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Development of a novel test system for *in situ* catalytic, electrocatalytic and electrochemical studies of internal fuel reforming in solid oxide fuel cells

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A test system based around a thin-walled extruded solid electrolyte tubular reactor has been developed, which enables the fuel reforming catalysis and surface chemistry occurring within solid oxide fuel cells and the electrochemical performance of the fuel cell to be studied under genuine operating conditions. It permits simultaneous monitoring of the catalytic chemistry and the cell performance, allowing direct correlation between the fuel cell performance and the reforming characteristics of the anode, as well as enabling the influence of drawing current on the catalysis and surface reaction pathways to be studied. Temperature-programmed reaction measurements can be carried out on anodes in an actual SOFC, and have been used to investigate the reduction characteristics of different anode formulations, methane activation and methane steam reforming, and to evaluate the nature and level of carbon deposition on the anode during reforming.

Keywords: solid oxide fuel cells, electrocatalysis, catalysis, electrochemistry, anode, fuel reforming, steam reforming, methane, carbon deposition

1. Introduction

Fuel cells offer tremendous potential as a more efficient and cleaner alternative method of electricity generation than conventional methods, and thus are attracting much interest at present [1–4]. Solid oxide fuel cells (SOFCs) offer potential advantages in terms of cost and efficiency over other types of fuel cell because the high operating temperature allows the possibility of running the cell directly on natural gas or other hydrocarbon fuels. The fuel is internally reformed within the fuel cell, since at these temperatures methane and higher hydrocarbons react readily with steam or oxygen [1,4–7]. Internal reforming of the fuel within the SOFC is considered essential in order for SOFCs to ever be economic, since this increases operational efficiency through chemical recuperation of waste heat from the stack into the fuel supply and simplifies the balance of plant [1,4,5]. However, there are several major problems associated with internal reforming which remain to be solved before such cells can be routinely operated on hydrocarbon fuel. These include the problems of carbon formation on the anode, sintering of the anode particles, and leaching and delamination of the anode, all of which lead to deactivation, loss of cell performance and poor durability [4–6]. Another problem is associated with the strongly endothermic nature of steam reforming, particularly under start-up conditions and operation at low loads. There is therefore much interest in developing and evaluating optimised anode formulations for internally reforming SOFCs, and studying the influence of anode formulation, pre-treatment and process operating conditions [4,5,8].

A particular problem in carrying out such studies on internal reforming in solid oxide fuel cells is the development of a suitable test system which enables the catalytic chemistry within the SOFC to be studied, as well as the cell performance to be evaluated, on an actual fuel cell under realistic operating conditions. The design and construction of a system with the capacity to study both the catalytic chemistry and the electrical performance of the SOFC, and in particular to be able to make catalytic measurements on a working SOFC, is not straightforward. The following problems must be overcome [9,10]:

(i) the ceramic cell must be heated to operating temperature at a reasonable rate;

(ii) the ceramic material must be able to be thermally cycled;

(iii) sealing the fuel cell so that the fuel at the anode and the air at the cathode are kept separate;

(iv) obtaining gas-tight connections between the gas feed and the cell inlet; and

(v) obtaining gas-tight connections between the cell outlet and an on-line gas analysis system.

Overcoming these problems and being able to make both electrochemical and gas analysis measurements is particularly difficult with planar SOFCs [11].

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The SOFC anode is generally a nickel/solid electrolyte cermet, and can be considered to be somewhat analogous to supported nickel methane steam reforming catalysts, which have been studied extensively [12–15]. It is therefore possible to study the catalytic behaviour of these anodes in powder form inside a conventional catalytic reactor; several research groups, including ourselves, [7,16,17] have demonstrated this approach. In many other fuel cell studies the primary focus is the electrical performance and durability of the cell, frequently using hydrogen rather than a realistic fuel as the fuel, in which the influence of electrode composition, structure and other experimental parameters are monitored by measuring changes in the current or power densities [18–20]. There is a genuine lack of studies in which the fuel reforming catalysis and surface chemistry have been studied in an actual SOFC.

In this paper we describe a test system which we have developed, based on a small diameter, thin-walled extruded yttria-stabilised zirconia tubular SOFC [21], which can be used for *in situ* catalytic and electrocatalytic studies of internal fuel reforming catalysis and surface chemistry in SOFCs, as well as the electrical performance and durability of the fuel cell. This allows a direct correlation to be made between the fuel cell performance and its reforming characteristics. Furthermore, the test system allows the reforming catalysis of a working SOFC to be continuously monitored, enabling the influence of drawing current on the reforming activity, surface reaction pathways and carbon deposition to be investigated in an actual SOFC [21].

