

# Sensitivity of nickel cermet anodes to reduction conditions

Christian Mallon\*, Kevin Kendall

*Chemical Engineering, University of Birmingham, Edgbaston B15 2TT, UK*

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## Abstract

The direct use of methane as fuel for solid oxide fuel cell (SOFC) without pre-reforming would reduce running costs and enable higher efficiencies. But methane generally causes carbon deposition on the nickel anode and subsequent power degradation. This paper shows that carbon deposition from methane is very sensitive to anode reduction conditions. The effect of direct methane on microtubular SOFC reduced at two different conditions was studied at temperatures above 800 °C. Reducing the cells at high temperature gave good performance on hydrogen but the current degraded quickly on methane, suggesting that carbon was blocking the nickel surfaces. This was not recoverable by bringing in hydrogen to replace the methane. Cells reduced under low temperature conditions gave higher current on methane than on hydrogen, showing that carbon deposited from the methane improved nickel anode conductivity in this case. These cells also did not degrade on methane under certain conditions but lasted for a long period. Extracting the carbon by feeding the cell with hydrogen interrupted this newly formed linkage between the nickel particles, reducing the electrical conductivity, which could be recovered by reintroducing methane. The conclusion was that nickel cermet anodes are very sensitive to reduction conditions, with low temperature reduction being preferred if methane is to be used as the chosen fuel.

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## 1. Introduction

There has been a lot of recent interest in the direct operation of solid oxide fuel cells (SOFCs) on methane, which normally degrades nickel anodes because of carbon deposition or coking. Usually, this has been solved by internal reforming, adding large amounts of steam and/or CO<sub>2</sub> into the fuel stream to prevent the carbon formation [1]. Recently, however, it has been shown that SOFCs can also work directly with pure methane without coking [2], when particular structures of nickel anodes were formulated. Changing the anode composition by adding ceria [3] and operating at higher temperatures [4] were effective in preventing carbon formation. Such results show that nickel anodes can be used directly on methane but the anodes need to be specially formulated in distinct compositions. In this paper, we show that conven-

tional nickel/zirconia cermet anodes can be used directly on methane, providing that their morphology has been defined by proper reduction conditions. It appears that the structure and performance of nickel/zirconia anodes depends to a significant extent on the reduction conditions.

## 2. Experimental

Fig. 1 shows the design of microtubular SOFCs used in the experiments. These cells were based on 5 cm long extruded thin walled yttria stabilised zirconia oxide (YSZ) tubes with active surface area of 0.5 cm<sup>2</sup>. The electrolyte tubes with a diameter of 2 mm were produced with a wall thickness of approximately 275 μm after extrusion and drying, shrinking to 225 μm after sintering at 1450 °C [5]. Because these tubes had such a small diameter, they were resistant to fracture by heat shock and thermal cycling [6].

\* Corresponding author.

*E-mail address:* CDM107@bham.ac.uk (C. Mallon).

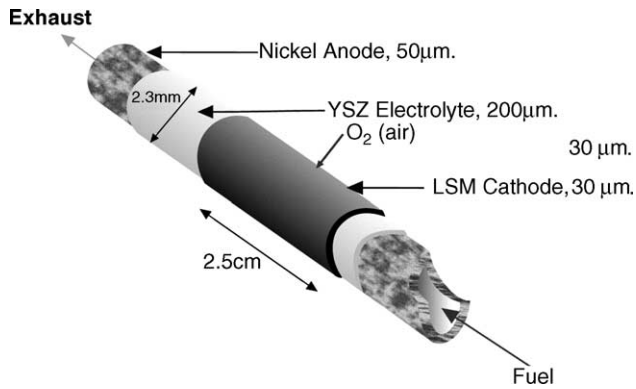


Fig. 1. Design of a microtubular SOFC [5].

The anode was prepared as a slurry ink by vibromilling nickel oxide (44 wt.%), 8YSZ (12%), acetone (41.4%) and KD2 surfactant (2.6%) to form an ink which was injected into the electrolyte tube with a syringe, dried at 378 K and sintered

at 1573 K for 1 h [7]. A second composition of anode containing more nickel oxide (47%), 3.2% cerium oxide and less 8YSZ (6%) was vibromilled in the same way and deposited on the first layer to enhance electronic conductivity and to help match the anode and electrolyte thermal expansion coefficients [8].

