The effect of current density and temperature on the degradation of nickel cermet electrodes by carbon monoxide in solid oxide fuel cells

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1 Abstract

The oxidation of dry Carbon Monoxide (CO) in Intermediate Temperature Solid Oxide Fuel Cells (IT-SOFCs) has been studied using a three electrode assembly. Ni/CGO:CGO:LSCF/CGO three electrode pellet cells at 500, 550 and 600°C were exposed to dry carbon monoxide for fixed periods of time, at open circuit and under load at 50 and 100 mA cm⁻², in an aggressive test designed to accelerate electrode degradation. It is shown that if the anode is kept under load during exposure to dry CO, degradation in anode performance can be minimised, and that under most conditions the anode showed significant irreversible degradation in performance after subsequent load cycling on dry H₂. Only at 500°C and at 100 mA cm⁻² was the degradation in performance after operation on dry CO and subsequent load cycling on dry H₂ within the background degradation rates measured. Where anode performance was compromised, this appeared to be caused by a reduction in the exchange current density for hydrogen oxidation, and the relatively large degradation after load cycling on dry H₂ was primarily caused by an increase in the series resistance of the anode. It is suggested that this increase in series resistance is associated with the removal of carbon deposited in the non-electrochemically active region of the electrode during operation on dry CO, and that operation under load inhibits carbon deposition in the active region.

2 Introduction

Investigations of Ni cermet anodes operating on CO or CO/CO₂ mixtures have been reported by a number of authors (Mizusaki, Aoki et al. 1990; Eguchi, Setoguchi et al. 1993;

Mizusaki, Tagawa et al. 1994; Yoshida, Yamamoto et al. 1994; Aaberg, Tunold et al. 1996; Holtappels, De Haart et al. 1999; Matsuzaki, Hishinuma et al. 1999; Matsuzaki and Yasuda 2000; Lauvstad, Tunold et al. 2002; Weber, Sauer et al. 2002; Jiang and Virkar 2003; Gemmen and Trembly 2006; Sukeshini, Habibzadeh et al. 2006). However these have so far been limited to YSZ containing anodes, and temperatures of 700°C and above. Furthermore, thermodynamics predict that in both dry fuels and at temperatures of 600°C and below, which are of interest for IT-SOFC operation, carbon deposition is a significant problem. This requires dilution of carbon containing fuel streams with the products of oxidation, or oxygen.

The steam to carbon ratio is often used to predict the propensity of carbon deposition under such conditions, most often presented in the form of C-H-O diagrams as shown by Sasaki and Teraoka (2003). However, thermodynamic predictions are only applicable in ideal conditions, and in an operating fuel cell the reaction kinetics must also be considered. In addition it is also known that; maintaining a fuel cell at reasonable currents can have a protective effect by reducing carbon deposition in the electrochemically active region of the anode (Weber, Sauer et al. 2002; Gunji, Wen et al. 2004); and that novel anode materials can help prevent carbon deposition demonstrated by Brett, Atkinson et al. (2005); and even that some carbon deposition can be beneficial as suggested by Mallon and Kendall (2005). In this paper we explore further the effect of current on carbon deposition via the Boudouard reaction as shown in equation 1, expanding on work presented previously by Offer and Brandon (2008).

When conducting investigations into carbon monoxide oxidation at temperatures below 700°C it is very difficult to decouple effects caused by carbon deposition, and effects caused by changes in the electrochemical performance of the anode. A complete decoupling of these effects is not achieved in this paper, nor is a discussion of the mechanism of the carbon monoxide electrochemical oxidation reaction (COOR) at intermediate temperatures; instead an empirical comparison of fuel cell performance after subjection to aggressive testing in dry CO is presented and discussed. In further papers we will publish results for an SOFC using Ni/CGO anodes operating on CO/CO₂ mixtures at temperatures between 500 and 600°C, the use of ex-situ Raman spectroscopy, and comments on the mechanism of the COOR.

3 Experimental

Gadolinium doped ceria (CGO) pellets were prepared by pressing CGO (CGO-10, FuelCellMaterials, USA) powder at 1 Tonne pressure for 30 s, before firing at 1400°C for 3 hours at a ramp rate of 2°C min⁻¹. The pellets were polished to ensure uniform thickness (average 1mm) before nickel oxide cermet ink (50:50 NiO/CGO, FuelCellMaterials, USA) as the anode and

