

Short communication

An internal reformer for a pressurised SOFC system

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Received 1 November 2005; received in revised form 18 November 2005; accepted 23 November 2005

Available online 23 January 2006

Abstract

A novel reformer design has been demonstrated that converts the methane required for a multi kilowatt SOFC stack. Results show the influence of temperature and the benefits of operating at elevated pressure on the reforming-catalyst fundamental reaction kinetics. Due to the high heat demand of the steam reforming reaction, efficient heat transfer between the SOFC stack and the reforming catalyst is essential. Parameters such as the volume/surface area ratio, choice of catalyst, and catalyst metal loading are key to the design, and these have been determined through a combination of computer modelling and experimental measurements. The thermal properties of the unit have been evaluated over a range of temperatures and fuel compositions that simulate system operating-conditions in the final product.

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Keywords: Internal-reforming; Kinetics; Heat-transfer; Catalyst

1. Introduction

Of the various fuel cell technologies available, the solid oxide fuel cell (SOFC) is the preferred option for large-scale stationary power production [1]. There are a number of issues that make hydrogen uneconomic as a choice of primary fuel for stationary power applications, not least, the high cost of fuel transportation, difficulty in fuel storage and large and complex fuel processing plants [2]. Low temperature technologies require a very pure source of hydrogen, so in that particular case, fuel processing becomes a significant issue. Contrary to this the SOFC operates at high temperature and in principle can operate on a variety of fuels, provided they can undergo oxidation at the anode [3–6]. As the operating temperature of SOFCs is high enough to facilitate fuel processing, the direct use of fuels such as natural gas in such systems becomes a possibility. Its high operating temperature also makes the SOFC more tolerant to impurities, which also reduces the cost and complicity of fuel processing. The ability to process hydrocarbon fuels therefore makes the SOFC a much more attractive option than other technologies for stationary power systems, as the direct use of hydrocarbon fuels

removes the problematic issues of hydrogen transportation and storage [7].

The development of the SOFC for stationary power generation has been underway at Rolls-Royce for a number of years [8]. Rolls-Royce fuel cell systems (RRFCS) is currently developing 1 MW_e pressurised hybrid systems for stationary power applications. The systems are designed to run on natural gas, and one of the key processes within the system is conversion of methane to synthesis gas. Using natural gas as a primary fuel source makes economic sense as one can tap into a vast global reserve that is fairly evenly distributed. Current global reserves are estimated to be approximately 180,000 km³, equivalent to 1.75×10^{15} kWh_t. The bulk of these reserves lie in Russia, with sizable quantities in the Middle East, Pacific Asia, Europe and North America [9].

Although the SOFC can be run directly on hydrocarbons, in practice this results in carbon deposition on the fuel cell anodes, which significantly compromises stack life [10,11]. Thus, in a commercial SOFC system, very little fuel slippage through the reformer can be tolerated. Fuel processing is therefore a fundamental step in any fuel cell system operating on hydrocarbons. Where natural gas is the primary fuel, the key processes upstream of the main stack block are desulphurisation, pre-reforming of higher hydrocarbons and internal reforming of methane to synthesis gas. Any commercial internal reformer design has to be

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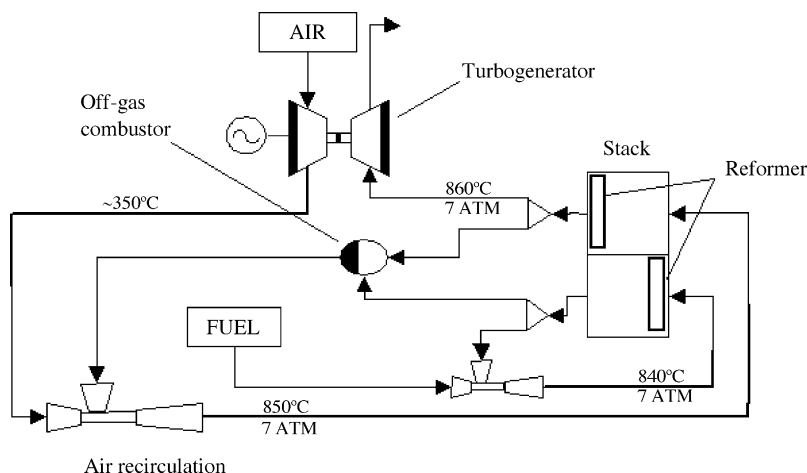