To make the cathode,  $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$  (44%) was mixed with 8YSZ (12%), acetone (42%) and KD2 surfactant (1.2%) and vibromilled to form an ink which was painted on the outside of the electrolyte tube. A second layer containing 58% lanthanum strontium manganite, 40.7% acetone and 1.2% KD2 was vibromilled and deposited on top of the first layer, dried at 378 K and sintered to 1373 K [7] to improve electronic conductivity. The overall cross-section of a fractured cell revealed by scanning electron microscopy (SEM) is shown in Fig. 2.

The current collection from the anode was a nickel wire inserted into the tube to make contact with the anode [5]. To make the positive connection, a silver wire was wound

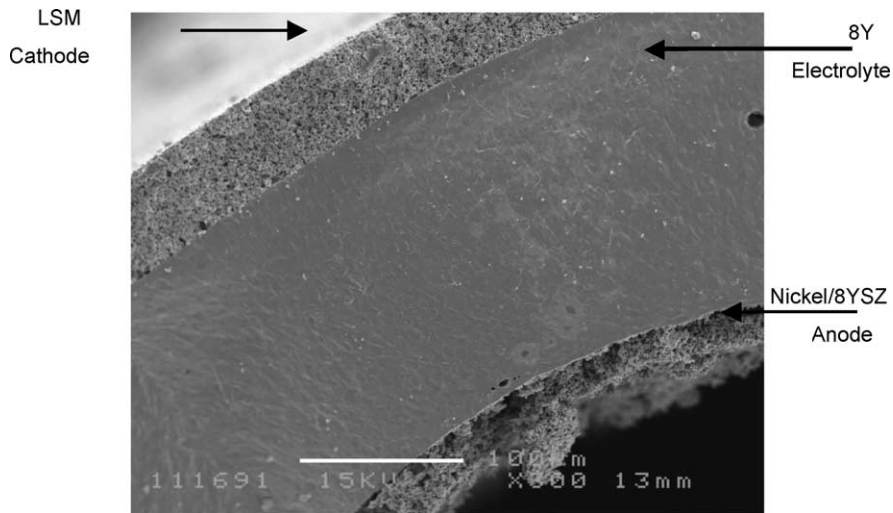


Fig. 2. SEM cross-section of a microtubular SOFC [5].

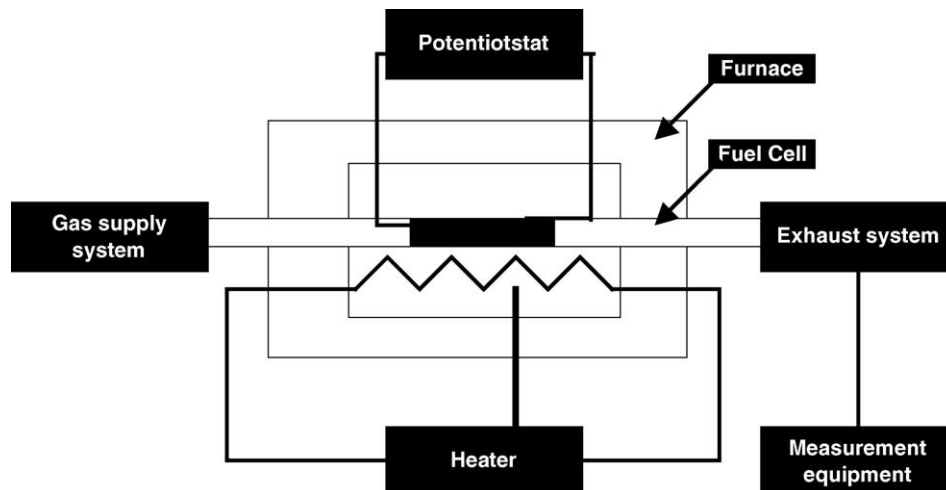


Fig. 3. Experimental set-up for measuring fuel cell performance.

