Short-term strong cathodic polarization of Ni/YSZ and Pt/YSZ

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The Ni-YSZ composite electrode is the common hydrogen-water electrode used in SOEC’s and SOFC’s. In both functions the efficiency depends on electrodes with a high triple phase boundary (3PB) area. SOFC anode performance degrades due to e.g. coarsening of the Ni particles and the resulting decrease in 3PB length and electronic percolation. A so-called reverse current treatment, RCT, has been used to create and restore a microporous Ni-YSZ interfacial structure in the anode. With this technique, a short cathodic high density current (0.5–2 A cm⁻²) is applied for 10 s. The mechanism of the activation is that during the pulse, YSZ in contact with Ni is reduced and a metallic Ni-Zr phase is formed. In the reoxidation process following the pulse, a nanoporous Ni-zirconia structure is formed. In SOEC’s the Ni cathode can at high current densities be polarized to potentials where a partial reduction of YSZ occurs. The importance of this for the cell degradation is not present at present, but it emphasizes that the Ni-YSZ interface is a dynamic structure that may change with varying current load and polarization.

In a recent work strongly polarized Ni wire point electrodes on polished YSZ surfaces were investigated at 900 °C in a humidified hydrogen atmosphere. It was shown that at polarizations down to −2.4 V relative to the standard oxygen potential for 140–160 h, the Ni|YSZ interface was drastically changed by a partial reduction of the YSZ and formation of intermetallic Ni-Zr compounds. Complex plane plots of impedance measurements were initially simple capacitive depressed arcs, but with time an inductive loop developed at low frequencies, and later the capacitive arc split up into two arcs. A similar impedance behavior has also been reported for Ni and Pt microelectrodes in 9 % humidified hydrogen at 650 °C, where the low frequency loop was explained by a widening of the triple phase reaction zone caused by an increase of the electronic conductivity of the YSZ with polarization.

In very recent SOEC degradation studies with rather large active electrode areas, inductive low frequency loops were observed and attributed to an adsorption process that allows H₂O reduction on Ni sites polluted with Si impurities from the sealing. Electronic conduction through the YSZ electrolyte or reduction of YSZ.

Except for the RCT works mentioned above, most studies of Ni-YSZ reactions have been carried out in a timescale of days. In the present work, the focus is on the initial stages of the Ni|YSZ reduction ranging from minutes to a few hours. The aim is to determine the potential where the reaction is initiated, the growth rate of the reduced intermetallic layer and the microstructural development. To follow the processes with high sensitivity, a number of linear potential sweep techniques are applied. Under favorable conditions with low DC current, linear sweeps are very sensitive and may resolve processes down to formation of monolayers.

**Experimental**

Ni wires (99.999% purity, Johnson Matthey, 0.5 mm in diameter) were bent to a U-shape and heat treated for 72 h at 1000 °C in 9 % H₂/3 % H₂O in N₂. After mounting them in a double bore alumina tube they were electropolished to obtain a smooth and clean surface.

A Pt wire was melted in one end to form a spherical electrode. It was then mounted in a double bore alumina tube similarly to the Ni electrodes.

8 mol% yttria-stabilized zirconia (YSZ, TZ8Y, Tosoh) disks were pressed, sintered at 1500 °C for 2 h in air and then polished on one side, ending with a 0.1 μm diamond suspension. The disks were approximately 2.5 mm in thickness and had a diameter of 1.5 cm. The unpolished sides of the YSZ disks were painted with Pt paste and placed on a Pt mesh for current collection. The YSZ disks were mounted in a two-electrode set-up where the Ni wires/Pt wire were pressed against the polished YSZ surfaces with a load of 300 g thus forming a point electrode. The set-up held four samples. Comparing the counter electrode area of 1.8 cm² with the Ni electrode contact area of less than 1 mm² it was considered safe to use the simple two electrode configuration rather than introducing a separate reference electrode and risk increased noise sensitivity and decreased AC bandwidth.

Polarization experiments were carried out at 650 and 750 °C, initially in 9 % H₂/3 % H₂O in N₂, but for the later experiments in 4 % H₂/3 % H₂O in N₂, because of a general change in the laboratory gas supply. The 3 % H₂O was obtained by bubbling the dry gases through a flask with water at room temperature (~ 25 °C). From thermodynamic data the equilibrium potential relative to the standard oxygen potential, E°(O₂), is calculated to −1.060 V and −1.035 V for the 9 % H₂ atmosphere at 650 and 750 °C, respectively. The corresponding values for the atmosphere containing 4 % H₂ are −1.015 V and −0.985 V. Assuming the open circuit potential (OCP) to be the same as the equilibrium potential, potentials relative to the standard oxygen potential are obtained by adding these values to the polarizations. In the graphs, the polarization as well as the potential relative to E°(O₂) are given.
Results from four types of electrochemical experiments are reported in the present work (Fig. 1).

1) Potential sweeps, where the electrode was cycled from the equilibrium potential to a polarization, \( \eta \), of \(-1.6\) V and back, with sweep rates decreasing through the sequence 100, 50, 20, 10, 5, 2 and 1 mV s\(^{-1}\) with three cycles per sweep rate. The series was carried out with decreasing sweep rates to postpone irreversible changes as much as possible. After each sweep rate, electrochemical impedance spectra (EIS) were recorded at the equilibrium potential. The sequence is illustrated in Fig. 1a.

2) Potential-stepped EIS (Fig. 1b). The potential was stepped down from the equilibrium potential, either in a series from 0 V down to a polarization of \(-1.0\) V and further to \(-1.6\) V with steps of \(-0.2\) V, or from 0 V down to \(-1.6\) V in steps of \(-0.1\) V. After a conditioning time of 5 min on each potential step, an impedance spectrum was recorded yielding a total polarization time on each step of 20 min.

3) Potential step (Fig. 1c). The electrodes were polarized with a constant potential for a certain time and then cooled at a rate of 100 °C/h while maintaining the polarization.

4) Stepped potential sweeps (Fig. 1d). The electrode potential was swept with a rate of 20 mV s\(^{-1}\) to the conditioning potential where it was kept for 300 s and then swept back to 0 V with 20 mV s\(^{-1}\). After 300 s the sequence was repeated with a new conditioning potential. The conditioning potentials were chosen as a staircase with steps of \(-0.1\) V from \(-0.1\) V to \(-2\) V.