Fig. 1. RRFCS hybrid cycle.

both highly compact and efficient. The simplest solution is to closely integrate the internal reformer with the SOFC stack [12]. Methane steam reforming is an efficient means of hydrogen production [13] and the waste steam and heat from the SOFC stack can be used effectively to achieve this.

The RRFCS system (Fig. 1) is designed to operate at 7 bar_a. Fuel (methane) is introduced to the anode side through an anode ejector, where it is mixed with the recycled exhaust anode stream (anode-off-gas) from the stack. This methane/anode-off-gas mixture is fed to the internal reformer, where the mixture is converted into a hydrogen/carbon monoxide rich mixture and subsequently fed to the SOFC stack. The internal reformer is closely coupled to the SOFC stack in such a way that the waste heat generated from the electrochemical reactions is used to facilitate the endothermic methane steam reforming reaction.

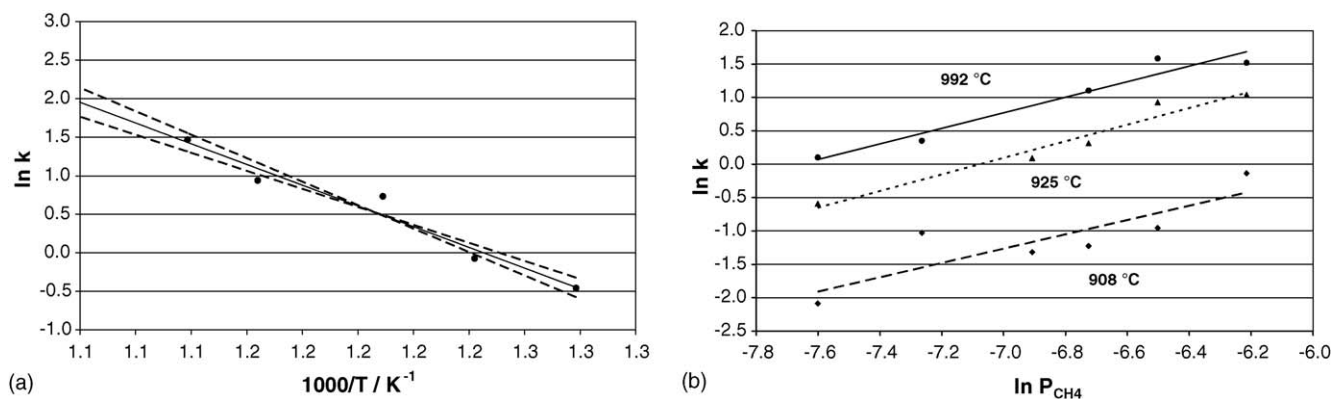
In the design of any internal reformer a proper understanding of parameters such as heat-transfer efficiency, catalyst activity and residence time are fundamental. In addition, the SOFC stack itself is ceramic, so large variations in localised temperature should be avoided as these can lead to thermal shock. Space is also an issue in the design for any SOFC components, and it is important that any reformer design is also compact.

In this paper the basic principles used in the design of the internal reformer are discussed, and the performance of a reformer suitable for an 8 kW_e stack is described under simulated operating conditions. The performance of a 7.5 kW_e stack block operating on reformed methane is also described in detail.

The results presented here demonstrate the achievement of an internal reformer design that meets the required specifications for an SOFC system, i.e. generating the required level of methane conversion through efficient heat transfer from the stack block with high catalytic activity.

