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Carbon formation on and deactivation of nickel-based/zirconia anodes in solid oxide fuel cells running on methane

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Abstract

Nickel/zirconia fuel reforming anodes in solid oxide fuel cells (SOFCs) running on methane have been studied using a test cell based on a tubular SOFC. The anodes have been characterised using temperature-programmed reduction (TPR) which reveals that two distinct types of nickel oxide are present in the anode prior to reduction. The steam reforming activity and surface chemistry of two different nickel/zirconia anode formulations and a molybdenum doped nickel/zirconia anode have been studied. All three show good activity towards methane steam reforming. It is found that the quantity of carbon deposited on the anode during methane reforming is strongly affected by the operating temperature and the methane/steam ratio. The addition of small quantities of molybdenum leads to a significant reduction in the amount of carbon deposited, whilst having little effect on the reforming activity or cell performance. Temperature-programmed oxidation (TPO) has revealed that three types of carbon are formed on the anodes during high temperature reaction of methane. As current is drawn from the cell, increased methane conversion occurs together with reduced carbon deposition, through reaction via partial oxidation and oxidative coupling with the flux of oxygen ions through the solid electrolyte. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Solid oxide fuel cells; Methane; Nickel; Reforming; Carbon; Zirconia

1. Introduction

Fuel cells have tremendous potential as a more efficient and cleaner alternative method of electricity generation than heat engines, steam and gas turbines and combined cycles, since they operate electrochemically, so are not limited by the Carnot cycle, and they are catalytic, with much lower emissions of NO_x in particular, and also CO_2 and unreacted hydrocarbons, than conventional generators. In addition they do not suffer appreciably from the problems of lubrication, wear, leakage and heat loss, which affect the reliability of traditional heat engines and inhibit small-scale applications. Consequently fuel cells are currently attracting a great deal of interest [1]. The solid oxide fuel cell (SOFC) is the ideal device for small-scale application, offering the potential of cheap, clean production of electrical power from natural gas and other hydrocarbons, as it operates at temperatures where methane (and other hydrocarbons) react readily with oxygen and steam. The possibility of internal reforming of methane and other hydrocarbon fuels directly on the anode, together with the flexibility in the choice of fuel, is one of the main advantages of SOFC compared to other fuel cell systems [2–4]. This

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also results in increased efficiency through improved heat utilisation.

However, several major problems of internal reforming remain to be solved before such cells can ever be routinely operated on hydrocarbon fuel. These include the problem of carbon deposition on the anode at the high operating temperatures involved and the subsequent deactivation of the anode which leads to a loss of cell performance and poor durability [4], obtaining the optimum anode formulation and designing a suitable test cell. For this reason many SOFC studies are carried out using hydrogen as the fuel, and there is a relative lack of studies on SOFCs using hydrocarbons as fuels, particularly ones involving any detailed catalytic, spectroscopic and structural characterisation. In this paper we have studied the fuel processing reactions and the catalytic chemistry which occurs at the anode surface under operating conditions, with an aim to develop anodes which will efficiently reform methane whilst giving the desired electrical performance over long time periods.

The SOFC can be divided into three main components; the anode, the solid oxide electrolyte and the cathode. The anode is generally nickel-based and can, in some respects, be considered to be analogous to supported nickel methane steam reforming catalysts, which have been studied by many workers [5–10]. Although the addition of steam to the fuel may be beneficial for the removal of carbon deposits, this is somewhat undesirable in fuel cell operation, as addition of oxygen atoms to the anode side of the cell reduces the electrical potential according to the Nernst equation [11]. The addition of additives can lead to lower rates of carbon formation. Alkali additives, traditionally potassium in the form of potash, are added which serve both to accelerate the reaction of carbon with steam and to neutralise the acidity of the catalyst support, and hence reduce carbon deposition [12–14]. Some transition metals have also been investigated as possible additives [15].