Table I shows the experiment type and experimental details for all samples.

All the electrochemical experiments, except the stepped potential sweeps, were carried out with a 125S Solartron Frequency Response Analyser and 1287 Electrochemical Interface. In the stepped potential sweeps, a Gamry FAS2 potentiostat was used. A few of the experiments ended with the last sample being polarized during cooling to keep the reduced state for microstructural analysis.

After the experiments, the YSZ and metal wires were examined with scanning electron microscopy (SEM, Zeiss Merlin). Initially, no carbon coating and low acceleration voltage (2 kV) were used to capture details of the surface microstructure. Later carbon coating was applied to be able to use higher acceleration voltage for the backscatter detector and to perform energy-dispersive X-ray spectroscopy (EDS). Finally, cross-sections were made of selected electrodes and electrolytes by casting them in epoxy and polishing from one side until the contact area was visible. These samples were all carbon-coated to avoid charging. Secondary electron (SE) and back-scattered electron (BS) images were obtained.

Results

Potential sweeps.—Figs. 2–5 show selected sweeps from series of potential sweeps with rates 100, 50, 20, 10, 5, 2 and 1 mVs\(^{-1}\) on Ni/YSZ and Pt/YSZ for overvoltages from 0 V to \(-1.6\) V and back at 650 °C and 750 °C. Three cycles were recorded at each sweep rate, but—except for Fig. 3—only the second sweep is shown in the figures.

The full range sweeps in Figs. 2a, 4a and 5a look very similar without appreciable hysteresis, and only in the overvoltage range \(-0.6\) V to \(-1.0\) V small deviations from a smooth curve are seen.

The expanded Figs. 2b and 4b show clear oxidation peaks that are decreasing with decreasing sweep rate for the Ni electrodes. For the sweep rate 100 mV s\(^{-1}\), a small reduction peak is seen in the downwards sweep just below the onset of the oxidation peak in the upwards direction.

To illustrate the development from the first to the third sweep at a given sweep rate, Fig. 3 shows these sweeps for a sweep rate of 20 mV s\(^{-1}\). The base level for the peaks is lowered with the repetition, but only minor changes in the peak shapes and sizes are seen.

The coupled oxidation-reduction peaks indicate that an—at least partially—reversible redox couple has been created during the sweeps. The expanded Pt electrode sweeps in Fig. 5b also shows oxidation, but the peak currents are an order of magnitude lower than those on Ni.

To reveal the potential where the redox reaction is initiated, a Ni/YSZ electrode was conditioned for 300 s at the equilibrium potential and then swept with 20 mV s\(^{-1}\) to a conditioning polarization, where it was kept for 300 s. Hereafter, it was swept back to 300 s equilibration without polarization. The sequence was repeated with conditioning potentials stepped down from \(-0.1\) V to \(-2.0\) V with 0.1 V steps. Results are shown in Fig. 6 and 7. For conditioning polarizations of \(-1.1\) V and above at 650 °C and of \(-1.0\) V and above at 750 °C, the sweep curves are coinciding; smooth and without any characteristic features, and all except the last sweeps have been omitted in the figures. At 650 °C a well-defined reoxidation peak is seen for a conditioning polarization of \(-1.3\) V and the cathodic current has increased Fig. 6. Actually, a close examination of the curve for \(-1.2\) V reveals a tiny peak and the increase in current is evident. Decreasing the conditioning potential further makes the peak grow, develop a shoulder and turn into a wide peak. For polarizations below \(-1.6\) V, the cathodic current increases but no new features are seen, and the curves are therefore not included in the graphs.

When the temperature is raised to 750 °C (Fig. 7) the \(-1.1\) V curve shows a very small reoxidation peak followed by a strong increase of
the cathodic current following the peak. When the conditioning potential is lowered, the reoxidation current is seen as a double-shouldered peak that separates into two peaks in the $-1.6$ V curve.

**Impedance.—**Before and after each triple of sweeps shown in Figs. 2 and 4, impedance spectra were recorded at the equilibrium potential. The results for Ni|YSZ at 650 °C (Fig. 2) are shown in Fig. 8 and display a remarkable decrease in impedance after each of the first few sets of sweeps.
1.3 V an inductive low frequency loop becomes more and more dominating. Furthermore, a hint of a high frequency capacitive arc seems to develop.

To investigate whether this polarization-induced activation seen in Fig. 9 is permanent or not, impedance spectra were recorded at the equilibrium potential before the stepped potential sweep series at 750 °C (in Fig. 7) and during a period of 110 h after the last sweep. The spectra recorded before and just after the sweeps are given in Fig. 10 and show that the low frequency impedance has decreased by three orders of magnitude during the sweeps, and that the spectrum is composed of two slightly suppressed arcs.

**Microstructure of contact surfaces.**—Optical inspection of the YSZ electrolytes revealed the general trend that samples cooled during a polarization of −1.2 V or below showed a greyish or brownish spot around the contact area.

SEM of contact areas on YSZ electrolytes and metal electrodes, where strong cathodic polarization was applied at 650 °C, showed that severe changes had occurred to the interface regions. A relatively thick reaction layer between YSZ and Ni had formed. A number of general features could be distinguished in the interface region for both reoxidized and reduced samples. Figure 11 shows images of the reoxidized electrode and electrolyte Ni34−1 that exemplify the microstructural features. Figures 11a and 11b show the contact areas on the YSZ and the Ni, respectively. The contact areas are easily recognizable and features can be correlated between them and it is obvious that a reaction layer has formed between the Ni and YSZ. A part of the reaction layer is missing on the YSZ and is instead adhering to the Ni. Figure. 11c shows the edge of the reaction layer and the fracture surface to the YSZ, which seems rough. Figure 11d shows YSZ grains adhering strongly to the reaction layer. Figure 11e shows a hole in the YSZ where such a grain has been torn out. A thin layer is located along the grain boundaries and is visible both where a grain was torn out and in grain boundaries on the fracture surface. The layer is also present on the corresponding YSZ grains that have been torn out. Figure 11f shows an example of a surface of a reaction layer with quite complex microstructures. A schematic of the interface region is shown in Fig. 11g.

