A novel test system for *in situ* catalytic and electrochemical measurements on fuel processing anodes in working solid oxide fuel cells

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A novel test system based around an extruded solid electrolyte tube enables the study of both the catalytic chemistry of fuel processing anodes in working solid oxide fuel cells and the electrochemical performance of the cell under the same conditions, allowing a direct correlation to be made between the fuel cell performance and the reforming characteristics of the anode.

Fuel cells are currently attracting a great deal of interest because they offer the possibility of more efficient and cleaner power generation. Solid oxide fuel cells (SOFCs) offer potential advantages over other fuel cell types because the high operating temperatures allow the possibility of running the cell directly on natural gas and other hydrocarbon fuels, internally reforming the fuel.[1–3] When a natural gas/steam mixture is passed over an SOFC anode at operating temperature, steam reforming (2) occurs, in addition to the methane decomposition (1) which results in carbon deposition. The CO produced by steam reforming may then undergo further reaction *via* the Water Gas shift reaction (3) and the Boudouard reaction (4).

$$CH_4 \rightarrow C_{(ads)} + 2H_2 \quad (1)$$

$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad (2)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (3)$$

$$2CO \rightarrow C_{(ads)} + CO_2 \quad (4)$$

The CO and H_2 produced at the anode *via* internal reforming can then react with the oxygen ions [reactions (5) and (6)] that are formed at the cathode [reaction (7)] and pass through the solid electrolyte to the anode.

Anode cell reactions $H_2 + O^{2-} \rightarrow H_2O + 2e^-$ (5)

$CO + O^{2-} \rightarrow CO_2 + 2e^-$ (6)

Cathode cell reactions $O_2 + 4e^- \rightarrow 2O^{2-}$ (7)

However, several major problems of internal reforming remain to be solved, including the problem of carbon deposition on the anode and its subsequent deactivation which leads to poor durability,[3] obtaining the optimum anode formulation and the design of a suitable test system. Consequently, many SOFC studies use hydrogen as a fuel, and there is a lack of studies using hydrocarbons, whilst other studies have focused on important aspects of materials development.

In terms of obtaining the optimum anode formulation and cell operating conditions, one of the key problems is the design of a suitable test system to study the catalytic chemistry occurring at the anode and to evaluate the cell performance. The design and construction of such a system is not straightforward. In particular the problems of rapid heating of the cell to operating temperature, thermal cycling, sealing, obtaining gas tight connections and being able to make both electrochemical and gas analysis measurements all have to be overcome; a particular difficulty with planar-type devices.

Nickel/zirconia cermet anodes can be considered to be somewhat analogous to supported nickel steam reforming catalysts, which have been studied extensively.[4–6] It is therefore possible to study the catalytic behaviour of nickel-based anodes in powder form inside a conventional catalytic reactor; this approach has been demonstrated by several research groups.[2,7] In many other studies the primary focus is the electrochemical performance of the cell, and the influence of electrode composition or structure and other experimental parameters are monitored by measuring current or power densities.[8–10] There are a lack of studies in which the catalytic chemistry of the fuel reforming anode is studied when the anode is part of an actual SOFC.

Here, we report the development of a test system based on a small diameter, thin-walled extruded yttria-stabilised zirconia tubular reactor which can be used to study the catalytic activity of the fuel reforming anode, the chemistry occurring at the anode surface and the electrochemical performance of the fuel cell. This allows a direct correlation between the cell performance and the reforming characteristics of the anode. In addition the test cell can be readily used to study the problems of carbon deposition and poor durability in operation. The particular benefits of this test cell are that it can be rapidly assembled, heated and cooled, and it has no sealing or leakage problems, which many test devices suffer from. The zirconia reactor is housed in a furnace operated by a temperature controller which allows linear control up to 1373 K. As yttria-stabilised 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 furnace is at 1373 K. The test cell inlet is linked to a stainless-steel gas manifold which allows complete flexibility in the choice of fuel and fuel/steam ratio. The gas feed can be instantly switched between H_2, O_2, inert gas and fuel and gas mixtures of any combination can be achieved, enabling evaluation over a wide range of operating conditions and fuel compositions. The reactor outlet is linked to an on-line mass spectrometer which permits the fuel processing reactions at the anode to be directly studied in the actual SOFC under operating conditions, and allows the chemistry occurring at the anode surface to be investigated using temperature programmed measurements.

