure 8b) of this pore also reveals the presence of nano-sized particles along this round-shaped part of the pore. Energy dispersive spectroscopy (EDS) has been obtained in the region where these nano-particles are present and in regions of pores/YSZ interfaces where no nano-particles could be observed in the SEM images. These EDS measurements reveal that the observed nano-particles contain Ni and traces of sulfur either in, on or in the vicinity of these nano-particles.
(R_{LSN}) and half of the R_{high}; all determined from the analysis of IS. A pO\textsubscript{2} of \(4 \times 10^{-17}\) atm in the anode compartment locally is not sufficiently high for Ni oxidation to occur at 850 °C which can be expected at a pO\textsubscript{2} around \(10^{-13}\) atm.\textsuperscript{45} Based on thermodynamic calculations and the overall cell test conditions (i.e. externally controlled conditions such as set temperature and fuel composition) one should not expect formation of nickel sulfide (Ni\textsubscript{3}S\textsubscript{2}) either.\textsuperscript{52,53} However, the given test conditions and values for pO\textsubscript{2}/aneo-compartment are “overall” numbers for the entire anode utilization volume and do not provide information on exact conditions on the nanometer scale of the anode at – or in the nano-scale vicinity of - the TPB at which the pO\textsubscript{2}, gas composition and temperature can be significantly different. Kishimoto and co-workers reported that the Ni-S system is complex and includes Ni-S eutectics between Ni and Ni\textsubscript{3}S\textsubscript{2}; and showed thermodynamic data for the significant increase (\(\sim\) doubling) of the solubility of oxygen and sulfur in Ni when increasing the oxygen potential, pO\textsubscript{2}, by one order of magnitude.\textsuperscript{3} Furthermore, work by Loehsontorn et al.\textsuperscript{54} indicates that the presence of sulfur will give rise to increased Ni diffusion and sintering. These reported data render it probable that O and S solubility, Ni sintering and Ni diffusion will be affected by high oxygen potential and sulfur exposure. This will inevitably lead to enhanced mobility of Ni in the active anode thus potentially enhanced close to the anode-electrolyte interface where the highest oxygen potential is present. Finally it should be noted that a high pO\textsubscript{2} locally in the active anode will lead to significant quantities of Ni\textsubscript{3}S\textsubscript{2} to be present in YSZ,\textsuperscript{49} which will affect the ionic conductivity of the YSZ-skeleton\textsuperscript{50,51} and in turn can be expected to lead to an increase in the impedance at high frequencies (above \(\sim 15\) kHz).\textsuperscript{26,27}

To summarize our findings and combine the impedance analyzes results with the post-mortem SEM results Figure 9 shows a sketch of the initial state of the Ni/YSZ anode microstructure (Figure 9a), and after long-term test with no irreversible degradation i.e. test YSZ-Low and YSZ-no-S (Figure 9b) and after long-term test with sulfur exposure at high overpotential with irreversible degradation i.e. YSZ-Hi test (Figure 9c). In the initial state (Figure 9a), the Ni particles are well distributed and a well percolating network exists. This means a high TPB density in the few microns of the anode close to the electrolyte and O\textsuperscript{2-} ions will find a TPB at the anode/electrolyte interface or only need to be conducted few microns in the YSZ skeleton of the anode. In other words; the utilization volume is expected to be contained within the innermost 5–10 μm of the anode. Figure 9b illustrates the anode microstructure after test YSZ-Low and YSZ-no-S. In both cases Ni coarsening has occurred, but there is still a well percolating Ni network present in the entire anode. The coarsening of the Ni particles means a slightly lower TPB density per given nominal electrode volume which in turn corresponds to a slightly expanded reaction volume, and we can expect the electrode area corrected R_{Ni-TPB} to have increased slightly which was also observed from the analyzes of IS. However in the anode structure of Figure 9b the YSZ skeleton and the percolating Ni network in the innermost part of the anode is still intact which in turn means that the O\textsuperscript{2-} ions still have a short path to be conducted to find an active TPB, and the high frequency part of the impedance response (R\textsubscript{i} and R\textsubscript{high}) should therefore not have changed significantly for the structure in Figure 9b. This was also observed from the IS from the YSZ-Low and YSZ-no-S test. The observed slight increase in R_{Ni-TPB} for YSZ-Low, even after long recovery time, can also be partly due to traces of Ni-S species still being present in the anode structure but not detectable via SEM/EDS. Such traces of sulfur need to be investigated by e.g. TEM/EDS and/or ToF-SIMS as illustrated by Schubert and co-workers.\textsuperscript{54} Figure 9c illustrates the Ni/YSZ anode after long-term H\textsubscript{2}S exposure at high overpotential. In this degraded anode, a percolating Ni network is lacking in the 2–4 μm of the anode layer closest to the electrolyte. This irreversible change means that the O\textsuperscript{2-} ions now have a longer path to reach an active TPB in the anode, which in terms of expected impedance response fits well with the observed irreversible increase in R\textsubscript{i} for YSZ-Hi. The electrochemical reactions will now take place significantly further away from the electrolyte. Furthermore, in this outer layer of the anode, the Ni particles have coarsened as well, leading again to an increased reaction volume compared to that of the initial anode. In terms of impedance response these should lead to a slight irreversible increase in R_{Ni-TPB} even in the case where all surface adsorbed sulfur species desorb from the Ni particles. For an anode supported cell the reaction utilization volume can in principle extend into the anode support layer either if the long-term test period is prolonged or in case thinner active anodes are applied and will become limited by the ionic conduction in the porous YSZ network especially if the reaction utilization volume is to be extended to the anode support layer in which YSZ is used. To investigate these effects further cell tests with anode thickness variations in line with those reported by Park and co-workers could provide valuable information regarding the long-term irreversible degradation.\textsuperscript{55}

