Catalysis Letters Vol. 81, No. 1–2, July 2002 (©2002)

Implications for using biogas as a fuel source for solid oxide fuel cells: internal dry reforming in a small tubular solid oxide fuel cell

John Staniforth and R. Mark Ormerod *

Birchall Centre for Inorganic Chemistry and Materials Science, School of Chemistry and Physics, Keele University, Staffordshire ST5 5BG, UK

Received 16 October 2001; accepted 15 December 2001

The feasibility of operating a solid oxide fuel cell (SOFC) on biogas has been studied over a wide compositional range of biogas, using a small tubular solid oxide fuel cell system operating at 850 °C. It is possible to run the SOFC on biogas, even at remarkably low levels of methane, at which conventional heat engines would not work. The power output varies with methane content, with maximum power production occurring at 45% methane, corresponding to maximal production of H_2 and CO through internal dry reforming. Direct electrocatalytic oxidation of methane does not contribute to the power output of the cell. At higher methane contents methane decomposition becomes significant, leading to increased H_2 production, and hence transiently higher power production, and deleterious carbon deposition and thus eventual cell deactivation.

KEY WORDS: solid oxide fuel cells; biogas; dry reforming; methane; nickel; yttria-stabilized zirconia; coke formation.

1. Introduction

Biogas is a complex and variable mixture of methane, carbon dioxide and other gases [1]. It is cheap and readily available and can be considered as an underexploited energy reserve, for example, in power sources. It is currently used for heating and cooking purposes in Third World countries such as India and China [2]. One of the principal limitations of biogas in certain applications is its variability of composition, not only in different locations but also over time, which presents difficulties in its use in conventional power systems [3]. As the proportion of CO_2 in the biogas increases the fuel becomes progressively more difficult to ignite, and eventually the proportion of CO_2 becomes such that ignition can no longer be maintained [4]. In practice, conventional heat engines are not operated at methane levels below 50%, and hence large quantities of biogas are presently vented to the atmosphere, making a significant contribution to greenhouse gas emissions, whilst at the same time wasting a potentially clean, renewable energy resource.

Fuel cells are currently attracting tremendous interest because of their great potential as a more efficient and cleaner alternative method of power generation than conventional methods, combining significantly higher efficiency with very much lower emissions of SO_x, NO_x and residual hydrocarbons and reduced CO_2 emissions. Solid oxide fuel cells (SOFCs) offer potential advantages in terms of efficiency, flexibility and cost over other fuel cell types because of their tolerance to carbon monoxide and other poisons and impurities in the fuel, and because the high operating temperatures allow the possibility of running the fuel cell directly on natural gas or other hydrocarbon fuel sources, internally reforming the fuel within the fuel cell [5,6]. It is generally accepted that for SOFCs to be cost effective, direct or indirect reforming of the hydrocarbon fuel within the fuel cell is essential [7]. Although natural gas is the most commonly used practical fuel for SOFCs, other hydrocarbon fuels such as propane and butane are particularly suitable for certain applications.

Biogas can therefore be considered as a possible source of fuel for the solid oxide fuel cell. At CO_2 levels which are too high for conventional power generation, SOFCs could, in theory, still extract the power available from the methane content of biogas. Thus, in principle, SOFCs offer the possibility of using even biogas that is depleted in methane, consuming methane which would otherwise be vented wastefully and harmfully to the atmosphere, thus acting as an environmental clean-up device, significantly reducing the contribution to greenhouse gas emissions (methane being a greenhouse gas 26 times more potent than CO_2), whilst at the same time producing useful energy.

Conventionally, in SOFCs steam is added to the natural gas, converting it to syngas via steam reforming, either using an external reformer, or more realistically by internal reforming, either indirectly using a reforming catalyst or directly on the nickel-based anode [8,9]. There are several major problems associated with internal reforming in SOFCs, in particular the problem of carbon deposition on the anode, which leads to deactivation and poor durability. There is therefore much interest in developing and evaluating optimized anode formulations for internally reforming SOFCs [10–12]. Partial oxidation

---

* To whom correspondence should be addressed.
E-mail: r.m.ormerod@keele.ac.uk

1011-372X/02/0700-0019/0 © 2002 Plenum Publishing Corporation

of the natural gas using oxygen, or potentially air, is a possible alternative to steam reforming [13–16], though carbon deposition is also a major problem with partial oxidation over nickel catalysts [15,17].