strontium cobalt doped lanthanum ferrite ink (50:50 $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ / CGO, FuelCellMaterials, USA) as the cathode were screen printed (error of $\pm 125\text{ }\mu\text{m}$ in the placement of electrode geometries) and fired sequentially at 1300°C and 1125°C respectively. The electrodes were approximately $20\text{ }\mu\text{m}$ thick as produced. The anode was a circular disk 11 mm in diameter with a surface area of 0.95 cm^2 and the cathode was an identical circular disk, surrounded by a ring with an internal diameter of 17 mm , and an external diameter of 19 mm . All data was collected using a three electrode configuration with the anode as the working electrode and a full description of the three electrode experimental apparatus and the correction procedure used to calculate the polarisation characteristics of the pellets is described in previous work by Offer, Shearing et al. (2008). This is necessary because there are limitations when using a reference electrode in a pellet cell configuration that under certain conditions can cause large errors (Winkler, Hendriksen et al. 1998; Adler, Henderson et al. 2000). In summary the correction procedure applied involves measuring the potential response at a series of current densities, and correcting for the uncompensated ohmic resistance (R_s) at that current density to calculate the overpotential, and build up an i - η curve. An example of this correction procedure is presented below. The cell was taken up to the operating temperature at a ramp rate of 2°C min^{-1} with the anode side exposed to a $2.5\%\text{ H}_2\text{O}$, $48.75\%\text{ N}_2$ / $48.75\%\text{ H}_2$ atmosphere. During testing the atmosphere was either dry $50\%\text{ N}_2$ / $50\%\text{ H}_2$ or dry $50\%\text{ N}_2$ / $50\%\text{ CO}$. For the electrochemical measurements, an Autolab PGSTAT302 (Eco Chemie BV, The Netherlands) with an FRA module was used. The electrochemical impedance spectroscopy (EIS) response was measured in the frequency range 0.01 Hz to 100 kHz with one point measured at each decade and a stimulus potential amplitude of 10 mV(rms) used throughout. Autolab NOVA 1.3 software was used to log and analyse the measurements. The EIS data was fitted with a standard electrochemical circuit incorporating a resistor (R_s), in series with a resistor (R_p) and a constant phase element in parallel.

In these experiments, the fuel cell anodes were maintained at a range of currents and temperatures and exposed to dry CO , the fuel utilisation was low ($<1\%$) such that the reaction products from the electrochemical reactions would not be expected to have a large effect (assuming thermodynamic equilibrium and no diffusion limitations within the anode). Therefore any differences are attributed to local effects caused by surface species, significant residence times of reaction products within the cermet electrodes, or inadequacies in assuming thermodynamic equilibrium within a cermet electrode.

The experimental procedure was as follows:

1. The cell was characterised under operation on wet H_2 overnight with a 40 point characterisation i - η curve with EIS at each point from 0 to 100 mA cm^{-2} .

2. The cell was characterised under operation on wet H₂ with a 5 point characterisation i-η curve with EIS at each point from 0 to 100 mA cm⁻². Comparison with the performance measured in step 1 at identical current densities enabled a background degradation rate to be estimated.
3. The cell was switched over to dry H₂ and purged for 2 hours.
4. The cell was characterised under operation on dry H₂ with a 5 point characterisation i-η curve with EIS at each point from 0 to 100 mA cm⁻².
5. The carbon monoxide experiment was performed, see below.
6. The cell was characterised under operation on dry H₂ with a 5 point characterisation i-η curve with EIS at each point from 0 to 100 mA cm⁻².
7. The fuel stream was switched to dry N₂ and the furnace allowed to cool to room temperature as quickly as possible without cracking the pellet.

The cells were exposed to carbon monoxide according to the following procedure:

- 5.a. The cell was polarised at the specified current on dry H₂.
- 5.b. The cell was held at this current for 1 hour, and the fuel stream was then switched over to dry CO.
- 5.c. During operation upon CO an EIS spectra was taken approximately every 10 minutes whilst maintaining the current.
- 5.d. After 1 hour the fuel stream was switched back to dry H₂ and the current maintained for a further 60 minutes whilst continuing to collect EIS spectra approximately every 10 minutes.

In order to assess the performance of the cells before and after carbon monoxide exposure an i-η curve with EIS at each point is needed (steps 4 and 6), however, for the experiments at zero current this will produce some water at the anode which may not be entirely removed during the hour equilibration step prior to the introduction of carbon monoxide.

In addition the nature of CGO as a mixed ionic/electronic conductor means there will always be some leakage current, and therefore in a H₂ atmosphere a small amount of water will always be present, which could effect the rate of carbon deposition.

The conditions studied here were at temperatures of 500 °C, 550 °C, and 600 °C and current densities of 0 mA cm⁻² (zero), 50 mA cm⁻² (low), and 100 mA cm⁻² (high).

3.1 Example correction procedure

The dataset before exposure to CO at 600 °C for the pellet exposed at 100 mA cm⁻² is arbitrarily selected here to demonstrate the importance of applying the correct procedure when calculating anode overpotentials from current potential curves obtained using pellet cells.

