INTERNAL REFORMING AND ELECTROCHEMICAL PERFORMANCE STUDIES OF DOPED NICKEL/ZIRCONIA ANODES IN SOFCs RUNNING ON METHANE

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ABSTRACT

The effects of doping nickel/zirconia cermet anodes with small quantities of molybdenum and gold on the steam reforming characteristics of the anode and the SOFC performance have been studied over the temperature range 1023 K to 1173 K, and a range of methane/steam ratios. Temperature programmed reduction (TPR) has been used to study the anode reduction characteristics and post-reaction temperature programmed oxidation (TPO) has been used to determine the level of carbon deposition and its strength of interaction with the anode. Both gold and molybdenum-doped anodes are shown to offer significantly increased resistance to carbon deposition, increased methane conversion and improved durability, particularly at lower reforming temperatures, and lower, more realistic, methane/steam ratios.

INTRODUCTION

In order for SOFCs to be economic, internal reforming of natural gas is considered essential, since this increases efficiency and simplifies the balance of plant (1-3). There is therefore much interest in developing improved anode formulations for internally reforming SOFCs. One of the major operational problems associated with internal reforming in SOFCs is that of carbon deposits formed on the anode, which leads to deactivation, and a loss of cell performance and poor durability (1,3). The deposition of carbon on the fuel reforming anode in SOFCs running on natural gas is thus an important area requiring further study. The anode is generally nickel-based and can be thought of as being somewhat analogous to supported nickel methane steam reforming catalysts where the carbon deposition on the catalyst has been extensively studied (4-6). It is well known that the rate of carbon formation on nickel steam reforming catalysts can be reduced by the introduction of additives to the catalysts. Traditionally potassium in the form of potash is added, which serves both to accelerate the reaction of carbon with steam and to neutralise the acidity of the alumina support, and hence reduce carbon deposition (7,8). Recent work has identified molybdenum (9-11) and gold (12,13) as also having promotional effects in terms of reducing carbon deposition, even at extremely low levels.
In this paper we report briefly the results of a detailed study of the effects of doping nickel/zirconia cermet anodes with small quantities of molybdenum and gold on the steam reforming characteristics of the anode, and in particular the problems of carbon deposition on the anode and poor durability, as well as the effects on the electrical performance of the SOFC. The study has been carried out using the SOFC test system which we have developed, which uses a tubular zirconia SOFC (14-16), and is ideally suited to studying internal reforming in SOFCs, as well as the performance of the SOFC (15-19). Different anode formulations can readily be evaluated over a range of relevant operating conditions. In addition to studying the reforming activity of the anode in the SOFC under operating conditions, temperature programmed spectroscopy has been used to study the anode reduction characteristics, and the nature and quantity of carbon deposition on the anode. This paper briefly summarises some of our findings, the results will be described in detail elsewhere (20,21).

EXPERIMENTAL

All the experiments described in this paper were carried out using the SOFC test system developed in our laboratory (14-16). Briefly the apparatus consists of a 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. Thus evaluation is possible over a full range of operating conditions and fuel compositions. The test cell outlet is linked via a heated quartz capillary 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 inside of the furnace is at temperatures as high as 1373 K.

The anodes used in this work were prepared by adding a physical mixture of nickel oxide (Alfa Chemicals) and 8 mol% yttria-stabilised zirconia (Unitec FYT11) to a solvent. The resultant slurry was milled for three hours, with a small quantity of binding agent added at the end of the milling period. Molybdenum was added as molybdenum trioxide at levels of 1 wt% and 5 wt% prior to milling. The anode slurry was coated onto the inside of the fired zirconia electrolyte tube prior to a second firing. Following drying in air at room temperature, the coated zirconia tubes were fired to two different temperatures, 1273 K and 1573 K. The lower firing temperature was also studied as molybdenum oxide is known to be highly mobile at elevated temperatures, and thus the loading following firing at 1573 K was only a fraction of the initial loading. Gold was added as finely dispersed gold powder at a level of 1 wt% prior to milling. Following application to the zirconia electrolyte the anodes were fired at 1573 K. Two nickel loadings were used in the anodes, corresponding to 50 vol% NiO and 90 vol% NiO. For cell performance measurements strontium-doped lanthanum...
manganite (Seattle Speciality Chemicals) was used as the cathode, and was applied to the outside of the zirconia electrolyte as an ink. Following drying in air the cells were fired to 1573 K using the same procedure as for the anode. Nickel wire was used to collect current from the anode, whilst silver wire wound round the cathode was used for current collection from the cathode.