The work described in this paper has been carried out on a unique, simple robust test cell based on a tubular SOFC, which has been developed in this laboratory and described previously [16,17]. The cell consists of a nickel-based anode, a tubular yttria-stabilised zirconia (YSZ) electrolyte, and a strontium-doped lanthanum manganite cathode. The test cell can be readily used to study the problems of carbon deposition and poor durability in operation, and the optimum anode formulation. The benefits of this test cell are that it can be rapidly assembled, heated, cooled, and it has no sealing or leakage problems, which devices based on the more commonly used planar cells suffer from. Thus different anode formulations can be easily evaluated for their electrical performance and durability. In addition the apparatus is linked to a computer-interfaced mass spectrometer which permits the methane reforming reaction to be studied in the actual SOFC under operating conditions and the methane activation and chemistry occurring at the anode surface to be thoroughly investigated using in situ temperature-programmed measurements. These have been used to study the calcination and reduction of the nickel anode, and to obtain detailed information about the methane activation process, reforming and partial oxidation of the methane, and the nature and level of carbon deposition on the anode. Furthermore, the apparatus allows the catalytic and surface chemistry of a working SOFC to be monitored enabling direct correlation of the reforming activity and surface chemistry with the cell performance [17,18].

In this paper, two different nickel/zirconia anode formulations and a molybdenum-doped nickel/zirconia anode have been studied. The effect of adding steam to the methane, the influence of operating temperature, and the effect of doping the nickel/zirconia anode with a small quantity of molybdenum, on the methane reforming activity of the anode, the surface chemistry and the nature and level of carbon deposition, have been investigated.

2. Experimental

All the experiments described here were carried out on a custom-built catalytic and electrochemical reactor, which has been described in more detail in a recent publication [16]. The essential components of the apparatus are a ceramic furnace which is operated by a Eurotherm temperature controller which allows the heating rate to be linearly controlled between room temperature and 1350 K; heating rates of between 1 and 20 K min^{-1} are possible. The reactor temperature is measured using a K-type thermocouple. The reactor inlet is fed by a supply of hydrogen, oxygen, helium and methane via a stainless-steel gas manifold which allows complete flexibility in gas handling; helium is used both as a carrier gas for the reactant stream and as an inert flow for the reactor bypass system. The flow of helium, hydrogen and oxygen is controlled by needle flow-control valves, whilst the methane flow is controlled by a mass flow controller (Unit Instruments). Water was removed from helium, hydrogen and oxygen using 13X molecular sieve traps. Research grade methane was used without further purification. Water can be introduced into the reactant gas stream via a water saturator. The gas manifold has been designed in such a way that any methane/water or methane/oxygen ratio can be achieved. A 4-way sampling valve (Whitey) placed before the reactor inlet can be used to divert reactant gases through the bypass system, allowing reactant gas composition to be changed whilst maintaining the reactor under a continuous flow of helium. A schematic of the apparatus is shown in Fig. 1. A particular advantage of the tubular SOFC design is that it can be used in the same way as a conventional catalytic reactor. As the yttria-stabilised zirconia is a good thermal insulator, the ends of the tubular electrolyte which project beyond the outer walls of the furnace remain cool enough for a gas-tight seal to be made. The exit from the reactor is connected to the gas analysis system, which is heated to 383 K to avoid the problem of water condensation. Gas analysis is carried out by an on-line computer–interfaced mass spectrometer (Leda-Mass Satellite).

The fuel cell anodes used in this work were prepared by physically mixing nickel oxide powder (Alfa Chemicals) and 8 mol% yttria-stabilised zirconia (YSZ) (Unitec-FYT11). To this a mixture of methanol, 1,1,1-trichloroethane and glycerol trioleate were added as a solvent and the resultant slurry was milled for 3 h, with a small quantity of poly-vinyl butyrol added at the end of the milling period as a binding agent. The anode sample can then be studied in the powder form following firing, or as an actual anode coated on the tubular zirconia electrolyte. In this case the anode slurry was sucked into the electrolyte tube prior to firing. All the experiments reported here were carried out on anodes coated on zirconia electrolyte as

