Short communication

Microtubular SOFC anode optimisation for direct use on methane

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Abstract

The main problems of small-scale solid oxide fuel cell (SOFC) devices are the rapid start-up, durability and operation on available fuels such as methane. This paper describes how microtubular anode-supported SOFCs can be started rapidly and run on methane. However, the key factor was the activity of the nickel anode, especially its surface area and conductivity, which were found to depend on the reduction method and the operating fuel. Controlled reduction experiments in hydrogen at temperatures between 650 and 850 °C were performed. Reduction temperature and gas composition were altered and the resultant electrical performance and exhaust gases recorded. The conclusion was that microtubular SOFC can be successfully run on methane to outperform pure hydrogen by up to 9%.
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1. Introduction

Solid oxide fuel cells (SOFCs) are energy conversion devices that produce electricity via electrochemical reactions of fuel and oxidant gases across an ionic-conducting ceramic. Fuel cells convert fuel directly to electricity, with heat as a by-product, at efficiencies greater than any single conventional energy conversion technology [1,2]. Their modular nature coupled with their ability to generate electricity cleanly and efficiently make them attractive for a wide variety of applications and markets [2,3].

SOFCs have attracted special interest as a method of power generation because of the available catalysts and the fuel options [2]. Present development of SOFCs is focused on lowering the operating temperature to below 800 °C and using available fuels such as methane and butane [4]. The advantages of reduced temperature operation include wider material choice, better long-term performance, and system compactness, potentially leading to lower manufacturing costs [5].

SOFCs employ a solid-state electrolyte and typically operate near 800 °C. The SOFC typically uses a solid yttria-stabilised zirconia (YSZ) ceramic material as the electrolyte layer. During operation, oxidant (usually air) enters the cathode compartment and after the electrode reaction, oxygen ions migrate through the electrolyte layer to the anode where hydrogen is oxidised. The operating temperatures of SOFCs are sufficiently high to provide the necessary heat for the endothermic reforming of hydrocarbons on the nickel/YSZ anode. SOFCs are therefore more tolerant of fuel impurities and can operate using hydrogen and hydrocarbon fuels directly at the anode; this has been well documented [6–14]. However, several issues exist with direct internal reforming such as carbon deposition. This is traditionally overcome with the use of dopants such as ceria and molybdenum in the anode [14]. Moreover, recent developments include the use of barrier and catalyst layers to suppress coke formation [15,16]. In this paper we discuss an alternative method of operating a microtubular SOFC directly with methane without significant coking by modification of the Ni/YSZ anode reduction technique.

2. Methods and materials

2.1. Cell manufacture

NiO/YSZ-supported micro-tubes were supplied by Adaptive Materials Inc., USA (AMI). These tubes were of 55 mm length and were coated with YSZ electrolyte of approximately 15 μm. Two cathode layers of LaSrMnO$_3$ (LSM) were prepared by vibro-milling into an ink. More detail on ink preparation can be found in Mallon and Kendall [7].

