STUDY OF SURFACE CARBON FORMED ON WORKING ANODES OF SOFCs RUNNING ON METHANE

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ABSTRACT

Surface carbon formed on Ni-cermet anodes in working SOFCs operating on methane has been characterised using Temperature Programmed Oxidation (TPO), and electrochemical measurements. It is found that the quantity of carbon deposited on the anode is significantly reduced by: lowering the operating temperature, increasing the steam/methane ratio, and introducing small quantities of additives such as molybdenum into the anode. TPO has revealed that three types of surface carbon species are formed during high temperature reaction of methane. Each of these species has been found to form at different rates on the Ni anode.

INTRODUCTION

One of the main problems which still has to be overcome in solid oxide fuel cell research is that of the formation of carbon deposits on the anode when the fuel cell is run on hydrocarbons. In SOFC designs a nickel-based anode is frequently used (1). The anode can, in some respects, be considered to be analogous to Ni methane steam-reforming catalysts, where the formation of carbon deposits on the catalysts continues to attract much interest (2-6). It is generally accepted that the rate of carbon formation on nickel-based catalysts can be reduced in one of two ways: increasing the steam/fuel ratio during the steam reforming process, or by the addition of additives or promoters to the catalyst.

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 electrolyte reduces the electrical potential according to the Nernst equation (7). The addition of additives to the catalyst can, in principle, lead to lower rates of carbon formation without the need for the addition of steam. Traditionally potassium is used as an additive (8), however some transition metals have also been investigated as possible additives (9).

In this paper we present work carried out on tubular-design SOFCs containing nickel/ytria-stabilised zirconia anodes (10). The influence of adding steam to the fuel
feed, the operating temperature, the anode formulation, and the effect of doping the anode with a small amount of molybdenum on the nature and level of carbon deposition and the cell performance have all been investigated using both catalytic measurements and electrochemical tests.

EXPERIMENTAL

All experiments in this work were performed in a tubular-design SOFC previously developed in this laboratory (10). The fuel cell anodes were prepared by physically mixing NiO powder with 3 wt% yttria-stabilised-zirconia (Unitec FYT11). To this a mixture of methanol, 1,1,1-trichloroethane and glycerotrioleate was added as solvent. The mixture was then milled for 3 hours with the addition of poly-vinyl butyral towards the end of the milling period to act as a binder. The resultant slurry was then dried at room temperature and fired in air to form the powdered anode using the following regime: heating to 773 K at 1 K min⁻¹, and then heating from 773 K to 1573 K at 5 K min⁻¹, followed by an isothermal period of one hour at 1573 K, and finally cooling from 1573 K to room temperature at 10 K min⁻¹. The anode sample could either be studied in the powdered form as a conventional catalyst or, as in this paper, as a working fuel cell anode. In the case of the latter the slurry was sucked into a zirconia tube prior to firing, and the anode slurry and the zirconia tube were then fired simultaneously.

Three samples were prepared for detailed study: 50 vol% Ni/ZrO₂, 90 vol% Ni/ZrO₂, and 1 wt% MoO₃-50 vol% Ni/ZrO₂ (respectively known as 50/50, 90/10, and 1% Mo-50/50). The molybdenum-doped sample was prepared by adding MoO₃ to the anode mixture prior to milling and firing.

All samples were studied in a purpose-built rig designed so that both catalytic and electrochemical measurements could be made simultaneously. The apparatus consisted of a micro furnace, linear temperature controller and stainless steel gas handling system. The reactants and products of reaction were all analysed by an on-line mass spectrometer (Leda-Mass Ltd.) interfaced to a computer. The apparatus used in this study is discussed in detail in another publication (11). All samples were reduced in-situ prior to reaction at 1173 K using a 19% H₂/He gas mixture. Steam reforming reactions were carried out by passing a CH₄/H₂O/He gas mixture over the anode. The water was added to the mixture by passing a CH₄/He gas mixture through a water saturator at 293 K; the CH₄/water ratio could be adjusted by changing the CH₄ flow rate. Temperature Programmed Oxidation (TPO) was used to characterise the carbon deposits following steam reforming. Experiments were generally performed by passing an 8% O₂/He gas mixture over the anode, and using a heating rate of between 5 and 10 K min⁻¹.
RESULTS

Catalytic Measurements

The three anode samples were characterised using Temperature Programmed Reduction (TPR). It was found that the TPR reduction profiles were composed of two peaks. In all samples it was observed that reduction was complete by 1173 K. Temperature Programmed Methane Adsorption (TPMA) over a 50/50 cermet showed that dissociative methane adsorption occurred at temperatures above 780 K. This was apparent from an uptake of methane 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; these can be removed by Temperature Programmed Hydrogenation (TPH). The TPH of the 50/50 cermet 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 was followed by a TPO experiment, and it was found 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 K 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 the surface carbon was essentially hydrogen free, i.e. all the adsorbed methane had completely dissociated to form a carbonaceous overlayer.