2. Reformer design

To design a suitable reformer, a number of key parameters have to be determined. These include the choice of active catalyst and metal loading, the surface area required based on the thermal duty, and the overall size and shape. The quantity of catalyst required is dependant on the reaction kinetics. The temperature-dependant rate constant, k , and reaction order, were measured in a small-scale atmospheric test rig and the results are given in Fig. 2. Results were fitted to a simple power-rate expression (1). The rate of reaction, $-d(\text{CH}_4)/dt$, followed a 1st order dependence on the methane partial pressure, P_{CH_4} , and was inde-

Fig. 2. (a) Arrhenius plot for CH₄ conversion over reforming catalyst. (b) ln–ln plot to determine CH₄ reaction order for reforming catalyst.

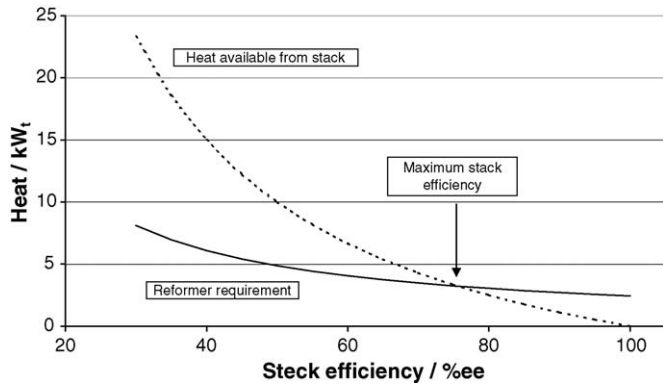


Fig. 3. Relationship between stack efficiency and reformer duty for a 10 kW_e system, with 90% CH₄ converted in the reformer.

pendent of the partial pressure of the other components, over the temperature and pressure range studied.

$$-\frac{d(\text{CH}_4)}{dt} = kP_{\text{CH}_4} \quad (1)$$

The value of the reaction rate constant, k is given by the Arrhenius Eq. (2), where A is the pre-exponential factor, R is the universal gas constant, and T the absolute temperature.

$$k = A e^{-E_a/RT} \quad (2)$$

The apparent activation energy for the disappearance of methane, E_a , calculated from the Arrhenius plot shown in Fig. 2a, was $112 \pm 15 \text{ kJ mol}^{-1}$. For correct reactor sizing the required residence time has to be calculated. This was done with a model tubular-reformer operating in a custom-built pressurised rig. Residence times of about 1 s are typically required for steam reforming [14].

Due to the highly endothermic nature of the steam reforming reaction (3), effective heat transfer is perhaps the most important aspect of the reformer design.



For a self-sustaining system, the bulk of the heat required to facilitate methane conversion is generated from Ohmic heating through losses within the stack. The amount of heat available and the electrical efficiency of a fuel cell system are dependent on the area specific resistance, ASR of the fuel cells, defined as the voltage drop for a given current density. The relationship between stack efficiency and available heat is illustrated in Fig. 3 for a system consisting of a 10 kW_e stack and internal reformer. Stack efficiency, η_{stack} , is defined as:

$$\eta_{\text{stack}} = \frac{P_{\text{out}}}{\text{LHV}_{\text{in}}} \times 100\% \quad (4)$$

where P_{out} is the total electrical power generated by the stack, and LHV_{in} is the total power available from the incoming fuel, based on its lower heating value. For any given system the total fuel requirement drops with increasing electrical efficiency, and this is matched by a corresponding drop in the thermal duty of the internal reformer. However, the heat available from the stack drops more markedly with increasing stack efficiency, which

leads to a theoretical maximum stack efficiency, above which steam reforming cannot be sustained by heat generated from the stack alone. For example, in a system where 90% of the incoming methane has to be converted in the reformer, the thermal requirement of the reformer can only be met if the stack efficiency is below 76%, assuming there are no additional thermal losses. The reformer design becomes increasingly challenging the closer one approaches to this point, as heat transfer efficiency has to increase accordingly.