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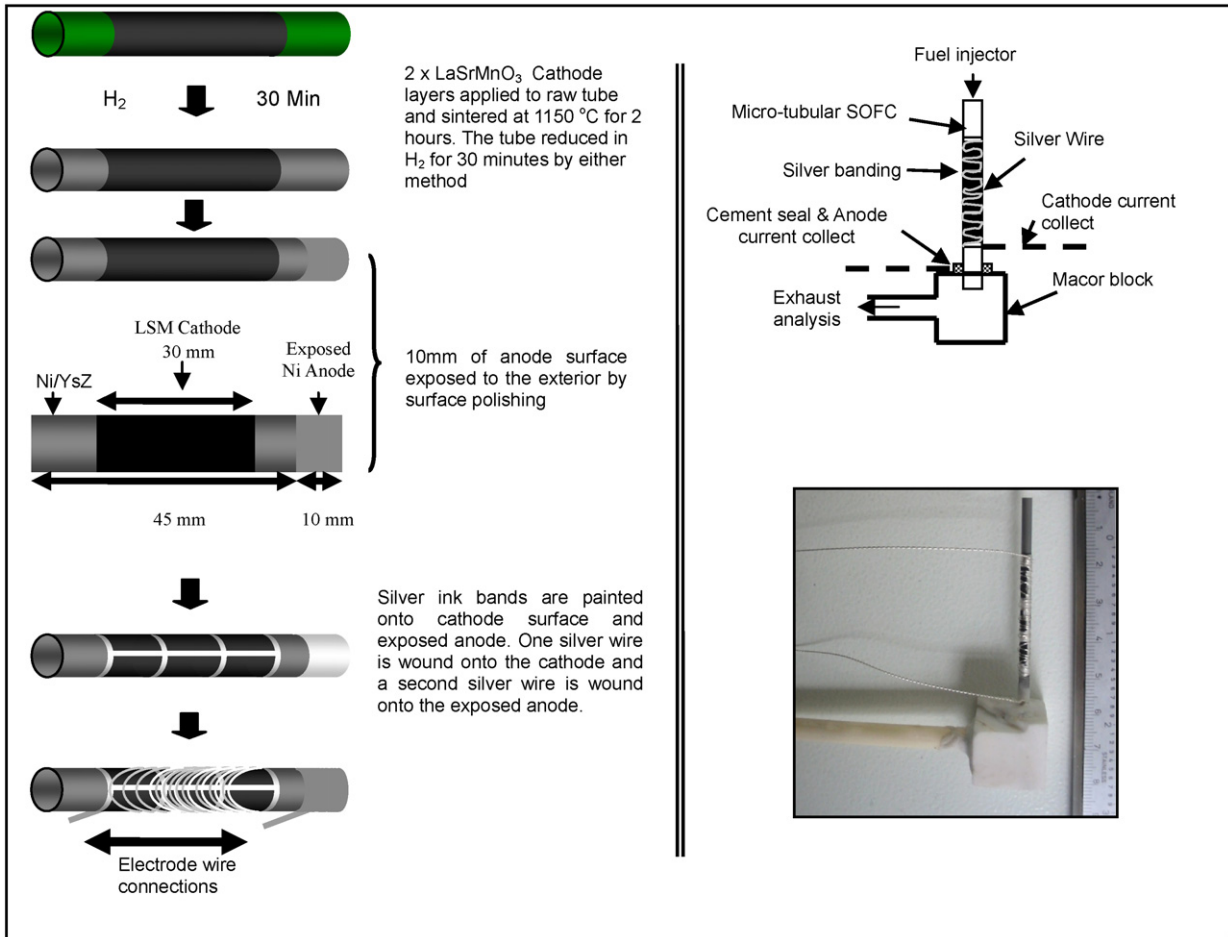*E-mail address:* axd853@bham.ac.uk (A. Dhir).

Fig. 1. This figure outlines the steps involved in manifolding a microtubular SOFC for simultaneously obtaining electrochemical and catalytic performance.