A comparison of the stability towards coking was made between the 50/50 cermet and the 90/10 cermet. A dry CH₄/He gas stream was passed over each sample for a 30 minute period at three different temperatures, 673 K, 823 K and 973 K. Following each methane adsorption the surface carbon was analysed by TPO. Table I summarises the results.

Table I. Characteristics of carbon species deposited on 5050 and 9010 cermets

| CH₄ adsorption temperature / K | 5050 Cermet | 9010 Cermet |
|-------------------------------|-------------|-------------|
| T_max / K | μmol carbon | T_max / K | μmol carbon |
| 673 | 705 | 5.2 | 725 | 0.2 |
| 823 | 825 | 20.6 | 838 | 9.6 |
| 973 | 873 | 133.9 | 873 | 39.0 |

It can be seen from the table that as the methane adsorption temperature is increased the temperature at which the maximum rate of surface carbon oxidation occurs increases. This indicates that the surface carbon is more strongly bound when the methane adsorption temperature is higher. For both the 50/50 and 90/10 anode the peak maxima occur at about the same temperature. However, the quantity of carbon adsorbed on the 50/50 and 90/10 cermets is substantially different. In all experiments the quantity of carbon...
adsorbed on the 90/10 cermet was substantially less than that adsorbed on the 50/50 cermet; at 973 K less than one third of the quantity of carbon deposited on the 50/50 cermet was found to be deposited on the 90/10 cermet. The addition of steam to the CH₄/He feed alters the reactions taking place on the anode. Methane steam reforming [1] becomes the dominant reaction, though the Water Gas Shift Reaction [2], and carbon deposition due to the Boudouard reaction [3], and methane dissociation [4] also take place.

\[
\begin{align*}
\text{CH}_4 + \text{H}_2\text{O} &= \text{CO} + 3\text{H}_2 \quad [1] \\
\text{CO} + \text{H}_2\text{O} &= \text{CO}_2 + \text{H}_2 \quad [2] \\
2\text{CO} &= \text{C}_{\text{ads}} + \text{CO}_2 \quad [3] \\
\text{CH}_4 &= \text{C}_{\text{ads}} + 2\text{H}_2 \quad [4]
\end{align*}
\]

Steam reforming reactions were performed on the 50/50 cermet using a CH₄/H₂O ratio of 5.5, for a period of 30 minutes. Upon introduction of the fuel/steam mixture to the cermet a large uptake in methane was observed together with hydrogen evolution. At the same time a large quantity of CO₂ was produced, although after only a couple of minutes the CO₂ level was found to drop off and there was an increase in CO production. After about 5 minutes the cermet anode reached equilibrium, with relatively constant production of CO, CO₂ and H₂. The effect of steam on the rate of coking for the 50/50 cermet was measured at various temperatures. The effect of adding steam to the fuel feed was most marked at the highest reaction temperature of 823 K where it was found that 88 μmol of carbon was deposited after a 30 minute reaction period compared with 109 μmol when dry methane was used. The two TPO traces are shown in Figure 1. Methane steam reforming on 1% Mo-50/50 cermet for 30 minutes at 823 K with a CH₄/H₂O ratio of 5.5 resulted in the deposition of 24 μmol of surface carbon, compared to 88 μmol deposited on the 50/50 cermet anode operating under the same conditions. The length of exposure time was also found to alter significantly the quantity of carbon adsorbed on the cermet anodes and the nature of the carbon species. The result of a variation in the CH₄/H₂O exposure time is shown in Table II for 1% Mo-50/50 operating at 973 K with a CH₄/H₂O ratio of 5.5. The surface carbon species were analysed by TPO.