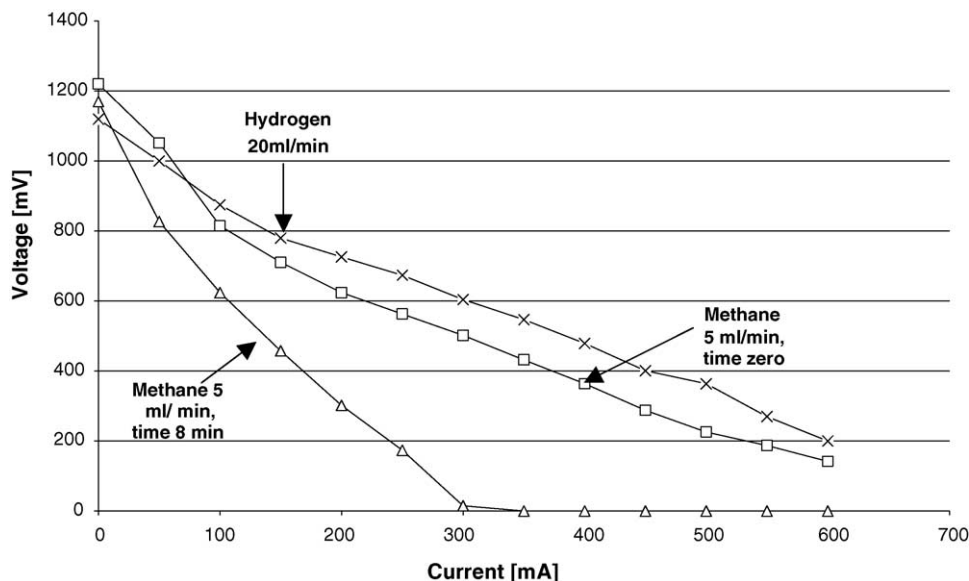


Fig. 4.  $V$ - $I$  curves for the SOFC reduced at high temperature. Hydrogen gave good performance which was almost the same as methane at first. But the cell output degraded after 8 min on methane.

onto the outside of the cathode, with silver paste to increase electrical contact and catalyze oxygen ionization [4].

The microtubular cell was inserted into the experimental set-up shown in Fig. 3. This was an electrically heated furnace controlled by a Eurotherm system. The gases were supplied from cylinders, metered by mass flow controllers, mixed and then passed to the fuel cell. The exhaust gas was analysed with a mass spectrometer and the electrical output after reduction was monitored by a potentiostat. To study the sensitivity to reduction conditions, two methods of reduction, high temperature and low temperature, were employed and the cell performance and anode microstructure were subsequently measured.

### 3. Performance after high temperature reduction

To reduce at high temperature, the SOFC was heated in air at  $20 \text{ K min}^{-1}$  to  $850^\circ\text{C}$  such that the nickel oxide was not reduced prematurely. Then hydrogen was passed into the anode compartment at  $20 \text{ ml min}^{-1}$  for 20 min to ensure that all the nickel oxide in the anode was reduced into nickel metal. The open circuit voltage was 1.120 V. Current was then drawn from the cell using the potentiostat to plot out the  $V$ - $I$  curve shown as crosses in Fig. 4. The current at 0.5 V was 375 mA corresponding to  $750 \text{ mA cm}^{-2}$  and the cell performed steadily as indicated by the crosses in Fig. 5 which shows current output from the cell with time.