Cathode layer 1 was painted onto the external surface of the tube to a length of 30 mm and left to dry overnight. Cathode layer 2 was then applied and sintered at 1150 °C for 2 h. The active cathode area was 1.6 cm². The cells were then reduced from NiO to Ni via two different methods—Ramped and Constant Temperature (see Section 2.3). Anode current collection was achieved by exposing the anode by carefully removing the thin electrolyte from the surface (10 mm length) [17]. Silver conductive ink was applied to the exposed anode surface to enhance the contact with the silver wire. Silver wire was then wound around the outside of the exposed anode and high-temperature cement was used to seal the surface of the silver wire when manifolding for testing. Silver wire was wound onto the outside surface of the cathode to act as the external current collector. Contact of the silver wire and the cathode surface was enhanced by using four silver ink bands. SOFCs were manifolded using high-temperature cement
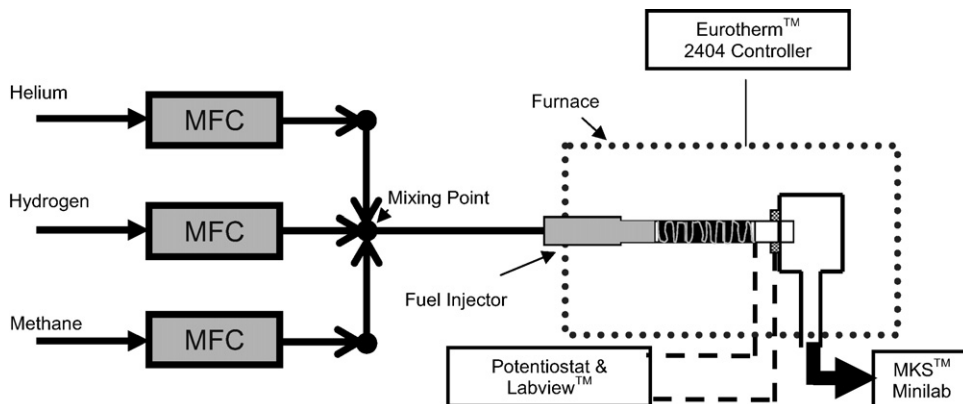

Fig. 2. Schematic of the test equipment. 3× Unit Instruments mass flow controllers, a Eurotherm 2404 furnace controller, Potentiostat and a MKS mass spectrometer.
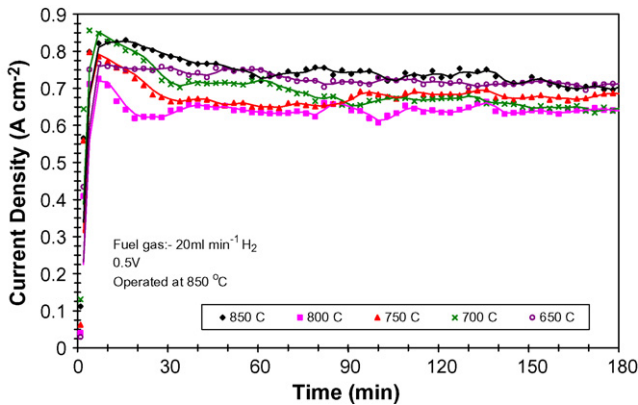
Fig. 3. Comparison of the ramped reduced tubes and the performance on 20 ml min^{-1} hydrogen at 0.5 V.

into drilled Macor blocks to allow simultaneous exhaust gas analysis and electrical measurements. Fig. 1 shows these steps and picture of the final product.

2.2. Materials

Anode supported tubes of 55 mm length and diameter 2.3 mm were supplied by AMI, USA. They had a 300 μm nickel oxide/YSZ cermet and a 15 μm 8% YSZ electrolyte.

Gases were supplied by British Oxygen Company (BOC), UK, as follows:

- Helium 99.99%.
- Hydrogen high purity 99.95%.
- Methane CP grade 99.95%.

2.3. Cell reduction

The micro-tubes were reduced using two different methods: Ramped and Constant Temperature. The temperature range investigated here was 650 to 850 °C at 50 °C intervals.

2.3.1. Ramped reduction

20 ml min^{-1} of H$_2$ was supplied to the tube for 30 min. The temperature was then raised from ambient to the test target temperature at a rate of 100 °C min^{-1}. The tube was then cooled back to ambient temperature in a 50:50 mixture of helium and hydrogen to avoid oxidation.

2.3.2. Constant temperature reduction

The tubes were raised from ambient to the test target temperature in air for a period of 10 min, then 20 ml min^{-1} H$_2$ was supplied for an exposure time of 30 min. The furnace was then cooled back to ambient temperature in a 50:50 mixture of helium and hydrogen to avoid oxidation.