Carbon dioxide (dry) reforming of methane,

$$CH_4 + CO_2 \rightarrow 2H_2 + 2CO, \qquad (1)$$

is a potentially very attractive route for methane conversion [18,19], though again carbon deposition is a major problem which limits its usefulness [20,21].

Carbon dioxide is inherently present in biogas, in addition to methane, and hence in principle biogas may be used directly in the SOFC without the addition of either steam or air/oxygen. One obvious drawback is the variable composition of biogas, and hence the variable carbon dioxide/methane ratio, rather than the stoichiometrically preferred equimolar quantities.

In this paper we demonstrate the feasibility of running solid oxide fuel cells on biogas using a small-diameter thin-walled extruded tubular SOFC system developed in this laboratory [22]. The test system allows both the performance and durability of the fuel cell and the reforming catalysis to be evaluated within the actual SOFC [23]; we have previously demonstrated the value of such *in situ* catalytic measurements on working SOFCs [24–26]. We report the influence of the methane/CO_2 ratio on the cell performance and the exit gas composition, at a cell operating temperature of 850 °C, and comment on the potential use of biogas as a fuel for SOFCs.

2. Experimental

All the experiments described in this paper were carried out using the SOFC test system, which we have developed [23,25], based on a small-diameter, thin-walled extruded yttria-stabilized zirconia tubular reactor. Briefly, the apparatus consists of a custom-built furnace which houses the tubular SOFC. The test cell inlet was linked to a gas handling system which allowed control of gas composition, enabling evaluation over a full range of operating conditions and fuel compositions. The exhaust gas from the SOFC was monitored by gas chromatography (Unicam ProGC), enabling the catalytic reforming reactions of the biogas to be directly studied in the actual SOFC. The gas chromatograph had a thermal conductivity detector, which because of incompatibilities in the thermal conductivities meant that a different carrier gas was required for the detection of hydrogen. Hence each experiment had to be repeated in order to detect the H_2 in the exit gas. The nature of the sampling system prevented detection of water in the exit gas. A particular advantage of the tubular SOFC design is that it can be housed in the furnace in the same way as a conventional catalytic reactor [24,25]. As zirconia is a good thermal insulator the ends of the electrolyte tube which project beyond the walls of the furnace remain sufficiently cool for a gas-tight seal to be maintained under operating conditions.

The SOFC anode was constructed in two layers. Both layers were prepared by milling nickel oxide (Alfa Chemicals) and 8 mol% yttria-stabilized zirconia (YSZ) (United-FYT11). 10.5 g NiO and 5.0 g YSZ were mixed for the inner anode layer and 9.5 g Nb and 0.9 g YSZ for the outer layer. 0.5 g of cerium(IV) oxide (Avocado) was also added to the outer layer mixture. A mixture of methanol, 1,1,1-trichloroethane and glycerol was added to each as a solvent and the resultant slurry was milled for 3 h. A small quantity of polyvinyl butyrol (~0.15 g) was added at the end of the milling period as a binding agent. The anode ink was then applied to the inside of the electrolyte tubes and dried in air at 150 °C before being fired at 1300 °C for 1 h, using a specific firing procedure.

Strontium-doped lanthanum manganite (Seattle Speciality Chemicals) was used as the cathode and again applied in two layers. The inner layer was a 50 : 50 wt% mixture of $La_{0.5}Sr_{0.5}MnO_3$ and yttria-stabilized zirconia, with a methanol, 1,1,1-trichloroethane, glyceroltrioleate mixture used as the solvent. The outer layer was $La_{0.82}Sr_{0.18}MnO_3$ mixed with acetone using KD1 as a dispersant. After applying the inks to the outside of the tubular electrolyte, the tubes were dried in air at room temperature before firing to 1573 K using the same procedure that was used for the anode. Nickel wire was used to collect current from the anode and silver wire was used for current collection from the cathode.