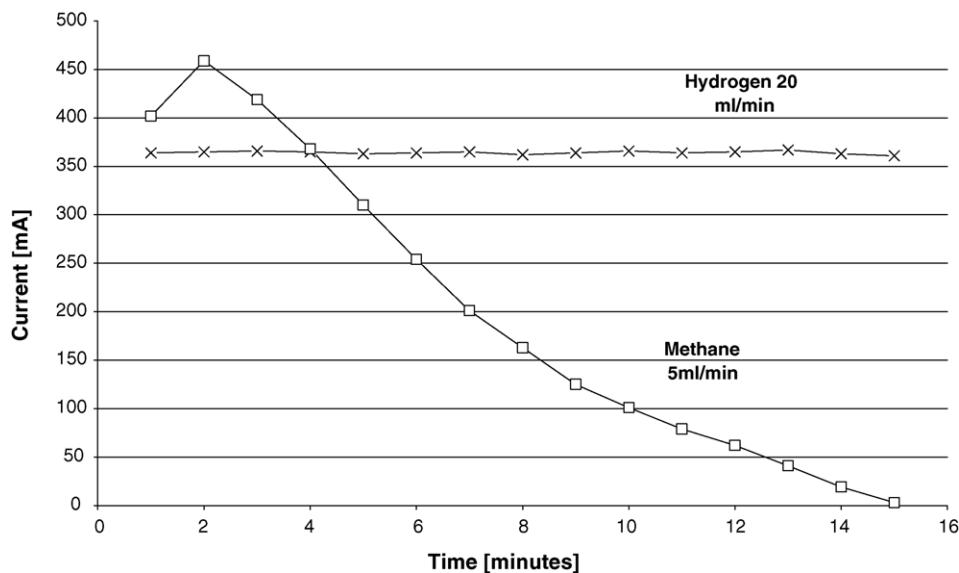


Fig. 5. Current output vs. time at 0.5 V. Hydrogen gave steady performance whereas methane produced a slight early increase followed by irreversible degradation.

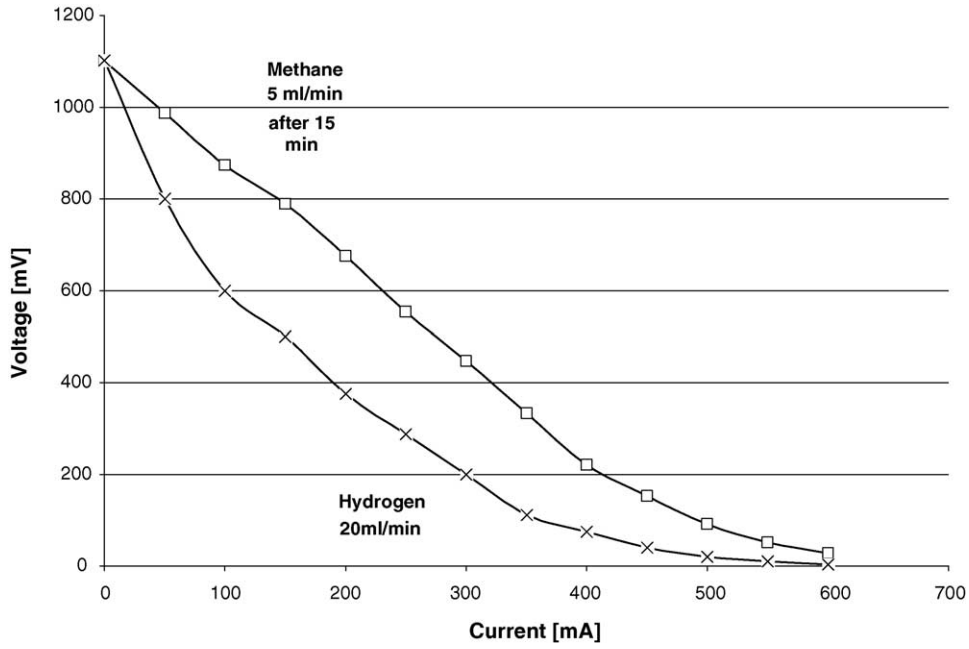


Fig. 6. Voltage current curves at 825 °C for microtubular SOFCs after low temperature reduction.