Samples subjected to strong cathodic polarization at 750 °C show some of the same features but in most cases the contact volume adheres to the electrode and a lot of fragments are present in and around the fracture (Fig. 12a). The fracture surface shows that grains were torn out and the fractures primarily occurred along grain boundaries (Fig. 12b). The rough grain surfaces indicate that reaction has occurred along them and remnants of a grain boundary phase is present (Fig. 12c).

**Microstructure and EDS of cross sections.**—Figure 13 shows the contact area and a cross section of part of a contact volume. As the specimen was cooled during polarization, the reaction layer is still reduced. It is dense and uniform in thickness and has a sharp boundary to the YSZ below. The original YSZ surface runs through the layer (Fig. 13b). EDS shows that the layer consists of a Ni-Zr intermetallic phase. The thickness is approximately 1.6 μm. Figure 13b is a backscatter image and thus shows phase contrast.

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**Figure 3.** 20 mV s\(^{-1}\) sweeps from the sweep series shown in Fig. 2 (Ni32−0). Dotted lines indicate sweeps with decreasing potential and full lines shows sweeps with increasing potential. In the insert, the reoxidation peaks have been moved vertically for a better comparison.

**Figure 4.** Potential sweeps from 0 V to −1.6 V polarization and back on Ni∥YSZ (Ni33−0) at 750 °C in 9 % H\(_2\)/3 % H\(_2\)O. Sweeps in the negative potential direction are shown with dotted curves and those in the positive direction are shown with full lines. (a) Full potential range. (b) Expanded segment of (a).
At the edge (3PB), there is a darker area, and an EDS line scan from the intermetallic reaction layer to the dark area shows a higher O/Zr and a lower Ni/Zr as compared to the intermetallic phase (Fig. 15e), i.e. contains more oxygen than the brighter part of the layer. A similar area is found at the opposite edge.

Figure 14a displays a cross section of Ni$_{33}$$–$$3$ where the polarization was kept during cooling from 750 °C. The intermetallic reaction layer is easily recognizable between YSZ and Ni. Fractures are evident in YSZ and the intermetallic layer, corresponding to the surface structures (Fig. 12). The thickness is around 8 $\mu$m where the layer is thickest and 3–4 $\mu$m in the thinner part.

The reoxidized layer of Ni$_{34}$$–$$1$ is shown in Fig. 14b. Two phases are present in a network structure, i.e. the nanostructured oxidation products from the intermetallic Ni-Zr phase, Ni (bright) and ZrO$_2$ (dark).

Figure 15a shows an EDS line scan of Ni$_{32}$$–$$2$ through the reaction layer and into YSZ. Figures 15b–15d show element ratios for the reduced Ni$_{32}$$–$$2$ and the reoxidized Ni$_{34}$$–$$1$. Figure 15b presents the Zr/O ratio, which is much larger ($\sim 1.9$) in the reduced intermetallic compound compared to the reoxidized phase ($\sim 0.5$). The nominal ratio for 8 mol% YSZ is 0.44. The Ni/Zr ratio is similar ($\sim 2.6$) for both the intermetallic and the reoxidized phase. Y is present in both phases with a Y/Zr around 0.2. The nominal ratio is 0.17.

During line scan acquisition, the counting time in each point is relatively low which may result in a large uncertainty, i.e. curves are
not smooth. Point EDS measurements show a variation in the Ni/Zr ratio from $\sim 2.3$ to $\sim 2.9$.

Figure 16 shows contact area and cross section of Ni$_{34}$-3 that was polarized at $-1.2$ V for 25 min before it was cooled to room temperature at 200 °C $h^{-1}$ under polarization. A 200–300 nm thick intermetallic layer had formed with some pores on the Ni side.

Figure 17a shows the contact area on YSZ of the only Pt electrode investigated. The backscatter image shows phase contrast, and EDS confirmed that the brighter areas contain Pt. An intermetallic layer has formed at the interface and a part of the reaction layer had a stronger attachment to the Pt electrode (Fig. 17b). The layer shows remnants of YSZ grain shapes. In one location, a piece of YSZ has been torn out and is now attached to the Pt wire (Fig. 17b).

Figure 7. Stepped potential sweeps on a Ni[YSZ electrode (Ni$_{41}$–3) in 4% H$_2$/3% H$_2$O from equilibration for 300 s at the equilibrium potential to 300 s conditioning at varying polarizations (given in legends) and back to 0 V at 750 °C. Sweeps in the negative potential direction are shown with dotted curves and sweeps in the positive direction are shown with full lines. (a) Full potential range and zoom of the downward reduction peak in insert. (b) Expanded oxidation peak.

Figure 8. Impedance at OCV for Ni[YSZ (Ni$_{32}$–0) at 650 °C before the first and after each sweep from the series in Fig. 2. The key numbers indicate the sweep rates in mV s$^{-1}$. Except for the "before (bfr)" spectrum, where a limited frequency range (82.5 kHz-121 Hz) was applied, the range was 82.5 kHz-0.01 Hz with 6 frequencies per decade.
Discussion

The cyclic voltammogram sketched in Fig. 18 summarizes the processes discussed in the following, and is intended to serve as an overview through the discussion.

The electrochemical sweep measurements on Ni|YSZ in Figs. 2, 4–7 show a reduction process proceeding with a rate that increases almost exponentially with the cathodic polarization. To investigate this further, the downward sweeps of the Figs. 2, 4 and 5 with sweep rate 1 mV s⁻¹ and the potential stepped sweeps in Figs. 6 and 7 with sweep rate 20 mV s⁻¹ are shown as Tafel plots in Fig. 19. In spite of the difference in technique, they are all very similar and only that for Pt stands out with a steeper increase below −0.9 V. The logarithmic plot shows two regions. From 0 V down to −0.5 V or lower—depending on the electrode and temperature—the current flattens out after the initial steep increase. The slope of the curve in the inflection

Figure 10. Impedance spectra obtained at 750 °C before and after the sweep series on the Ni|YSZ electrode (Ni41−3) shown in Fig. 7. (a) Impedance spectrum acquired at OCV before the first sweeps, frequency range 82 kHz–56 mHz. (b) Impedance spectrum acquired at OCV just after the last sweep, frequency range 82 kHz–8.2 mHz.