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. Steam reforming was carried out by passing the methane/steam mixture over the fired and pre-reduced anodes at reaction temperature. Water was added by passing a methane/helium gas mixture through a water saturator. 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 AND DISCUSSION

Anode reduction characteristics

Temperature programmed reduction was used to study the reduction characteristics of the molybdenum and gold-doped anodes. 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. Addition of 1 wt% molybdenum leads to an increase in the reduction temperature of the nickel oxide, whilst at higher loadings a second higher temperature reduction peak is observed which can be attributed to the reduction of molybdenum oxide. Addition of 1 wt% gold also leads to an increased reduction temperature, though the effect is less marked than for molybdenum.

Methane reforming activity and carbon deposition

5:1 methane/steam mixtures were passed over pre-reduced 1 wt% Mo-doped and the standard undoped 50 vol% Ni/zirconia anodes. It was found that the 1 wt% Mo-doped anode gave increased methane conversion over the entire temperature range studied, 1023 K - 1173 K. For the 90 vol% Ni anodes, similar increased reforming activity was observed for the 1 wt% Mo-doped anodes at the lower temperatures studied, though there was much less of an effect at higher reforming temperatures. At the higher 5 wt% Mo loading deactivation is observed, suggesting that at higher levels molybdenum actually inhibits reforming, probably by blocking active sites on the nickel surface.

Doping the 90 vol% nickel/zirconia anode with 1 wt% gold leads to increased steady-state methane conversion, particularly at lower reforming temperatures and higher methane/steam ratios, with a significant increase in the H₂/CO ratio relative to the undoped 90 vol% nickel anode, as well as in the CO selectivity, at lower reforming temperatures, suggesting that the presence of gold causes an enhancement in the relative rate of the Water Gas Shift reaction at lower reforming temperatures. The amount of carbon deposited on the gold doped anode during reforming is actually
substantially higher than on the undoped 90 vol% Ni anode under equivalent conditions. Given the appreciably higher methane conversion, this suggests that the carbon deposited on the gold doped anode is much less detrimental to its reforming activity, suggesting that the carbon is not in a deactivating form.

The influence of molybdenum on carbon deposition is complex. Addition of 1 wt% Mo to the 50 vol% nickel cermet leads to a decrease in carbon deposition at lower reforming temperatures but increased carbon deposition at higher reforming temperatures, though it should be noted that under these conditions increased methane conversion is nevertheless occurring. Following firing at 1573 K the 1 wt% Mo doped 90 vol% nickel cermet shows no carbon deposition at all at reforming temperatures below 1173 K, and shows substantially less carbon deposition following reforming at 1173 K than the undoped 90 vol% nickel cermet.

TPO measurements also provide an insight into the strength of interaction of the carbon with the anode. On the standard undoped 50 vol% and 90 vol% Ni anodes, the carbon is removed from the anode in distinct processes, around 900 K. The temperature of both carbon removal peaks increases with increasing reforming temperature and increasing methane/steam ratio, whilst the relative amount removed in the higher temperature process increases with increasing reforming temperature, with increased methane/steam ratio and with increased reforming times. Although both anodes show similar carbon removal temperatures, carbon deposited under the same reforming conditions is removed at lower temperature from the 90 vol% Ni anode. Carbon is still removed in these same two processes from the Mo-doped anodes following reforming, suggesting the existence of the same two carbon species as on the standard nickel anodes. However, the addition of molybdenum leads to a reduction in the thermal stability of these two species. In addition, on the Mo-doped 90 vol% anode formation of the lower temperature carbon species is favoured even at the highest reforming temperature studied, 1173 K, in marked contrast to the undoped 90 vol% Ni anode. This is shown in figures 1 and 2 which show TPO spectra from the undoped 90 vol% Ni anode and the 1 wt% Mo-doped 90 vol% Ni anode following reforming at 1173 K in a 5:1 methane/steam ratio for 60 minutes.

