H₂-H₂O-Ni-YSZ ELECTRODE PERFORMANCE AND SEGREGATION TO THE INTERFACE

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ABSTRACT

Impurities present in YSZ and nickel segregate to the interfaces and cause decreased performance of impure electrodes. A clear separation between pure (99.995%) Ni and impure (99.8%) Ni was found, and OCV data showed that the best pure electrodes were a factor of 100 better than the impure electrodes in a plot of log(LSR⁻¹) versus 1000/T. Comparing these values with literature data showed that values for most literature electrodes are consistent with those for the impure electrodes.

INTRODUCTION

Interfaces in solid oxide fuel cells (SOFCs) play an important role in determining the performance of the cells. Ni-yttria-stabilised zirconia (YSZ) cerments are designed for the maximisation of the length of the three-phase boundary (TPB) between nickel, YSZ, and hydrogen because it is the general assumption that the electrochemical reactions take place at or very close to the TPB. This means that the nature of the TPB and also of the Ni-YSZ interface is essential for the performance of Ni-YSZ electrodes.

The Ni-YSZ interface has previously been examined with respect to changes in microstructure and chemical composition (1-3) after one week at 1000°C with and without polarisation. It was found that the interface changed during both non-polarised and polarised conditions. The segregation of impurities to the Ni-YSZ interface was also examined (4), and it was found that the interface between 99.8% nickel and YSZ as well as that between 99.995% Ni and YSZ contained several different impurity elements. The impurity phase was characterised as a glassy alkali silicate phase (3). The development of the series and polarisation resistance with time has been treated previously (1, 2).

In this paper, more detailed data are presented, and more information on the Ni-YSZ interface and the processes during OCV and polarisation is revealed. The performance of pure and impure nickel point electrodes are compared with several types of electrodes from the literature.

EXPERIMENTAL

A nickel-YSZ interface was created by pressing a bent nickel wire against the surface of a YSZ three-electrode pellet (Figure 1A) with a load of 82 g. This resulted in average pressures over the contact areas of more than 10 MPa. The surfaces of the 8 mol% YSZ
pellets for the three-electrode setup were polished in several steps ending with 1 μm diamond paste. Two different nickel wires were used:

- Impure: 99.8 % Ni, 0.38 mm in diameter (Johnson Matthey)
- Pure: 99.995% Ni, Puratronic, 0.5 mm in diameter (Johnson Matthey).

The raw nickel wires were rough and electropolishing was performed to achieve a smooth surface.

Figure 1B shows the three-electrode setup. The working electrode is the nickel wire, which is connected to a platinum wire. The reference electrode is a platinum ball positioned in the bore of the hollow pellet, and the platinum paste counter electrode is painted on the lower narrow part of the pellet (Pt paint type 5542, ESL Europe). The rig with the pellets was mounted in a furnace and heated (6°C/min) to a temperature of 1000°C in an atmosphere of 9% H₂/3% H₂O in nitrogen. At 1000°C the atmosphere was changed to 97% H₂/3% H₂O. The electrochemical characterisation was done by impedance spectroscopy. The examined samples were subjected to one of the following treatments:

- Open circuit voltage (OCV); impedance measurements were performed.
- Anodic polarisation (100 mV); impedance measurements were performed during polarisation and at OCV before and after the polarisation.
- Cathodic polarisation (100 mV); impedance measurements were performed during polarisation and at OCV before and after the polarisation.

After stabilisation at OCV (typically after 24–72 hours), either anodic or cathodic overvoltages of 100 mV were applied to the respective pellets. The polarisations were continued for 2–7 days, after which the pellets were left for up to two days at OCV before cooling down. Impedance measurements were generally repeated every 4-6 hours in the first experiments and every 0.5–2 hours in later experiments during both OCV and polarisation. The experiments lasted 100–300 hours.

A Solartron 1260 impedance/gain-phase analyser was used for measurements at OCV; for polarised samples, a Solartron 1286/1287 potentiostat and a Solartron 1250 frequency response analyser were used. The amplitude of the potential applied was 14 mV RMS. The impedance spectra were recorded in the frequency ranges 0.1 Hz to 65 kHz (1250) and 0.05 Hz to 1 MHz (1260) at 9 or 11 points per decade. All instruments were operated from a PC running FCL (5). The impedance spectra were analysed with EQUIVCRT (6).

After the furnace had cooled down, the samples were dismounted. The nickel and the YSZ separated easily from one another, making it possible to examine both surfaces. All samples were examined with scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). Some samples were further analysed with atomic force
RESULTS AND DISCUSSION

The impedance spectra (Figures 2 and 3) generally show a depressed arc, which can be fitted to 1–4 semicircles with the EQUVCRT software (6). Due to the nature of the experiments, a detailed interpretation of the spectra is not possible because it would require additional experiments at other temperatures, other polarisation voltages, or in other atmospheres to observe the effect of these parameters (7). However, some general features may be extracted from the impedance analysis.