Figure 11. SEM (SE) images of Ni34−1, which is reoxidized after a maximum polarization −1.6 V at 650 °C. Examples of the general microstructural features that form during short strong cathodic polarization. (a) Contact area on YSZ. A piece of the reaction layer has been torn out and another piece is loose (arrow). The red square indicates the location of Fig. 11c. (b) Contact area on Ni where the missing piece (arrow) from 10a is located. The red square indicates the location of 10d. (c) The formed reaction layer (oxidized in this case) on YSZ. (d) Torn out YSZ grains (arrows) adhering to the backside of the reaction layer. (e) Grain boundary phase (arrows). (f) Complex microstructures on the exposed surfaces of the reaction layer. (g) Sketch showing the microstructural features observed after strong cathodic polarization.
point close to $-0.5$ V corresponds to a Tafel slope of $\sim 1.5$ V decade$^{-1}$, i.e. a value far too large to be attributed to a charge transfer reaction. Thus, the curvature below $-0.5$ V strongly indicates that diffusion-controlled water reduction is the dominating process in this region (orange and light blue in Fig. 18). At still lower potentials, the current increase accelerates and a region with only a minor bending is obtained. To discover whether the curvature is a consequence of the electrolyte resistance, the curves in this region are fitted with a Tafel expression including a linear ohmic term:

**Figure 12.** SEM (SE) images of surface structures of Ni33–1, which is reoxidized after a maximum polarization of $-1.6$ V at 750 °C. (a) Contact area on YSZ. Most of the reaction volume is attached to the Ni electrode and many fragments are present. (b) Fractures occurred along grain boundaries. (c) Surfaces of grains left in the crater show rough grain faces and a grain boundary layer (arrow).

**Figure 13.** SEM images of Ni32–2 where the polarization of $-1.4$ V was kept during cooling from 650 °C. (a) Contact area (SE image) on YSZ with approximate location of the cross section and b) cross section (BS image). The dotted line indicates that original polished YSZ surface. The dashed line surrounds a darker area where the O-content is higher. An EDS scan line parallel to the dotted line and through the darker area is shown in Fig. 15e.

**Figure 14.** (a) SEM cross section of the reduced interface of Ni33–3 (BS image, 750 °C). “R” indicates the reaction layer. (b) SEM cross section of the reoxidized interface of Ni34–1 (SE image, 650 °C).
Figure 15. (a) EDS line scan across the interface between YSZ and the reduced intermetallic layer (Ni32–2). (b)–(d) Zr/O, Ni/Zr and Y/Zr element ratios from EDS line scans of Ni32–2 (red line) and Ni34–1 (reoxidized intermetallic layer, blue line). The yellow areas signify the reduced or reoxidized reaction layer. (e) Element ratios from EDS scan line in the intermetallic layer (Ni32–2, Fig. 13). The green area is the darker area towards the 3PB.

Figure 16. SEM images of Ni34–3 which was polarized at −1.2 V for 25 min at 650 °C and cooled during polarization. (a) SE image of the contact area on Ni with attached YSZ (SE). The dashed line indicates the approximate location of cross section. (b) BS image of the entire cross section. The intermetallic reaction layer is present everywhere between Ni and YSZ. (c) BS image of a magnified part of the intermetallic reaction layer.
where the symmetry factor and \( n \) is the number of electrons in the rate determining charge transfer reaction.

As seen from Fig. 19, the dashed fit lines are close approximations to the experimental curves. The fit parameters are shown in Table II. The \( \beta n \) product gives values between 0.35 and 0.5 for the Ni electrodes and a somewhat higher value for the Pt electrode. These values indicate a single electron transfer process. Comparing the \( R_s \) values from the fit with the electrolyte resistance, \( R_s(OCV) \), determined by impedance measurements at OCV and also given in Table II, shows that \( R_s \) is three to four times lower than \( R_s(OCV) \). This may at first appear surprising, but as seen from Fig. 9 impedance measurements show that the high frequency impedance decreases by almost a factor of two when the polarization is changed from \(-1.3\) to \(-1.6\) V, and the indication of a capacitive arc at frequencies above the experimental range points towards even lower values. In a recent study with PtIr cantilever electrodes, a decrease of more than a factor of 100 was obtained when the electrode was polarized by \(-2\) V. Calculations based on literature data indicate, albeit with a substantial extrapolation, that the electronic conductivity equals the ionic for a polarization of \(-1.2\) V (\(-2.2\) V vs \(E^0(O_2)\)) at 650 °C. The decreasing high frequency impedance combined with the calculated estimate strongly indicate that the \( R_s \) values in Table II mainly reflect the electronic conductivity, i.e. transport of electrons from the working electrode through the YSZ to the counter electrode (gray shaded region in Fig. 18). Although the electronic conductivity is by far lower in the less reducing areas.
environment of the counter electrode, the widening of the current path compensates for the decrease.

Where the downward sweeps in the Figs. 2, 4–7 are smooth, the return sweeps show distinctive oxidation peaks (dark red in Fig. 18), and it is noted that the rate of the oxidation process exceeds the rate of the water reduction resulting in a positive net current until the oxidation is completed. A closer inspection of the expanded voltamograms in Figs. 2b and 4b reveals that for a sweep rate of 100 mV s⁻¹, a reduction peak (green in Fig. 18) has developed on the downwards sweep just below the onset of the oxidation peak in the upwards sweep. Thus, another redox process is proceeding simultaneously with the water reduction and the electronic conduction. A comparison of the charge transferred in the “exponential” region with that in the reoxidation peaks shows that the electron transfer is by far the dominating process and that reduction processes involving oxide ion conduction only plays a minor role.

The Ni-Zr phase diagram shows a number of intermetallic compounds. This indicates a negative free energy of formation of such compounds, which facilitates the reduction of zirconia into a Ni-Zr intermetallic phase when in contact with Ni, compared to the reduction of zirconia to pure Zr. Thus, the reduction of zirconia in contact with Ni will take place at potentials higher than the standard reduction potential of −2.35 V vs E°(O₂) at 650 °C calculated from thermodynamic data tables. The threshold oxygen partial pressure for the electrochemical reduction of Zr from YSZ in contact with Ni was in a previous investigation estimated to an oxygen partial pressure of 3.2 10⁻¹⁰ bar, corresponding to a potential in the range 1.59 ± 0.17 V vs E°(O₂). Considering the difference in temperature and experimental uncertainties, this indicates that the coupled reduction/oxidation peaks between −1.8 and −1.9 V vs E°(O₂) are most likely due to formation and reoxidation of a Ni-Zr intermetallic phase on the interface. The fact that the peaks do not overlap strongly supports the presence of a two-phase reaction, where a coexistence potential between the peaks separates the thermodynamic stability ranges of the phases.