CFD modelling using Fluent has been used to predict the heat and mass transfer characteristics of the reformer design [15]. The design must allow for a high gas diffusion rate, to prevent the overall conversion being diffusion limited. The bulk gaseous diffusion coefficient for a binary system, D_{12} (5) was calculated from the Chapman-Enskog theory [16], where M_1 and M_2 are the molecular weights of the two species, P is absolute pressure and σ_{12} is the collision diameter calculated from the Lennard-Jones potential parameters (6).

$$D_{12} = \frac{1.86 \times 10^{-3} T^{3/2} (1/M_1 + 1/M_2)^{1/2}}{P \sigma_{12}^2} \quad (5)$$

$$\sigma_{12} = \frac{1}{2}(\sigma_1 + \sigma_2) \quad (6)$$

In addition to good heat transfer to the walls of the reformer, good heat transfer within each gas stream is essential to obtain an overall high efficiency. The thermal conductivity of each gas stream, k_t , is calculated from kinetic theory [17] where σ is the collision diameter (7).

$$k_t = \frac{1.99 \times 10^{-4} \sqrt{T/M}}{\sigma^2} \quad (7)$$

Radiation must also be included in the modelling process as this has a significant contribution to heat transfer at the reformer operating temperature.

Using this combination of small-scale catalyst testing and CFD modelling a reformer unit has been constructed that is sized to convert enough methane for a 8 kW_e stack; this is referred to as an 8 kW_e reformer unit.

3. Reformer tests

The 8 kW_e reformer unit has been tested under simulated operating conditions in a custom-built pressure rig designed to operate at temperatures up to 1000 °C and a pressure of 7 bar_a. The reformer is divided into two flow streams, designated the anode stream which is the methane/anode-off-gas mixture, and the cathode stream which is the exhaust air from the SOFC stack. Hot air was supplied to the reformer at a mass flow-rate equivalent to design conditions. The fuel stream was preheated before entering the reformer. The fuel stream was mixed externally to the test rig and steam was added via a custom-built steam generator. The flow-stream and reformer-body temperatures are given in Table 1.

The composition of the anode stream is given in Table 2. The reformer achieved an overall methane conversion of $89.9 \pm 1.6\%$, which met the design target (91%). The outlet fuel

Table 1
Flow-stream and reformer-body temperatures for 8 kW_e reformer test

Flow stream temperature (°C)	Reformer body temperature (°C) ^a		
		Anode side	Cathode side
Cathode (in)	945		
Anode (in)	804	827	909
Cathode (out)	791	820	882
Anode (out)	803	814	882

^a The temperature of the outer walls of the reformer was measured at six points. Three of these points were influenced mainly by the anode stream, and three by the cathode stream.

Table 2
Anode stream compositions for 8 kW_e reformer test

Component	Composition (vol.%)		
	Inlet	Outlet	
		Design	Measured
H ₂	14	43	38
CO	9	18	20
CH ₄	15	1	1
CO ₂	20	15	14
H ₂ O	42	23	27

composition contained less H₂ and more CO than the target composition, although the percentage of total flammables (H₂ and CO) was almost identical to the design specification. This is likely due to the effect of the water-gas shift reaction (WGSR) (8), which was assumed to be at equilibrium in the design calculations.



Previous tests at RRFCs have shown the performance of cells running on CO to be almost the same as that of cells running on H₂, so the difference between the design and measured outlet compositions does not present any problems.

4. Anode-cycle tests

To demonstrate SOFC stack operation on methane, the complete anode cycle (Fig. 4), including reformer has been tested in a custom-built pressurised rig, designed for stacks up to 10 kW_e (Fig. 5). In order to determine reformer performance, gas chromatography (GC) was used to analyse the anode stream at various points around the cycle (labelled A-F). The stack, composed of eight units, termed half-strips, was rated for 7.5 kW_e and had been used in two previous tests. The gas composition from the GC analyses is given in Table 3, where the stack was

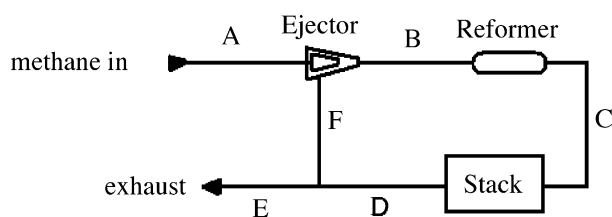


Fig. 4. Schematic of anode cycle.