![Figure 1](image-url)

**Figure 1.** Temperature programmed oxidation of carbon deposited on a 90 vol% nickel cermet following reforming for 60 minutes in a 5:1 methane/steam mixture at 1173 K.
On the 1 wt% molybdenum doped 90 vol% Ni cermet which had been fired to 1273 K, the higher temperature carbon species becomes the more favoured, and is more thermally stable than when the anode was fired to 1573 K. Increased carbon deposition is observed, together with a decrease in the methane conversion. These observations are consistent with our proposal that increased carbon deposition and loss of catalytic activity are mainly due to formation of the higher temperature carbon species.

Doping the 90 vol% Ni anode with 1 wt% gold has little effect on the thermal stability of the carbon species formed compared to the undoped cermet. However, the formation of the higher temperature carbon species is almost totally inhibited at reforming temperatures below 1173 K, which taken with the appreciably higher reforming activity of the gold doped anodes at lower temperatures is again consistent with the higher temperature carbon form being the more detrimental in terms of catalyst deactivation. Following reforming at 1173 K the higher temperature carbon species becomes dominant, and a large increase in carbon deposition is observed. The substantially higher methane conversion observed on the gold doped anode at higher methane/steam ratios is also consistent with the gold dopant increasing activity and reducing deactivation by limiting carbon deposition at the active sites, in agreement with recent work on gold doped supported nickel steam reforming catalysts (12,13).

Even under reforming conditions which are known to promote carbon deposition both the molybdenum and gold doped nickel anodes have higher methane conversions, again suggesting it is not actually the amount of carbon deposited that causes initial deactivation but the nature of the deposited carbon.

Extended reforming over 48 hours showed that the molybdenum-doped anodes were more stable in terms of methane conversion, undergoing a much smaller decrease...
in activity than the undoped nickel cermet. Over 48 hours, the methane conversion over the undoped 50 vol% and 90 vol% Ni cermet fell by 7% and 2%, respectively, whereas only a 1% decrease was observed for the 1 wt% and 5 wt% Mo-doped Ni anodes, whilst the 1 wt% Mo-doped 50 vol% Ni anode showed significantly increased durability compared to the undoped 50 vol% Ni anode. The gold doped 90 vol% Ni cermet proved to be the most durable anode with no decrease in activity after 48 hours reforming. Thus addition of small levels of either gold or molybdenum to the nickel/zirconia cermet leads to increased durability of the anode, in terms of methane conversion.

Post-reaction TPO measurements indicated that there was only the higher temperature form of carbon present on the anode after 48 hours reforming, indicating that neither the molybdenum or the gold actually stops the formation of this higher temperature state, but that their presence can slow its formation. This is shown in Table I, which shows the amount of carbon deposited on each anode following reforming for 48 hours at 1123 K, at a methane/steam ratio of 5:1, and clearly shows that both the molybdenum and gold dopants very substantially reduce long term carbon deposition, with the most dramatic effect being seen for the 1 wt% molybdenum-doped 90 vol% nickel cermet, which reduces carbon deposition by more than a factor of thirty over the 48 hours, whilst at the same time providing increased methane conversion. Although carbon is not as significantly reduced on the gold-doped 90 vol% Ni anode, the methane conversion is almost 20% higher over this anode, which suggests that the increased deposition relative to the molybdenum doped 90 vol% anodes has no detrimental effect on the catalytic activity.

