

# Internal reforming over nickel/zirconia anodes in SOFCs operating on methane: influence of anode formulation, pre-treatment and operating conditions

Caine M. Finnerty, R. Mark Ormerod \*

*Birchall Centre for Inorganic Chemistry and Materials Science, Department of Chemistry, Keele University, Staffordshire, ST5 5BG, UK*

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## 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 of the anode have been investigated under actual operating conditions. Post-reaction 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 H<sub>2</sub> at 1173 K leads to a more active reforming catalyst. Carbon is removed from the anodes in two processes during TPO, suggesting two types of carbon species. As the reforming temperature increases both carbon types are removed at higher temperature, and there is an increase in the relative population of the more strongly bound form of carbon. © 2000 Elsevier Science S.A. All rights reserved.

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## 1. Introduction

Natural gas is the most appropriate fuel for SOFCs; 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, lead to deactivation of the anode, 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 [4–6].

Study of internal reforming over nickel/zirconia cermet anodes, investigating the influence of anode pre-treatment, steam/methane ratio and operating temperature, as well as the durability of the anode in terms of reforming activity and carbon deposition is now reported. The work has been performed on an SOFC test system, based on a small diameter, thin-walled extruded yttria-stabilised zirconia tubular reactor, which has developed [7–9]. This system can be used to study the internal reforming catalysis and surface chemistry in SOFCs, including the problems of carbon deposition on the anode and poor durability, as well as the electrical performance of the SOFC [8–14]. Hence, different anode formulations and pre-treatment procedures can be readily evaluated over a range of relevant operating

\* Corresponding author. Fax: +44-1782-712378.

*E-mail address:* r.m.ormerod@keele.ac.uk (R.M. Ormerod).

conditions. The system permits internal reforming to be studied in an SOFC under actual operating conditions and the chemistry occurring on the anode surface to be investigated using temperature-programmed spectroscopy. This has 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, which occurs on the anode during steam reforming and the kinetics of carbon removal.

## 2. Experimental

All experiments were carried out using the SOFC test system developed in this laboratory [7–9]. The apparatus consists of a custom-built furnace operated by a temperature controller enabling 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. Thus, evaluation is possible over a full range of operating conditions and fuel compositions. The reactor outlet is directly linked 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 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 electrolyte inside the furnace is at elevated temperatures.

The anodes 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 3 h, with a small quantity of polyvinyl 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 production SOFC. Following drying in air at room temperature, the coated zirconia tubes were fired in air to 1573 K, according to a specific firing regime, and held at 1573 K for 1 h. Two nickel oxide/zirconia cermet anodes were prepared for detailed study; a 50-vol.% NiO/zirconia anode and a 90-vol.% NiO/zirconia anode. These were chosen to type by the two extremes of composition likely to be of interest. Both anodes have been characterised by XRD, BET, SEM and particle size analyses.

Following firing, the tubular SOFC was sealed into the test system. Pre-reduction of the anode was carried out in

the test system at 1173 K in flowing hydrogen for 30 min. Methane steam reforming was carried out by passing a methane/steam mixture over the fired, and generally 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 TPO was used to determine the amount of carbon deposited following each reforming experiment and the strength of its interaction with the anode. TPO measurements were carried out using a heating rate of 10 K min<sup>-1</sup> in a 10% O<sub>2</sub>/He mixture.

## 3. Results

### 3.1. Influence of 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 pre-reduced anodes at temperatures of 1023 K, 1073 K, 1123 K and 1173 K; these temperatures cover the realistic operating temperature range of zirconia-based SOFCs. These results are summarised in Table 1.

