ELECTROCHEMICAL CHARACTERISTICS OF A Ni-YSZ CERMET ELECTRODE ON YSZ IN A H$_2$-H$_2$O-CO-CO$_2$ SYSTEM

Yoshio Matsuzaki, Masakazu Hishinuma and Isamu Yasuda
Fundamental Technology Research Laboratory
Tokyo Gas Co. Ltd.
1-16-25 Shibaura, Minato-ku, Tokyo, 105-0023 Japan

ABSTRACT

The electrochemical reaction in a H$_2$-H$_2$O-CO-CO$_2$ system at the interface of a porous Ni-YSZ cermet electrode and YSZ electrolyte has been studied using complex impedance spectroscopy and direct-current polarization measurements at 1023 and 1273 K under a constant oxygen partial pressure. The polarization resistance in a H$_2$-H$_2$O-CO-CO$_2$ system increased when the CO concentration, P(CO)/(P(H$_2$)+P(CO)), exceeded specific levels of 0.2 and 0.5 at 1023 and 1273 K, respectively. The electrochemical oxidation rate of H$_2$ was found to be 1.9-2.3 times and 2.3-3.1 times higher than that of CO at 1023 and 1273 K, respectively, and the shift reaction was found to be much faster than the electrode reaction at both temperatures.

INTRODUCTION

Because of the high operating temperature of solid oxide fuel cells (SOFCs), a wide variety of fuels, including natural gas, are expected to be used in SOFCs with high fuel-to-electricity conversion efficiencies. To estimate the performance of the SOFCs operated with natural gas fuel, it is necessary to clarify the electrochemical properties of a cermet electrode in a gas mixture of H$_2$, H$_2$O, CO and CO$_2$ produced by steam reforming of CH$_4$ which is the main component in natural gas.

If the electrochemical oxidation rate of CO differs from H$_2$, the concentration ratio of CO to H$_2$ in the downstream of fuel flow will be different from the ratio in the reformed CH$_4$ when the SOFC is operated at a high fuel utilization. Mizusaki et al. (1) reported that Pt electrodes in CO-CO$_2$ have higher polarization resistance than in H$_2$-H$_2$O. For the cermet electrodes of a mixture of nickel and yttria stabilized zirconia, Ni-YSZ, Eguchi et al. (2) found no differences in the polarization resistance in CO-CO$_2$ and H$_2$-H$_2$O systems, which is in contrast to Aaberg et al. (3) who observed 2-3 times higher polarization resistance in a CO-CO$_2$ system than in a H$_2$-H$_2$O system.
It should be noted that the electrode kinetics of SOFC anode is largely dependent on oxygen partial pressure, $P(O_2)$ \((1,4)\). However, there has been no previous study in which the influence of $P(O_2)$ was separated to discuss the difference in the electrochemical oxidation rate of CO and H\textsubscript{2}. Therefore we studied the electrochemical oxidation of CO and H\textsubscript{2} on the Ni-YSZ cermet electrode under a constant $P(O_2)$. The effect of the CO concentration in a H\textsubscript{2}-H\textsubscript{2}O-CO-CO\textsubscript{2} system on electrochemical properties of the electrode and the shift reaction rate compared with that of electrochemical reactions are discussed.

**EXPERIMENTAL**

**Test Cell Preparation**

Dense pellets (20 mm in diameter and 2 mm in thickness) of 8 mol% YSZ were used as the electrolytes of electrochemical cells. NiO powder with an average grain size of 0.9 \(\mu\)m (Nihon-Kagaku-Sangyo) was dispersed in a mixed toluene solution of zirconium octylate (\(Zr(C_4H_9CH(C_2H_5)CO_2)\), Nihon-Kagaku-Sangyo) and yttrium octylate (\(Y(C_4H_9CH(C_2H_5)CO_2)\), Nihon-Kagaku-Sangyo), and then screen-printed onto one side of the electrolyte pellet before firing at 1723 K for 2 hrs to prepare a porous Ni-YSZ cermet electrode. The YSZ content in the cermet electrode was 10 wt\%. The thickness and porosity of the electrode were about 25 \(\mu\)m and 45 \%, respectively. For a counter electrode, Pt paste (Tokuriki Kagaku 8103) was painted symmetrically to the Ni-YSZ cermet electrode on the other side of the pellet and fired at 1273 K for 2 hrs. For a reference electrode, the Pt paste was painted at the perimeter of the pellet and fired at 1273 K for 2 hrs.