Figures 2 and 3 show sequences of selected impedance spectra for a pure and an impure anodically polarized nickel electrode and a pure and an impure cathodically polarised nickel electrode. Included are the series and polarisation resistance curves (Figures 2A, B, F, J and 3A, B, F, J) with indications of the time when the selected impedance spectra were acquired. These spectra represent typical examples of the specific treatment of the samples. The reported ASR and frequency values indicate the typical range when all samples are considered. The spectra change with time both during OCV and during the polarisation periods. Figures 2C and 3C show that impure electrodes display an increasing ASR with time at OCV (spectra a and b), from 25–60 Ωcm² to 55–100 Ωcm² and a small decrease in the summit frequency of the depressed arc from 8–17 Hz to 1–2 Hz. Upon polarisation (Figures 2D and 3D) the ASR drops considerably (spectrum c) to 2–15 Ωcm², and the summit frequency increases to 4–30 Hz. During the polarisation period the ASR decreases (spectrum c and d) and the summit frequency does not change considerably. At the change back to OCV conditions (Figures 2E and 3E) the ASR increases (spectrum e and f) and the summit frequency decreases to about 1 Hz. There is apparently no difference between the anodically and cathodically polarised impure electrodes except that the ASR seems to be higher in cathodically polarised electrodes.

The spectra from the samples with pure electrodes (Figures 2 F-J and 3 F-J) show a trend at OCV opposite to the samples with impure electrodes. Initially (Figures 2H and 3H, spectra a and b) the polarisation resistance decreases from 50–180 Ωcm² to 20–60 Ωcm². There is no general trend for the behaviour of the summit frequency. It may decrease (from 50 to 6 Hz), increase (from 8 to 17 Hz) or stay the same. Upon anodic polarisation (Figure 2I, spectra c and d) the ASR decreases to below 1 Ωcm² for anodically polarised samples. The summit frequency increases to 100–200 Hz. At OCV after polarisation (Figure 2J) the polarisation resistance increases slightly (spectra e and f) and the summit frequency decreases to 70–80 Hz. Cathodic polarisation causes the ASR to decrease (Figure 3I, spectra c and d) to 7–12 Ωcm² and the summit frequency to increase. On the change back to OCV, contrary to the anodically polarised samples, the polarisation resistance decreases further (Figure 3J), resulting in ASRs between 1.5 and 3 Ωcm² and a summit frequency between 100 and 200 Hz.

It is clear that initially the interfacial region changes for both types of samples. This is due to the increasing contact area with time, consistent with the decrease in Rₛ (Figures 2-3A and F) and the migration of impurities to the interface and TPB.
Figure 2. Impedance spectra from the anodically polarised sample 112a with an impure electrode and from the anodically polarised sample 224a with a pure electrode. A and F show $R_s$ and B and G show $R_p$ versus time. A through F show the positions of the impedance spectra; C and H show impedance spectra at OCV; D and I show impedance spectra during polarisation; E and J show impedance spectra at OCV after the polarisation period had ended. The numbers in the spectra indicate frequencies.
Figure 3. Impedance spectra from the cathodically polarised sample 71c with an impure electrode (A-E) and from the cathodically polarised sample 241c with a pure electrode (F-J). A and F show $R_s$ and B and G show $R_p$ versus time. A through F show the positions of the impedance spectra; C and H show impedance spectra at OCV; D and I show impedance spectra during polarisation; E and J show impedance spectra at OCV after the polarisation period had ended. The numbers in the spectra indicate frequencies.
Figure 4 shows that on samples with impure electrodes an accumulation of impurities at the TPB results in a rim ridge 1–2 μm high and up to 3 μm wide (1). Apparently this restricts the electrochemical reactions, as seen from the increasing polarisation resistance found for samples with impure electrodes.

Figure 5 shows that impurity ridges were also observed on samples with pure electrodes (2). Samples with pure electrodes show a decreasing trend of polarisation resistance that can be ascribed to the increasing contact area and TPB length. The impurities may restrict the electrochemical reactions for those samples even though it is not obvious from the polarisation resistance trend.

Further investigation into the distribution of impurities in and around the contact area revealed not only the impurity ridges but also a film of impurities on the YSZ away from the contact area and a more or less covering impurity film between the Ni and YSZ (4). It is well known from the literature that SiO₂ and Na₂O segregate to the external surface (8, 9), and it is likely that this film may affect the water formation reaction occurring near the TPB (3). A blocking impurity phase at the nickel-YSZ interface is likely to be a serious factor in limiting electrode performance.

The decreasing R_p upon polarisation signifies a change in condition in the interfacial region. This is thought to be from a current-induced redistribution of the impurity phase.
From the impedance spectra the polarisation resistances were deduced, and by multiplying the area and the contact area boundary length, the area (ASR) and length-specific polarisation resistances (LSR) were calculated. A summary of the polarisation resistance data from (1) and (2) is given in Table 1.