The particular benefits of the test cell are that it can be rapidly assembled, heated and cooled, and it has no sealing or leakage problems, which many devices based on the more commonly used planar cells suffer from. Thus different anode formulations can be easily evaluated for their performance and durability. In addition the apparatus is linked to an on-line mass spectrometer which permits fuel reforming to be studied in the actual SOFC under operating conditions and the hydrocarbon activation and chemistry occurring at the anode surface to be investigated using *in situ* temperature-programmed measurements. Temperature-programmed reduction (TPR), oxidation (TPO) and reaction measurements are used to study the reduction characteristics of the anode, and to obtain detailed information about the hydrocarbon activation process, methane steam reforming and partial oxidation, and the reactions occurring at the anode surface, as well as enabling the nature and level of carbon deposition on the anode, and the kinetics of carbon removal to be investigated [22].

2. Design and development of test system

2.1. SOFC test system design

A particular advantage of this tubular SOFC design is that it can be housed in a typical furnace and used in the same way as a conventional continuous-flow catalytic microreactor. As yttria-stabilised zirconia is a good thermal insulator the ends of the tubular electrolyte 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 gas-tight sealing of the yttria-stabilised zirconia tubular reactor to the gas inlet and the on-line gas analysis system keep the fuel at the anode and the air at the cathode totally separate, and ensure a fully gas-tight system, which was achieved using specially machined PTFE Swagelock ferrules, which enable routine gas-tight connections to be made to the stainless-steel gas inlet and outlet using standard Swagelock fittings. The system has been designed so that either a conventional reactor or an extruded tubular yttria-stabilised zirconia reactor can be used.

The apparatus consists of a custom-built insulated, resistively heated ceramic furnace of length 140 mm and internal diameter 45 mm. The furnace is operated through a temperature controller which allows linear temperature control between room temperature and 1373 K; ramp rates between 0.1 and 50 $\mathrm{K\,min^{-1}}$ are possible. The furnace temperature is precisely measured using a K-type thermocouple. 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/oxidant ratio, through a combination of on/off valves, precision needle valves and mass flow controllers. The gas feed can be instantly switched between gases using a four-way sampling valve. Thus evaluation is possible over a full range of relevant operating conditions and fuel compositions. Helium is used both as a carrier gas for the reactant stream and as an inert flow for the reactor bypass system. Research grade gases were used. Any water present in the gases was removed by the use of 13x molecular sieve drying traps. The total system operating pressure was just above 1 bar and flow rates of up to 100 $\mathrm{ml\,min^{-1}}$ could be used. Water can be introduced into the reactant stream via a stainless-steel temperature-controlled water saturator, linked to the gas manifold by a four-way valve. The reactor outlet is linked to the gas sampling system. The valve system allows monitoring of either the gas flow from the reactor outlet or from the reactor bypass, enabling precise conversions to be determined. The entire gas sampling system was heated to 383 K to avoid the problem of water condensation, and is fed by a heated quartz capillary to a continuously sampling on-line mass spectrometer (Leda-Mass Satellite). This permits the fuel processing reactions to be continuously and directly studied in the actual SOFC under operating conditions, and allows the chemistry occurring at the anode surface to be investigated using temperature-programmed reaction measurements. A line diagram of the test equipment is shown in figure 1, whilst a schematic of the SOFC test reactor itself is shown in figure 2.

2.2. Anode and cell preparation

The anodes used in this work were prepared by physically mixing nickel oxide (Alfa Chemicals) and 8 mol%

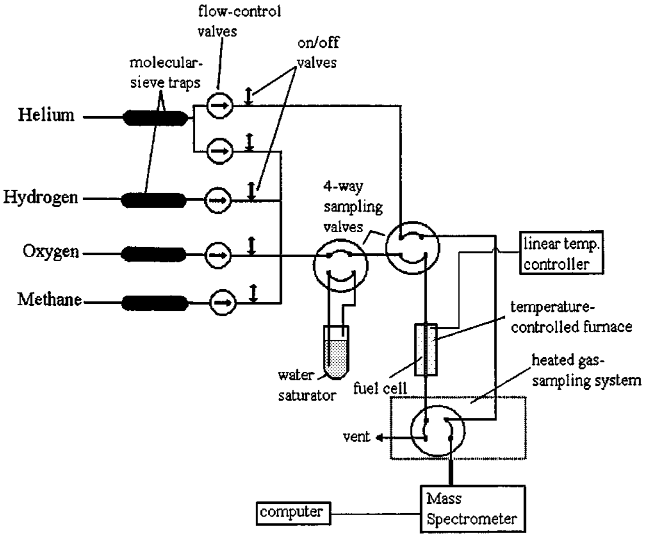

Figure 1. Schematic line diagram of the SOFC test system used for *in situ* catalytic, electrocatalytic and electrochemical measurements.