The data shown in 0 (a) is the potential between the anode and the reference electrode as a function of current density. In order to begin the correction procedure this must first be converted into overpotentials by subtracting the open circuit potential, as shown in 0 (b). It should be noted that the overpotential at this point is a function of the anode polarisation resistance, and some portion of the electrolyte resistance. Therefore, in order to subtract the uncompensated resistance between the working and reference electrodes it is normal to determine the series resistance (R_s) using impedance spectroscopy at open circuit, and to subtract this from the overpotentials using $V = IR$. This is acceptable if the series resistance between the working and reference electrodes does not change with current density. However, this is not true in the majority of pellet cell configurations used by SOFC investigators, and the errors that can be introduced by this effect can be considerable (Winkler, Hendriksen et al. 1998; Adler, Henderson et al. 2000). To mitigate this, it is possible to create a i - η curve by determining the R_s at multiple points using impedance spectroscopy at load, and then use the correct R_s values to compensate for the uncompensated resistance at that current and therefore current distribution. In this work we perform a 5 point characterisation measurement for the results presented. Figure 2 shows the anode overpotentials calculated using the single R_s value and the overpotentials calculated correctly using the different R_s values at load. The data presented in Figure 4 is the corrected data calculated using this procedure, and it is worth noting that if the correction procedure had not been applied the overpotentials of the anodes would have been overestimated by almost an order of magnitude, as shown in Figure 2.

The corrected results shown in Figure 4 are then fitted to the Butler-Volmer equation (equation 2) to extract the anode exchange current density and transfer coefficient.

4 Results

Images of the anodes investigated are shown in Figure 3. Features to note in Figure 3 are the different regions characterised by the presence or absence of a 1mm wide flow channel which was positioned horizontally across the pellets as depicted, and a central region where the fuel impinged upon the pellet. It is clear that the different regions of the pellet have experienced different operating conditions and have been affected in different ways. This is likely to have an effect upon the electrochemical performance of the different regions, and as such the electrochemical performance reported here is an average of these. Effects of this type should be avoided if at all possible, although it was not possible in the present work. However, it is worth

noting that these effects are likely to occur in a real operating fuel cell, and as such will be investigated further in a future study.

Figure 4 shows an analysis of the i - η performance of the anodes before and after exposure to dry CO, shown as a comparison of the exchange current density for hydrogen oxidation on the anodes.

Example chrono-amperometric data and EIS spectra for the experiments conducted at 500°C and 100 mA cm⁻² are shown in 0, and an analysis of the series resistance (R_s) and the low frequency polarisation resistance (R_p) from the EIS spectra for all the experiments shown in Figure 6.

Visually inspecting Figure 4 suggests that the electrochemical performance of the anodes is worse for those that were exposed to dry CO at the lowest current densities. The damage to the electrochemical performance of the anodes held at 100 mA cm⁻² appears to be minimised, and at 500°C the damage is negligible. The results shown in Figure 4 were fitted using the Butler-Volmer equation 2 below, and the results are presented in Table 1.

$$j = j_0 \left(\exp \left(\frac{\alpha F}{RT} \eta \right) - \exp \left(\frac{-(1-\alpha)F}{RT} \eta \right) \right) \quad \text{Equation 2}$$

Where j is the current density, j_0 is the exchange current density, T is the temperature, α is the transfer coefficient and η is the overpotential. R and F have their usual values of 8.314 J K⁻¹ mol⁻¹ and 96485 C mol⁻¹ respectively.

500°C	0 mA cm ⁻²		50 mA cm ⁻²		100 mA cm ⁻²		Average
	Before	After	Before	After	Before	After	Before
$j_0 / \text{A cm}^{-2}$	0.055	0.045	0.054	0.047	0.044	0.043	0.051
α	0.47	0.23	0.51	0.32	0.48	0.52	0.49
Variance j_0	27%	28%	5.00%	8.30%	25%	27%	n/a
Variance α	37%	38%	6.70%	11.50%	32%	33%	n/a
$R_{ct} / \Omega \text{ cm}^2$	1.15	1.42	1.17	1.35	1.44	1.48	1.25

550°C	0 mA cm ⁻²		50 mA cm ⁻²		100 mA cm ⁻²		Average
	Before	After	Before	After	Before	After	Before
$j_0 / \text{A cm}^{-2}$	0.118	0.033	0.244	0.124	0.082	0.073	0.148
α	0.5 *	0.5 *	0.5 *	0.5 *	0.5 *	0.5 *	0.5
Variance j_0	7.64%	8.54%	3.01%	2.08%	6.40%	4.00%	n/a
Variance α	n/a	n/a	n/a	n/a	n/a	n/a	n/a
$R_{ct} / \Omega \text{ cm}^2$	0.60	2.16	0.29	0.57	0.87	0.97	0.59

600°C	0 mA cm ⁻²		50 mA cm ⁻²		100 mA cm ⁻²		Average
	Before	After	Before	After	Before	After	Before
$j_0 / \text{A cm}^{-2}$	0.133	0.05	0.086	0.064	0.257	0.175	0.158
α	0.49	0.39	0.45	0.36	0.5 *	0.5 *	0.48
Variance j_0	24.50%	21.50%	14.60%	8.40%	1.80%	3.80%	n/a
Variance α	78.80%	29.50%	32.70%	20.20%	n/a	n/a	n/a
$R_{ct} / \Omega \text{ cm}^2$	0.57	1.5	0.87	1.18	0.29	0.43	0.47

Table 1. Table comparing the fits at 500, 550 and 600°C to the Butler-Volmer equation 2 using Origin 6.1 non-linear curve fitting function for the results shown in Figure 4, showing extracted electrode parameters for hydrogen oxidation before and after exposure to dry CO for one hour, at 0, 50, and 100 mA cm⁻². (* Where the error values for the transfer coefficient were too large, a value of 0.5 was assumed).

