



Characterisation of electrical performance of anode supported micro-tubular solid oxide fuel cell with methane fuel

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ABSTRACT

The reduction and operation of Ni–YSZ anode-supported tubular cells on methane fuel is described. Cells were reduced on pure methane from 650 °C to 850 °C, varying reduction time and methane flow rate. The effect on electrochemical performance with methane fuel was then investigated at 850 °C after which temperature-programmed oxidation (TPO) was employed to measure carbon deposition. Results showed that carbon deposition was minimized after certain reduction conditions. The conclusion was that 30 min reduction at 650 °C with 10 ml min⁻¹ methane reduction flow rate led to the highest current output over 1.2 A cm⁻² at 0.5 V when the cell operated at 850 °C between 10 ml min⁻¹ and 12.5 ml min⁻¹ methane running flow rate. From these results, it is evident that solid oxide fuel cell (SOFC) performance can be substantially improved by optimising preparation, reduction and operating conditions without the need for hydrogen.

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1. Introduction

In recent times, there has been increasing interest in the direct operation of solid oxide fuel cells (SOFCs) on methane because natural gas is a widely available fuel. Short chain hydrocarbon (HC) fuels have advantages for SOFCs because internal reforming on the nickel anode is possible, although generally some prereforming is used in practice. This reduces running cost and helps to achieve higher working efficiencies [1]. In particular, HCs such as liquid petroleum gas or natural gas are expected to be suitable fuels which benefit from lower cost and lower pressure for storage. However, anode deterioration due to carbon deposition on the nickel anode microstructure has been a common problem. This is known to lead to a decrease in cell performance resulting from the deactivation of electrocatalytic area for fuel oxidation [2].

It has been shown that SOFCs with Ni-based anodes can be operated stably with methane at temperatures above 800 °C [3]. Under these conditions, the cells are able to oxidize the mixture of hydrogen and carbon monoxide formed as nickel catalyses the conversion of methane to H₂ and CO.

Most previous investigations of SOFCs have been carried out using hydrogen as the fuel, and there is a relative lack of scientific literature on SOFC's using HC as fuels, particularly ones involving any detailed catalytic, spectroscopic and structural characterization

[4]. Porous yttria stabilized zirconia (Ni/YSZ) cermet is currently the most common anode material for SOFCs because it is stable in reducing atmospheres at high temperature and its thermal expansion coefficient is close to that of YSZ–electrolyte. Nickel serves as an excellent reforming catalyst and electrocatalyst but it can become coated with carbon from the fuel and this is a substantial durability issue [5–7].

The aim of this work was to study the effect of reduction and operating of micro-tubular SOFCs using methane as both reductant and fuel. Also temperature-programmed oxidation (TPO) was employed to measure the carbon deposition on the anode in order to assess potential damage to the cermet catalyst. In this study the micro-tubular SOFCs were both reduced and operated using methane, in contrast to previous reports where the cell was reduced in hydrogen and subsequently operated on methane. Reduction and operation on methane is shown to give performance benefits while eliminating the need for additional hydrogen infrastructure.

2. Experimental

The experimental cells were based on 55 mm long extruded anode-supported NiO/YSZ tubes of 2.5 mm outside diameter coated with YSZ electrolyte of 15- μ m thickness (supplied by Adaptive Materials Inc. USA). Cathode layer 1 was applied using a LSM/YSZ ink; La_{0.5}Sr_{0.5}MnO₃ (Seattle Speciality Ceramics), YSZ (Tosoh TZ8Y), acetone, KD2 surfactant and glycerol trioleate vibro milled for 24 h. The ink was painted on the outside of the SOFC tube and left to dry overnight. A second layer formulation was