**Electrochemical Measurements**

Figure 1 shows the test geometry used in the electrochemical measurements. Two Sr-doped LaCrO\textsubscript{3} plates with grooves were used as both manifolds and current collectors. Air and a fuel were fed into the doped LaCrO\textsubscript{3} plates from the top and bottom of a furnace, respectively. Air was supplied to the reference and counter electrodes, and the fuel was supplied to the Ni-YSZ cermet electrode. Platinum wires were used as voltage terminals for the working and reference electrodes. An equilibrium $P(O_2)$ in the fuel was checked by measuring OCV between these electrodes.

The fuel gas compositions used in this study are listed in Table 1. The equilibrium $P(O_2)$ in F1 to F6 at 1023 K was $10^{20.75}$ atm which was equal to the equilibrium $P(O_2)$ in CH\textsubscript{4}-H\textsubscript{2}O at steam/carbon ratio (S/C) of 2. The equilibrium $P(O_2)$ in F7 to F12 at 1273 K was $10^{15.68}$ atm which was also equal to the equilibrium $P(O_2)$ of CH\textsubscript{4}-H\textsubscript{2}O (S/C=2). F1 and F7 were mixed gases only of H\textsubscript{2} and H\textsubscript{2}O. F5 and F11 were mixed gases only of CO and CO\textsubscript{2}. F2 to F4 were mixed gases of F1 and F5, and F8 to F10 were mixed gases of F7 and F11. Of these, F2 and F8 had the equilibrium compositions of reformed CH\textsubscript{4} at S/C=2 at 1023 and 1273 K, respectively. The equilibrium compositions of F6 and F12.
both consisting only of CO and H2O, were corresponding to F4 and F10, respectively.

The complex impedance measurements were made over the frequency of 1 mHz-100 kHz with an applied amplitude of 10 mV using the three-terminal method. The system for the impedance measurements was composed of a frequency response analyzer (Solartron 1260), a potentiostat (Solartron 1287) and a personal computer (Compac Armada 1120T). Steady-state polarization was measured by a current interruption method using a current-pulse generator (Hokuto Denko HC-110).

RESULTS AND DISCUSSION

Complex Impedance Analysis

Figure 2 (a) and (b) show the complex impedance spectra measured at 1023 K using the fuels F1 to F5 and the spectra measured at 1273 K using the fuels F7 to F11, respectively. It is found that the size of the impedance arcs increased significantly when the CO concentration, $C(\text{CO})$, defined by

$$ C(\text{CO}) = \frac{P(\text{CO})}{[P(\text{H}_2) + P(\text{CO})]} \quad [1] $$

exceeded specific levels of 0.2 and 0.5 at 1023 and 1273 K, respectively, where $P(\text{CO})$ and $P(\text{H}_2)$ are CO and H2 partial pressures. At 1023 K, the impedance spectra measured in a H2-H2O gas mixture of F1 and in a H2-H2O-CO-CO2 gas mixture of F2 with a reformed CH4 composition were almost identical. The spectra in F7 and F8 at 1273 K also showed a close correspondence. These results indicate that the electrode kinetics of the Ni-YSZ cermet electrode in reformed CH4 is almost equal to that in a H2-H2O system under the same $P(\text{O}_2)$, which is in line with the work of Kawada et al. (5-7) who reported that the oxidation of hydrogen is the main electrode reaction on the Ni-YSZ cermet electrode in a CH4-H2O system when S/C is higher than unity. The impedance arcs appeared in a CO-CO2 system of F5 and F12, however, these were much larger than the arcs in a H2-H2O system, which indicates that the Ni-YSZ cermet electrode in a CO-CO2 system has higher polarization resistance than in a H2-H2O system under the same $P(\text{O}_2)$, and the electrochemical oxidation rate of CO on the electrode is lower than that of H2.