Table I. Amount of carbon deposited on different nickel/zirconia anodes fired at 1573 K, during reforming for 48 hours at 1123 K (methane/steam ratio = 5:1).

| Anode                | Quantity of carbon deposited / μmoles mg⁻¹ |
|----------------------|-------------------------------------------|
| 50 vol% Ni           | 935.0                                     |
| 90 vol% Ni           | 87.6                                      |
| 1 wt% Mo-doped 50 vol% Ni | 66.6                                    |
| 1 wt% Mo-doped 90 vol% Ni | 2.9                                      |
| 5 wt% Mo-doped 90 vol% Ni | 15.4                                     |
| 1 wt% Au-doped 90 vol% Ni | 43.3                                     |

Molybdenum-doped nickel cermet fired at 1273 K were found to be more active than those fired at 1573 K if the anode was not pre-reduced in H₂ prior to reforming. The 1 wt% Mo-doped 50 vol%, 1 wt% Mo-doped 90 vol% and 5 wt% Mo-doped 90 vol% nickel cermet gave methane conversions of 47.3%, 53.1% and 68.1%, respectively, and gave a much smaller decrease in activity over time. The activity of the 5 wt% Mo-doped anode is the highest for any anode that we have observed under our experimental conditions. The increased activity is thought to be due to the formation of some form of active molybdenum carbide, through using methane rather than H₂ as the reductant. Previous work has shown that molybdenum carbides are very active for methane conversion (9). Again there is an observed correlation between increased
formation of the high temperature carbon species and increased carbon deposition and loss of reforming activity, again consistent with this carbon species being the more detrimental; anodes which favour formation of the lower temperature carbon species give higher methane conversion and a greater resistance to carbon deposition.

**Electrical Performance**

The electrical performance of tubular SOFCs containing the standard nickel/zirconia cermet anodes and the molybdenum and gold doped anodes, running on a 5:1 methane/steam mixture, was measured. The respective current densities at an applied potential of 0.7 V are tabulated in Table II.

Table II. Current densities of SOFCs containing different nickel/zirconia anodes operating on a 5:1 methane/steam mixture at 1173 K (anodes fired at 1573 K and pre-reduced in H₂ at 1173 K unless stated).

| Anode                      | Current density at 0.7 V / mA cm² |
|----------------------------|----------------------------------|
| 50 vol% Ni                 | 171                              |
| 90 vol% Ni                 | 171                              |
| 1 wt% Mo-doped 50 vol% Ni  | 154                              |
| 1 wt% Mo-doped 90 vol% Ni  | 171                              |
| 5 wt% Mo-doped 90 vol% Ni  | 233                              |
| 5 wt% Mo 90 vol% Ni (fired at 1273 K) | 220          |
| 5 wt% Mo-doped 90 vol% Ni (unreduced) | 346          |
| 1 wt% Au-doped 90 vol% Ni  | 282                              |

The electrical performance of tubular SOFCs containing these anodes, in terms of current density correlates very well with the observed reforming activity of these anodes; the pre-reduced Au-doped and the unreduced 5 wt% Mo-doped 90 vol% Ni anodes give both the highest current density and the highest reforming activity. The highest cell performance also correlates well with the lowest apparent water conversions, which along with other observations suggests that it is the electrochemical oxidation of H₂ to water which is the dominant electrochemical reaction, and it is the rate of this reaction, and not the electrochemical oxidation of CO which most determines the cell performance.

We propose that molybdenum acts as a promoter for electrocatalysis partially by providing additional oxygen ion exchange sites which leads to increased ionic conductivity of the anode. This would account for its greater influence on the 90 vol% Ni anodes, as well as with increased molybdenum concentration. The gold dopant increases cell performance due to the increased reforming activity caused by the gold limiting the formation of detrimental carbon, thus providing more H₂ for electrochemical oxidation. The gold dopant also appears to reduce power losses during current collection.
Reforming under load

Post-reaction TPO measurements carried out after reforming under load conditions, show that under these conditions the molybdenum and gold doped anodes lead to a substantial reduction in the amount of carbon deposited compared to that deposited during reforming under the same conditions but without drawing any current. This is in contrast to the undoped standard nickel/zirconia cermet anodes where there is actually increased carbon deposition during reforming under load conditions compared to reforming over the anode in an unloaded cell.