**Table 1. ASR and LSR (1, 2) and Later Results.**

| Electrode              | ASR \( [\Omega \text{cm}^2] \) Impure nickel | Pure nickel | LSR \( [\Omega \text{cm}^2] \) Impure nickel | Pure nickel |
|------------------------|---------------------------------------------|-------------|---------------------------------------------|-------------|
| OCV                    | 24-135                                      | 10-35       | 4752-24150                                  | 1719-7189   |
| Anodically polarised   | 3-13                                        | 0.26-3.8    | 679-2447                                    | 62-657      |
| Cathodically polarised | 12-14                                       | 7-17        | 2479-2820                                   | 2169-4344   |

The LSR values at OCV are compared with literature data in Figure 6 for different electrodes. Some overlap exists between the pure and impure electrodes. The inset shows the detailed distribution of values. The pure electrodes cover a range of values up to 2 orders of magnitude larger than the impure electrodes in the log(LSR) versus 1000/T plot. The point electrode from Guindet et al. (10) is the only one that comes close to the pure electrodes from this study; the exact purity of their nickel ball electrode was not specifically mentioned, only that it was pure. The electrolyte was polycrystalline 10 mol% YSZ.

Extrapolating the lines for the data from de Boer (11), Bieberle (12), and Yamamura (13) we realised that the best pure electrodes are at least two orders of magnitude above that. Considering the presence of the rim ridge and other impurities and that the impurity phase is described as an alkali silicate glassy phase containing a multitude of elements (e.g., Na, K, Mn, Mg, Ti, Al) (3) (4), it is not surprising that the impurities are able to reduce the performance of the electrodes, especially when considering that impurities were found in all locations (4) where electrochemical reactions are supposed to occur.

Glassy impurity phases that have segregated to internal YSZ grain boundaries are known to contribute significantly to the total resistivity of the electrolyte material (14,15). Badwal (15) suggests that the oxygen ion transport across grain boundaries takes place only where the YSZ grains are in direct contact; impurity phases in YSZ appear to have low oxygen ion conductivity.

de Ridder et al. (9) probed the surface of 3 and 10 mol% YSZ samples by low energy ion scattering (LEIS). By a combination of annealing at 300°C and oxidation with atomic oxygen they achieved a clean YSZ surface before annealing at 300–1600°C for 5 hr in oxygen. The LEIS surface analysis revealed that below 900°C no impurities were detected on the surface, but at temperatures above 1000°C the surface was completely covered by Si, Na, and Ca. The impurities were restricted to one atomic layer. The bulk content of the impurities is stated to be less than 300 ppm. de Ridder et al. have found that the impurity layer practically prevents oxygen exchange at the surface, which is believed to be responsible for the bad performance of SOFC (9). Considering the results we obtained with the nickel/YSZ interface, this may be a one-sided explanation for the bad performance. The impurities migrating out of the YSZ are important, but the nickel contributes with impurities and the TPB zone is affected by the impurity phase. A similar problem with impurities may exist at the cathode/electrolyte interface with impurities from both the YSZ and the cathode material (16).
Figure 6. Log(LSR\(^{-1}\)) versus 1000/T. Data from this study are plotted with data from (11) and (12). Additional LSR values from Ni/YSZ anodes in the literature (17,13) have been included. pH\(_2\)-pH\(_2\)O values for the data are listed in Table 2. The inset shows the distribution of the points for pure and impure electrodes.

Table 2. pH\(_2\)-pH\(_2\)O Values for the Data Plotted in Figure 6.

| Reference                     | Electrode type | pH\(_2\) [atm] | pH\(_2\)O [atm] |
|-------------------------------|----------------|----------------|-----------------|
| Guindet et al. (13)           | Point          | 0.2            | 0.0027          |
| Norby et al. (17)             | Point          | 0.0012         | 0.006           |
| Mizusaki et al. (17)          | Pattern        | 0.01-0.05      | 0.012-0.0165    |
| Norby (13)                    | Point          | 0.1-1.0        | 0.0085          |
| Yamamura et al. (13)          | Pattern        | 0.01           | 0.0085          |
| de Boer (11)                  | Porous, Cermet| 0.905          | 0.021           |
| Bieberle (12)                 | Pattern        | 0.136          | 0.0005          |
| This work                     | Point          | 0.97           | 0.03            |

The cermet structure of real Ni-YSZ anodes is, of course, different from the simplified interface used in the present study.

Recent results on the effects of impurities in NiO on the microstructure of Ni/YSZ cermet-YSZ half cells reveal that anodes containing more e.g. SiO\(_2\) and Na\(_2\)O degrade faster than anodes with a lower content of impurities. The impurity phase segregates to and accumulates at the anode/electrolyte interface and this changes the microstructure by grain boundary corrosion (18).
CONCLUSIONS

The impurity content in the nickel influences the area and length specific polarisation resistance. For OCV samples, the log(LSR^1) vs. 1000/T graph showed a differentiation between the samples with impure and pure electrodes. The data for impure electrodes were consistent with most literature data. The pure electrodes were up to a factor of 100 better than the impure electrodes.

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