Steady-State Polarization

The steady-state current density measured in a H2-H2O-CO-CO2 system at a constant overvoltage is shown in Fig. 3 as a function of the CO concentration; (a) and (b) show the results at 1023 and 1273 K. It can be seen that the current densities decreased largely when the values of $C(\text{CO})$ exceeded 0.2 and 0.5 at 1023 and 1273 K, respectively, and reached minimums in the fuels containing no H2 (F5 and F11). In F2 and F8, the current densities are almost equal to those in F1 and F7, respectively. These results agree well with the results in the polarization resistance evaluated by the complex impedance analysis.
In order to compare the electrochemical oxidation rate of CO at the interface of the Ni-YSZ cermet electrode and the YSZ electrolyte with that of H₂, the ratios of the current density in H₂-H₂O and CO-CO₂ systems are plotted in Fig. 4 as a function of the electrode overvoltage. Since the current density is proportional to the rate of electrochemical reaction, the vertical axis shows the ratio of the electrochemical oxidation rate of CO to H₂. The ratio was found to be more than 1.9 and 2.3 at 1023 and 1273 K, respectively, and increased with the overvoltage. The overvoltage dependence of the electrochemical reaction rate ratio is larger at 1273 K than at 1023 K.

Shift Reaction

The electrode kinetics for the reformed CH₄ was found to be equivalent for H₂-H₂O as already shown in Figs. 2 and 3. Due to the difference in the electrochemical oxidation rate of CO and H₂, however, there is a possibility that when the SOFC is operated at a high fuel utilization the value of C(CO) in the downstream of the fuel shifts to a CO-rich direction resulting in increased polarization resistance. In such a case, the concentration of H₂O produced by the electrochemical oxidation of H₂ should also increase, which will prevent the increase of C(CO) if the shift reaction given in the following equation proceeds fast enough.

\[
\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2
\]  

In order to evaluate the effect of the shift reaction on the electrochemical property of the electrode, the complex impedance spectrum was measured in a CO-H₂O system and compared to that measured in the corresponding equilibrium composition. Figure 5 (a) and (b) are the results at 1023 and 1273 K. The spectrum in a CO-H₂O system and in the corresponding equilibrium composition showed no difference at both temperatures. When no shift reaction takes place, C(CO) in a CO-H₂O system is 1, which should give larger arcs in the impedance spectrum in a CO-H₂O system than in the corresponding equilibrium composition. The identical impedance spectra therefore suggest that the rate of the shift reaction is much higher than that of the electrochemical reaction and that even when the SOFC is operated at a high fuel utilization the shift reaction will prevent the increase of the C(CO) and the polarization resistance in the downstream of fuel flow. This may be one of the important factors for our successful operation of a 1.7 kW module at high fuel utilization (~70%) with direct internal reforming of CH₄ (8).

CONCLUSIONS

The electrochemical oxidation rate of H₂ at the interface of a porous Ni-YSZ cermet electrode and YSZ electrolyte has been found to be 1.9-2.3 times and 2.3-3.1 times higher than that of CO at 1023 K and 1273 K, respectively, under a constant P(O₂). The complex impedance semi-circle in a H₂-H₂O-CO-CO₂ system was found to expand when the CO concentration, P(CO)/(P(H₂)+P(CO)), exceeded specific levels of 0.2 and 0.5 at 1023 and 1273 K, respectively. The steady-state d.c. current density under a constant
overvoltage also significantly decreased when the CO concentration exceeded these levels. The complex impedance and the steady-state polarization characteristics of the electrode in the reformed CH$_4$ showed a good correspondence with those in a H$_2$-H$_2$O system, and the shift reaction was found to be faster than the electrode reaction, from which it can be concluded that the electrode performance in the reformed CH$_4$ will be equivalent to that in a H$_2$-H$_2$O system even at high fuel utilizations.