2.4. Cell testing

The microtubular fuel cells were tested in a brick furnace, controlled by a Eurotherm^{TM} 2402 controller. 3× Unit Instru-
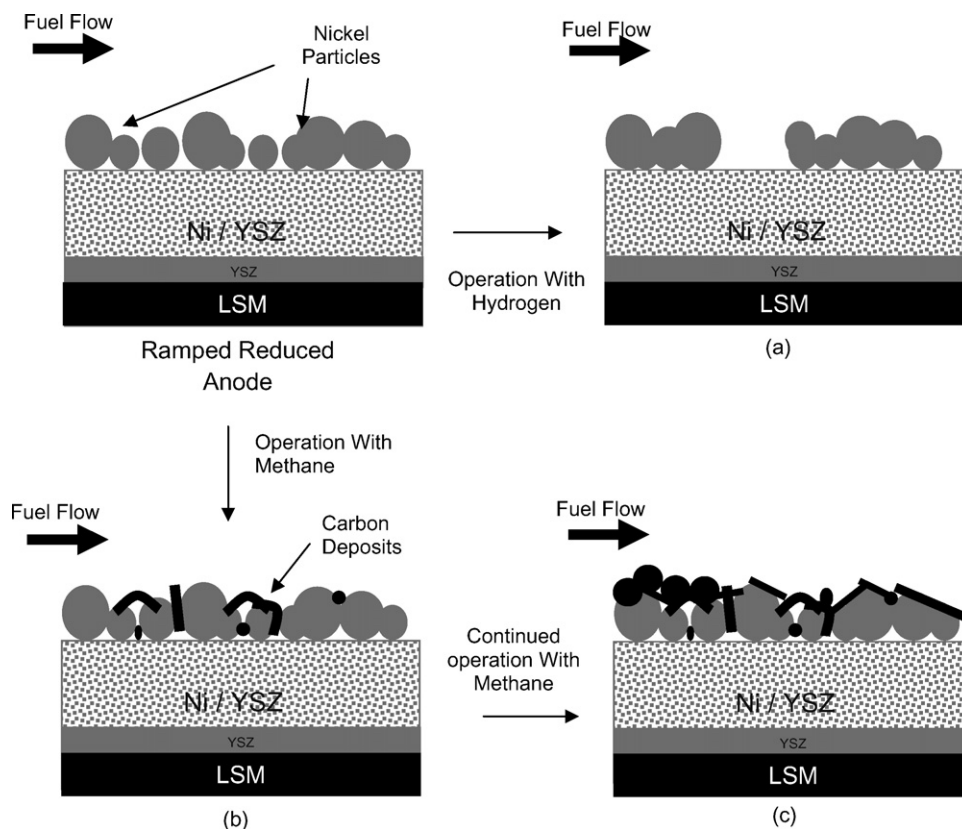

Fig. 4. Proposed anode structure under ramped reduction when (a) hydrogen and (b) methane are used as fuels (c) continues on methane.

ments 7300 mass flow controllers were utilised to control the flow of gases to the system. The cell was loaded using a university built potentiostat and data was logged using a Labview[TM] interface. Exhaust gases were analysed using a MKS[TM] mini lab mass spectrometer and *Process Eye 2000* software. The system was linked together using several swagelok[TM] valves and pipes. The layout can be seen in Fig. 2.

20 ml min^{-1} of helium carrier gas was used throughout to enable gas analysis. Each tube weighing 0.5 g Ni/YSZ was supplied with 3 ml min^{-1} methane, ramped at 100 °C min^{-1} and operated at 850 °C. The cell was loaded to 0.5 V once OCV had stabilised at 1.2 V. Fuel gases were not preheated or humidified during these experiments. All preheating was conducted within the delivery tube in the furnace.