From Table 1 it is possible to state that, whilst there is some scatter in the electrochemical performance of the anodes before testing there is a clear improvement in the performance of the anodes as the temperature increases, with the exchange current density (j_0) increasing from an average of 51 mA cm⁻² at 500°C to 158 mA cm⁻² at 600°C. The transfer coefficient (α) did not appear to change, suggesting that the mechanism of the hydrogen oxidation reaction does not change across this temperature range, with values approaching 0.5. At times the scatter in the data did not permit the transfer coefficient value to be extracted and instead a value of 0.5 had to

be assumed. It should be noted that for anodes exposed to CO at 0 mA cm⁻² the subsequent characterisation of the anode may remove some of the deposited carbon, either by direct oxidation to CO₂ or CO, or via reforming reactions with product water. We suggest that this results in the performance of the anode decreasing over the timescale of the characterisation, resulting in a lower apparent transfer coefficient because of levelling off of the *i*- η curve over time. This also occurred for some results at load. This was unavoidable, and further discussion of the transfer coefficient is therefore avoided.

It was demonstrated that direct oxidation of deposited carbon to CO₂ or CO was possible by repeating an experiment and switching to dry N₂ after exposure to CO and then drawing current. Significant current densities were possible for many minutes with the initial performance approaching that on dry H₂ but with continuous irreversible degradation in performance which was not recoverable upon switching to dry or wet H₂. The anode had effectively become a carbon battery.

After testing it can be seen that the performance is worse for all the anodes except 100 mA cm⁻² at 500°C, with the exchange current density decreasing significantly. Statistical significance was taken to be outside the bounds of errors calculated using Origin 6.1, although the tests at 0 mA cm⁻² are discounted because of large errors caused by experimental noise. However, from Figure 4 it is clear that the performance is worse after exposure at OCP. Therefore the only anode for which the performance is not worse is the one which was maintained at 100 mA cm⁻² at 500°C.

For all anodes for which the exchange current density has been affected it is suggested that this is associated with a reduction in the number of percolated three phase boundaries. In this paper we suggest the most plausible explanation is that the deposition and subsequent removal of the carbon has caused stresses in the anode which are proportional to the destruction of the mechanical integrity (and concomitant electrical interconnectivity) of the anode. In addition it is possible that carbon deposits remaining on or in the anode have modified the nickel surface such that the surface diffusion of species involved in the hydrogen oxidation reaction are inhibited.

The charge transfer resistance R_{ct} can be estimated from the exchange current using equation 3.

$$R_{ct} = \frac{RT}{Fj_0} \quad \text{Equation 3}$$

The charge transfer resistance calculated using equation 3 for the nine anodes before and after dry CO exposure is also shown in Table 2. In order to assess the extent of degradation caused by the exposure to dry CO, the increase in charge transfer resistance for the anodes after testing is plotted in Figure 7.

It can be seen in Figure 7 that the performance of the anodes shows a clear trend in both temperature and current density during exposure, with the worst degradation occurring at open circuit. The only increase in charge transfer resistance which can be fully accounted for by the background degradation rate is that for the experiment conducted at 500°C and 100 mA cm⁻². The total time for the experiments was roughly 3½ hours and a charge transfer resistance background degradation rate of approximately 0.01 Ω cm² hour⁻¹ was calculated from repeats of the performance prior to exposure over 24 hours.

It can be seen that the effect of the CO upon the impedance spectra across the range of experiments appears to be complex and inconclusive. In addition, because of the leakage currents caused by the electronic conductivity of CGO in reducing atmospheres; which increase with increasing temperature above 500°C (Steele 1994; Inaba and Tagawa 1996; Wang, Kobayashi et al. 2000), it has been reported by Atkinson, Baron et al. (2004) that it is not possible to make quantitative interpretations of the spectra with confidence. A brief qualitative assessment of the data shown in Figure 6 is therefore made.

At 500°C there appear to be some clear trends. For all current densities the series resistance appears to be minimally affected by exposure to dry CO. However, for the experiments conducted at 0 and 50 mA cm⁻² there is a large increase in the series resistance after reverting back to operation on hydrogen. At 500°C it appears that operation on dry CO is characterised by an increase in the polarisation resistance of the anode during operation. The impact of current density appears to mitigate this effect, with increasing current density minimising the relative increase. At zero, low and high current the polarisation resistance decreases rapidly and exponentially upon switching the fuel stream back to hydrogen, although the increase only appears to be fully reversible at the higher current density.

At 550°C the series resistance behaves very differently at 0 mA cm⁻² compared to the experiment at 500°C, with a large increase during operation on dry CO, although the experiments at higher current densities appear to show similar behaviour with little increase. The polarisation resistance behaviour appears to be similar to the experiments at 500°C except for the experiment at 100 mA cm⁻² which does not seem to be consistent with any other results and may be anomalous.

