

# The effect of fuel cell operating conditions on DIR-MCFC system selection

Richard Fellows

*British Gas, Gas Research Centre, Ashby Road, Loughborough, Leics. LE11 3QU, UK*

## Abstract

The use of natural gas and 'direct internal reforming' allows very simple molten carbonate fuel cell systems to be devised. The compositions and flow rates of the anode and cathode stack inlet and outlet gas flows can be described by five dimensionless system variables. These variables describe the total air flow, the cathode recycle, the overall fuel utilisation, the anode recycle, and the amount of steam addition. The equilibrium stability limits of carbon are presented and related to the system variables. A simplified stack model has been developed and a parametric analysis has been performed to determine the effect of the system variables on the stack performance. Two atmospheric pressure systems are presented which are suitable for combined heat and power applications of less than 1 MWe.

**Keywords:** Molten carbonate fuel cells; Direct internal reforming

## 1. Introduction

Many molten carbonate fuel cell (MCFC) systems have been proposed. There is a vast number of possible variations involving different arrangements of heat exchangers and blowers. However, the gas flows through the stack are determined by a small number of system variables such as inlet air flow rate and recycle fractions. The balance-of-plant, therefore, influences the performance of the stack only through these system variables. In this paper the stack performance is characterised in terms of the system variables without reference to specific system configurations.

The performance of a real stack can be predicted accurately only by using a full three-dimensional non-isothermal model. However, this degree of complexity is not needed for system studies purposes. A simplified stack model is presented here.

The formation of carbon in the stack can be avoided by recycling anode exit gas to the anode inlet or by adding steam to the fuel stream. It will be shown how the amount of anode recycle and steam addition affect the propensity for carbon deposition at the stack inlet.

## 2. Scope of the study

The analysis presented here is applicable to MCFC systems using 'direct internal reforming' (DIR) powered by natural gas with a power output of less than 1 MW. At this scale advanced techniques such as  $H_2$  transfer are not considered to be economic.

Although large systems may benefit from pressurisation it is considered that atmospheric pressure operation is appropriate for the application addressed here.

The oxidant is taken to be air and the fuel is assumed for simplicity to be methane.

## 3. System variables

Fig. 1 shows a schematic of the gas flows. It is applicable to any relevant system configuration, whatever the arrange-

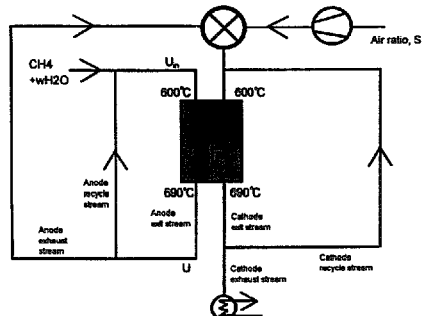


Fig. 1. MCFC gas flows.

ment of heat exchangers and blowers. Anode and cathode recycle streams are shown and steam may be added to the fuel stream. The anode exhaust gas is combusted using the feed air and the product is passed to the cathode inlet.

For a fixed fuel flow rate, the flow rate and composition of all four stack inlet and outlet flows are determined by five independent system variables. The following, dimensionless variables have been selected for convenience:

- (i)  $S$ , air ratio, defined as the feed air flow rate divided by that required for stoichiometric combustion of the feed fuel;
- (ii)  $C$ , cathode gas recycle ratio, defined as the cathode exit gas flow rate divided by the cathode exhaust gas flow rate. This definition is convenient as it simplifies the expression for cathode gas compositions;
- (iii)  $w$ , the steam/carbon molar ratio of the feed fuel stream;
- (iv)  $U$ , the overall fuel utilisation, i.e. the proportion of the fuel fed to the system that is used in the stack, and
- (v)  $U_{in}$ , the inlet oxidation factor; this factor can be used to describe the composition of the anode inlet gas and is given by the overall fuel utilisation multiplied by the ratio of the recycle stream flow rate to the anode exit flow rate:

$$U_{in} = UR_a \quad (1)$$

It is a more useful term than anode recycle,  $R_a$ , as it determines the atomic composition of the anode inlet gas.

The cathode exit gas  $O_2$  and  $CO_2$  concentrations must not fall below certain minimum values so it is important to note that these concentrations depend only on  $S$ , assuming that there is no net addition of water to the system.

#### 4. Nernst voltage

The performance of the stack depends on the local Nernst voltages within it.

The Nernst equation can be written as:

$$E = E_0 + \frac{RT}{2F} \ln \left\{ \frac{P_{H_2}}{P_{H_2O} P_{CO_2}} \right\} + \frac{RT}{2F} \ln \{ P_{CO_2} P_{O_2}^{1/2} \} \quad (2)$$

Let

$$V_a = \frac{RT}{2F} \ln \left\{ \frac{P_{H_2}}{P_{H_2O} P_{CO_2}} \right\} \quad (3)$$

and

$$V_c = \frac{RT}{2F} \ln \{ P_{CO_2} P_{O_2}^{1/2} \} \quad (4)$$

where  $V_a$  is the component of the Nernst voltage that depends on the anode gas composition, whereas  $V_c$  depends only on the cathode gas.  $V_c$  varies from stack inlet to stack outlet. The average value of  $V_c$  can be calculated analytically from the system variables  $S$  and  $U/C$ . It is plotted for a cell temperature of 645 °C, see Fig. 2, which shows that a high average value of  $V_c$  is given by a high value of  $U$  and low values of  $S$  and  $C$ .