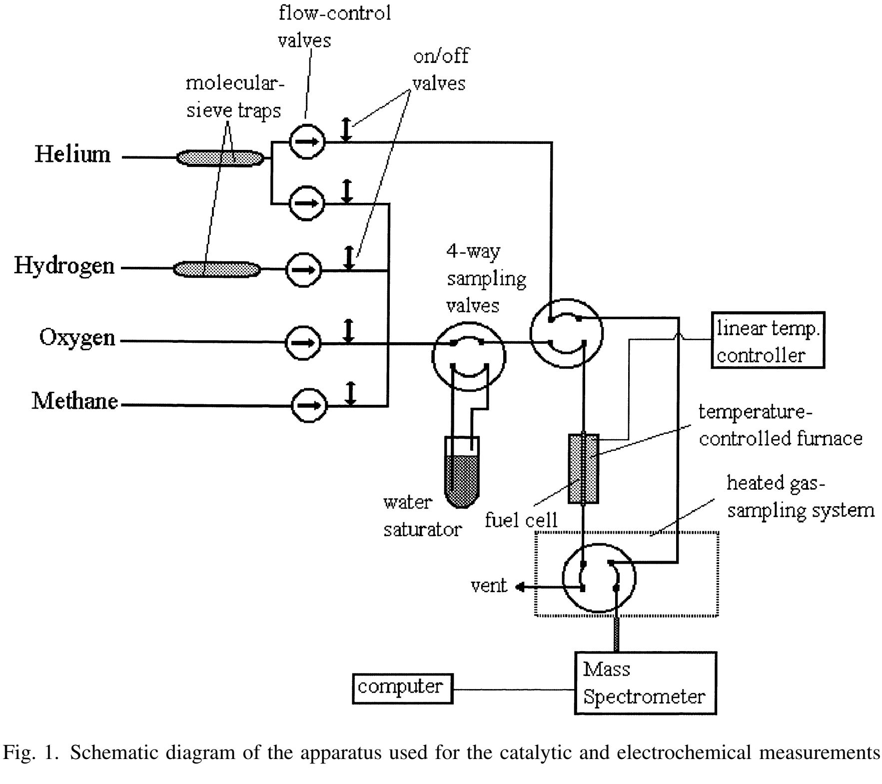

Fig. 1. Schematic diagram of the apparatus used for the catalytic and electrochemical measurements.

in a working SOFC. Following drying at room temperature in air, they were calcined in a static air oven according to the following procedure: heated to 773 K at 1 K min^{-1}, and then from 773 to 1573 K at 5 K min^{-1}, held at 1573 K for 1 h, before being cooled to room temperature at a rate of 10 K min^{-1}. Following firing the anodes were reduced in the reactor at 1173 K for 30 min in a 10% H_2/He stream to convert the NiO to metallic nickel. We have shown previously that this results in complete reduction of NiO [19].

Three anode samples were prepared for detailed study: 50 vol% Ni/YSZ, 90 vol% Ni/YSZ and 1 wt.% MoO_3 doped 50 vol% Ni/YSZ. These are referred to as 50/50, 90/10 and 1% Mo-doped 50/50 Ni/ZrO_2 anodes, respectively. The molybdenum doped sample was prepared by adding MoO_3 (BDH Chemicals) to the anode ink prior to milling and firing.

Temperature-programmed reduction (TPR) measurements were carried out in a 10% H_2/He mixture, using a heating rate of 5 K min^{-1}. Temperature-programmed oxidation (TPO) was used to characterise the nature and quantity of surface carbon. All TPO experiments were carried out using an 8% O_2/He mixture and a heating rate of 5 K min^{-1}.

3. Results

The three anode samples were characterised using TPR. The results are presented for the reduction of 50/50, 90/10 and 1% Mo-doped 50/50 anodes in Table 1. Also shown are the results for the reduction of a physical mixture of NiO and YSZ (1:5) and a 10% Ni/YSZ sample prepared by wet impregnation of YSZ with an aqueous solution of nickel (II) nitrate. In all samples it was observed that reduction was complete by 1173 K.

Table 1
Results of TPR studies on different anode formulations, a NiO/YSZ physical mixture and a Ni/YSZ catalyst prepared by wet impregnation

Anode composition	Temperature of peak maxima (K)
50/50	758
90/10	707, 850 (shoulder)
1% Mo doped 50/50	760
NiO/YSZ physical mixture (1:5)	673
10% Ni/YSZ (prepared by impregnation)	815, 894

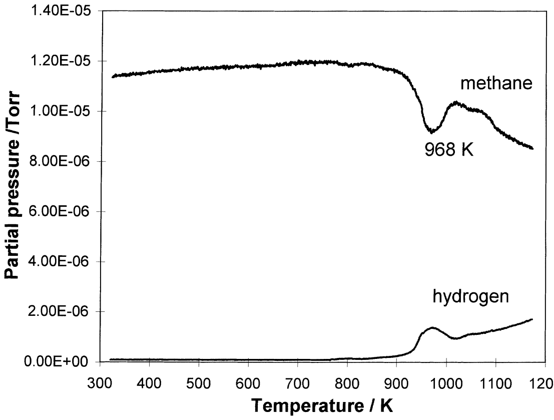

Fig. 2. Temperature-programmed reaction spectrum of the reduced 50/50 Ni/YSZ anode carried out in a dry methane/helium gas mixture.