At 600°C the behaviour of the series resistance appears broadly consistent with that at 550°C, with a large increase during operation at 0 mA cm⁻² and little increase at higher current densities. However the polarisation resistance behaviour at 0 mA cm⁻² at 600°C is inconsistent with that at the other two temperatures, although at higher current densities it is consistent. This may reflect the impact of the electronic conductivity of the CGO electrolyte, which increases with

temperature, but which is offset as current density increases as reported by Leah, Brandon et al. (2005).

It is clear that the impedance results confirm the problems with performing such measurements under reducing conditions using CGO as reported by Atkinson, Baron et al. (2004) and with non steady-state conditions, and the difficulties in interpretation therein. The use of more carefully defined conditions at open circuit (i.e. with a defined partial pressure of CO_2), faster electrochemical impedance analysers, and nickel CGO cermet anodes on YSZ pellets will be explored in future work, as although no firm conclusions could be made from the EIS here there is clearly the potential for future insight into CO reaction kinetics using this methodology.

It is noted that at open circuit potential (OCP) the nature of the reversible electrochemical couple is ill defined in dry CO with no CO_2 . However, the nature of the CGO electrolyte means that some leakage current exists even under conditions of no external load, such that it is likely that some CO_2 is formed. A stable OCP is therefore possible, although its relationship to the electrochemical species composition is not known. It should also be noted that this set of experiments was specifically chosen to investigate the effect of the formation of carbon by the Boudouard reaction and not to establish equilibrium conditions with a well defined $\text{CO}:\text{CO}_2$ couple, experiments of this type will be reported in a further paper.

To summarise, the results presented in this paper suggest that maintaining the anode at load during exposure to dry CO appears to mitigate the damaging effects of carbon deposition on the anode, with higher loads and lower temperatures offering the best protection against degradation. Although the R_p and R_s values are affected during operation it was not possible to fully interpret the EIS results. However, further work using multi-frequency impedance analysers should enable more reliable data to be obtained, shortening the data collection time and therefore minimising changes in the anode during the data collection period. It is suggested that it is not the carbon deposition but the removal of the carbon that causes the most damage, at least over the timescale of these experiments, and this irreversibly damages the electrochemical performance of the anode.

5 Discussion

Applying equilibrium calculations to reforming reactions may be straightforward (Sasaki and Teraoka 2003; Sasaki and Teraoka 2003) but is often misleading as reported by Walters, Dean et al. (2003), requiring the kinetics of the various reactions to be considered. However, as soon as the step is taken to include the kinetics a large number of reactions all occurring simultaneously must be considered. As described by Van Hook (1980), these reactions include hydrocarbon cracking, polymerization, steam reaction with surface carbon hydrogen residues, methanation, hydrocracking (hydrogenolysis), dehydrogenation, carbon monoxide disproportionation (Boudouard

reaction), water-gas shift, and even dehydrocyclization reactions. The most important aspect to consider is that all of these reactions are associated with a steady state concentration of carbon-hydrogen-oxygen residues on the catalyst surface. Some reactions are "carbon" producing and others are "carbon" removing reactions, and considerable attention must be given to the catalyst and operating variables in order to maintain an acceptable level of steady-state "carbon" on the catalyst. In the experiments conducted in this paper the choice of dry CO was made over CO/CO₂ mixtures in order to investigate the formation of carbon from a single reaction; the Boudouard reaction, under harsh conditions. The purpose was in part to establish a baseline for conditions that could represent an accelerated degradation test for SOFC anodes that need to be resistant to conditions where carbon formation is favoured. Therefore the only CO₂ present is produced by the electrochemical oxidation of CO or C, and the carbon formation inhibition or carbon removal effect of current density could therefore be investigated directly. This could also be achieved by providing a known CO/CO₂ mixture and monitoring changes in the oxygen content at different operating conditions. When using yttrium stabilised zirconia (YSZ) electrolyte such conditions give rise to unstable open circuit potentials (OCP), however when using gadolinium doped ceria (CGO) some CO₂ may be produced at open circuit because of the leakage currents arising from the mixed conductivity of CGO under reducing conditions and at elevated temperatures; hence a stable OCP is possible.

In order to test the electrochemical performance of the anodes under 'ideal' steady state and comparable conditions the pellets were tested on dry hydrogen before and after the exposure to CO. An unavoidable consequence of this is that a significant percentage of the carbon deposited within or on the anode will be removed by either direct electrochemical oxidation of the carbon, or removal via various reforming reactions. This means that steady state conditions cannot be guaranteed. However, once the carbon has been removed, steady state conditions should be achievable and for this reason the anodes were maintained at their specified current density for an hour after exposure to CO. This appeared to result in stable operation for all anodes except those held at OCP, where further degradation occurred during the characterisation procedure. Apart from the results at OCP, this was considered acceptable because the experiments accurately reflect the conditions that nickel anodes have to endure, both carbon formation and carbon removal reactions, although the carbon formation and removal reactions have been separated.