Methane/CO_2 mixtures covering the composition range 15% to 85% methane were made up to reproduce the composition of all biogas sources. The gas mixture was introduced to the SOFC at a controlled rate using a mass flow control valve at an operating temperature of 850 °C. The anodes were not pre-reduced but were exposed directly to the methane/CO_2 mixture. The measurements were carried out at a cell operating temperature of 850 °C and a cell potential of 0.7 V. Before each reading was taken the cells were operated for at least 20 min on each biogas mixture in order to reach a steady power output.

3. Results

The influence of the biogas composition (methane/CO_2 ratio) on the cell performance was studied using two different flow regimes, these being constant methane flow rate and constant total flow rate.

Figure 1 shows the power output from the SOFC at 850 °C as a function of methane content of the biogas at a constant gas flow rate of 6 ml min^{-1}, *i.e.* methane flow rate is varying, whilst figure 2 shows the power output as a function of methane content of the biogas at a constant methane flow rate of 1 ml min^{-1}, *i.e.* total flow rate is varying.

Figure 3 shows the exit gas composition from the SOFC as a function of methane content at a constant

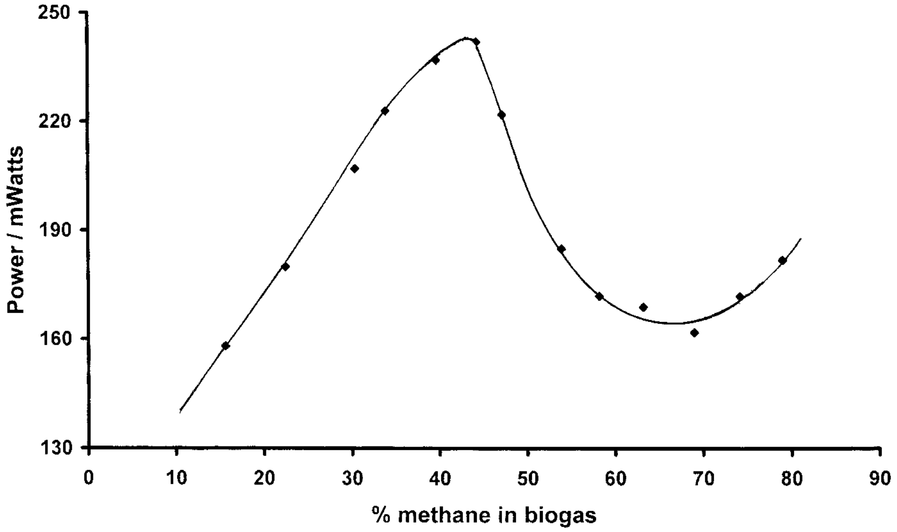

Figure 1. Power output from a small tubular SOFC running on biogas at 850 °C, as a function of methane content in the biogas, at a constant flow rate of 6 ml min^{-1} (cell potential 0.7 V).