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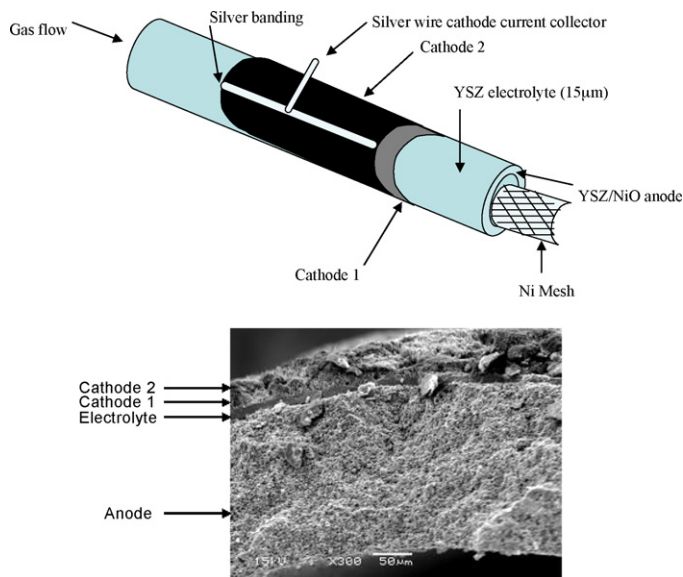


Fig. 1. (a) Schematic of a micro-tubular anode-supported SOFC and (b) SEM cross-section of micro-tubular SOFC.

then mixed by adding LSM (Merck $\text{La}_{0.82}\text{Sr}_{0.18}\text{MnO}_3$), KD2, and acetone. This was milled for 24 h after which 2 g of terpineol was added. The second layer was then applied and dried at 100°C before sintering at 1150°C [8].

The current was collected from the anode using a nickel mesh and pin inserted into the tube to make contact with the anode [9]. The positive connection was made by winding a silver wire onto the outside of the cathode (Fig. 1a). Fig. 1b shows a scanning electron microscope (SEM) cross-section of a typical tube indicating the anode support, the electrolyte membrane and the cathode structure.

The objective of the reduction experiments was to find the optimum conditions of temperature and flow rate using pure methane. Six cells were inserted into a 15-mm diameter silica tube placed in a furnace and various flows of methane were injected into the tube at several temperatures. The results showed that the minimum possible reduction temperature at 10 ml min^{-1} methane flow rate was 650°C because the reaction was slow and patchy below that, whereas above 850°C the metal connections degraded. Therefore, five reduction conditions were studied at 10 ml min^{-1} methane flow; 650°C , 700°C , 750°C , 800°C and 850°C . Each condition was

observed at four times; 15 min, 30 min, 45 min and 60 min. The cells were then measured for carbon deposition using TPO.

Electrochemical performance of the reduced cells was tested using the experimental setup shown in Fig. 2b. An electrically heated furnace was controlled by a thermocouple and eurotherm system. The pure methane gas was delivered from cylinders, metered by mass flow controller and passed to the fuel cell. The electrical output at 850°C was monitored by a potentiostat.

3. Results and discussion

3.1. Influence of reduction time and temperature on carbon deposition from methane

Fig. 3a shows the effect of reduction conditions on carbon deposition measured by TPO. The mass of each cell Ni/YSZ cermet anode was 1 g. Each cell was cooled to room temperature and oxygen was passed through the cell as temperature was ramped up steadily. The peak of CO_2 measured on the mass spectrometer trace was used to calculate the mass of carbon on the anode. It can be seen that carbon deposition had increased steadily with reduction time and temperature. Under the worst condition, 850°C for 60 min, 6% of carbon was coating the nickel and this caused blockage. The best reduction conditions were at 650°C and 700°C for 30 min, giving only 1% carbon on the anode. This amount did not block the anode but instead enhanced the electrochemical performance as shown in Fig. 3b.

Fig. 3b illustrates the peak in electrochemical performance, measured at 0.5 V and 850°C in 10 ml min^{-1} pure methane, for the anode reduced at 650°C for 30 min. The current density was almost 1.6 A cm^{-2} , some 60% higher than outstanding high temperature reduction cells performance of 1 A cm^{-2} at 0.5 V. This is a significant result because it shows that the deposition of carbon under optimum conditions can have a beneficial effect. Under these circumstances, the Ni/YSZ cermet anode is viewed as a composite of Ni particles connected by C nanostructures which provide improved electrical connection and robust mechanical and thermal properties [10–12].

From the above results, 30 min reduction time at 650°C with 10 ml min^{-1} methane was the optimum condition for electrical performance of SOFCs.