Previous experiments had demonstrated that exposure to dry CO at OCP was particularly detrimental to anode performance, and therefore the experiments had to be designed to ensure that anodes exposed at load were not exposed to CO at OCP. Hence it was necessary to switch from H₂ to CO and back again under load, with the unavoidable consequence of water being produced within the anode, such that residual H₂ and or H₂O may have an impact on the subsequent exposure to dry CO. Initially it was thought that this would reduce the amount of

damage, however the opposite was shown by Yoshida, Yamamoto et al. (1994) who studied the role of hydrogen in carbon deposition on Ni at 425 °C by determining the respective rates of the carbon formation reactions, the reverse water gas shift (WGS) reaction, equation 4, and the Boudouard reaction, equation 1.

The most interesting and relevant (for this work) conclusions were that equation 1, as expected, increased in proportion to the partial pressure of H_2 , however, equation 4 was catalysed by the addition of an extremely small amount of H_2 , such that the rate became about eight times that for pure CO but hardly varied as more H_2 was added. They interpreted their results in terms of a surface OH species proposed as an intermediate for both of the carbon forming reactions studied. In the second reaction, the presence of the OH species promotes the removal of carbon layers covering the catalyst, which exposes fresh active sites enabling further carbon deposition to occur. The background rate of carbon deposition was associated with the progressive separation of Ni particles from the surface. They noted that as the H_2 concentration increases, excess hydrogen can remove carbonaceous deposits to form methane and this must be considered at high H_2 partial pressures (>0.01 bar).

It is known that the WGS and the Boudouard reaction are both significant at the temperatures of operating SOFCs, and the temperatures studied in this paper, therefore it is not unreasonable to suspect that H_2 should have a similar effect on the Boudouard reaction in our experiments. Therefore, if this mechanism is also occurring at the temperatures studied in this paper, then we should see results that are worse under wet CO than dry CO.

In order to test this hypothesis the experiment at 50 mA cm⁻² and 550°C was repeated but in wet H_2 and CO (3% H_2O) rather than dry. The images of the two pellets are shown in Figure 8. It can clearly be seen that the amount of carbon deposited under wet conditions is far higher than dry, with significant delamination of the anode and visible carbon deposits. The electrochemical performance for the pellet exposed under wet conditions, as shown in 0 is also much worse with the exchange current density under wet CO changing from 193 mA cm⁻² to 44 mA cm⁻², corresponding to an increase in the R_{ct} of 1.25 Ω cm² compared to an increase of 0.28 Ω cm² under dry CO. This result is therefore consistent with the above mechanism.

Mallon and Kendall (2005) reported that the propensities of nickel cermet anodes towards carbon formation when operating on methane were very sensitive to the anode reduction conditions. Differences in performance when operating on methane were observed to be related to reduction temperature with better performance possible when reduction was commenced at low temperature (300 °C) compared to high temperature (850 °C). The explanation offered for this

behaviour was that, following a low temperature reduction the nickel particles are small and separated, with poor electronic conductivity. After operation under methane the carbon deposits form linkages between the particles improving the conductivity, and the nickel has a high surface area which is not readily blocked by carbon deposits. The explanation offered for the improvement in performance caused by an increase in conductivity by carbon deposits for the nickel seems reasonable, although to be conclusive this would need to be verified by an observed difference in particle size. However, it is not adequately explained why the differently reduced nickel anodes show different propensities towards the irreversible site blocking carbon deposited by methane. Nor is it adequately proved that there are two different types of carbon formation, although the data is suggestive.

In summary it is clear that the reduction method can influence the performance of a nickel cermet anode, and that under certain conditions some carbon deposition can be beneficial. However, the exact mechanism of these effects need further study in order to be independently verified. That low temperature reduction increases the triple phase boundary length could be verified by ex-situ analysis techniques (Wilson, Kobsiriphat et al. 2006; Shearing, Chater et al. 2008) using 3-D reconstruction from focused ion beam milling. However, equally plausible is that differences in the microstructure of the anode could influence the transport properties of the anode such that gas composition gradients within the anode occur under certain conditions, allowing some regions of the anode to be free of carbon deposition permitting stable performance. It is likely that the reduction procedure and the oxidation state and morphology of the nickel anodes will have an effect upon the effect of CO as well as methane, therefore the present study would benefit from such validation too. In these experiments the anodes were reduced by being taken up to the operating temperature at a ramp rate of $2^{\circ}\text{C min}^{-1}$ with the anode side exposed to a 2.5% H_2O , 48.75% N_2 / 48.75% H_2 atmosphere throughout. This was found to give the best and most reproducible results. However, the end point of the ramp rate was different for the different temperatures, and therefore differences in the oxidation state and morphology of the nickel anode at the different temperatures studied is likely and could explain the lack of observable trends in the EIS data. Further studies where the anodes were all taken up to the highest temperature and allowed to equilibrate before the operational temperature was selected would be needed to verify this.