The amount of carbon deposited on the SOFC anode was determined by exposing the anode to an oxygen atmosphere and then monitoring the evolution of CO and CO_2 as the carbon was oxidized — a technique called temperature programmed oxidation (TPO). The silver wire was removed from the used cells which were then placed into a quartz glass tube. The tube was then placed in a furnace in the experimental rig described above. A constant flow of helium (20 ml min^{-1}) and oxygen (5 ml min^{-1}) was supplied, and the furnace was heated to 850 °C at a rate of 10 °C min^{-1}. As the temperature was raised, different types of carbon reacted to form CO or CO_2 at different times. Amorphous (adsorbed) carbon tends to oxidise around 300 °C, whereas graphitic oxidises around 600 °C. CO and CO_2 levels were monitored by an online mass spectrometer. The quantity of carbon was then quantified using an internal calibration.

3. Results and discussion

Two different methods of reduction, Ramped and Constant Temperature (as explained in Section 2.3) have been examined. A temperature range of 650 to 850 °C (at 50 °C intervals) was investigated on both hydrogen and methane giving electrochemical results, data on the reforming products and the amount of carbon deposited.
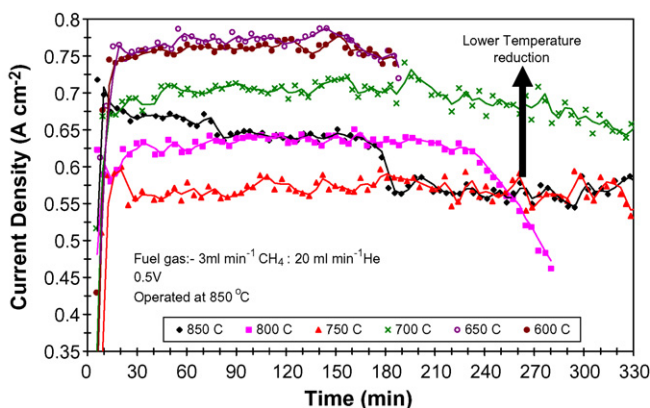
3.1. Ramped reduction

Fig. 3 shows the results for tubes that had been ramped reduced and operated with hydrogen. It can be quite clearly seen that in the first 30 min of operation the cell performance degraded substantially. This 20% degradation in performance is common at all temperatures, indicating that this response of the micro-tubes is independent of the reduction temperature. After this initial drop, the performance only degrades by 2% up to 36 h. After 36 h [17] of operation there was no further drop in performance.

The cells exhibit good performance (with hydrogen, 0.7 A cm^{-2}) with this reduction technique. Fig. 4 displays a pictorial representation of the postulated anode structure when ramped reduction is used. As the NiO/YSZ cermet is subjected to a range of temperatures during the reduction phase, particle size is non-uniform, with smaller particles at lower temperatures. As reduction continues at the higher temperatures, nickel becomes mobile and leads to the formation of larger particles.

When the SOFC is used at the high operating temperature of 850 °C the particles become mobile, from which agglomeration and sintering of these multi-sized particles (at both the bulk and interface) can take place when hydrogen is the choice of fuel. This is indicated in Fig. 4a, leading to a disjointed anode structure were the conductivity for the electrons is decreased, hence leading to a drop in electrical performance.