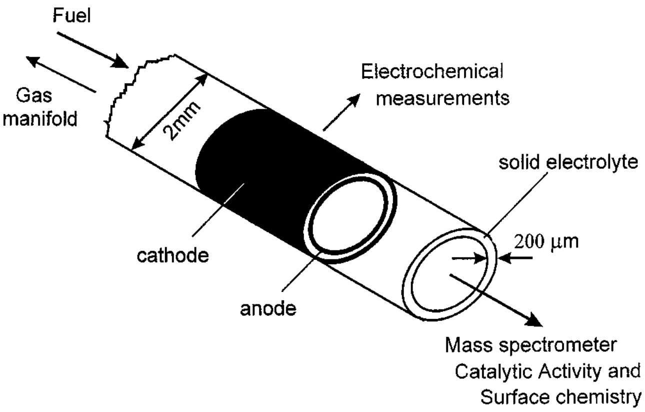

Figure 2. Schematic of the SOFC test system used for *in situ* catalytic, electrocatalytic and electrochemical measurements.

yttria-stabilised zirconia (YSZ) (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 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, in a conventional reactor; an approach which has been used previously by ourselves [17] and other workers [7,16], or as an actual anode coated on the tubular zirconia electrolyte. In this case the anode slurry is coated onto the inside of the zirconia electrolyte tube prior to firing as in an actual SOFC. The experiments reported here were carried out on anodes coated on zirconia electrolyte as in a working SOFC. Following drying at room temperature in air, the coated zirconia tubes were fired in a static air oven to 1573 K, using a specific firing regime. Strontium-doped lanthanum manganite was used as the cathode and was applied to the zirconia electrolyte as an ink. Following drying in air at room temperature the cells were fired to 1473 K, using the same procedure that was used for the anode. Spiralled 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. Current/voltage measurements were carried out using a specially designed passive potentiostat.

2.3. Experimental conditions

Following firing pre-reduction of the anodes, when carried out, was performed in the test system at 1173 K for 30 min in a 10% H_2/He stream. Steam reforming and partial oxidation reactions were carried out by passing the fuel mixtures over reduced and unreduced anodes at reaction temperature. The reactions were carried out using a gas mixture of 10% reaction gas in helium. Temperature-programmed measurements were carried out using a heating rate of 10 $\mathrm{K\,min^{-1}}$. Temperature-programmed reduction (TPR) and oxidation (TPO) measurements were carried out in 10% H_2/He and 10% O_2/He mixtures, respectively.

3. Capabilities of the test system

The following sections outline the capabilities of the SOFC test system in terms of studying the internal reforming catalysis and surface chemistry in an actual solid oxide fuel cell, and the electrochemical performance and durability of the SOFC, under genuine operating conditions.

3.1. Temperature-programmed reaction measurements on SOFC anodes

Temperature-programmed reduction (TPR) can be used to study the reduction characteristics of different anode samples. The reduction characteristics of the SOFC anodes are markedly different from either a simple physical mixture of NiO and zirconia, or a sample prepared by wetness impregnation of the nickel component. In the former case reduction of the nickel oxide occurs at rather lower temperatures (673 K), whilst in the latter case reduction of the nickel oxide component does not occur until significantly higher temperatures (815 and 894 K). The reason for the difference in reduction temperature can be attributed to the smaller particle size and stronger interaction of the NiO with the zirconia in the sample prepared by wetness impregnation [23,24]. The reduction characteristics of the SOFC anodes indicate that although the cermet anodes are formed from a physical mixture of NiO and zirconia, a fairly strong interaction occurs between the NiO and the zirconia following the extended milling procedure and the high-temperature calcination treatment used in anode preparation. The detailed interpretation of these results is reported elsewhere [22].