6 Conclusion

In this paper we have shown that the effect of both temperature and current density upon carbon deposition from exposure to dry CO is significant. The results show that, under moderate current density, carbon formation does not appear to damage the electrochemical performance of the anode, at least over the timescale of one hour, until it is removed by switching back to

hydrogen, whereupon large changes can occur to the anodes resulting in irreversible damage to performance. It is demonstrated that, by operating at a current density of 100 mA cm^{-2} at 500°C , carbon formation can be minimised and that the anode can be protected from these otherwise harsh conditions, such that the anode performance before and after operating on dry CO for an hour can be maintained within the background degradation limits measured here. The operation of SOFC pellet cells on CO under conditions where carbon deposition is favourable can therefore irreversibly affect the performance of the anodes, indicating that any investigations into the CO oxidation reaction mechanism are also likely to be affected. It is therefore important to decouple these effects when investigating CO oxidation under conditions where carbon deposition is favourable. However, as long as the cell is maintained at reasonable current densities (100 mA cm^{-2} or above) then the damage does not affect the electrochemical performance of the cell, and investigations into the CO oxidation reaction mechanism in an intermediate temperature SOFC should be possible.

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8 References

- Aaberg, R. J., R. Tunold, et al. (1996). Oxidation of CO and H₂ on Ni/YSZ cermet electrodes. *High Temperature Electrochemistry: Ceramics and Metals*: 511-518.
- Adler, S. B., B. T. Henderson, et al. (2000). Reference electrode placement and seals in electrochemical oxygen generators. *Solid State Ionics* **134**(1-2): 35-42.
- Atkinson, A., S. A. Baron, et al. (2004). AC impedance spectra arising from mixed ionic electronic solid electrolytes. *Journal of the Electrochemical Society* **151**(5): E186-E193.
- Brett, D. J. L., A. Atkinson, et al. (2005). Methanol as a direct fuel in intermediate temperature (500-600 degrees C) solid oxide fuel cells with copper based anodes. *Chemical Engineering Science* **60**(21): 5649-5662.
- Eguchi, K., T. Setoguchi, et al. (1993). *Science and Technology of Zirconia*. S. P. S. Badwal, M. J. Bannister and R. H. J. Hannink. Basel, Technomic Publishing Co: 694-704.
- Gemmen, R. S. and J. Trembly (2006). On the mechanisms and behavior of coal syngas transport and reaction within the anode of a solid oxide fuel cell. *Journal of Power Sources* **161**(2): 1084-1095.
- Gunji, A., C. Wen, et al. (2004). Carbon deposition behaviour on Ni-ScSZ anodes for internal reforming solid oxide fuel cells. *Journal of Power Sources* **131**(1-2): 285-288.
- Holtappels, P., L. G. J. De Haart, et al. (1999). Reaction of CO/CO₂ gas mixtures on Ni-YSZ cermet electrodes. *Journal of Applied Electrochemistry* **29**(5): 561-568.
- Inaba, H. and H. Tagawa (1996). Ceria-based solid electrolytes - Review. *Solid State Ionics* **83**(1-2): 1-16.
- Jiang, Y. and A. V. Virkar (2003). Fuel composition and diluent effect on gas transport and performance of anode-supported SOFCs. *Journal of the Electrochemical Society* **150**(7): A942-A951.