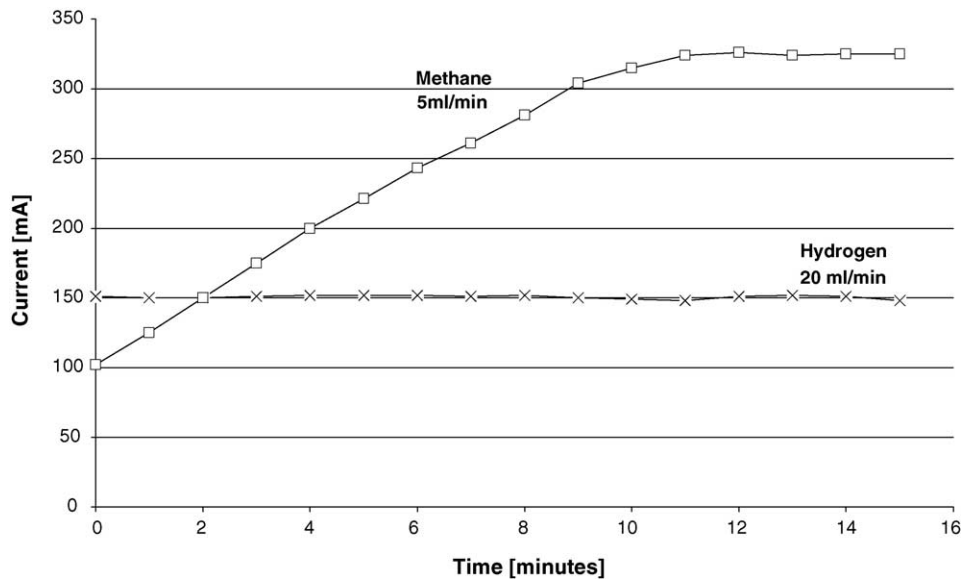


Fig. 7. Effect of time on the current reading for hydrogen and methane, for low temperature reduced nickel cermet anode.

After switching the hydrogen off, 4 ml min<sup>-1</sup> of methane was introduced to give the *V–I* curve shown slightly below the hydrogen line in Fig. 4. The open circuit voltage was slightly higher at 1.22 V, suggesting carbon formation. This carbon

deposition on the nickel seemed to connect the nickel particles together because the current was seen to rise slightly over the first few minutes of methane operation. Subsequently, degradation to the cell performance was observed, giving the

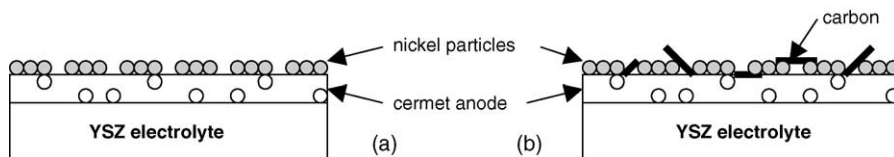


Fig. 8. Schematic of nickel cermet structure for low temperature reduction: (a) after reduction and (b) after running on methane.

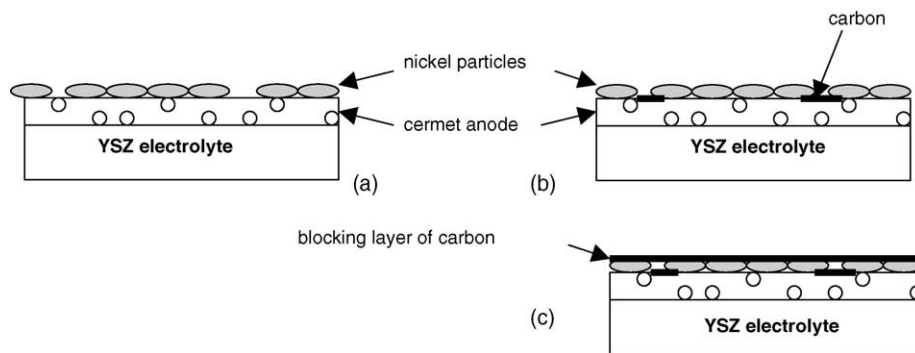


Fig. 9. Structure of anode when reduced with hydrogen at high temperature and run on methane: (a) after reduction; (b) small amount of carbon improves connectivity; (c) large amount of carbon blocks the anode.

$V$ – $I$  curve after 8 min as shown in Fig. 4. Within 15 min, the anode was completely blocked and the current was almost zero. This carbon blockage was not recoverable by the re-introduction of hydrogen because no current reading could be drawn.

#### 4. Performance after low temperature reduction

To reduce the anode at low temperature, the microtubular SOFC was fed with  $20 \text{ ml min}^{-1}$  hydrogen starting at room temperature and ramped at  $20 \text{ K min}^{-1}$  to  $850^\circ\text{C}$  in flowing hydrogen, allowing reduction of the nickel oxide around  $300^\circ\text{C}$ . After reaching  $850^\circ\text{C}$ , the open circuit voltage was  $1.12 \text{ V}$  as before (Fig. 6, crosses). Current was then drawn from the cell using the potentiostat to plot out the  $V$ – $I$  curve shown in Fig. 4, where the current at  $0.5 \text{ V}$  was  $375 \text{ mA}$ .