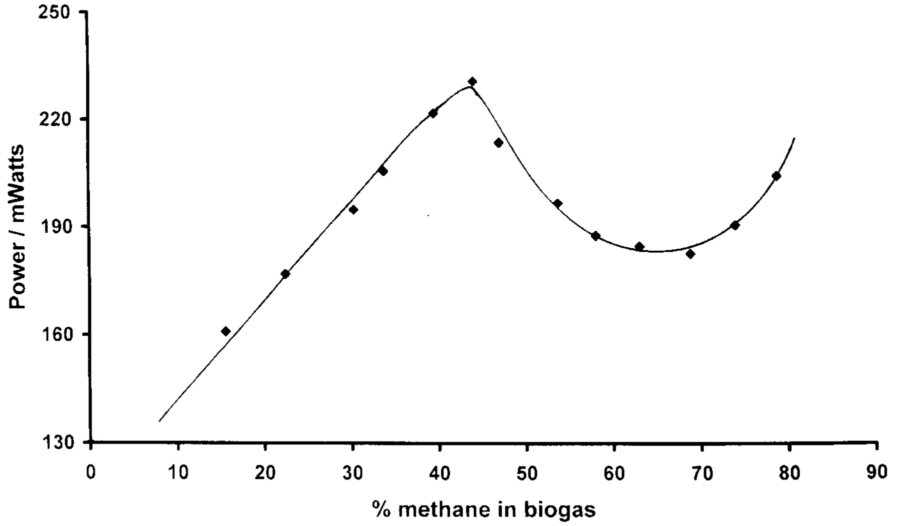

Figure 2. Power output from a small tubular SOFC running on biogas at 850 °C, as a function of methane content in the biogas, at a constant throughput of methane of 1 ml min^{-1} (cell potential 0.7 V).

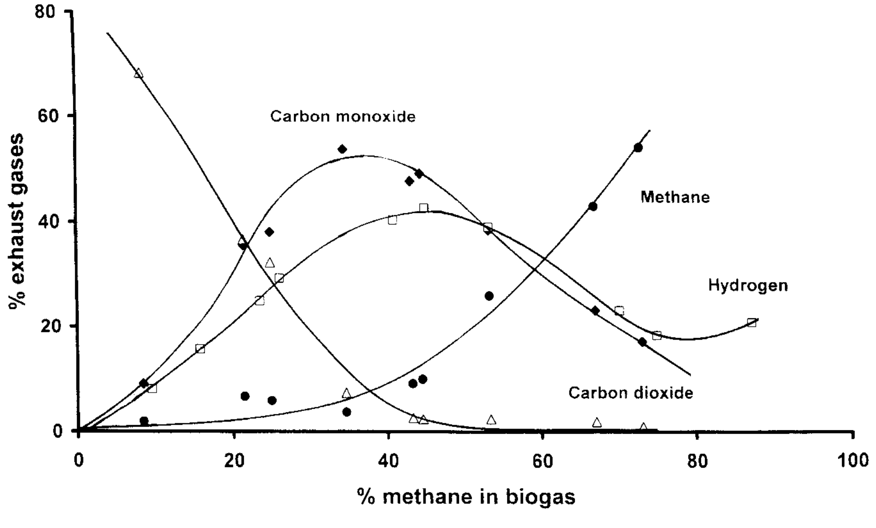

Figure 3. Exit gas compositions from an unloaded small tubular SOFC running on biogas at 850 °C, as a function of methane content in the biogas (gas flow rate of 6 ml min^{-1}).

gas flow rate of $6\,\text{ml}\,\text{min}^{-1}$, *i.e.* under the same experimental conditions as figure 1, except that in this case measurements were made with the cell not under load in order to prevent interference from the electrochemical cell reactions.

4. Discussion

The electrical power output of a solid oxide fuel cell depends on many factors, including the oxygen ion flux and the fuel composition at the anode. At a given temperature and cell potential, for a given electrolyte thickness, there is a particular flux of oxygen ions which limits the power output. In these experiments the oxygen ion flux should be essentially the same, as are nearly all the other experimental parameters, and hence changes in the measured power output can be largely attributed to the gas composition at the anode and hence the availability and type of fuel.

Figures 1 and 2 show the same general trend, with a steady increase in power output from 160 mW at 15% methane content to maximum power outputs of 245 and 235 mW, respectively, for biogas with a methane content of 45%. As the methane content in the biogas exceeds 45% the power output decreases, initially quite quickly and then more slowly, reaching a minimum of 160 and 175 mW, respectively, for biogas with methane contents of around 65–70%, corresponding to methane flow rates of 4.2 and $1\,\text{ml}\,\text{min}^{-1}$, respectively. An increase in power output is observed for biogas with methane contents above 70%, with power outputs of, respectively, 182 and 205 mW, observed for biogas with a methane content of 79%, corresponding in the former case to a methane flow rate of $4.8\,\text{ml}\,\text{min}^{-1}$, and in the latter to one of $1\,\text{ml}\,\text{min}^{-1}$.