Temperature-programmed oxidation (TPO) and temperature-programmed reaction measurements can be carried out in the system in an analogous manner to the TPR experiments, using a flow of oxygen or reactant gas, respectively, in place of flowing hydrogen. TPO experiments

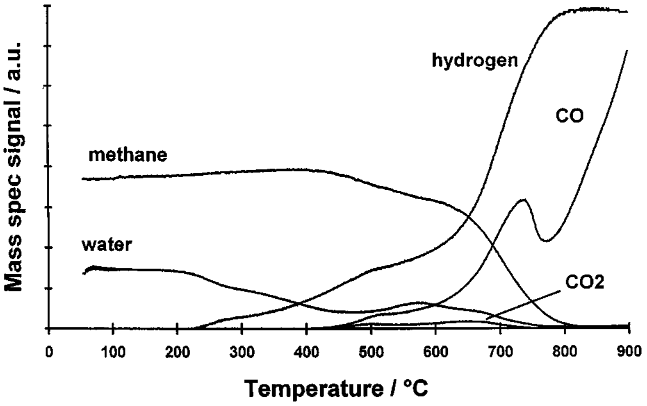

Figure 3. Temperature-programmed reaction profile of a pre-reduced 50 vol% Ni/zirconia anode exposed to a 2 : 1 methane/steam mixture.

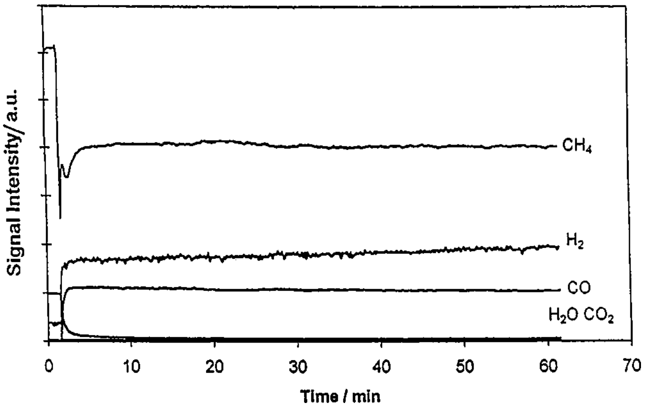

Figure 4. Exit gas compositions following exposure of a pre-reduced 50 vol% Ni/zirconia anode to a 5 : 1 methane/steam gas mixture at 1123 K.

have been used very extensively to evaluate the nature and quantity of surface carbon deposited on the anode following reforming, whilst temperature-programmed reaction measurements have been used to study methane activation, methane steam reforming and partial oxidation, and the reaction pathways occurring at the anode surface [22,25]. An example of this is shown in figure 3, which shows the temperature-programmed reaction profile of a pre-reduced Ni/zirconia anode in a 2 : 1 methane/steam mixture. It can be seen that dissociative adsorption of methane starts to occur at ∼680 K, as evidenced by the onset of carbon oxide evolution. The rate of methane adsorption increases with temperature with a rapid increase in methane conversion, and H_2 and CO formation, occurring above ∼920 K, and complete methane conversion occurring above ∼1100 K. The CO evolution profile is complex, with a local maximum in CO production observed at ∼1000 K followed by a sharp increase in the CO yield above ∼1040 K.

3.2. On-line catalytic measurements on SOFC anodes

The system design enables catalytic measurements to be carried out on the SOFC using the mass spectrometer to continuously monitor the exit gas composition. The four-way valve and the reactor bypass enable precise conversions and product selectivities to be calculated. The continuous real-time sampling of the mass spectrometer allows transient reaction phenomena to be observed; such transient phenomena cannot be detected using a gas chromatograph. Figure 4 shows the exit gas compositions when a reduced 50 vol% Ni/zirconia anode is exposed to a 5 : 1 methane/steam mixture at 1123 K. Upon introduction of the methane/steam mixture to the anode a large uptake of methane is observed together with hydrogen and CO evolution. Initially some CO_2 is also produced but this quickly falls off to very low levels, with almost total selectivity towards CO formation. Under these conditions the stability of the nickel anode as a reforming catalyst can be readily seen. It should be noted that figure 4 represents the isothermal analogue of figure 3. Heating the reaction mixture to 1123 K and holding it at this temperature should produce the steady-state reaction profile shown in figure 4.

As outlined in section 2, the gas manifold has been designed to allow any steam/methane or oxygen/methane ratio to be obtained. Thus the system can be used to study the reforming characteristics of different anode formulations over the full range of fuel cell operating conditions of temperature, gas flow rate and methane/oxidant ratio.