Potentiostat values were much lower than those obtained after high temperature reduction. At  $0.5 \text{ V}$ , the current was only  $100 \text{ mA}$ , suggesting that the nickel particles formed during low temperature reduction were not well connected within the anode cermet structure. This current remained steady with time as shown in Fig. 7 (crosses). By contrast, when the hydrogen was switched off and  $4 \text{ ml min}^{-1}$  of

methane flowed through the anode, the current began to rise with time, eventually stabilising at  $450 \text{ mA}$ , and subsequently remaining steady for several hours (Fig. 7). In this case, the hydrogen and methane  $V$ – $I$  curves were similar at first, but the methane gave much better current after 15 min operation, suggesting that carbon deposition improved conductivity by linking the nickel particles together in the cermet anode. In addition, this carbon was less electrochemically damaging because it did not block the active sites within the nickel cermet as time progressed.

It was clear in this case that the nickel cermet anode reduced at low temperature gave a much better performance on methane than on hydrogen. Moreover, the methane did not degrade the anode but instead gave a steady performance with time over the 30 h duration of the test.

#### 5. Discussion of anode structure

The logical explanation for these results is that under low temperature hydrogen reduction, the nickel particles are small and somewhat separated, giving poor power output on hydrogen, as indicated schematically in Fig. 8. Because of the gaps between the small nickel particles, the electronic

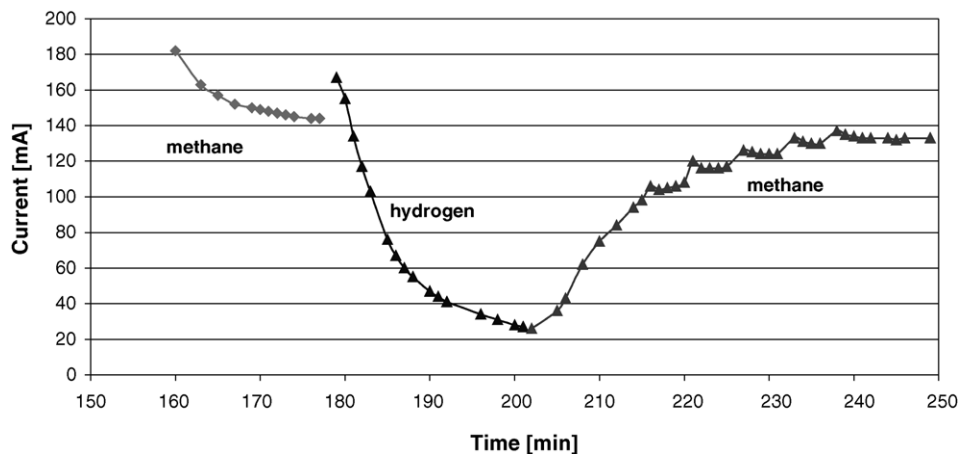


Fig. 10. Fall in current with time when hydrogen was used to remove the carbon deposit on low temperature reduced nickel anode followed by improved current when methane was reintroduced.

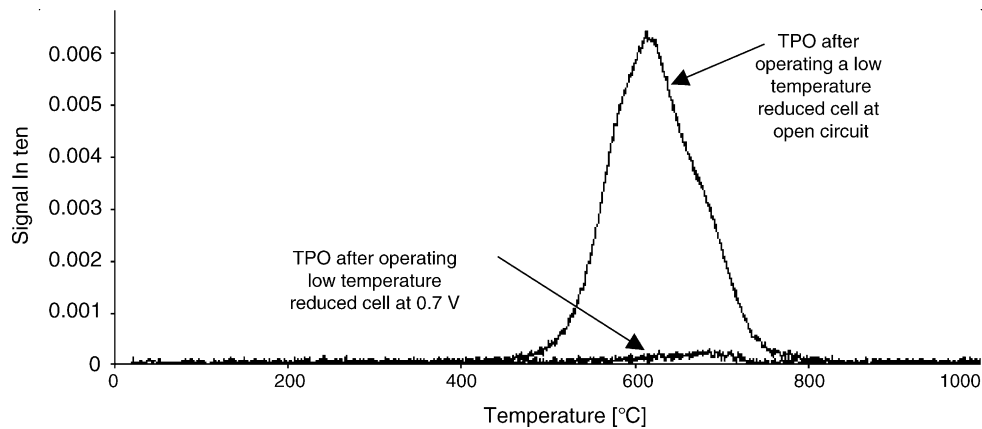


Fig. 11. TPO results for low temperature reduced cell running on pure methane at 850 °C, 4 ml min<sup>-1</sup> [10].