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Table I. Gas compositions used as fuel.

| Temperature (K) | Fuel No. | H₂ (%) | H₂O (%) | CO (%) | CO₂ (%) | \( P(\text{CO}) + P(\text{H}_2) \) in equilibrium | \( \log(P(O_2)/\text{atm}) \) | Note |
|-----------------|----------|--------|---------|--------|---------|-----------------------------------------------|------------------|------|
| 1023 | F1 | 80.0 | 20.0 | 0 | 0 | 0 | -20.75 | - |
| | F2 | 64.2 | 16.0 | 14.9 | 4.9 | 0.19 | -20.75 | - |
| | F3 | 38.8 | 9.7 | 38.8 | 12.6 | 0.50 | -20.75 | Equilibrium composition of \( \text{CH}_4-\text{H}_2\text{O}, \text{S/C}=2 \), at 1023 K |
| | F4 | 18.8 | 4.7 | 57.8 | 18.8 | 0.75 | -20.75 | Equilibrium composition of Fuel [8] at 1023 K |
| | F5 | 0 | 0 | 75.5 | 24.5 | 1 | -20.75 | - |
| | F6 | 0 | 23.5 | 76.5 | 0 | 1 | -20.75 | - |
| 1273 | F7 | 78.5 | 21.5 | 0 | 0 | 0 | -15.69 | - |
| | F8 | 62.8 | 17.2 | 17.2 | 2.8 | 0.21 | -15.69 | Equilibrium composition of \( \text{CH}_4-\text{H}_2\text{O}, \text{S/C}=2 \), at 1023 K |
| | F9 | 41.0 | 11.2 | 41.0 | 6.8 | 0.50 | -15.69 | - |
| | F10 | 12.0 | 3.3 | 72.8 | 12.0 | 0.86 | -15.69 | Equilibrium composition of Fuel [12] at 1273 K |
| | F11 | 0 | 0 | 85.9 | 14.1 | 1 | -15.69 | - |
| | F12 | 0 | 15.3 | 84.7 | 0 | 1 | -15.69 | - |

Fig. 1. Test geometry used in the electrochemical measurements. A: working electrode, B: reference electrode (Pt), C: counter electrode (Pt), D: YSZ pellet, E: Pt mesh for current collection, F: Sr-doped \( \text{LaCrO}_3 \) plate for current collection and manifold, G: \( \text{Al}_2\text{O}_3 \) plate for manifold, H: Gasket (Pt), I: glass seal and J: push-rod.
Fig. 2. The frequency dispersion diagram of the complex impedance spectra of the electrode.
(a) in the fuels F1 to F5 at 1023 K.
(b) in the fuels F7 to F11 at 1273 K.

Fig. 3. Dependence of anodic current on CO concentration under constant electrode polarization.
(a) at 1023 K, (b) at 1273 K.
Fig. 4. Ratio of the electrochemical oxidation rate of H₂ and CO as a function of electrode polarization.

Fig. 5. A complex impedance spectrum in a CO-H₂O system compared with a spectrum in the corresponding equilibrium composition. (a) at 1023 K, (b) at 1273 K.
INTERNAL REFORMING OVER NICKEL/ZIRCONIA ANODES IN SOFCs: INFLUENCE OF ANODE FORMULATION, PRE-TREATMENT AND OPERATING CONDITIONS

Caine M. Finnerty, Robert H. Cunningham and R. Mark Ormerod
Birchall Centre for Inorganic Chemistry and Materials Science, Department of Chemistry, Keele University, Staffordshire, ST5 5BG, United Kingdom

ABSTRACT

Internal methane reforming over nickel/zirconia cermet anodes has been studied in detail using a thin-walled extruded zirconia tubular SOFC reactor. The influence of anode formulation, anode pre-treatment, operating temperature and methane/steam ratio on the reforming characteristics, resistance to carbon deposition and durability have been investigated under actual operating conditions. Post-reaction temperature programmed oxidation (TPO) has been used to determine the amount of carbon deposition and its strength of interaction with the anode. A 90 vol% nickel/zirconia anode shows higher activity than a 50 vol% Ni anode at higher reforming temperatures, and shows very good durability. Pre-reducing the anodes in H₂ at 1173 K leads to a more active reforming catalyst. Carbon is removed from the anodes in two processes during temperature programmed oxidation, suggesting two types of carbon species. As the reforming temperature increases there is an increase in the temperature of both carbon removal processes, and an increase in the population of the higher temperature state.