Table II. Influence of Exposure Time on the Quantity and Nature of Carbon Species Deposited on a 1% Mo-50/50 Cermet Anode

| Exposure Time / min. | Carbon Deposited / μmol | T_max of Major Peaks / K |
|----------------------|-------------------------|--------------------------|
| 30                   | 24                      | 880, 1069                |
| 60                   | 59                      | 870, 900(s), 1008        |
| 97                   | 121                     | 869, 930, 1050 (s), 1254 |
| 120                  | 294                     | 870 (s), 923, 1150       |

* (s) denotes shoulder

The TPO traces are shown in Figure 2. It can be seen both from Table II and Figure 2 that at least three types of carbon species are formed on the anode. These carbon species are
referred to as; type I carbon, removed from the cermet at about 870 K, type II carbon which is removed from the cermet just above 900 K, and type III carbon which can only be removed by oxygen from the cermet at temperatures above 1000 K. It can be seen from Figure 1 that as the exposure time increases, the relative quantities of the different carbon species changes. After a relatively short exposure time of 30 minutes it is found that the most strongly bound carbon species (Type III) was the main species formed, and in addition a small quantity of type I carbon was also formed. As the exposure time was increased to 60 minutes it was found that type I species is the most dominant species. As the exposure time increases there is an increase in the quantity of both type I and II carbon species, 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.

Electrochemical Measurements

The results in the previous section show that the addition of steam to the fuel feed significantly reduced the rate of carbon deposition on the cermet anode, as did the addition of 1 wt% MoO3 to the anode. A fuel cell containing a 50/50 cermet anode and one containing a 1% Mo-50/50 anode were run at 1173 K with 5.5% H2/He as fuel to compare the electrochemical performance of the Mo-doped anode with that of the standard cermet anode. The results are summarised in Table III and shown in Figure 3.

| Table III. Electrochemical Measurements in a 50/50 Cell and a 1% Mo-50/50 Cell |
|-----------------------------------------------|-----------------------------------------------|
| Open circuit voltage / V | 50/50 Cell | Voltage / V | Current density / mA cm² | 1% Mo-50/50 Cell | Voltage / V | Current density / mA cm² |
|------------------------------|-----------|-------------|------------------|----------------|-------------|------------------|
| 1.048                        | 1.0       | 92.5        | 1.215            | 1.0            | 74.4        |
| 0.9                          |           | 117.1       | 0.9              |               | 99.6        |
| 0.8                          |           | 146.2       | 0.8              |               | 127.5       |
| 0.7                          |           | 157.9       | 0.7              |               | 138.5       |
| 0.6                          |           | 196.0       | 0.6              |               | 178.6       |
| 0.5                          |           | 231.6       | 0.5              |               | 212.9       |

It was found that the open circuit voltage for fuel cells containing the 1% Mo doped cermet anode was 16% higher than that of the fuel cell containing the standard 50/50 anode. It can be seen from Figure 3 that over the entire voltage range tested the current density measured in the 1% Mo doped cell is approximately 15% less than that measured in the standard 50/50 cell. The average power densities for the two cells were: 109.8 mW cm⁻² for the standard 50/50 cell, and 96.1 mW cm⁻² for the 1% Mo-50/50 cell.

The effect of drawing current from a 90/10 cell running on methane has also been investigated using the standard CH4/H2O ratio of 5.5. The experimental results are presented in Figure 4, where the methane consumption and product formation are shown as a function of current drawn. Both the methane consumption and hydrogen production
are found to increase as the current drawn increases. Of particular interest is the formation of higher hydrocarbons which increase with increasing current drawn. This was evident from an increase in both the mass 27 and mass 28 signals.

DISCUSSION

The two peaks observed in the TPR profiles of the cermet anodes are consistent with TPR profiles of supported Ni catalysts. It is generally accepted that the low temperature peak corresponds to reduction of bulk NiO particles whilst the higher temperature peak is due to NiO in intimate contact with the support material (12). The results indicate therefore that although the cermet anodes are formed from a physical mixture of NiO and ZrO₂, a strong interaction occurs between the two species following the high temperature calcination treatment used in anode preparation.

Although methane dissociative adsorption begins on the cermet anodes at about 780 K, the surface carbon which is formed during this reaction is likely to become strongly bound as the final temperature of the TPMA experiment is 1173 K. It is believed that the local maximum in methane adsorption observed at 975 K is due to a rate limiting step in the process. This could be due to one of three possibilities: metal-adsorbed carbon species spilling over to the support, surface carbon migrating into the nickel bulk, or the formation of carbon filaments. It is known that on nickel catalysts both the formation of carbon filaments and the formation of nickel carbide can occur (2,13). The strength of carbon adsorption following the TPMA is demonstrated by the fact that not all the carbon can be reduced from the anode using hydrogen alone.