Temperature-programmed measurements were carried out on the reduced 50/50 Ni/ZrO_2 anode in a dry methane/helium gas mixture (temperature-programmed methane adsorption (TPMA)). These show that dissociative methane adsorption occurs at temperatures above 780 K, as can be seen in Fig. 2. This was apparent from an uptake of methane by the anode and simultaneous production of hydrogen. The rate of methane adsorption was found to increase with temperature, although a local maximum in the adsorption rate was observed at 975 K. Dissociative adsorption of dry methane leads to the formation of surface-adsorbed carbon species. The anode sample was then subjected to a temperature ramp in a H_2/helium gas mixture (temperature-programmed hydrogenation (TPH)) to establish if the surface carbon species could be removed by hydrogenation. The TPH of the 50/50 Ni/YSZ anode following high temperature methane adsorption revealed a maximum in methane production at 835 K. However, methane was still evolved at the highest reaction temperature of 1173 K, indicating that hydrogenation alone was not effective in removing all the adsorbed carbon from the surface. The TPH experiment was immediately followed by a TPO measurement, which confirmed that a substantial quantity of carbon did indeed remain on the anode following TPH. Two maxima were observed in the rate of carbon removal during TPO, at 920 and 1075 K, indicating the presence of two types of surface carbon species. The major product of oxidation was carbon dioxide. No water was produced during TPO indicating that all the adsorbed methane had completely dissociated to from a carbonaceous overlayer.

A comparison of the stability towards surface carbon formation was made between the 50/50 and 90/10 Ni/YSZ anodes. A dry methane/helium gas stream was passed over each sample for 30 min at three different temperatures; 673, 823 and 973 K. Following each methane exposure the surface carbon formed was analysed by TPO. It was observed that as the reaction temperature is increased the temperature at which the maximum rate of removal of surface carbon by oxidation occurs also increases, indicating that the surface carbon formed is more strongly bound at increasing methane reaction temperatures. For a given reaction temperature the TPO maxima occur at similar temperatures for both anodes. However, the quantity of carbon adsorbed on the two anodes is different. In each case the quantity of carbon adsorbed on the 90/10 Ni/YSZ anode was slightly less than that adsorbed on the 50/50 Ni/YSZ anode.

The effect of adding steam to the methane feed was studied using the 50/50 Ni/YSZ anode, using a methane/steam ratio of 19.3:1. Upon introduction of the methane/steam mixture to the anode a large uptake of methane was observed together with the hydrogen evolution. A large quantity of CO_2 was also produced, although after a couple of minutes the CO_2 level was found to decrease and there was a parallel increase in CO production. After about 5 min equilibrium was reached with relatively constant production of CO and H_2 and only very low levels of CO_2. The methane conversion rate was about 25%, with essentially 100% selectivity towards CO. The effect of adding steam to the methane feed on the formation of surface carbon was determined at various reaction temperatures. The effect was most marked at the highest reaction temperature of 823 K, where it was found that 20% less carbon was deposited after a 30 min reaction period when steam was added to the methane. The two TPO profiles are shown in Fig. 3.

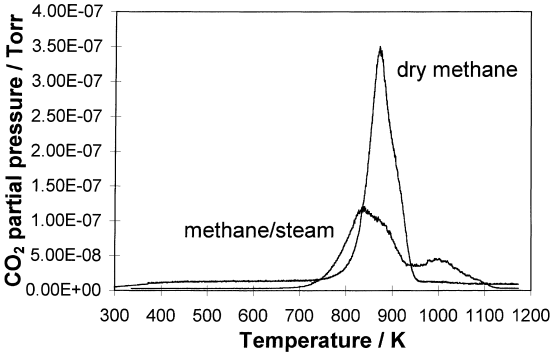

Fig. 3. Temperature-programmed oxidation of the 50/50 Ni/YSZ anode following exposure to dry methane and a 19.3:1 methane/steam mixture at 823 K for 30 min.