INTRODUCTION

Natural gas is the most relevant fuel for SOFCs, and it is generally accepted that for SOFCs to be cost effective direct or indirect internal reforming of natural gas is essential, since this both increases efficiency through chemical recuperation of waste heat into the fuel supply and simplifies the balance of plant (1-3). However, there are several major problems associated with internal fuel reforming, in particular the problem of coking of the anode at the high operating temperatures (3), and sintering, leaching and delamination of the anode material, which all contribute to a loss of cell performance and poor durability.

There is therefore much interest in developing and evaluating optimised anode formulations for internally reforming SOFCs, and studying the influence of anode pre-treatment and process operating conditions. Such studies require a suitable test system to allow the reforming catalysis and surface chemistry to be investigated and the performance and durability of the fuel cell to be evaluated. The anode is invariably
nickel-based and can be considered to be analogous, in some respects, to supported nickel methane steam reforming catalysts, where the formation of carbon deposits on the catalysts continues to attract much interest (4-8).

In this paper we report the results of an extensive study of internal reforming over nickel/zirconia cermet anodes, investigating the influence of anode pre-treatment, steam/methane ratio and operating temperature. The work has been performed on the SOFC test system, based on a small diameter, thin-walled extruded yttria-stabilised zirconia tubular reactor, which we have developed (9-11), which can readily be used to study the internal reforming catalysis and surface chemistry in SOFCs, including in particular the problems of carbon deposition on the anode and poor durability, as well as the electrical performance of the SOFC (10-16). Hence different anode formulations and pre-treatment procedures can be readily evaluated over a range of operating conditions. Briefly the system permits steady-state internal reforming to be studied in the actual SOFC under operating conditions and the chemistry occurring on the anode surface to be investigated using temperature programmed spectroscopy. These have been used to study the anode reduction characteristics and to obtain detailed information about the methane activation process, methane steam reforming, the nature and quantity of carbon deposition on the anode and the kinetics of carbon removal.

EXPERIMENTAL

All the experiments described in this paper were carried out using the SOFC test system developed in our laboratory (9-11). Briefly the apparatus consists of a custom-built furnace operated by a temperature controller which allows linear temperature control up to 1373 K. The test cell inlet is linked to a stainless-steel gas manifold which allows complete flexibility in gas handling, gas composition, the choice of fuel and fuel/steam ratio. The gas feed can be instantly switched between gases using a 4-way sampling valve. Thus evaluation is possible over a full range of operating conditions and fuel compositions. The reactor outlet is linked via a heated gas sampling system to a continuously sampling on-line mass spectrometer (Leda-Mass Satellite) which permits the fuel processing reactions in the actual SOFC to be continuously monitored under operating conditions, and allows the surface chemistry occurring at the anode surface to be investigated using temperature programmed spectroscopy. A particular advantage of the tubular SOFC design is that it can be heated in the furnace and used in the same way as a conventional catalytic reactor. As zirconia is a good thermal insulator the ends of the electrolyte tube which project beyond the outer walls of the furnace remain sufficiently cool for a gas tight seal to be made, even when the inside of the furnace is at temperatures as high as 1373 K.

The anodes used in this work were prepared by physically mixing nickel oxide (Alfa Chemicals) with 8 mol% yttria-stabilised zirconia (Unitec FYT11). A mixture of methanol, 1,1,1-trichloroethane and glycerol trioleate was added as a solvent and the resultant slurry was milled for three hours, with a small quantity of poly-vinyl butyrol added at the end of the milling period as a binding agent. The anode slurry was coated onto the inside of the fired zirconia electrolyte tube prior to a second firing, as in an actual SOFC. Following drying in air at room temperature, the coated zirconia tubes were...
fired in air to 1573 K. Two nickel oxide/zirconia cermet anodes were prepared for
detailed study, a 50 vol% NiO/zirconia anode and a 90 vol% NiO/zirconia anode.