3.3. Study of carbon deposition on the SOFC anode during internal reforming

Following fuel reforming over the SOFC, post-reaction temperature-programmed oxidation is used to determine the amount of carbon deposited on the anode during reforming, the nature and strength of interaction of the deposited carbon with the anode, and to study the kinetics of carbon removal, using a method we have described elsewhere [17]. Figure 5 shows the TPO spectra obtained following steam reforming in a 5 : 1 methane/steam mixture for 60 min over a 50 vol% Ni/zirconia anode at 1123 and 1173 K. Under these fuel-rich reforming conditions significantly increased carbon deposition at 1173 K compared to at 1123 K can readily be seen. At both reaction temperatures the carbon is removed in two distinct processes. In addition to the carbon being removed at higher temperatures following reforming at higher temperatures, indicating stronger interaction, the higher temperature carbon species predominates at the higher reforming temperature.

3.4. Cell performance measurements

The test system can be used to carry out current/voltage measurements on the same cell with an identical experimental arrangement to the catalytic and temperature-programmed reaction measurements, allowing a direct correlation to be made between the reforming characteristics of the anode and the fuel cell performance. Thus the electrochemical performance and durability of the SOFC can be studied for different anode formulations and following different pre-treatment procedures over a range of

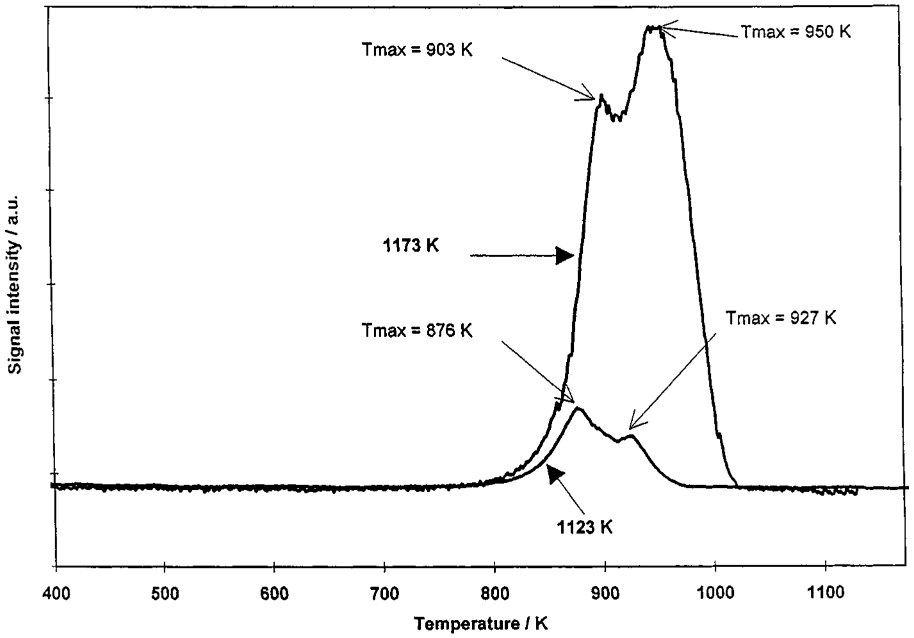

Figure 5. Temperature-programmed oxidation of carbon deposited on a 50 vol% Ni/zirconia anode following methane steam reforming for 60 min in a 5 : 1 methane/steam mixture at 1123 and 1173 K.

relevant operating conditions (temperature, gas flow rate, steam/methane ratio). An example of cell performance data obtained using this test system has been reported elsewhere [10].

3.5. Simultaneous electrochemical and catalytic (electrocatalytic) measurements on a working SOFC

A particularly powerful feature of the test system is the capability to simultaneously monitor the catalytic chemistry occurring at the fuel reforming anode and the electrochemical performance of a working SOFC under actual operating conditions, allowing direct correlation of the reforming characteristics and the cell performance, as well as enabling the influence of drawing current from the SOFC on the reforming activity, the reaction pathways occurring at the anode, and the level of carbon deposition, to be studied in detail. Figure 6 shows the effect of drawing current from an SOFC with a 50 vol% Ni/zirconia anode, operating at 1123 K in a 10 : 1 methane/steam mixture, on the reforming reaction. It can clearly be seen that as the potential across the ytttria-stabilised zirconia electrolyte is lowered from the open-circuit voltage, which leads to an increase in the oxygen ion flux across the solid electrolyte from the cathode to the anode, and an increased current can be drawn from the SOFC, there is increased methane conversion and stepwise increased production of hydrogen and CO. In addition to significantly increased CO and H_2 production, the formation of C_2 species is observed, which parallel the increase in H_2 and CO production. The formation of ethane and ethene was deduced from the 30 and 27 amu signals in the mass spectrometer, respectively. Post-reaction TPO experiments indicate that reduced carbon deposition occurs on the anode when the cell is operated under identical operating conditions of temperature and methane/steam ratio, but under load (generally 0.7 V) rather than on an unloaded cell.