The stepped potential sweeps in Fig. 6b show that when the electrode has been polarized to −1.1 V (−2.12 V vs E°(O₂)) and lower potentials at 650 °C, the water reduction current following the reoxidation peak (light blue in Fig. 18) is higher than that in the downwards sweep (orange in Fig. 18), and the difference increases with decreasing conditioning potentials. The reoxidation peak that is initiated at −1.85 V vs E°(O₂) is clearly seen after conditioning with −1.3 V polarization, but also for −1.1 and −1.2 V there are weak indications of the process. After stronger polarizations the peak develops a shoulder and grows into a broad peak. After the peak, the current is almost proportional to the overvoltage, and water reduction is the dominating process. The increase of the current-voltage slope with lower conditioning potentials—or rather the thickness of the layer being oxidized—demonstrates the enhanced activity for water reduction of the phase formed by the reduction-reoxidation cycle. This increase in activity has been the subject for a number of studies where a reverse current treatment was used as a means to form a nanoporous, highly active Ni/YSZ structure in SOFC anodes.

At 750 °C the picture has changed somewhat due to the higher reaction rates at this temperature. Figure 7b shows that the enhanced cathodic current after the peaks in the return sweep is present after a polarization of −1.1 V (−2.1 V vs E°(O₂)), and a very small reoxidation peak can be identified at −1.86 V vs E°(O₂). With decreasing conditioning potential the broad-shouldered reoxidation peak observed at 650 °C appears at 750 °C as two weak but clearly separated peaks. For a conditioning polarization of −1.3 V, the first peak appears at −1.86 V vs E°(O₂) and the second peak at −1.58 V vs E°(O₂)). With the decreasing conditioning potential and formation of a thicker intermetallic layer, the initially large overlap changes and for the −1.6 V conditioning polarization, the peaks have separated and are seen as two distinct peaks. Except for the −1.6 V curve, where the reoxidation has not been completed during the sweep, they all end up with an enhanced water reduction rate close to the equilibrium potential. Additionally, the insert in Fig. 7a shows that at 750 °C the reduction peaks develop at −1.92 V vs E°(O₂) for the two lowest conditioning potentials, i.e. 0.06 V below the onset of the first reoxidation peak at −1.86 V vs E°(O₂) (Fig. 6b). The broadening of the initially sharp reoxidation peak at 650 °C and the formation of two separate peaks at 750 °C is a strong indication of the formation of more than one intermetallic phase at the interface.

The reoxidation peak is not observed before the electrode has been polarized to a potential below −2.1 V vs E°(O₂) at 650 °C and −2.09 V vs E°(O₂) at 750 °C, i.e. 0.2 V below the potential where the reduction peak later is seen in the downward sweeps. This shows that a process with a high activation energy like a nucleation or disruption of YSZ crystal structures at the Ni-YSZ interface is needed to initiate the reduction. The increase in charge in the reoxidation with decreasing conditioning potential shows that the amount of YSZ being reduced increases from cycle to cycle, either because of interface modifications caused by the repetitive reduction-oxidation cycles or the increased cathodic polarization.

EDS line scans on cross sections of interfaces that has been polarized to −1.4 V and −1.6 V and cooled with and without polarization are shown in Fig. 15. It is seen from Fig. 15c that the Ni/Zr ratio in both the reduced phase (cooled during polarization) and the reoxidized layer is in the interval 2.3–2.9 and there is no significant difference between the two. The Y/Zr ratio in Fig. 15d is in accordance with the nominal value of 0.17 for the TZ8Y and no difference is seen between the reduced, reoxidized and unaltered YSZ phases, which supports that the reduction process has been accompanied by a Ni diffusion into an immobile Y-Zr containing phase. Reduction of TZ8Y to Zr-metal and yttria results in a Zr/O ratio of 3.8. The ratio close to 2 seen in Fig. 15b is substantially lower and corresponds to the composition (Y₂O₃)ₓ(ZrO₂)₁₋ₓ, i.e. only 88% of the Zr¹⁷⁻ content has been reduced. This indicates that zirconia clusters have been encapsulated in the metallic phase without ionic contact to the main YSZ phase in the reduction process. The scan parallel to the original Ni/YSZ interface in Fig. 15e shows a Ni/Zr ratio that decreases from 2.5 to 1 accompanied by an O/Zr ratio increasing to a value close to that for YSZ at the 3PB. So, apparently the supply of water combined with the local ohmic resistance has been sufficient to restrict YSZ reduction at the 3PB.

Another indicium of Ni being actively involved in the reduction of zirconia is that on platinum cathodes the reduction proceeds with a rate that is an order of magnitude lower than that on Ni anodes as seen from a comparison of Figs. 2 and 5. Additionally, the post

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**Table II. Parameters for the fit of Eq. 1 to the curves in Fig. 19, and series resistance at OCV.**

<table>
<thead>
<tr>
<th>Experiment</th>
<th>aV</th>
<th>β</th>
<th>Rₒ(ohm)</th>
<th>Rₒ(OCV)/ohm</th>
<th>R/Rₒ(OCV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni, 650 °C, Fig. 2</td>
<td>−3.19</td>
<td>0.36</td>
<td>269</td>
<td>1080</td>
<td>0.25</td>
</tr>
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<td>Ni, 650 °C, Fig. 6</td>
<td>−2.92</td>
<td>0.44</td>
<td>746</td>
<td>2020</td>
<td>0.37</td>
</tr>
<tr>
<td>Ni, 750 °C, Fig. 4</td>
<td>−2.42</td>
<td>0.51</td>
<td>168</td>
<td>433</td>
<td>0.39</td>
</tr>
<tr>
<td>Ni, 750 °C, Fig. 7</td>
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<td>163</td>
<td>538</td>
<td>0.30</td>
</tr>
<tr>
<td>Pt, 650 °C, Fig. 5</td>
<td>−2.29</td>
<td>0.70</td>
<td>605</td>
<td>2250</td>
<td>0.27</td>
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</table>
mortem SEM images in Fig. 17 shows that the reaction layers are less developed on the Pt/YSZ interface.