Fig. 5. Pressurised rig for testing 10 kW_e stack blocks.

run at 7 bar_a and an operating temperature of 950–1000 °C. The test was run on methane for a total of 13.5 h.

The presence of nitrogen in the fuel stream (Table 3) indicates some leakage in the system. Leak test analysis of the reformer prior to testing demonstrated it to be leak tight, and detailed analysis of the GC measurements indicated that this was also the case under test conditions. The most likely source of leakage during the test was within the stack, and this was confirmed by the gas analysis.

A summary of the reformer performance is given in Table 4. As with the stand-alone reformer test described above, the methane conversion target of 91% was met during this test. In addition, this performance was achieved with a turn-down ratio of 1.25, and demonstrates that there is a degree of flexibility built into the reformer design, allowing the component to be used with various sized stack blocks.

The stack performance is summarised in Table 5. In total 5.4 kW_e was drawn from the stack, however, current was not drawn from one of the half-strips. The reason for this half strip

Table 3
Gas composition of anode cycle during anode-cycle test

Component	Composition (vol.%)			
	Primary (A)	Ref. Inlet (B)	Stack inlet (C)	Stack outlet (D)
H ₂	–	7.38	45.1	9.4
CO	–	3.52	23.5	4.51
CH ₄	100	21.9	0.67	–
CO ₂	–	16.9	5.59	21.7
H ₂ O	–	33.5	14.1	42.9
N ₂	–	16.8	11.0	21.5

Table 4
Summary of reformer performance during anode-cycle test

Gas stream temperature (°C)		Performance details	
Cathode (in)	918	Reformer rating (kW _e)	8.0
Anode (in)	818	Fuel input (kW _L)	11.8
Cathode (out)	846	Turn-down ratio	1.25
Anode (out)	874	Methane conversion (%)	95.6

The turn-down ratio is the ratio of the reformer thermal rating (14.7 kW_L) over the actual fuel input (11.8 kW_L).

Table 5
Summary of stack performance during anode-cycle test

Run time (h)	13.5
Temperature (°C)	950–1000
Load current (A)	2.4
Fuel utilisation (%)	76
Output power (kW _e)	5.4
Stack efficiency (%)	45.9 (a) 52.5 (b)

being operated under open-circuit conditions was purely due to problems with the external electrical connections. If current had been drawn from all eight half-strips, the stack should have delivered 6.2 kW_e. Similarly, the stack efficiency (a) has been calculated based on the total methane flow into the cycle. The higher value of 52.5% (b) is based on the calorific value of the fuel fed through the seven working half-strips.

The stack used for this test had been used in two previous tests, and consequently the stack had been subjected to two full temperature cycles. In addition the stack had suffered a number of minor temperature cycles and at least one redox cycle during the course of the previous tests. The effect of these cycles on the stack performance is illustrated in the mean OCV for operation on an H₂/N₂ mixture. At the start of the test detailed here, the mean OCV was 0.996 V per cell under a humidified blend of 70% H₂/N₂. This can be compared with a mean OCV of 1.16 V per cell under the same conditions at the end of the first stack test; this amounts to a 14% drop in OCV. The stack produced a total of 7.3 kW_e on H₂/N₂ during the initial test. Taking into account the drop in performance evident from the lower OCV, it can be concluded that the stack would have produced 7.1 kW_e during the initial test had it been running on methane.

5. Conclusions

A reformer suitable for a pressurised SOFC hybrid system has been designed and tested. The reformer meets the required

methane-conversion target necessary to avoid stack deactivation through carbon formation. This reformer design has been demonstrated in an integrated system incorporating a 7.5 kW_e stack block and fuel recycle. The results show that the stack performance on reformed methane is similar to that obtained on H₂/N₂, where all the steam necessary for the reforming reaction was provided from the anode-off-gas recycle, and all heat was supplied from the stack. The flexibility of the system has been demonstrated through the use of the stack block for successive tests, and the ability to operate the reformer with a fuel turn-down ratio. The results in this paper clearly demonstrate that the RRFCs system can be run effectively on methane.

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