Fig. 5 conveys the results obtained with 3 ml min^{-1} methane on the ramped reduced tubes. When methane is used as a fuel this initial 20% degradation is not witnessed. In fact the performance seems to increase on those tubes that have been reduced at the lower temperatures (<750 °C). When methane is the choice of fuel, agglomeration and sintering can be overcome. This is illustrated in Fig. 4b. Here the products of methane reforming contribute to the behaviour of the anode structure. The carbon that is deposited in the early stages of the reforming "sits" between the disjointed multi-sized particles. Carbon creates a bridging effect [7,18], which keeps the normally mobile nickel particles apart. With the ability of carbon to conduct electrons, the conductivity is also increased. Hence when methane is used the performance increases at first, but continued oper-
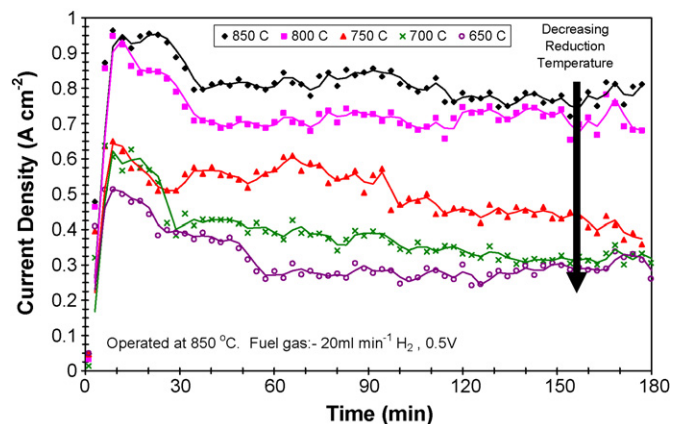

Fig. 5. Performance at 0.5 V of the ramped reduced tubes at different temperatures using 3 ml min^{-1} methane as fuel.

Fig. 6. A comparison of the constant temperature reduced tubes on 20 ml min^{-1} hydrogen at a 0.5 V.
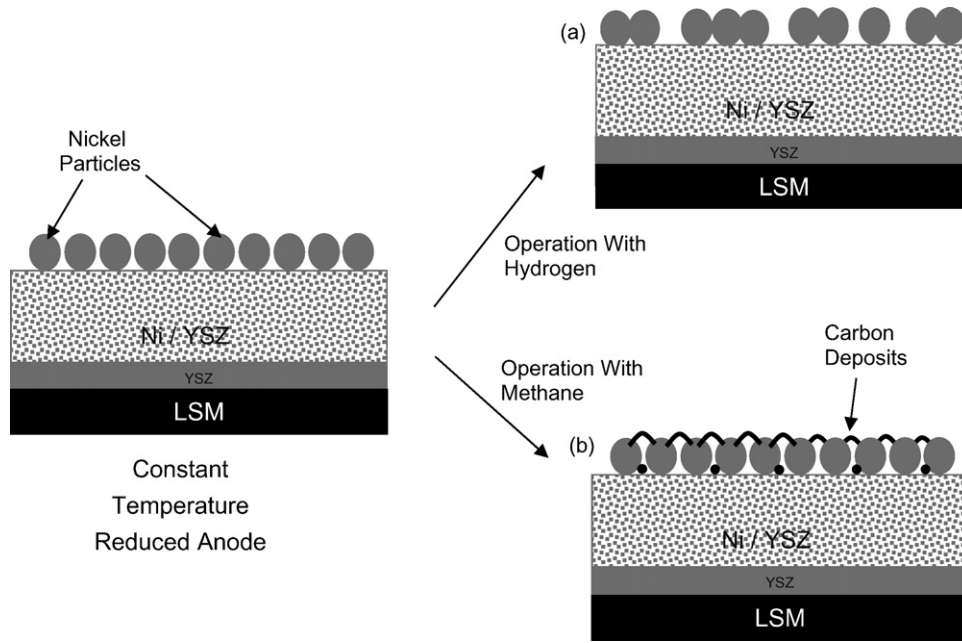
Fig. 7. Proposed anode structure after constant temperature reduction in hydrogen, then operated on (a) hydrogen and (b) methane.

ation (Fig. 5) leads to more carbon deposition (Fig. 4c) which blocks the anode after a few hours. This is evident in those tubes that have been reduced at the higher temperatures (>750 °C). Tubes that have been reduced at a lower temperature show this behaviour after longer operation. At the higher temperatures of reduction the surface area of the nickel anode is decreased, hence there are less active catalytic sites. With low temperature reduction there is an increase in surface area and thus an increase in reforming sites, hence it takes longer for the deposition to occur.