In a study of electrochemical reduction of YSZ in a symmetrical Ni/YSZ/Ni cell with dense 1 mm thick electrodes polarization to −2 V and a current of 40 mA cm−2 at 1200 K for 130 min resulted in a 10 μm thick interfacial layer of Ni5Zr at the interface. In a subsequent experiment, a 1 h polarization was followed by a relaxation period at OCV where the potential recorded against the NiO/Ni electrode formed at the anode gave a value of −0.97 V for the Ni5Zr/YSZ/NiO/Ni cell. Using the standard potential of the Ni|NiO electrode calculated for 1200 K of −0.686 V vs E°(O2) from thermodynamic data15 gives an equilibrium potential for Ni5Zr/ZrO2 of 1.66 V vs E°(O2). Considering the main temperature dependence to be mainly due to the entropy of formation for zirconia, the equilibrium potential is estimated to have a value that is lower by less than 0.9 V at 750 °C, or somewhat above −1.75 V vs E°(O2), i.e. in between the two reoxidation peaks in Fig. 7b.

In a recent investigation of reverse current treatment as a means to increase the triple phase boundary length in SOFC anodes, a single crystal YSZ cell equipped with a thin film Ni electrode and a porous composite Ni/YSZ counter electrode, the Ni film was exposed to a cathodic current pulse of 2 A cm−2 for 10 s at 700 °C in a H2O/H2 atmosphere.6 Hereafter, a constant open circuit potential of −0.95 V was recorded for the next 10 s before it decayed to 0 V. The potential was interpreted as the equilibrium potential for the Ni-Zr-Y alloy/YSZ interface formed by the current pulse—measured against the porous counter electrode in equilibrium with the gas atmosphere. From thermodynamic data15 and the gas composition, a value of −2.07 V for the potential vs E°(O2) is calculated. This value is substantially below the value estimated above and those found from the sweeps in Figs. 2, 4, 6 and 7. However, if it is assumed that the porous counter electrode behaves as a Ni|NiO electrode with a potential of −0.783 V vs E°(O2) at 700 °C (calculated from15) a value of −1.73 V vs E°(O2) is obtained. This value is very close to the −1.75 V as the lower limit at 750 °C estimated above from the former work,19 and also the results of the present work.

On the basis of the discussion above, it seems reasonable to suggest a mechanism where Ni in contact with YSZ at a sufficiently strong cathodic potential diffuses into the YSZ accompanied by a simultaneous reduction of the zirconia. Most likely, the initial reduction results in the formation of a solid solution at the interface. Later when the Ni concentration has increased, a separate phase consisting of stoichiometric Ni3Zr may nucleate from the solid solution at the Ni surface resulting in a two phase system. With further increase of the Ni concentration close to the Ni surface, new phases with higher Ni concentration can form and create a layered structure of phases with decreasing Ni stoichiometry and a solid solution at the YSZ surface. Previously it has been shown that five intermetallic phases ranging from Ni5Zr to NiZr2 are formed by mutual diffusion at nickel-zirconium interfaces equilibrated at 1133 K for 24 h, and Kirkendall markers show that the mobility of Ni is significantly higher than the mobility of Zr as expected from the differences in atomic mass.20

In the following reoxidation process, first the solid solution on the YSZ side is oxidized at the same conditions as the original thin solid solution layer. Thereafter, the intermetallic Ni-Zr compound is oxidized. Due to the higher Ni content this requires a higher potential than that necessary for oxidation of the solid solution, and furthermore, the reaction is slowed down by the necessary oxide ion transport through the porous reoxidized zirconia layer, which has a lower ionic conductivity because of yttrium segregation during the reduction process.6,8,19 The segregation is a result of the free energy of formation for yttria being much lower than for zirconia,21 and the potential required for the reduction of yttria is 0.5 V below that for zirconia. Except for the assumption of the direct formation of the Ni-Zr phase—without metallic Zr as an intermediate—this mechanism is very similar to that described by Szász et al.8

The steep decline of the current after the peak maximum seen for the potential stepped sweeps in Fig. 6, and the fact that the current is zero when the gas phase equilibrium is reached indicate that at 650 °C the reoxidation process is completed during the sweep. This is further supported by a very small increase in reoxidation charge during the three consecutive sweeps in Fig. 3 and confirms a picture where—at these short polarization times at 650 °C—the interfacial structure is irreversibly modified, but the reduction-reoxidation processes are reversible in the sense that the amount of intermetallic phase formed is completely reoxidized. It should be noted that for the potential stepped sweeps at 750 °C in Fig. 7 the reoxidation has not been completed after the conditioning polarization of −1.6 V. There is a striking difference in shape and size of the reoxidation and the reduction peaks. As seen from the Figs. 2b, 4b, 6a and 6b, and 7a and 7b, the former are well-defined and large whereas the reduction peaks are only weak indications although the same amount of charge is involved in both processes. This may be a consequence of a slow Ni diffusion into the YSZ during the reduction, which broadens the peak combined with the exponentially increasing electronic current masking the peak.

To get an estimate of the amount of substance involved in the reversible part of the reaction, the charge, q, used for reoxidation was determined by integration of the peak currents in Fig. 6 with respect to time using an estimated linear baseline. It is assumed that the reoxidation process is 2:

$$Z_{\text{Ni}} = Zr^{4+} + 4e^-$$  \[2\]

where Z_{\text{Ni}} is zirconium that has diffused into the Ni phase and zirconium in the Ni-Zr layer formed outside the bulk Ni phase with simultaneous diffusion of Ni into the YSZ phase. Based on a SEM estimate, the area, A, of the Ni|YSZ contact area is 3.4 \times 10^{-3} cm^2 and the density of YSZ, ρ = 5.9 g cm^{-3}.22 The thickness, δ, of the reduced YSZ layer can then be calculated as 3:

$$\delta = \frac{q \rho_{\text{YSZ}}}{4FA\rho}$$  \[3\]