Following firing the tubular SOFC was sealed into the SOFC test system. Pre­
reduction of the anode was carried out in the test system at 1173 K for 30 minutes in a
10% H2/He stream. Methane steam reforming was carried out by passing the
methane/steam mixture over the fired and pre-reduced anode at reaction temperature.
Water was added by passing a methane/helium gas mixture through a water saturator; the
methane/steam ratio was adjusted by changing the methane flow rate. Post-reaction
temperature programmed oxidation (TPO) was used to characterise the nature and
amount of carbon deposited following each reforming experiment. TPO measurements
were carried out using a heating rate of 10 K min⁻¹ in a 10% O₂/He mixture.

RESULTS

Anode reduction characteristics

Temperature programmed reduction was used to study the reduction characteristics
of the anode samples. The 50 vol% NiO/zirconia anode shows a reduction maximum at
738 K, whilst the 90 vol% NiO/zirconia anode has a maximum rate of reduction at 665
K. This compared to a reduction temperature of 673 K for a simple 1:5 physical mixture
of NiO and zirconia, whilst two peaks at 815 K and 894 K are observed for reduction of a
10% NiO/zirconia sample prepared by wet impregnation of an aqueous solution of nickel
(II) nitrate.

Influence of methane steam reforming temperature

The influence of operating temperature on the methane steam reforming activity and
carbon deposition were studied by passing a 5:1 methane/steam mixture over each anode,
which had been pre-reduced in H₂ at 1173 K, at reaction temperatures of 1023 K, 1073
K, 1123 K and 1173 K; these temperatures covering the most likely operating
temperature range of zirconia-based SOFCs. These results are summarised in Table I.

Table I. Methane conversion over 50 vol% and 90 vol% nickel cermet anodes as a
function of reforming temperature (methane/steam ratio = 5:1).

| Reforming Temperature/K | % Methane Conversion |
|------------------------|---------------------|
|                        | 50 vol% Ni/zirconia | 90 vol% Ni/zirconia |
| 1023                   | 31.6                | 31.1                |
| 1073                   | 34.0                | 35.5                |
| 1123                   | 34.5                | 39.9                |
| 1173                   | 40.9                | 49.2                |

The most noticeable differences occur at the higher reforming temperatures, where
the 90 vol% Ni/zirconia cermet shows higher methane conversion; at lower reforming
temperatures both anodes show very similar activity. Under these conditions both anodes show very little degradation with time, indeed the 90 vol% anode shows a small increase in methane conversion over one hour at 1123 K and 1173 K, suggesting steady-state has not yet been reached. The methane conversion over both anodes during reforming for one hour at 1173 K is shown in figure 1.

![Figure 1](image.png)

**Figure 1.** Methane conversion over 50 vol% and 90 vol% nickel/zirconia cermet anodes at 1173 K in a 5:1 methane/steam mixture.

There are also noticeable differences in the product selectivities between the two anodes; the $\text{H}_2/\text{CO}$ ratio and the selectivity towards CO were determined for each experiment. Table II shows the CO selectivity for both anodes over the temperature range 1023 K to 1173 K for the 5:1 methane/steam reforming mixture.

**Table II.** CO selectivity over 50 vol% and 90 vol% nickel cermet anodes as a function of reforming temperature (methane/steam ratio = 5:1).

| Reforming Temperature/K | CO selectivity / % |
|-------------------------|--------------------|
|                         | 50 vol% Ni/zirconia | 90 vol% Ni/zirconia |
| 1023                    | 95.4               | 96.7               |
| 1073                    | 96.2               | 97.6               |
| 1123                    | 97.3               | 98.2               |
| 1173                    | 98.1               | 98.8               |
Both anodes show very high CO selectivity, and water conversion, under these conditions. However, it can be seen that the CO selectivity is always higher on the 90 vol% nickel cermet; the H2/CO ratio is also always higher for this anode. The CO selectivity of both anodes increases with reforming temperature.