3.2. Constant temperature reduced

The constant temperature reduced cells gave a wide range of current densities when operated on hydrogen (Fig. 6). This is to be expected because nickel oxide reduces to smaller (fine), separated, particles at lower temperatures, leading to a decrease in the electrical conductivity of the anode. When higher temper-
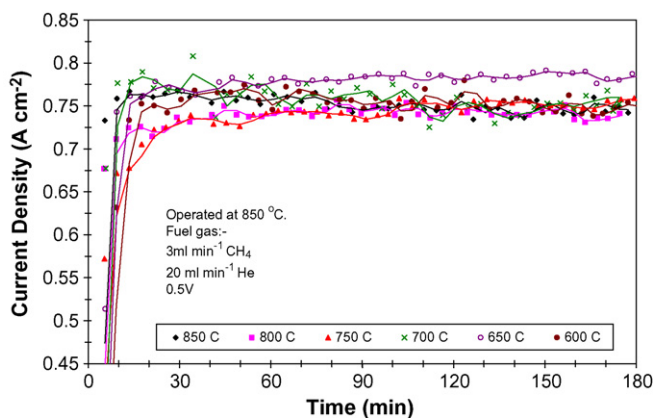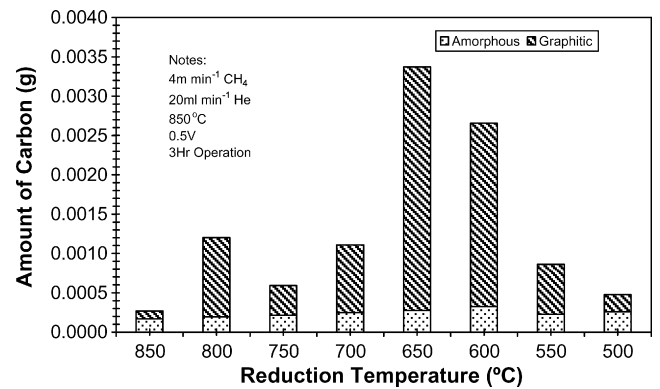

Fig. 9. Results of temperature programmed oxidation on each of the constant temperature reduced tubes after operation on methane. Carbon deposited on the surface of the anode is quantified into both graphitic and amorphous.

atures are used, larger (coarse) particles are obtained which are highly connected. A pictorial representation is given in Fig. 7 which postulates a difference in nickel structure when operated on the different fuels.

Fig. 8. Performance at 0.5 V of constant temperature reduced tubes using 3 ml min^{-1} methane.
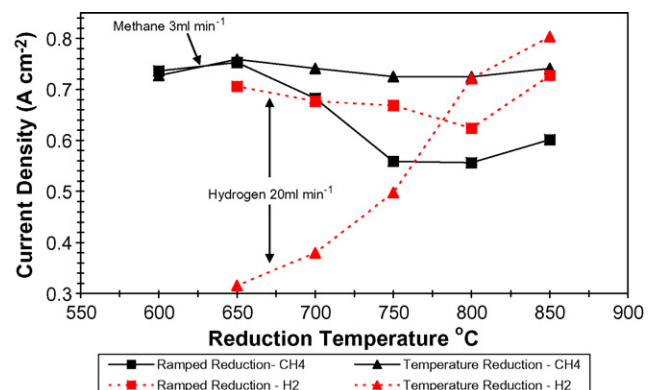

Fig. 10. Steady state current density at 0.5 V for both types of anode reduction.

Fig. 8 gives the current density of constant temperature reduced micro-tubes with 3 ml min^{-1} methane. It can be seen quite clearly in comparison to Fig. 6 that stable operation is achieved at 850 °C operation whatever the reduction temperature. Sintering and agglomeration can be overcome, Fig. 8 shows that electrical performance does not degrade with operational time, consistent with the model of Ni/YSZ structure given in Fig. 7b.

Lower temperature reduced tubes show an increase in current density by 4%. This can be explained by the increased catalytic activity of the anode due to the finer particles after low temperature reduction. With the lower temperature reduced cell, the active surface area is increased.