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 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 of reforming at 1123 K and 1173 K, suggesting steady-state had not been reached. The methane conversion over both anodes during reforming for 1 h at 1173 K is shown in Fig. 1. Both anodes show very high CO selectivity and water conversion under these conditions. CO selectivity is always higher on the 90-vol.% nickel cermet; the H<sub>2</sub>/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. At this methane/steam ratio both anodes showed a minimum in carbon deposition at a reforming

Table 1  
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

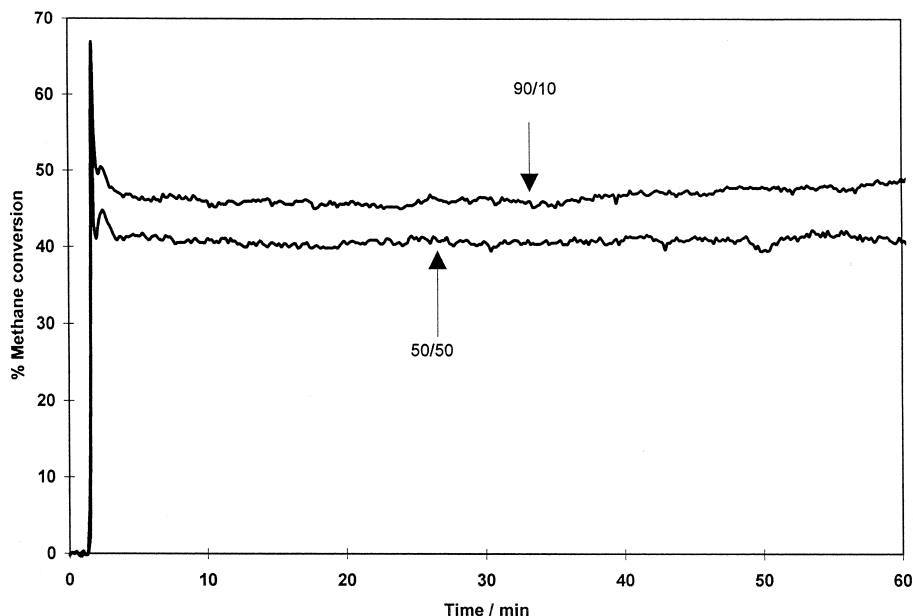


Fig. 1. Methane conversion over 50 vol.% and 90 vol.% nickel/zirconia cermet anodes at 1173 K in a 5:1 methane/steam mixture.

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, or the anode structure itself, also changes with changing reaction conditions of temperature and methane/steam ratio. Fig. 2 shows the TPO spectra following steam reforming for one hour over the 50-vol.% Ni anode at 1123 K and 1173 K in a 5:1 methane/steam mixture. The significantly increased car-

bon deposition at 1173 K compared to 1123 K can readily be seen. At both reaction temperatures, the carbon is removed in two processes. In addition to the carbon being removed at higher temperatures following reforming at 1173 K, indicating greater stability, the higher temperature carbon species predominates.

Following reforming at 1173 K on the 90-vol.% Ni anode, carbon is again removed in two stages, the  $\text{CO}_2$  desorbing principally in a peak at 927 K, with a small low temperature shoulder at 895 K, while at 1123 K, two  $\text{CO}_2$