TPO measurements were carried out after each reforming experiment to determine the quantity of carbon deposited, as well as the strength of interaction of the carbon with the anode. Under these conditions both anodes showed a minimum in carbon deposition at a reforming temperature of 1073 K, with no carbon deposition detected on the 90 vol% Ni anode. Overall, carbon deposition is similar on both anodes, though at all temperatures less carbon deposition occurs on the 90 vol% Ni anode. The nature of the carbon deposited also changes with reaction conditions (temperature, methane/steam ratio). Figure 2 shows the TPO spectra following steam reforming in a 5:1 methane/steam mixture for 60 minutes over the 50 vol% Ni anode at 1123 K and 1173 K.

![Figure 2. Temperature programmed oxidation of carbon deposited on a 50 vol% nickel cermet following methane steam reforming for 60 minutes in a 5:1 methane/steam mixture at 1123 K and 1173 K.](image)

The significantly increased carbon deposition at 1173 K compared to 1123 K can readily be seen. At both reaction temperatures the carbon is removed in two processes. The carbon deposited at the lower reforming temperature of 1123 K is removed at 876 K and 927 K, whilst the carbon deposited during reforming at 1173 K is removed at 903 K and 950 K. In addition to the carbon being removed at higher temperatures following reforming at 1173 K, indicating greater stability, the higher temperature carbon species predominates.

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Following reforming at 1173 K on the 90 vol% Ni anode, carbon is again removed in two stages, the CO₂ desorbing principally in a peak at 927 K, with a small low temperature shoulder at 895 K, whilst at 1123 K, two CO₂ desorption peaks are observed at 870 K and 902 K. Thus, for the same experimental conditions, although both anodes show similar carbon removal temperatures, carbon is removed at lower temperature on the 90 vol% Ni anode, and the higher temperature form of carbon is relatively more prevalent.

**Influence of methane/steam ratio**

The influence of methane/steam ratio on the methane reforming characteristics of the two anodes, in particular the carbon deposition, was studied. Methane/steam ratios ranging from 5:1 to 15:1 were studied at a reaction temperature of 1173 K. Table III summarises the methane conversion over both anodes after 30 minutes reforming at 1173 K.

Table III. Influence of methane/steam ratio on methane conversion over 50 vol% and 90 vol% nickel cermet anodes during reforming at 1173 K.

| Methane/steam ratio | % Methane Conversion |
|---------------------|----------------------|
|                     | 50 vol% Ni/zirconia | 90 vol% Ni/zirconia |
| 5                   | 38.0                 | 45.0                 |
| 7.5                 | 23.6                 | 24.9                 |
| 10                  | 22.1                 | 21.8                 |
| 15                  | 21.5                 | 14.1                 |

A clear correlation between methane conversion and the methane/steam ratio can be seen, with activity decreasing with decreasing water content. The decrease in activity over the 90 vol% Ni cermet is considerably more marked than that over the 50 vol% Ni cermet. At the highest methane/steam ratio of 15:1 the initial methane conversion over both anodes is similar, ~25%. There is then a small loss of activity over both anodes over the first 10 minutes, slightly more so over the 90 vol% anode. However, thereafter there is no further decrease in activity over the 50 vol% Ni anode, whereas the activity continues to decrease over the 90 vol% anode, indicating that deactivation is rapidly occurring.

The nature of the carbon deposited and the relative amounts of the two carbon species present alter as the methane/steam ratio is increased. At low methane/steam ratios only the low temperature species is present. As the methane/steam ratio is increased the higher temperature species is also formed, and at the highest methane/steam ratio this is the only carbon species formed, being removed at 950 K from both anodes.

**Influence of reforming time**

TPO measurements carried out following different reforming times suggest that the low temperature carbon species can be aged or transformed into the higher temperature
species with increased reforming time (17). Similar behaviour has been observed for supported nickel steam reforming catalysts (18,19).