Furthermore on the doped anodes, in many cases neither of the two carbon species observed previously is formed whilst reforming under load conditions, and instead a carbon species is formed which is not removed from the anode until significantly higher temperature. This high temperature species is only ever observed whilst reforming under load. Figure 3 shows the TPO spectra observed from the 1 wt% Au doped 90 vol% Ni anode following reforming in a 5:1 methane/steam mixture at 1123 K for 60 minutes; the only difference being that in one case the reforming was carried out under load conditions, with an applied potential of 0.7 V, whilst in the other reforming took place on an unloaded cell. The absence of the two carbon removal species typically observed following reforming on an unloaded cell and the formation of the new carbon species that is removed at appreciably higher temperature, can clearly be seen following reforming under load conditions.

![Figure 3. Temperature programmed oxidation of carbon deposited on a 1 wt% Au-doped 90 vol% nickel cermet following reforming for 60 minutes in a 5:1 methane/steam mixture at 1123 K, on an unloaded cell and at an applied potential of 0.7 V.](image)
The effects of doping nickel/zirconia cermet anodes with small quantities of molybdenum and gold on the steam reforming characteristics of the anode have been studied over the temperature range 1023 K to 1173 K, and a range of methane/steam ratios. In general, addition of molybdenum to nickel/zirconia cermet anodes at low levels gave increased methane conversion; over the entire temperature range studied on the 50 vol% Ni anodes, and at the lower temperatures studied on the 90 vol% Ni anodes. The influence of molybdenum on carbon deposition is complex, decreased carbon deposition occurs at lower reforming temperatures on the Mo-doped 50 vol% Ni anode but not at higher reforming temperatures, whilst on the 1 wt% Mo-doped 90 vol% Ni anode a dramatic reduction in carbon deposition is observed during reforming at 1173 K, whilst no carbon deposition at all is observed at reforming temperatures below 1173 K. The addition of molybdenum leads to a reduction in the thermal stability of the two carbon species formed during reforming, and on the Mo-doped 90 vol% Ni cermet, formation of the lower temperature carbon species is favoured even at the highest reforming temperature studied, in marked contrast to on the undoped 90 vol% Ni anode.

Very high activity was observed for the 5 wt% Mo-doped 90 vol% Ni cermet when the anode was fired to 1273 K and not pre-reduced in H₂. This is attributed to the formation of an active molybdenum carbide species.

The addition of gold leads to a strong inhibition of the higher temperature carbon species, particularly at reforming temperatures below 1173 K, as well as a significant increase in the steady-state methane conversion, especially at lower reforming temperatures and higher methane/steam ratios.

Molybdenum and gold doped nickel anodes show significantly improved resistance to deactivation, in particular the gold-doped anode, and much greater resistance to carbon deposition, particularly the 1 wt% Mo-doped 90 vol% Ni anode, relative to standard undoped nickel cermets, in extended reforming experiments. The addition of molybdenum and gold can actually result in significantly improved current densities; the pre-reduced Au-doped 90 vol% Ni anode and the unreduced 5 wt% Mo-doped 90 vol% Ni anode give appreciably higher current densities than the standard undoped nickel/zirconia cermets. Under load conditions the molybdenum and gold doped anodes lead to a substantial reduction in the amount of carbon deposited compared to that deposited during reforming under the same conditions but with no external load, in contrast to the undoped standard nickel/zirconia anodes where there is increased carbon deposition under load conditions. Under load conditions the two carbon species normally observed are not formed, and a new high temperature carbon species is observed, which is only ever detected when reforming under load conditions.

Thus, gold and molybdenum doped cermets have shown increased resistance to carbon deposition, increased methane conversion and increased durability, particularly at lower reforming temperatures and lower, more realistic, methane/steam ratios. They therefore represent more than just a viable alternative to conventional nickel/zirconia cermet anodes.

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cermet anodes, offering a realistic cheap, high performance and more durable improvement, particularly suited to lower temperature applications.

ACKNOWLEDGEMENTS

This work was supported by the UK Engineering and Physical Sciences Research Council through grant GR/K58647. The EPSRC Clean Technology Programme is also acknowledged for the award of a studentship to CMP.

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