3.2. Operating performance of SOFCs

The behaviour of cells prepared by different reduction methods was investigated using methane. Fig. 4a shows the effect of different methane flow rates during the reduction process. The cell was reduced at four different methane flow rates; 5 ml min^{-1} , 10 ml min^{-1} , 15 ml min^{-1} and 20 ml min^{-1} at the optimum reduction condition of 650°C for 30 min. Then the cells were all tested at 850°C and 0.5 V in order to find the best methane flow condition for reduction, measuring the current output with time as shown in Fig. 4a. 5 ml min^{-1} reduction flow rate gave a low output, while 10 ml min^{-1} gave the best output. Raising the reduction methane flow rate to 15 ml min^{-1} and 20 ml min^{-1} degraded the power output, suggesting that carbon was depositing too thickly and blocking the Ni catalyst sites.

A related effect was observed when the optimised cells were operated at 850°C and 0.5 V using a range of methane flow rates, as shown in Fig. 4b. 2.5 ml min^{-1} methane flow gave a low current of 1.17 A cm^{-2} when running for 10 min. Raising the methane flow rate, i.e. decreasing the fuel utilisation, gave increased current as expected, but it was found that 10 ml min^{-1} gave the maximum

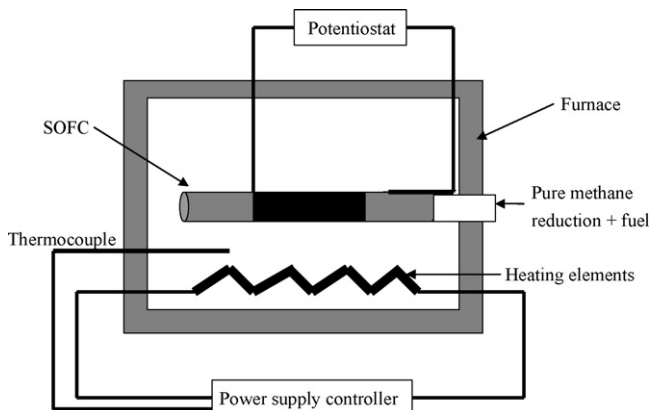


Fig. 2. Experimental setup for SOFC.

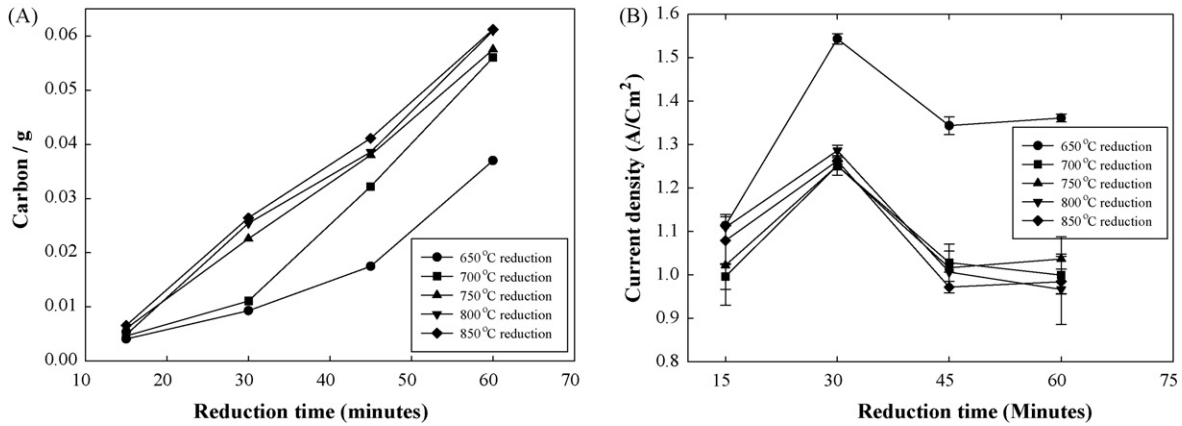


Fig. 3. (a) Carbon deposition results at five reduction temperatures and (b) SOFC performance at 850 °C and 10 ml min⁻¹ methane after five different reduction times.