The anodes were prepared from a slurry of nickel oxide and 8 mol% yttria-stabilised zirconia which was milled for 3 h, with a small quantity of binding agent added at the end of the milling period. The anode can then be studied as a powder in a conventional reactor following firing. However, in this case the anode slurry is applied to the inside of the electrolyte tube prior to firing as in an actual SOFC. Following drying, the coated zirconia tubes were fired to 1573 K. Strontium-doped lanthanum manganite was used as the cathode. Nickel wire was used for current collection from the anode and silver wire from the cathode. A specially designed potentiostat was used for the electrochemical measurements. Following firing the anodes were reduced in the reactor at 1173 K for 30 min in H_2. Reforming reactions were carried out by passing the fuel mixture over the reduced anode at reaction temperature.

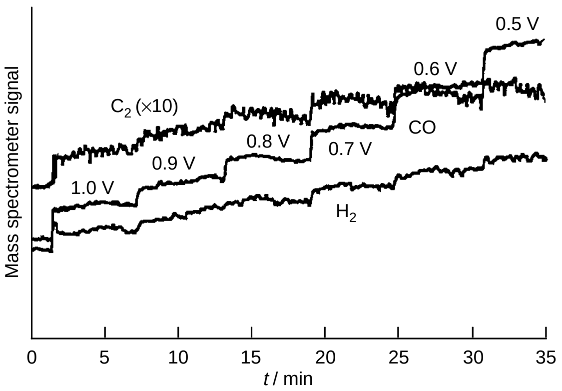

Fig. 1 The effect of drawing current on the reforming activity of a tubular SOFC with a nickel/zirconia anode running on a 19 : 1 methane–steam mixture at 1123 K

Thus the system allows the catalytic performance of the fuel reforming anode of an SOFC to be continuously monitored and 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 fuel composition. Importantly the anode is tested in an identical form and under the same conditions as in a working SOFC. The continuous real-time sampling of the on-line mass spectrometer enables any transient phenomena to be observed; such phenomena cannot be detected using a gas chromatograph. In combination with the linear temperature controller this also permits temperature programmed measurements to be carried out on the cells; temperature programmed reduction (TPR), oxidation (TPO) and reaction spectroscopy (TPRS). These have been used to study the firing and reduction characteristics (TPR, TPO), methane activation, methane steam reforming and the reaction pathways occurring at the anode surface (TPRS) and the nature and extent of carbon deposition following reforming (TPO). The detailed interpretation of these results will be reported elsewhere.[11] The same system and identical experimental arrangement can be used to carry out electrochemical measurements on the same cell, allowing a direct correlation to be made between the reforming characteristics of the anode and the fuel cell performance.

Furthermore, the system allows the chemistry occurring at the fuel reforming anode and the electrochemical performance of the SOFC to be simultaneously monitored under actual operating conditions. Fig. 1 shows the effect of drawing current from an SOFC with a nickel/zirconia anode, operating at 1123 K in a 19 : 1 methane–steam mixture, on the reforming reaction. It can clearly be seen that as the current drawn increases, *i.e.* as the cell potential decreases, there is increased methane conversion, stepwise increased production of hydrogen, and significantly increased formation of CO and C_2 species which parallel the increase in H_2 formation. Table 1 shows the corresponding cell performance. This demonstrates that we can directly correlate changes in the catalytic behaviour of the anode with the fuel cell performance.

Table 1 Electrochemical performance of a tubular SOFC running on a 19 : 1 methane/steam mixture at 1123 K

Cell potential/V	Current density/ mA cm^{-2}
1.0	93
0.9	117
0.8	146
0.7	160
0.6	197
0.5	232

In summary, we have developed an SOFC test system, based on an extruded zirconia tubular reactor, which can be used to investigate the catalytic behaviour of the fuel reforming anode, the anode surface chemistry and the electrochemical performance of the fuel cell, under genuine operating conditions. Catalytic measurements can be made on a working SOFC. Temperature programmed measurements can be carried out on anodes in an actual SOFC, and have been used to characterise different anode formulations, to study methane activation and reforming, and to evaluate the nature and level of carbon deposition on the anode during operation.

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Notes and References

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