From the experimental data in this work it is not possible to determine the exact mechanism, or at which point in time during testing the Ni particles leave their original position in the YSZ skeleton of the anode of the cell for the YSZ-Hi test. However it is clear that the nano-particles containing Ni and traces of sulfur are located in these Ni-lacking positions of the anode after test for the cell from the YSZ-Hi test. Even though the nano-particles contain Ni, the SEM images reveal that they do not constitute a percolating Ni network and therefore cannot act as new sites for the electrochemical reaction in the anode.

Cell overpotential was used as a test parameter to investigate the irreversible long-term performance loss due to H\textsubscript{2}S poisoning. Based on the results reported here we find that the observed long-term irreversible degradation is triggered by the combination of continued sulfur exposure and sufficiently high local oxygen potential (pO\textsubscript{2}) in the anode structure, particularly close to the electrolyte. In line with this, and based on long-term test for cells with Ni/YSZ and Ni/ScYSZ
based anodes, we further hypothesize that the reported increased tolerance toward sulfur for Sc-doped Ni-zirconia based anodes compared to Ni/YSZ based anodes is also closely related to the local pO2 in the anode structure, but the critical pO2 necessary to initiate the observed irreversible long-term degradation is not necessarily identical for Sc-doped Ni-zirconia anodes compared to Ni/YSZ anodes.

Conclusions

From the results presented here it can be concluded that:

- At 850 °C and a CH4/H2O/H2 fuel it is possible to obtain (after the initial and reversible performance loss) very stable cell performance for both Ni/YSZ-based and Ni/Sc/YSZ-based cells i.e. cells with and without scandia-doping of the zirconia during 500 h addition of 2 ppm H2S at 1 A/cm2.2,3,4
- At higher cell overpotential (by increasing current density, but keeping the same fuel utilization) both Ni/YSZ-based and Ni/Sc/YSZ-based cells can be forced into a regime where the initial and reversible degradation due to the addition of 2 ppm H2S is followed by an almost linear and irreversible degradation of the anode.
- Analyzes of electrochemical impedance spectra (IS) collected during galvanostatic testing for two Ni/YSZ-YSZ-LSM/YSZ-based cells show that for the low overpotential test (YSZ-Low) basically only Rsp,TRP is affected (reversibly) by H2S poisoning and only in the initial stages. In contrast, significant irreversible increase in the high frequency part of the IS (ohmic resistance and ionic conductivity in the anode) was observed for the high overpotential test upon prolonged H2S exposure (YSZ-Hi).
- The results from the non-sulfur high overpotential (YSZ-no-S) test in this work and previously reported test with similar cells with no H2S addition for a Ni/YSZ-based cell suggest that the irreversible long-term degradation for the high overpotential H2S-poisoning test (YSZ-Hi) is closely linked to the sulfur addition.
- The overpotential, rather than the current density or materials chemistry (since both YSZ and ScYSZ based anodes were tested), was found to be the key parameter for whether or not a given H2S-exposure led to long-term irreversible degradation of the Ni-Zirconia based SOFC anodes.
- Post mortem analyzes by SEM shows that the cell from sulfur test with low cell overpotential (YSZ-Low) test and the cell from the non-sulfur high overpotential (YSZ-no-S) test both have satisfying percolating Ni network and porosities as expected when compared with a non-long-term tested cell.
- Post mortem analyzes by SEM shows that the cell from the sulfur test with high cell overpotential (YSZ-Hi) has a significant lower phase fraction and number of percolating Ni particles in the few microns of the anode closest to the electrolyte. Furthermore, this anode has an increased phase fraction of porosity in this same region of the anode but similar number of pores when compared to other tested cells.
- Nano-sized particles containing Ni and traces of sulfur can be found at the borders of the large pores in the innermost 2–4 μm of the anode from the heavily degraded and not fully recovered cell from the test with sulfur and high cell overpotential (YSZ-Hi).

Acknowledgment

Colleagues at DTU Energy Conversion are greatly acknowledged for technical assistance and fruitful discussions; especially H. Henriksen, M. Davodi, K. Brodersen, research Professor M. Mogensen and Dr C. Graves. Furthermore the authors acknowledge the financial support from the project “Towards Smart Grid Ready SOFC”, Energinet.dk project no. 2012-1–10747.

References

32. C. Gruenve, Radvat vert.9.5, Dept. of Energy Conversion and Storage, Technical University of Denmark (2012).