When the 1% Mo-doped 50/50 Ni/YSZ anode was exposed to the 19.3:1 methane/water mixture for 30 min at 823 K, 24 μmol of surface carbon were formed compared to 88 μmol deposited on the undoped 50/50 Ni/YSZ anode operating under the same conditions. The presence of molybdenum causes a small reduction in methane conversion from 38% to 36% under reforming conditions.

Table 2 shows the effect of varying the exposure time of the 1% Mo-doped anode to the 19.3:1 methane/steam mixture at 973 K. The surface carbon formed was analysed by TPO, and the TPO profiles are shown in Fig. 4. It can be seen from Table 2 and Fig. 4 that the quantity of carbon adsorbed on the anode increases with increasing exposure time, and that at least three types of carbon species are formed on the anode. The carbon species are referred to as: type I carbon, removed from the anode at about 870 K, type II carbon which is removed from the anode just above 900 K, and type III carbon which can only be removed from the anode by oxygen at temperatures above 1000 K. The terminology type I, II and III carbon has been used on the basis of the temperature required to remove the carbon by reaction with oxygen, rather than the notation used by Bartholomew in his review

Table 2
Influence of exposure time on the quantity and nature of carbon species deposited on a 1% Mo doped–50/50 Ni/YSZ anode

Exposure time (min)	Carbon deposited (μmol)	T_{max} of major peaks (K)[a]
30	24	880, 1069
60	59	870, 900 (s), 1008
97	121	869, 930, 1050 (s), 1254
120	294	870 (s), 923, 1150

[a] (s) denotes shoulder.

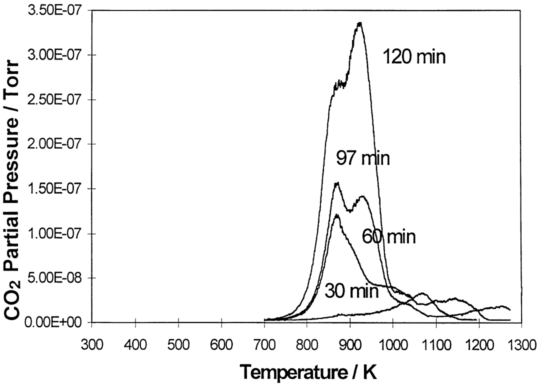

Fig. 4. Temperature-programmed oxidation of the 1% Mo-doped 50/50 Ni/YSZ anode following exposure to a 19.3:1 methane/steam mixture at 973 K for different time periods.

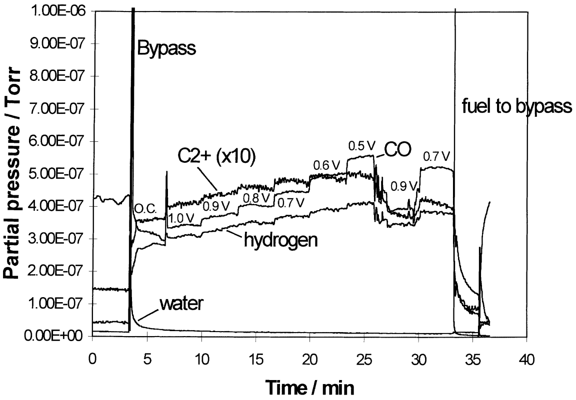

Fig. 5. The effect of drawing current on product formation for a 90/10 Ni/YSZ anode in a tubular SOFC running on a 19.3:1 methane/steam mixture at 1173 K.

of carbon formation on nickel catalysts [20], where the carbon type is classified according to the temperature at which it is formed. It can also be seen from Fig. 4 that the exposure time increases the relative quantities of the different carbon species. After a relatively short exposure time of 30 min it was found that the most strongly bound carbon species (Type III) was the main species formed, together with a small quantity of type I carbon. As the exposure time was increased to 60 min it was found that type I carbon becomes the most dominant species. Further increase in the exposure time results in an increase in the quantity of both type I and type II carbon, although the quantity of type II carbon becomes more significant. The quantity of type III carbon however, was not found to increase with exposure time.

The electrical performance of tubular SOFCs coated with these anodes have been studied using both H_2 and methane as a fuel, using the same test rig and experimental conditions. The results of these electrical tests will be described elsewhere [21].