Extended reforming experiments were carried out at 1123 K and 1173 K using a methane/steam ratio of 5:1. Under these conditions the 90 vol% Ni anode shows excellent stability with only a very small decrease in methane conversion over a 48 hour period. In contrast the 50 vol% anode shows an initial substantial decrease in activity and is observed to cycle varying considerably with time, suggesting anode deactivation and regeneration is occurring. This is supported by the variation in water conversion and H2/CO ratio which follow and mirror the methane conversion, respectively.

Post-reaction TPO reveals only one carbon species, removed at 927 K from the 90 vol% Ni cermet and at 940 K from the 50 vol% Ni cermet, indicating that after a certain reaction time only one form of carbon exists. Under these reforming conditions ten times less carbon is deposited on the 90 vol% Ni cermet than on the 50 vol% anode. Thus the 90 vol% anode is both more stable towards steam reforming and has a higher resistance to carbon deposition under these conditions.

**Influence of pre-reduction of the anode**

A series of experiments were carried out to investigate the effect of running the anode directly in the methane/steam fuel mix without pre-reducing the anode in H2. Experiments showed that pre-reducing the anodes isothermally at 1173 K rather than by temperature programmed reduction, resulted in very significantly reduced carbon deposition. These experiments were carried out at 1173 K using a methane/steam ratio of 5:1. After initially very high methane conversion corresponding to reduction of the nickel oxide, steady-state steam reforming is observed. Under these conditions conversions of 41.9 % and 33.0 % were observed over the 90 vol% and 50 vol% Ni anodes, respectively, compared to 49.2 % and 40.9 % conversions on the same anodes following pre-reduction in H2 at 1173 K. Thus at lower methane/steam ratios, pre-reducing the anode produces a more active reforming catalyst. Interestingly, following reforming over the unreduced anodes at 1173 K in a 5:1 methane/steam mixture, ten times more carbon is deposited on the 50 vol% Ni anode than on the 90 vol% Ni anode, whereas the amount of carbon deposition is only slightly less on the pre-reduced 90 vol% anode. The major difference is on the 90 vol% Ni anode where six times less carbon is deposited on the unreduced anode, whereas slightly more carbon is deposited on the unreduced 50 vol% Ni anode, compared to the pre-reduced anode. In both cases the carbon deposited on the unreduced anodes is removed at lower temperatures than on the pre-reduced anodes. Again both carbon species are observed, with the higher temperature state dominating.

**SUMMARY**

The methane reforming characteristics of two different nickel/zirconia cermet anodes, with 50 vol% Ni and 90 vol% Ni, have been studied over the temperature range 1023 K to 1173 K, and a range of methane/steam ratios. The 90 vol% anode shows higher activity than the 50 vol% anode at higher reforming temperatures, whereas both
anodes show very similar activity at lower reforming temperatures. As expected the activity increases significantly with increased reforming temperature.

Carbon is removed from the anodes in two processes, suggesting two types of carbon species. As the reforming temperature is increased carbon deposition increases, with an increase in the temperature of both carbon removal processes and an increase in the population of the higher temperature state.

As the methane/steam ratio is increased the reforming activity decreases, with a much more significant drop in activity occurring over the 90 vol% anode. At higher methane/steam ratios only the high temperature carbon species is formed. Following extended reforming the higher temperature state is also the only carbon species formed, suggesting that the lower temperature carbon species can be aged or transformed into the higher temperature species with increasing reforming time. In all cases carbon is removed at lower temperature from the 90 vol% anode than from the 50 vol% anode.

Comparison of anodes pre-reduced in H₂ and non pre-reduced anodes shows that the nature of anode pre-treatment is very important. Although steady-state reforming occurs over unreduced anodes, pre-reducing the anode leads to a more active reforming catalyst. However, significantly less carbon deposition occurs over the non pre-reduced 90 vol% Ni anode.

In summary it can be concluded that the factors influencing methane conversion and carbon deposition are complex, and that the precise operating conditions, in terms of temperature and fuel/steam ratio, have a very significant bearing on the optimum choice of anode formulation and anode pre-treatment.

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