Figure 20 shows the thickness of the reduced YSZ layer calculated from the sweeps in Fig. 6 vs the overvoltage in the conditioning period. As expected, the thickness increases with increasing negative overvoltage. The thickness is in the order of a few hundred nanometer and thus by far exceeds monolayer formation. At lower conditioning potentials, the curve flattens out indicating formation of a layer where the growth rate is limited by the layer thickness and diffusion of Ni through the layer as the rate-limiting step. The graph indicates that the layer formation is initiated just above −2.3 V vs E°(O2). However, the −1.1 V sweep in Fig. 6b does show a small reoxidation current above −1.9 V vs E°(O2) after conditioning at −2.1 V vs E°(O2). Probably the reduction process begins close to −1.9 V vs E°(O2), but with a very low rate that increases with increasing cathodic polarization. Also, Fig. 16 shows that an interfacial layer of 200−300 nm has developed at a Ni|YSZ interface that has been polarized with −1.2 V (−2.2 V vs E°(O2)) at 650 °C for 25 min before being cooled in the polarized state. For a similar polarization at −1.4 V the layer thickness was ~2 μm (Fig. 13b), i.e. far more than predicted by Fig. 20. For similar conditions at 750 °C layers of ~ 8 μm were obtained and in a recent long-term experiment at 900 °C an electrode polarized to −2.4 V vs E°(O2) gave a layer of 100−200 μm.8

In a series of studies on the structural changes induced by reverse current treatments on anode supported SOFC cells by Klotz et al.,3−5 cathodic current pulses with 2 A cm−2 and a duration of 10 s were applied to the Ni anode at 700 °C. The subsequent transmission electron microscopy analyses showed that a porous nanostructured layer with a thickness around 200 nm containing Ni, zirconia and yttria had been formed in the reduction-reoxidation process at the Ni|YSZ interface.

A subsequent investigation at the same conditions by Klotz et al.6 but with a YSZ single crystal cell equipped with a 400 nm thick Ni film working electrode and a composite Ni|YSZ counterpart electrode showed thicknesses from 290 nm for a 1 s pulse length to 1100 nm for
both onset at polarization and temperature. The reduction/reoxidation peaks are when first initiated, proceeds with a decaying rate promoted by polarization and temperature. The reduction/reoxidation peaks are both onset at $-1.9 \text{ V} \text{ vs E}^{\circ}(\text{O}_2)$ and, as seen from Fig. 2b, the reoxidation in the slowest sweep (1 mV s$^{-1}$) is completed at $-1.7 \text{ V} \text{ vs E}^{\circ}(\text{O}_2)$. This makes it tempting to conclude that YSZ in contact with Ni cannot be reduced at potentials above $-1.7 \text{ V} \text{ vs E}^{\circ}(\text{O}_2)$, and SEM on an electrode polarized to $-2.06 \text{ V} \text{ vs E}^{\circ}(\text{O}_2)$ for 90 min at 650 °C did not reveal any interfacial changes.

The impedance spectra recorded at stepwise decreasing potentials and shown in Fig. 9 demonstrate the general feature of electrode activation resulting from the strong polarization. Above polarizations of $-1.3 \text{ V} (-2.3 \text{ vs E}^{\circ}(\text{O}_2))$ simple suppressed arcs are obtained with DC impedances decreasing from an open circuit value of 350 kΩ to 4 kΩ at $-2.2 \text{ V} \text{ vs E}^{\circ}(\text{O}_2)$. Below $-2.3 \text{ V} \text{ vs E}^{\circ}(\text{O}_2)$ an inductive low frequency loop develops. This has previously been observed on Ni wire electrodes polarized to $-2.2 \text{ V}$ relative to $\text{E}^{\circ}(\text{O}_2)$ in pure humidified hydrogen at 900 °C$^9$ and Ni microelectrodes at 650 °C in humidified 9 % H$_2$ for polarizations below $-1.2 \text{ V}$, where the inductive behavior was referred to a broadening of the triple phase reaction zone caused by an increase in the electronic conductivity of YSZ with the cathodic polarization.$^{10}$ The inductive low frequency arc has not only been observed for simple point contact electrodes, but also on larger porous SOEC Ni electrodes, where it has been attributed to a competition between blocking Si impurities from glass cell packings and water adsorption,$^{12}$ introduction of electronic conductivity in the YSZ phase$^{13}$ and reduction of YSZ.$^{14}$

For polarizations from $-1.3 \text{ V}$ and down, the spectra in Fig. 9 show an indication of a capacitive arc at frequencies above the range used. At first, it may be taken as an experimental error caused by stray capacities in the experimental setup. However, as it is not seen at lower polarizations where the much higher impedances should increase the influence of stray capacities it does not seem likely, and it appears to be a common feature for the capacitive arc to separate into two arcs at sufficient cathodic polarizations.$^5,10$ The same observations have also been made on PtIr cantilever electrodes at 650 °C$^{11}$ and thus the behavior is mainly determined by the properties of YSZ, rather than the electrode material.

The decrease in impedance with polarization is a common feature for a charge transfer reaction like the water reduction process, and since no interfacial layer was seen by SEM on an electrode that had been polarized to $-1.0 \text{ V}$ for 90 min at 650 °C, the change in impedance from OCV down to $-1.1 \text{ V} (-2.12 \text{ V} \text{ vs E}^{\circ}(\text{O}_2))$ is ascribed to the water reduction process. For lower conditioning potentials the decrease also contains contributions from the interface modifications and the increased electronic conductivity of YSZ.

Similar to the impedance spectra recorded in-between the sweep series (Fig. 8), the spectra recorded before and after the potential stepped sweeps show a remarkable reduction of the impedance caused by the polarization. As seen from Fig. 10, the low frequency impedance has decreased by at least three orders of magnitude. The

![Figure 20.](image)

**Figure 20.** Thickness of the YSZ layer reoxidized during the anodic sweeps of the stepped potential sweeps obtained at 650 °C and shown in Fig. 6. The calculated thickness is based on a Ni/YSZ contact area of $3.4 \times 10^{-3} \text{ cm}^2$ estimated from SEM.

10 s. The main reason for the increase in layer thickness compared to the former experiment is most likely that the actual current density, and, thus, also the polarization has increased with the change from a high area porous composite electrode to a dense film electrode.