Of significance to this paper is the effect of drawing current from the SOFC on the reforming reaction. We have shown previously how the tubular SOFC design coupled to our apparatus permits the methane reforming reaction to be directly monitored in a working SOFC, enabling direct correlation of the reforming activity and surface chemistry with the cell performance [17,18]. Fig. 5 shows the effect of drawing current from an SOFC with a 90/10 Ni/YSZ anode, operating at 1173 K using 19.3:1 methane/steam mixture. It can readily be seen that as the current drawn increases there is an increase in the conversion of methane, and a stepwise increased production of hydrogen. There is also significantly increased formation of CO, which parallels the increase in the hydrogen production. In addition to increased CO and H_2 production, ethene and ethane formation is also observed; the level of which shows a similar increase with increasing current drawn.

4. Discussion

Temperature-programmed reduction has been used to study supported nickel oxide by a number of groups [22–25]. In general, several reduction peaks are observed in the TPR spectra. The two peaks observed in the TPR spectra of the anodes are consistent with TPR profiles of supported nickel catalysts. It is generally accepted that the low temperature peak corresponds to reduction of larger NiO particles which are similar in nature to pure bulk NiO particles, whilst the higher temperature peaks are due to NiO in intimate contact with the support material [25]. Our results indicate therefore, that although the cermet anodes are formed from a physical mixture of NiO and zirconia, a fairly strong interaction occurs between the two species following the extended milling procedure and the high temperature calcination treatment used in anode preparation. The precise degree of interaction between the NiO and the zirconia depends on the percentage of nickel in the anode formulation and will be discussed in more detail in a separate paper [26].

Although dissociative adsorption of methane starts to occur on the anodes at about 780 K, the surface carbon which is formed during the temperature-programmed reaction is likely to become more strongly bound as the final reaction temperature was 1173 K. The fact that no water was evolved in the subsequent TPO experiment indicates that all the adsorbed methane completely decomposes to form a purely carbonaceous overlayer. The local maximum in the methane adsorption observed at 975 K is most likely due to a rate-limiting step in the process. This could be due to carbon species adsorbed on the nickel spilling over onto the support, surface carbon migrating onto the nickel bulk, or the formation of carbon filaments. It is known that on nickel catalysts formation of carbon filaments and the formation of nickel carbide can both occur [8,20]. The strength of carbon adsorption following the temperature-programmed methane adsorption is demonstrated by the fact that not all the carbon can be removed from the anode by hydrogenation, even at temperatures as high as 1173 K.

The amount of surface carbon adsorbed on the anode increased with increasing methane reaction temperature, together with the temperature at which the maximum rate of removal of surface carbon occurs, confirming that the surface carbon does indeed become more strongly bound at increasing methane reaction temperature.

The addition of only a small quantity of steam to the methane led to a significant lowering in the rate of carbon formation on the anode surface. The methane/steam ratio of 19.3:1 is considerably higher than those typically used by other researchers [2], though it is nevertheless still sufficiently low to demonstrate the role of steam in reducing carbon deposition. The results also show that the anode formulation has a considerable influence on the level of carbon deposition.

The addition of small quantities of molybdenum to the Ni/YSZ anode leads to a very substantial reduction in the level of carbon deposition. The addition of as little as 1 wt.% MoO_3 to the 50/50 nickel oxide/YSZ anode mixture results in a four fold reduction in the quantity of carbon formed compared to the unloaded undoped 50/50 Ni/YSZ anode under the same reaction conditions. Doping the anodes with molybdenum does not lead to any significant lowering of the methane reforming activity of the anode, whilst electrochemical tests show only a small reduction in cell performance compared with the undoped anode under the same operating conditions [27]. These findings are consistent with previous work on conventional nickel steam reforming catalysts, which show that promotion with molybdenum reduces the quantity of surface carbon formed but does not result in a significant lowering of the catalytic activity [15]. Although some oxides of molybdenum are rather volatile, no loss of activity or selectivity due to leaching of molybdenum was observed. It should be noted that the anodes were fired to 1573 K before reduction and exposure to methane in the temperature range 1073–1173 K. Thus significant loss of molybdenum occurs in the firing step and the actual molybdenum loading during reforming is considerably less than 1 wt.%. Temperature-programmed reduction of MoO_3 indicate that at the cell operating temperature, pure MoO_3 is completely reduced to metallic molybdenum [27].