- Lauvstad, G. O., R. Tunold, et al. (2002). Electrochemical oxidation of CO on Pt and Ni point electrodes in contact with an yttria-stabilized zirconia electrolyte - I. Modeling of steady-state and impedance behavior. *Journal of the Electrochemical Society* **149**(12): E497-E505.
- Leah, R. T., N. P. Brandon, et al. (2005). Modelling of cells, stacks and systems based around metal-supported planar IT-SOFC cells with CGO electrolytes operating at 500-600 degrees C. *Journal of Power Sources* **145**(2): 336-352.
- Mallon, C. and K. Kendall (2005). Sensitivity of nickel cermet anodes to reduction conditions. *Journal of Power Sources* **145**(2): 154-160.
- Matsuzaki, Y., M. Hishinuma, et al. (1999). Electrochemical characteristics of a Ni-YSZ cermet electrode on YSZ in a H-2-H2O-CO-CO2 system. *Solid Oxide Fuel Cells (Sofc Vi)* **99**(19): 560-567.
- Matsuzaki, Y. and I. Yasuda (2000). Electrochemical oxidation of H-2 and CO in a H-2-H2O-CO-CO2 system at the interface of a Ni-YSZ cermet electrode and YSZ electrolyte. *Journal of the Electrochemical Society* **147**(5): 1630-1635.
- Mizusaki, J., M. Aoki, et al. (1990). Response and Electrode-Reaction of Zirconia Sensors in Co-Co2 Gas Atmospheres. *Denki Kagaku* **58**(12): 1169-1177.
- Mizusaki, J., H. Tagawa, et al. (1994). Kinetics of the Electrode-Reaction at the H2-H2O Porous Pt Stabilized Zirconia Interface. *Journal of the Electrochemical Society* **141**(6): 1674-1683.
- Offer, G. J. and N. P. Brandon (2008). A Study of CO Oxidation in Intermediate Temperature SOFCs. *8th European SOFC Forum*. U. Bossel. Lucerne, Switzerland, SOFC Forum: A0405.
- Offer, G. J., P. Shearing, et al. (2008). Using electrochemical impedance spectroscopy to compensate for errors when measuring polarisation curves during three-electrode measurements of solid oxide fuel cell electrodes. *Electrochimica Acta* **53**(26): 7614-7621.
- Sasaki, K. and Y. Teraoka (2003). Equilibria in fuel cell gases - I. Equilibrium compositions and reforming conditions. *Journal of the Electrochemical Society* **150**(7): A878-A884.
- Sasaki, K. and Y. Teraoka (2003). Equilibria in fuel cell gases - II. The C-H-O ternary diagrams. *Journal of the Electrochemical Society* **150**(7): A885-A888.
- Shearing, P. R., R. J. Chater, et al. (2008). 3D Reconstruction of SOFC Electrodes using Focused Ion Beam Techniques. *8th European SOFC Forum*, Lucerne Switzerland.
- Steele, B. C. H. (1994). OXYGEN-TRANSPORT AND EXCHANGE IN OXIDE CERAMICS. *Journal of Power Sources* **49**(1-3): 1-14.
- Sukeshini, A. M., B. Habibzadeh, et al. (2006). Electrochemical oxidation of H-2, CO, and CO/H-2 mixtures on patterned Ni anodes on YSZ electrolytes. *Journal of the Electrochemical Society* **153**(4): A705-A715.
- Van Hook, J. P. (1980). Methane-Steam Reforming. *Catalysis Reviews* **21**(1): 1 - 51.
- Walters, K. M., A. M. Dean, et al. (2003). Homogeneous kinetics and equilibrium predictions of coking propensity in the anode channels of direct oxidation solid-oxide fuel cells using dry natural gas. *Journal of Power Sources* **123**(2): 182-189.
- Wang, S. R., T. Kobayashi, et al. (2000). Electrical and ionic conductivity of Gd-doped ceria. *Journal of the Electrochemical Society* **147**(10): 3606-3609.
- Weber, A., B. Sauer, et al. (2002). Oxidation of H-2, CO and methane in SOFCs with Ni/YSZ-cermet anodes. *Solid State Ionics* **152**: 543-550.
- Wilson, J. R., W. Kobsiriphat, et al. (2006). Three-dimensional reconstruction of a solid-oxide fuel-cell anode. *Nature Materials* **5**(7): 541-544.
- Winkler, J., P. V. Hendriksen, et al. (1998). Geometric requirements of solid electrolyte cells with a reference electrode. *Journal of the Electrochemical Society* **145**(4): 1184-1192.
- Yoshida, N., T. Yamamoto, et al. (1994). Effect of Hydrogen on Carbon Deposition from Carbon-Monoxide on Nickel-Catalyst. *Catalysis Letters* **23**(3-4): 237-243.

Figure 1. Graph showing the cyclic voltammogram (solid line) and 5 characterisation points (X) measured using chrono-amperometry for the pellet at 600 °C before exposure to CO at 100 mA cm⁻² (a), and the same data presented as overpotentials (b)

Figure 2. Graph showing the anode overpotentials for the cyclic voltammogram data (solid line) and 5 characterisation point data (X) incorrectly corrected using the single R_s measurement calculated from the EIS measurement at open circuit. The overpotentials for the 5 characterisation point data correctly corrected using the R_s measurements calculated from the EIS measurements at load are also shown (■).

Figure 3. Images of the nickel cermet electrodes after testing on carbon monoxide for 60 minutes at different temperatures and current

Figure 4. Graph showing the electrochemical performance for hydrogen oxidation of the anodes before and after exposure to dry CO for an hour at different current densities at 500, 550 and 600°C

Figure 5. Example chrono-amperometric data (a) and EIS spectra (b) taken during and after exposure to dry CO for 1 hour at 500°C and 100 mA cm⁻². Spectra were taken every 10 minutes and took approximately 3 minutes to collect with indicative dotted lines shown; time zero was the initial exposure to CO and at 60 minutes the fuel gas is switched back to H₂. Frequency used was from 100 mHz to 100 MHz.

(a) 500°C

(b) 500°C

(c) 550°C

(d) 550°C

(e) 600°C

(f) 600°C

Figure 6. Graphs showing the changes in series and polarisation resistances of the anodes at 500, 550, and 600°C and at 0 mA cm⁻² (○), 50 mA cm⁻² (Δ), and 100 mA cm⁻² (□). The cell was first exposed to CO at zero minutes and the dotted line at 60 minutes represents the time when the CO was switched back to H₂.

Figure 7. Graph showing the increase in charge transfer resistance versus current density during exposure for hydrogen oxidation of the anodes after exposure to dry CO for an hour at 500 (■), 550 (●), and 600°C (▲).

Figure 8. Images of the nickel cermet electrodes exposed to dry and wet CO for 1 hour at 550°C and 50 mA cm^{-2}

Figure 9. Graph showing the electrochemical performance for hydrogen oxidation of the anodes before and after exposure to dry and wet CO for an hour at 50 mA cm⁻² at 550°C