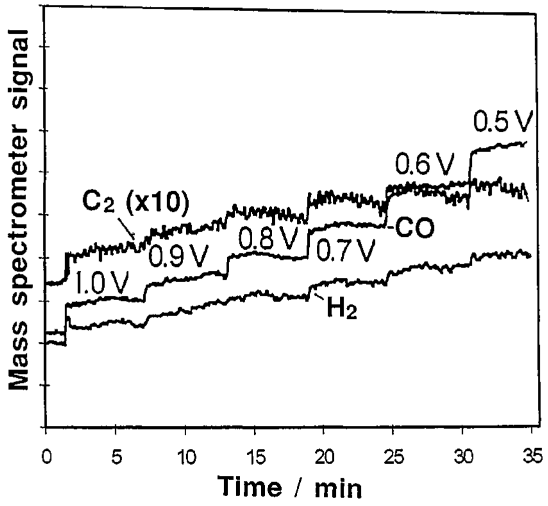

Figure 6. Effect of drawing current on the reforming activity of a tubular SOFC with a 50 vol% Ni/zirconia anode running on a 10 : 1 methane/steam mixture at 1123 K.

The increased methane conversion, and increased CO and H_2 production, can be attributed to a combination of increased steam reforming (and also dry reforming) activity through electrochemical production of steam and CO_2, and also because the flux of oxygen ions through the zirconia electrolyte causes some direct electrochemical partial oxidation of methane. The oxygen ions also provide an alternative electrocatalytic mechanism for carbon removal from the nickel anode, which partly accounts for the increased steam reforming activity. The other factor responsible for the increased reforming is the production of water and CO_2

via electrochemical oxidation of H_2 and CO; hence there are increased water levels and some CO_2 which lead to increased reforming activity, and also increased carbon removal. The formation of ethane and ethene indicates that in addition to being active for methane partial oxidation, removal of carbon, and electrochemical oxidation of H_2 and CO, the oxygen ion flux also results in some oxidative coupling of methane over the nickel/zirconia anode.

We have also used the test system to demonstrate the removal of carbon, deposited on the anode during operation, by the oxygen ion flux through the electrolyte. Thus if the fuel feed is switched off following reforming and a potential maintained across the cell, evolution of CO can be observed along with a measurable power output, due to electrochemical oxidation of the deposited carbon. In this way the removal of carbon deposited on the anode by the oxygen ion flux can be followed by mass spectrometry; when all the carbon is removed no further evolution of CO is observed, and the power output decreases. If the fuel feed is then restored maximum power output from the SOFC is again observed.

4. Summary

We have developed a test system for the *in situ* study of the fuel processing catalysis and electrocatalysis in solid oxide fuel cells, based on a thin-walled extruded yttria-stabilised zirconia tubular reactor. The system can be used to investigate the catalytic behaviour of the fuel reforming anode, the chemistry occurring at the anode surface and the electrochemical performance of the fuel cell, under genuine operating conditions. Catalytic measurements can be made on a fully working SOFC. The system therefore permits the fuel cell performance to be directly correlated with the reforming characteristics of the anode, and also enables the influence of applying an external load to the cell, and drawing current, on the catalytic activity and reaction pathways occurring at the anode to be established. Drawing a current from the cell results in a change in the reaction pathways occurring, with increased methane conversion, some via direct electrochemical partial oxidation, together with reduced carbon deposition, and the production of small quantities of ethene and ethane, via electrochemical oxidative coupling of methane. Electrochemical oxidative removal of carbon, deposited on the working SOFC anode during reforming, by the oxygen ion flux through the solid electrolyte can be directly monitored using on-line mass spectrometry.

Temperature-programmed measurements can be carried out on anodes in an actual SOFC. These have been used to investigate and characterise different anode formulations, to study methane activation and methane reforming, and evaluate the nature and level of carbon deposition on the anode during high-temperature operation, its strength of interaction with the anode, and the kinetics of carbon removal.

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