current cannot penetrate the anode, thus producing a higher resistance. However, when the methane replaces the hydrogen, carbon deposits are formed which connect the nickel particles together and improve current output. The nickel has a relatively high surface area which is not readily blocked by carbon deposits.

The structure formed by the normal high temperature anode reduction process has larger nickel particles with reduced surface area and much more continuous nickel structure, as shown by the schematic of Fig. 9, and so improves only slightly with carbon connections between the nickel grains, but then becomes blocked with a surface carbon layer which reduces performance. This structure could in principle be quantified by SEM.

In order to confirm that carbon was causing the improvement in the low temperature reduced anode, the methane flow was switched off and hydrogen at 20 ml min<sup>-1</sup> brought into the anode, which was operated at 0.5 V. This produced water which could react with the carbon to remove it. As the carbon was removed, the current began to fall, eventually reaching its original low level after its low temperature reduction, as shown in Fig. 10. Reverting to methane instead of hydrogen then caused another improvement in current by redepositing the carbon between the nickel particles, showing that this structural connection between the deposited carbon and the nickel anode was reversible.

It is known that the electrical performance of a Ni-YSZ cermet anode is highly influenced by its morphology such as triple phase boundary length and Ni grain connection [9]. It appears that low temperature reduction increased this triple phase boundary length. Improving the Ni connection with the deposition of carbon from the methane on the cermet anode then improved the electrical performance.

## 6. Measurement of carbon at anode

The amount of carbon deposited on the anode under various conditions was measured by temperature programmed

oxidation (TPO). A TPO measurement was made after the cell had been running. The cell was cooled to room temperature under flowing hydrogen. Then oxygen was passed through the anode while ramping up the cell temperature at 5 K min<sup>-1</sup>. This caused carbon dioxide to be produced as the temperature rose to about 500 °C where the carbon began to react with the oxygen [5]. Measuring the carbon dioxide as the ramp continued gave a peak as shown in Fig. 11. The total area under each plot is representative of the volume of carbon dioxide given from each cell during the TPO process.

Fig. 11 shows the difference in carbon deposition from methane as the operating voltage was changed. It was noted that at 4 ml min<sup>-1</sup> of methane flowing down the SOFC anode tube, the optimum voltage for minimum carbon deposition was 0.7 V for this particular handmade cell. Each cell had a measurable optimum voltage value, always somewhere between 0.5 and 0.7 V running on 4 ml min<sup>-1</sup> of methane. This 0.7 V cell gave only a small amount of carbon after 9 h of operation as shown by the bottom curve in Fig. 11. However, a similar cell operating at open circuit voltage deposited at least 20-fold more carbon, as shown by the upper curve after only 40 min of operation. This suggests that even after low temperature reduction the nickel anode was sensitive to carbon deposition from methane under certain conditions of voltage and flow rate.

## 7. Conclusions

The effect of carbon deposition on nickel cermet anodes has been studied after different reduction conditions.

High temperature reduction gave good performance of the cell on hydrogen, but changing to methane caused rapid fall in current as a result of carbon blocking.

Low temperature reduction gave a poor performance on hydrogen, but the current increased rapidly with methane, and the cells did not block with carbon at 4 ml min<sup>-1</sup> flow rate at 0.5 V.

This improvement was shown to be due to carbon linking the nickel anode particles. Reintroduction of hydrogen removed the carbon and degraded the cell performance, which could be recovered by reintroduction of methane.

The results of this study show that direct methane operation of microtubular SOFC with nickel cermet anodes seems to be possible, providing that the anodes are reduced at low temperature and the cell is then operated at suitable voltage and methane flow.

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