Fig. 9 shows that much more carbon is deposited on the anode after reduction at 650 °C which is consistent with higher nickel activity. Because most of this is graphitic carbon, better conductivity is expected.

3.3. Comparison of the two reduction methods

Fig. 10 shows a direct comparison of current density for both methods of reduction with both fuels. It can be seen that when ramped reduction was utilised the micro-tubes continued to produce in the region of 0.7 A cm^{-2} on both hydrogen and methane. Conversely when constant temperature reduction was used, the performance on hydrogen was poor on those tubes that had been reduced below 800 °C.

Fig. 11 shows the products of the internal reforming when running on methane. The current was drawn after 2 min coincident with the hydrogen peak. It can be seen that methane drops to zero after 5 min. The methane entering has been broken down into hydrogen, carbon dioxide, carbon monoxide, water and carbon.

Fig. 12 shows current density versus time for the same test. The curve for hydrogen peaks after 4 min and then declines by 10% whereas the methane shows a constant current density after a few minutes. The cell performed by up to 9% better on methane than on hydrogen. This increase in performance has been attributed to the amount of carbon that had been deposited
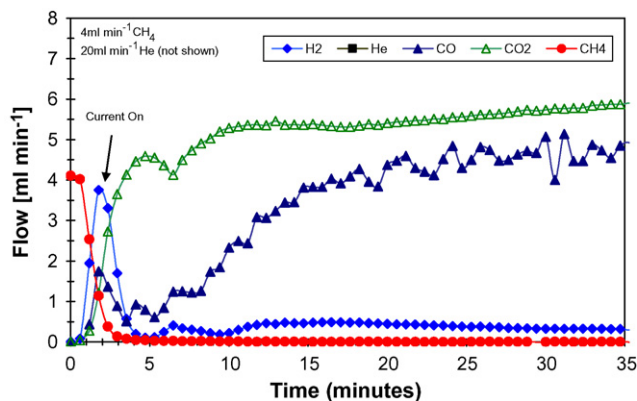

Fig. 12. Current density for constant temperature reduced tube on both H$_2$ and CH$_4$ at 850 °C and 0.5 V.

during the initial operation. The carbon deposition did not hinder the performance during the period of testing.

4. Conclusions

The effect of reduction technique on carbon deposition and performance with anode supported microtubular SOFC has been examined.

Reducing tubes at a specified temperature by constant temperature reduction yields consistent performance with methane. The best performance with methane of 0.85 A cm^{-2} is achieved by temperature reduction at 650 °C because carbon bridging maintains the anode structure and prevents sintering.

Methane has been shown to out perform hydrogen by up to 9% when using the optimal conditions of using constant temperature reduction at 650 °C. The tubes can be run successfully even with carbon deposition at these conditions.

Acknowledgments

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Fig. 11. Mass spectrometer results when a 650 °C constant temperature reduced SOFC is operated at 850 °C. After 35 min steady state is achieved.
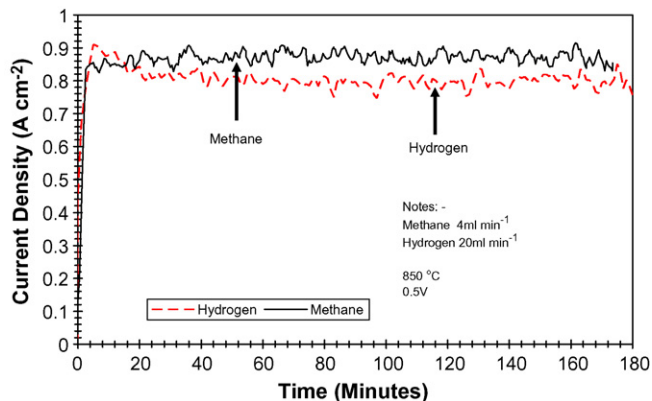
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