In spite of the different conditions for these results—in the point electrode experiments overvoltages are specified, in the thin cell experiments where reference electrodes are not applicable only the current density is known—they show that Fig. 20 does not reflect a true steady state but rather that the layer growth is a process that, when first initiated, proceeds with a decaying rate promoted by polarization and temperature. The reduction/reoxidation peaks are both onset at $-1.9 \text{ V} \text{ vs E}^{\circ}(\text{O}_2)$ and, as seen from Fig. 2b, the reoxidation in the slowest sweep (1 mV s$^{-1}$) is completed at $-1.7 \text{ V} \text{ vs E}^{\circ}(\text{O}_2)$. This makes it tempting to conclude that YSZ in contact...
spectra recorded for the next 110 h were fitted to the equivalent circuit shown in Fig. 21a, and the resulting resistance component values are plotted against time in Figs. 21b–21d. After 10 h, the values of $R_1$ and $R_2$ show a sudden decrease that disappears after 50 h. This jump is most likely due to a temporary local improvement in the reduction and reoxidation processes. Samples cooled during polarization at $0.45 \text{ V} > \text{E}°(\text{O}_2)$ show a sudden increase in electronic contact conductivity at $0.45 \text{ V} > \text{E}°(\text{O}_2)$ which is mainly reflecting the 3PB reaction. Apart from that, the values of $R_1$ and $R_2$ do not change much during the whole period. The dominating component is $R_2$, the width of the large low frequency arc, which increases by a factor of 10 during the period and does not show any sign of approaching a stable value. Most likely the initial decrease in the OCV impedance reflects that when the interfacial Ni-Zr alloy layer formed during polarizations below $2.1 \text{ V} > \text{E}°(\text{O}_2)$ is reoxidized through the process:

$$2\text{H}_2\text{O} (3\text{PB}) + \text{Ni}_3\text{Zr} (\text{alloy}) = \text{xNi} + \text{ZrO}_2$$

[4]

Ni is segregated in the reoxidized YSZ phase (Fig. 13b) as a more or less interconnected network which increases the electronic contact area between the Ni electrode and the YSZ. With time the connectivity decreases, probably because of disruption of the Ni threads driven by surface forces.

The microstructural investigations carried out after the electrochemical measurements reveal a number of characteristic features of the reduction and reoxidation processes. Samples cooled during polarization at $-1.2 \text{ V} > \text{O}_2$ or below exhibit an optically visible, diffuse grey/brown spot some millimeters in diameter. The color indicates presence of electronic conductivity in the YSZ and it is present in an area much larger than the contact point. The change in color was not observed for samples cooled at OCV. The reduced phase is sustained during cooling under polarization as evidenced by SEM backscatter images (Figs. 13b and 14a) and EDS (Fig. 15), and it can be clearly distinguished chemically and microstructurally from the reoxidized phase obtained when the polarization is released.

Both the reduced and the oxidized reaction layers are uniform and homogeneous in cross sections which points to the whole volume being reduced or oxidized completely during each redox cycle.

The interface between the reaction layer and YSZ is sharp and slightly wavy in cross sections. When the electrode is removed from the electrolyte, the interfacial reaction layer (RL) stays mainly intact and the fracture follows the electrode–YSZ interface allowing a closer inspection of the surfaces. As seen from Figs. 11c and 12b and 12c, the YSZ grains at the reaction front show a roughened RL interface, whereas just below it, the YSZ seems unaltered. The phase present in the grain boundaries (Figs. 11e and 12c) indicates that the reduction also proceeds along these and introduces a weak zone between the grains. This results in some YSZ grains being strongly attached to the RL and torn from the YSZ (Figs. 11d and 11e) in the separation.

The fracture surface between Ni and the reaction layer shows that despite uniformity in cross sections processes forming complex microstructures such as cell-like formations are active during the reduction process.

The tapered end of the reaction layer in the cross section in Fig. 13b shows that the reduction rate during polarization decreases from the central part of the contact area towards the gas/Ni[YSZ] triple phase boundary, where the reduction of YSZ competes with the reduction of water from the gas phase.

**Conclusions**

At $650 ^\circ \text{C}–750 ^\circ \text{C}$ and an atmosphere of $4\%–9\% \text{H}_2/3 \% \text{H}_2\text{O}$ the Ni[YSZ] electrode exhibits three overlapping electrode reactions when cathodically polarized:

1. For polarizations down to $-1.5 \text{ V} > \text{E}°(\text{O}_2)$ diffusion limited reduction of water at the triple phase boundary is the main reaction. After the first YSZ reduction/oxidation cycle the reaction rate is enhanced.

2. At lower potentials electronic conductance in the YSZ becomes significant and increases with polarization to exceed the ionic conductivity by a factor of two at $-2.6 \text{ V} > \text{E}°(\text{O}_2)$. Below $-1.7 \text{ V} > \text{E}°(\text{O}_2)$ the cathodic current increases almost exponentially and the dominating process is activation controlled transfer of electrons across the Ni[YSZ] interface followed by electron conduction through the YSZ to the counter electrode.

3. The first time the electrode is polarized below $-2.1 \text{ V} > \text{E}°(\text{O}_2)$ reduction of YSZ in contact with Ni is initiated within 5 min and a Ni-Zr metallic layer with inclusions of yttria is formed at the interface. In subsequent reduction/reoxidation cycles the processes are initiated at $-1.9 \text{ V} > \text{E}°(\text{O}_2)$, i.e. $0.45 \text{ V} > \text{O}_2$ above the standard potential for the reduction of zirconia to pure Zr. Thus, the Ni-Zr layer is formed directly, without Zr as intermediate, and the rate is limited by the diffusion of Ni through the reaction layer. This is further substantiated by the fact that on a Pt[YSZ] interface the reaction layer formation is much less pronounced compared to that on Ni[YSZ].

4. The presence of two reoxidation peaks in voltammograms indicates formation of two Ni-Zr phases with different compositions.

5. Microstructural investigations of samples cooled during polarization confirm the formation of a Ni-Zr intermetallic layer already at a polarization of $-1.2 \text{ V} > (-2.26 \text{ V} > \text{E}°(\text{O}_2))$ at $650 ^\circ \text{C}$ and the growth of the layer to a few microns thickness within a short time scale at stronger polarizations.

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