For biogas samples with methane contents in the range 15–45%, where a steady increase in power output is observed with increasing methane content, the exit gas composition from an identical, but unloaded, cell running under exactly the same conditions of temperature and flow rate shows that complete consumption of the methane occurs, together with the formation of H_2 and CO, the amount of which parallels the increase in power output, and a significant consumption of the CO_2 in the biogas. The balance of the exit gas under these conditions is water. Maximum formation of CO and H_2 occurs at almost exactly the same fuel composition at which maximum power output is observed, that is, ~45% methane, close to equimolar quantities of methane and CO_2. At this biogas composition essentially complete consumption of the CO_2 was observed. The exit gas compositions over this compositional range of biogas show clearly that internal dry reforming of the methane present in the biogas (reaction (1)) is occurring effectively, though some methane does remain unconverted. The fact that the production of CO is initially greater than the H_2 production, and reaches a maximum at a slightly lower methane content, and the more rapid decrease in the amount of CO_2 in the exit gas, suggests that the reverse water gas shift reaction (2) may be occurring:

$$CO_2 + H_2 \rightarrow H_2O + CO. \qquad (2)$$

As the methane content of the biogas exceeds 45% and the CO_2 content of the biogas starts to decrease, the amount of H_2 and CO formed start to decrease, with the quantity of CO produced decreasing more rapidly than the H_2 production. This behavior essentially precisely mirrors the power output over this composition range. Over this range the quantity of methane in the exit gas continues to increase. This clearly demonstrates that as the quantity of CO_2 in the biogas decreases, progressively less CO and H_2 are formed by dry reforming of the methane, and thus that it is the electrochemical oxidation of H_2 and CO which lead to power production. Direct electrochemical oxidation of the methane does not therefore contribute to power production, or at least only makes a very minor contribution.

For biogas with methane content around 75% the amount of H_2 in the exit gas reaches a minimum, with H_2 production increasing at methane contents above 75%, whilst CO production continues to decrease. In this biogas compositional range an increase in the power output was also observed. These observations can be rationalized in terms of catalytic methane decomposition (3) becoming progressively more important with increasing methane levels, providing a second route to H_2 production, which is then electrochemically oxidized to produce electrical power:

$$CH_4 \rightarrow C_{(ad)} + 2H_2. \qquad (3)$$

Thus the power output and exit gas compositions from the fuel cell over the entire biogas compositional range can be accounted for.

For biogas with high methane contents, significant carbon deposition occurs through catalytic methane decomposition (3), leading to eventual deactivation; deactivation is rapid for "biogas" with in excess of 85% methane. At low methane contents, and high carbon dioxide levels, dry reforming of the methane (1) should predominate over methane decomposition. Further, we have shown deposited carbon may be removed quite readily by reaction with carbon dioxide:

$$CO_2 + C_{(ad)} \rightarrow 2CO. \qquad (4)$$

It is particularly worth noting that the amount of power produced within the SOFC is still quite reasonable at methane contents as low as 15%, being ~70% of the maximum power output. Thus at methane contents where conventional heat engines would have long since stopped working, the solid oxide fuel cell is still able to produce a significant amount of power. Maximum power output occurs at ~45% methane, at which composition most heat engines would have difficulty operating.

A future paper will focus on more long-term durability experiments using biogas, with a particular emphasis on mixtures with high carbon dioxide contents, which is not only necessary for effective internal reforming of the methane, but which also minimizes or reverses any carbon deposited within the cell [27]. Another issue which we are currently investigating is the influence of different levels of sulfur in the biogas on the fuel cell performance, since sulfur can cause deactivation of the anode (or internal reforming catalyst) and biogas can contain up to 0.1% H_2S.

5. Conclusions

We have demonstrated that it is possible to run a solid oxide fuel cell directly on biogas, over a wide compositional range of methane and carbon dioxide. In particular, it is possible to run the SOFC with only a comparatively small loss of power output at significantly lower levels of methane than is possible with conventional heat engines, which are not operated at methane levels below 50%. Thus, poor quality biogas, which is presently disposed of by simply venting wastefully and detrimentally to the atmosphere, can potentially be used within an SOFC to produce useful quantities of power.