For all the anodes studied TPO has shown that more than one type of carbon species is formed during high temperature methane adsorption or steam reforming. As noted earlier the terminology type I, II and III carbon has been used on the basis of the temperature required to remove the carbon by reaction with oxygen, rather than the notation used in the review by Bartholomew [20] on carbon formation on nickel catalysts, where the carbon type (α, β, γ) is classified according to the temperature at which it is formed. This is because the temperatures used in this work are sufficiently high so that all three types of carbon identified by Bartholomew can be formed to a greater or lesser extent. It is also possible that some of the carbon formed in our experiments results from CO dissociation, and Bartholomew has proposed that additional types of carbon species are formed by high temperature dissociation of CO [20]. The length of the exposure time to methane was found to significantly influence both the quantity of carbon adsorbed on the anode surface as well as the nature of the carbon species, for all the anodes. These results indicate that each carbon type is either formed on different sites on the Ni/YSZ anode, or that one form of carbon is converted into another, either by higher temperature or by longer exposure. Very short exposure times result in predominantly the most strongly bound (type

III) carbon being formed. The quantity of type III carbon formed is found not to increase with exposure time beyond a certain relatively low level. It seems most likely that the strongly bound type III carbon species is graphitic carbon formed on the surface nickel sites. As the methane exposure time is increased the formation of the lower temperature type I carbon increases, such that after 60 min exposure time, type I carbon has become the dominant carbon species, and type II carbon has started to form. At longer exposure times, type II carbon becomes more significant, until after 120 min exposure, type II carbon is the major species, though the quantity of type I carbon also continues to increase. The results suggest that type II carbon is formed from the type I species, possibly via some sort of ageing process.

The total quantity of carbon measured after prolonged exposure to methane often exceeds the quantity of nickel present. This clearly indicates that the deposited carbon cannot be simply in the form of chemisorbed species on the nickel surface. A large proportion of the carbon must therefore, have spilled over onto the zirconia, or be in the form of filamentous carbon. We have studied the anodes using electron microscopy, and it is clear that the anodes suffer considerable damage when they are run under harsh coking conditions (high temperatures and high methane/steam ratios) in comparison to anodes which have been run purely on hydrogen, indicating that the carbon species formed break up the anode structure, suggesting that filamentous carbon is formed.

The addition of molybdenum seems to inhibit the formation of type I and type II carbon but not type III carbon, suggesting that the molybdenum may serve to inhibit the transition from type III carbon to type I and type II carbon.

The experiments on the working SOFC operating on the methane/steam gas mixture show clearly that drawing current from the SOFC results in increased conversion of methane, and increased production of hydrogen and CO, as well as the formation of ethene and ethane. Subsequent work has shown that there is a reduction in the quantity of carbon deposited on the anode compared to that under unloaded conditions, whilst electron microscopy has shown that the damage to the anode is not as severe when the cell is operated under load conditions [21]. As the current drawn from the SOFC increases, the flux of oxygen ions across the zirconia electrolyte, from the strontium-doped lanthanum manganite cathode to the Ni/YSZ anode, increases. The increased conversion of methane and the stepwise increase in CO and H_2 production with increasing current drawn, indicate that partial oxidation of methane to CO and H_2 by oxygen ions is occurring. The formation of the C_2 hydrocarbons indicates that in addition to partial oxidation, in the presence of oxygen ions transported through the zirconia the Ni/YSZ anode is also active towards the oxidative coupling of methane to ethane and ethene. The partial oxidation and oxidative coupling pathways which occur in the working SOFC, i.e. when current is drawn from the cell, lead not only to increased methane conversion but also reduced carbon deposition.

5. Conclusions

1. Ni/YSZ anodes in a tubular solid oxide fuel cell show good activity as methane steam reforming catalysts.
2. The formation of carbon from methane decomposition on the anodes increases with increasing operating temperature, and can be reduced by the addition of relatively low levels of steam to the methane.
3. Doping the anode with small quantities of molybdenum (<1%) is found to lead to a substantial reduction in the level of carbon deposited on the anode.
4. Temperature-programmed oxidation indicates that there are three types of surface carbon species formed on the anode surface during high temperature reaction of methane.
5. When an external load is applied to the cell increased methane conversion occurs together with reduced carbon deposition, through reaction via partial oxidation and oxidative coupling with the flux of oxygen ions through the zirconia electrolyte.

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