As expected, the rate of surface carbon formation was significantly reduced with the addition of only a small quantity of water to the fuel feed. The CH₄/H₂O ratio (5.5) is much higher that that typically used by other researchers (14), however it is still low enough to demonstrate the role of steam.

A further significant improvement to the stability of the anode towards coking is achieved by the addition of 1% MoO₃ to the cermet. It was found that the addition of molybdenum to the cermet anode results in the production of less than 30% of the carbon formed on an unpromoted cell working under the same conditions. Subsequent TPR experiments have shown that at the standard operating temperature of the cell, MoO₃ is completely reduced to metallic Mo.

It has been shown that for nickel steam reforming catalysts (9), unlike promotion with potassium, promotion with molybdenum reduces the quantity of surface carbon deposited but does not lead to a substantial reduction in catalytic activity. The electrochemical tests in this study support this, as the performance of the 1% Mo-50/50 cell running on H₂ was only 16% less than that of an unpromoted 50/50 cell.
For all the anodes studied, TPO has indicated that more than one type of carbon species is formed during high temperature methane adsorption or steam reforming. The results from experiments where the methane exposure time was varied indicate that each carbon type is either formed on different sites on the cermet anode, or that one form of carbon is converted into another, either with higher temperature or longer exposure times. With very short exposure times it is found that the carbon formed is predominantly type III. The quantity of type III carbon is found not to increase with exposure time. We therefore propose that the strongly bound type III species is graphitic carbon formed on the surface Ni sites.

As the methane exposure time increases, so does the formation of type I carbon, and after an exposure time of 60 minutes type I carbon becomes the most dominant species. At 60 minutes exposure time type II carbon is observed as a shoulder on the subsequent TPO trace (Figure 2). As the exposure time increases, type II carbon becomes more significant, until after 120 minutes, 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 probably via some sort of ageing process.

The total quantity of carbon measured after long exposure times often exceeds the quantity of nickel present. This clearly indicates that the deposited carbon cannot entirely be in the form of chemisorbed species bound to surface Ni sites. A large proportion of the carbon must therefore be sitting on the ZrO₂ or be in the form of filamentous carbon. We have studied used cermet anodes using electron microscopy and no evidence has been obtained for the formation of filamentous carbon. However, with harsh coking conditions (high temperatures and high CH₄/H₂O ratios) the anode seems to suffer more damage than either an unused anode, or one which has been run purely on hydrogen, indicating that the carbon species which are formed break up the cermet structure.

It is interesting that the addition of molybdenum seems to inhibit the formation of type I and II carbon but not type III carbon. We have suggested above that type III species are carbon species bonded to the Ni sites, and that type I and II carbon species are formed from the type I species. It appears that molybdenum serves to inhibit the transition to type I and II carbon species.

Electron microscopy has also shown that the damage to the cermet anode was not as severe when the cell was operated under load conditions. From Figure 4 it can be seen that as the current drawn from the cell is increased there is a parallel increase in the formation of C₂ and higher hydrocarbons. This indicates that in addition to the reactions described earlier, oxidative coupling of methane to ethene and ethane also occurs when current is drawn from the cell. This therefore provides an additional mechanism for the removal of surface carbon species from the anode.
CONCLUSIONS

We have shown in this study that the formation of carbon on cermet anodes can be reduced by the addition of steam to the fuel feed. The rate of carbon formation is also found to increase with temperature. We have found that the addition of a small percentage of molybdenum reduces the quantity of carbon deposited, but does not significantly affect the electrochemical performance of the fuel cell.

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Figure 1. Temperature Programmed Oxidation of 50/50 Ni/ZrO$_2$ cermet anode following exposure to dry methane and a 5.5 : 1 methane/steam mixture at 823 K for 30 minutes.

Figure 2. Temperature Programmed Oxidation of 1% Mo-50/50 Ni/ZrO$_2$ cermet anode following exposure to a 5.5 : 1 methane/steam mixture at 973 K for different times.
Figure 3. Comparison of current / voltage curves for 50/50 Ni/ZrO$_2$ and 1% Mo-50/50 Ni/ZrO$_2$ anodes, obtained at 1173 K.

Figure 4. Effect of drawing increasing current on product formation for a 90/10 Ni/ZrO$_2$ anode running on a 5.5:1 methane/steam mixture at 1173 K.