The electrical power produced varies with the methane content of the biogas and can be accounted for by internal reforming of the methane by CO_2 to produce H_2 and CO, which are electrochemically oxidized, and in addition, at high methane levels, by methane decomposition to surface carbon and H_2. Direct electrochemical oxidation of methane does not contribute to the power output of the cell, or at the most only makes a very minor contribution to the power output. High levels of methane in the biogas result in significant coking of the fuel reforming anode, and hence progressive deactivation and loss of cell performance occurs over time.

Acknowledgments

The UK Engineering and Physical Sciences Research Council is gratefully acknowledged for the award of an Advanced Research Fellowship to R.M.O.

References

[1] M. Hammad, D. Badarneh and K. Tahboub, Energy Conversion and Management 40 (1999) 1463.
[2] C. Bell, S. Boulter, D. Dunlop and P. Keiller, in: *Methane: Fuel of the Future* (Andrew Singer, Bottisham, 1973).
[3] J. Huang and R.J. Crookes, Fuel 77 (1998) 1793.
[4] S. Neyeloff and W.W. Gungel, in: *Energy, Agriculture and Waste Management* (Ann Arbor Science, Ann Arbor, MI, 1975).
[5] D. Hart, Chem. Ind. (1998) 344.
[6] A.C. Lloyd, Sci. Am. 281 (1999) 64.
[7] R.A. George, J. Power Sources 86 (2000) 134.
[8] N.Q. Minh, J. Am. Ceram. Soc. 76 (1993) 563.
[9] C.M. Finnerty, N.J. Coe, R.H. Cunningham and R.M. Ormerod, Catal. Today 46 (1998) 137.
[10] A.S. Carrillo, T. Tagawa and S. Goto, Mat. Res. Bull. 36 (2001) 1017.
[11] C.M. Finnerty and R.M. Ormerod, J. Power Sources 86 (2000) 390.
[12] A.L. Sauvet and J. Fouletier, J. Power Sources 101 (2001) 259.
[13] J.C. Slaa, R.J. Berger and G.B. Marin, Catal. Lett. 43 (1997) 63.
[14] C.T. Au and H.Y. Wang, Catal. Lett. 41 (1996) 159.
[15] V.A. Tsipouriari, Z. Zhang and X.E. Verykios, J. Catal. 179 (1998) 283.
[16] S. Tang, J. Lin and K.L. Tan, Catal. Lett. 51 (1998) 169.
[17] A.M. Diskin, R.H. Cunningham and R.M. Ormerod, Stud. Surf. Sci. Catal. 122 (1999) 393.
[18] J.R. Rostrup-Nielson, Catal. Today 18 (1993) 305.
[19] P.D.F. Vernon, M.L.H. Green, A.K. Cheetham and A.T. Ashcroft, Catal. Today 13 (1992) 417.
[20] G. Xu, K. Shi, Y. Gao, H. Xu and Y. Wei, J. Mol. Catal. A 147 (1999) 47.
[21] D. Duprez, M.C. Demichali, P. Marecot, J. Barbier, O.A. Ferretti and E.N. Ponzi, J. Catal. 124 (1990) 324.
[22] K. Kendall and M. Prica, in: *Proc. 1st Eur. Solid Oxide Fuel Cell Forum*, ed. U. Bossel (European Fuel Cell Forum, 1994), p. 163.
[23] J. Staniforth and K. Kendall, J. Power Sources 71 (1998) 275.
[24] C.M. Finnerty, R.H. Cunningham, K. Kendall and R.M. Ormerod, J. Chem. Soc. Chem. Commun. (1998) 915.
[25] C.M. Finnerty, R.H. Cunningham and R.M. Ormerod, Catal. Lett. 66 (2000) 221.
[26] R.M. Ormerod, Stud. Surf. Sci. Catal. 122 (1999) 35.
[27] J. Staniforth and R.M. Ormerod, in preparation.