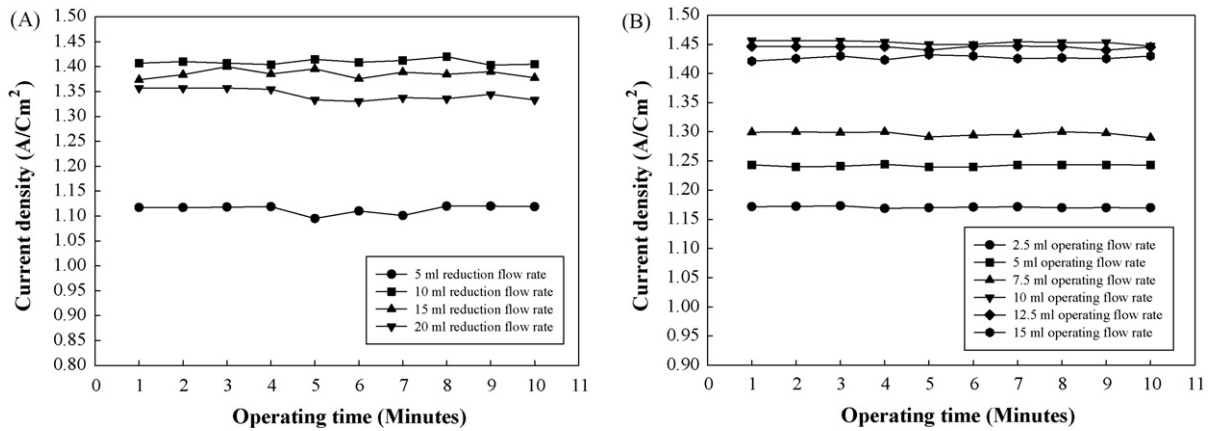


Fig. 4. Current output measurement after optimum 30 min reduction on methane at 650 °C. (a) Results for 0.5 V at 850 °C on 10 ml min⁻¹ methane after various reduction flow rates. (b) Results at 850 °C, 0.5 V for different operating flow rates after 10 ml min⁻¹ reduction flow rate.

current, after which further methane flow gave a decreasing power, indicating that carbon deposition was beginning to block the catalyst.

When dry methane gas is used as a fuel, carbon particles are created on the anode surface, but stream is also generated by the

react of methane with oxygen emitted at the anode. This stream reaction product will reform the methane at a rate which depends on the gas flow [13,14]. These reports on SOFC using dry fuel showed that methane was completely oxidized to carbon dioxide and water without carbon deposition on the anode surface at low methane flow rates. Fig. 5 shows similar results. 15 ml min⁻¹ of methane flow gave a diminishing performance with time, in contrast to the 2.5 ml min⁻¹ condition where the output remained steady.

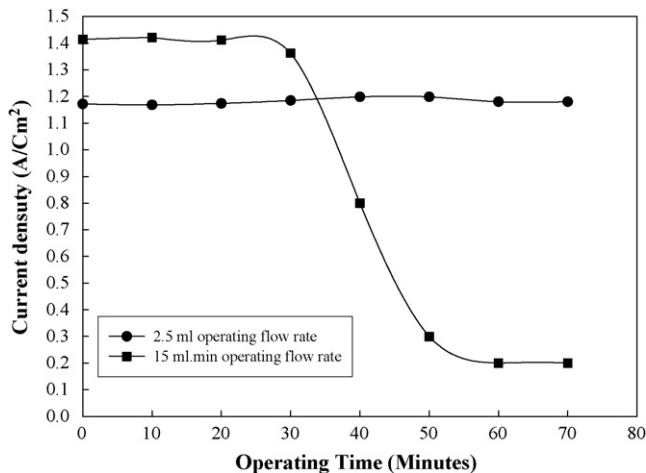


Fig. 5. Cell performance at 850 °C, 0.5 V on different operating flow rates showing effect of carbon deposition for high methane flow.

4. Conclusions

Pure methane can be used both as a reductant and a fuel for operating micro-tubular SOFCs, removing the need for a hydrogen supply.

By studying the reduction of SOFCs made from Ni/YSZ cermet anode supports, it was evident that the optimum reduction condition was 30 min reduction time with 10 ml min⁻¹ methane flow rate.

The optimum running condition at 850 °C was found to be 10 ml min⁻¹ methane flow rate but carbon deposition over long periods at low fuel utilisation was an issue.

The performance could be substantially changed by optimising preparation reduction conditions.

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