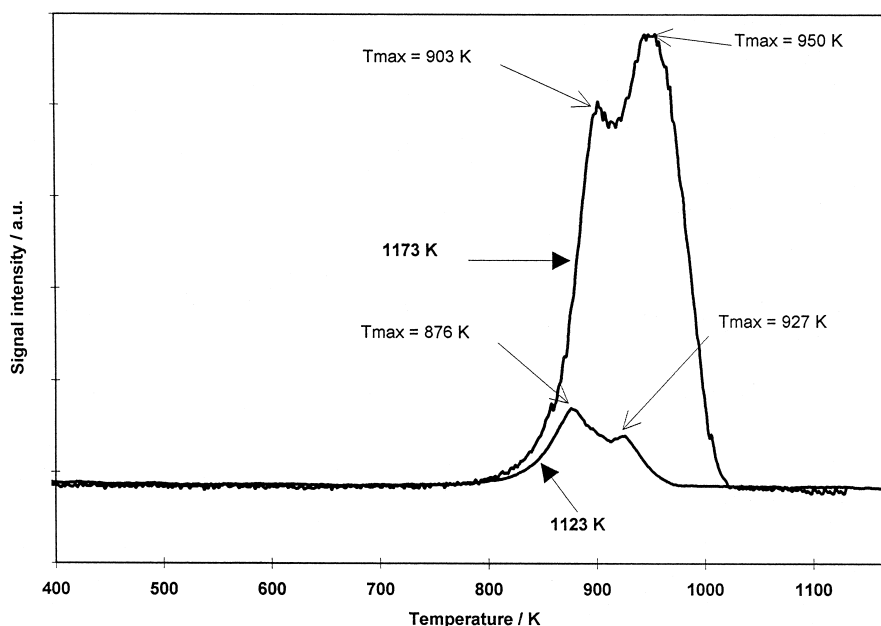


Fig. 2. Temperature-programmed oxidation of carbon deposited on a 50-vol.% nickel cermet following methane steam reforming for 60 min in a 5:1 methane/steam mixture at 1123 K and 1173 K.

desorption peaks are observed at 870 K and 902 K. Although both anodes show similar carbon removal temperatures, for the same experimental conditions, carbon is removed at lower temperature from the 90-vol.% Ni anode, but the higher temperature form of carbon is relatively more prevalent on this anode.

### 3.2. Influence of methane / steam ratio

The influence of methane/steam ratio on the reforming characteristics of the two anodes, and 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 2 summarises the methane conversion over both anodes after 30 min reforming at 1173 K.

A clear correlation between methane conversion and the methane/steam ratio can be observed, with activity decreasing with decreasing water content. The decrease in activity over the 90-vol.% Ni cermet is considerably more marked than over the 50-vol.% Ni cermet. At the highest methane/steam ratio of 15:1, the initial methane conversion over both anodes is similar at approximately 25%. There is, then, a small loss of activity being both anodes over the first 10 min, 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, or the anode structure, 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.

### 3.3. Influence of pre-reduction of the anode

The effect of operating the anode directly in the methane/steam fuel mix without pre-reducing the anode in  $H_2$  was investigated. Experiments showed that pre-reducing the anodes isothermally at 1173 K for 30 min,

rather than by temperature-programmed reduction to 1173 K, resulted in very significantly reduced carbon deposition. Reforming was carried out at 1173 K using a methane/steam ratio of 5:1. After initially very high methane conversion, which resulted in reduction of the nickel oxide, steady-state steam reforming was 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% conversion on the same anodes following pre-reduction in  $H_2$  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, 10 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 occurs for the 90-vol.% Ni anode where six times less carbon is deposited on the unreduced anode, compared to that on the pre-reduced anode. The carbon deposited on both 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.

### 3.4. Extended reforming experiments and 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 [15]. Similar behaviour has been observed for supported nickel steam reforming catalysts [16,17].

Extended reforming experiments were carried out at 1123 K and 1173 K using a methane rich fuel feed (methane/steam ratio = 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-h period. In contrast, the 50-vol.% anode shows a considerable cyclic variation in the methane conversion with time, after an initial significant decrease in activity, suggesting that anode deactivation and subsequent regeneration is occurring. This is supported by the variation in water conversion and  $H_2/CO$  ratio, which follow and mirror the methane conversion, respectively.

Post-reaction TPO reveals only one carbon species, removed at 927 K and 940 K from the 90-vol.% and 50-vol.% Ni cermets, respectively, 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, under these reforming conditions, the 90-vol.% anode is both more stable towards steam reforming and has a higher resistance to carbon deposition.

Table 2  
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

#### 4. Summary

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

Carbon is removed from the anodes in two processes, suggesting two distinct types of carbon species or a change in the anode structure. 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 relative 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 higher 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, or in more carbon rich fuel feeds. 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 H<sub>2</sub> and non pre-reduced anodes shows that the nature of anode pre-treatment has a very significant effect. 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 com-

plex, 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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