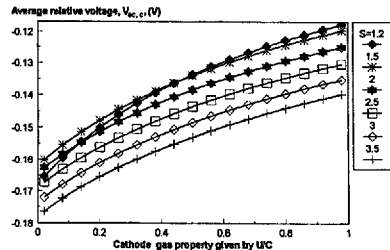


Fig. 2. Influence of  $U$  and  $C$  on  $V_{c,av}$  for six values of  $S$  with a cell temperature of 645 °C.

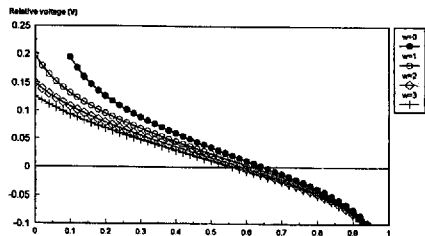


Fig. 3. Relative voltage,  $V_a$ , for equilibrated mixture of  $CH_4 + wH_2O + 4U_xCO_2$  at 645 °C (see text Section 6).

$V_a$  has been calculated for the anode gas in equilibrium at 645 °C. It is plotted against  $U_x$  in Fig. 3 for four values of  $w$ .

#### 5. Simplified stack model

It has been assumed for the purposes of this study that the gas flows in the MCFC stack are co-current and that the anode and cathode gas temperatures are equal. Unless otherwise stated, the gas inlet temperatures have been assumed to be 600 °C and an outlet temperature of 690 °C has been taken.

A simple isothermal stack model has been developed to calculate the stack power output and the required total stack cell area. The input for the model are the five variables defined above and the inlet and outlet temperatures. The anode outlet gas is assumed to be in equilibrium with respect to the reforming and shift reactions. First the composition of the gas streams is calculated from the five variables. The enthalpies of the streams are calculated and the stack electrical power output is then found from an overall energy balance for the stack. Stack heat loss is not accounted for. The current is calculated from the overall fuel utilisation. The voltage is then given directly from the power output and the current.

The total cell area depends on the difference between the average Nernst voltage in the stack and the actual voltage. Let us define the area factor,  $A_r$ , as the overall fuel utilisation divided by this voltage difference:

$$A_f = U / (V_{Nernst,av} - V) \tag{5}$$

$A_f$  is therefore a measure of the total cell area for a stack of a given cell resistance. The average Nernst voltage,  $V_{Nernst,av}$ , is computed by integration assuming a representative cell temperature of 645 °C and thermodynamic equilibrium throughout.

The current density, if required, can be calculated from:

$$\text{Current density} = U / (A_f \times \text{cell resistance area}) \tag{6}$$

### 6. Limits of thermodynamic stability of carbon

The formation of carbon is considered most likely on the reforming catalyst near the stack inlet. The possibility of carbon deposition is often determined using the 'criterion of equilibrated gas'. This states that carbon will only be formed in a particular gas if it would be thermodynamically stable in an equilibrated gas at the same temperature with the same atomic composition. Thus, assuming that this criterion is applicable, the propensity for carbon deposition depends only on the atomic composition of the anode inlet gas.

Anode gas contains  $CH_4$ ,  $H_2O$ ,  $CO_2$ ,  $CO$ , and  $H_2$ , which can react by the reforming and shift reactions:



The thermodynamic carbon stability boundary for an equilibrium mixture of these five species is often shown on a triangular H-O-C diagram. However, for MCFC systems studies it is instructive to resolve the gas mixture into the components  $CH_4$ ,  $H_2O$ , and  $CO_2$ , rather than into its atomic components. Thus, any anode gas can be represented as  $CH_4 + wH_2O + 4U_xCO_2$ , where  $U_x$  is the local oxidation factor. Fig. 4 shows the carbon stability limit for the case where  $w=0$ . Curves for the two forms of carbon are given. 'Dent' carbon is a form of carbon which has been reported to form on catalysts under conditions in which graphite does not form, even though it is thermodynamically stable [1]. It can be seen, for example, that at 600 °C, a typical inlet temperature, we require  $U_x$  to be 0.45 or more to ensure that graphite is

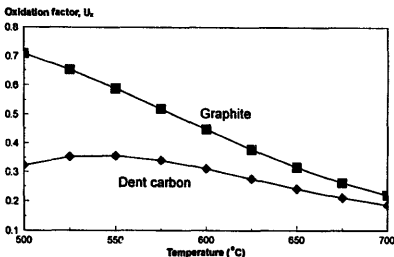


Fig. 4. Oxidation factor limit for carbon formation at equilibrium at 1 bar.

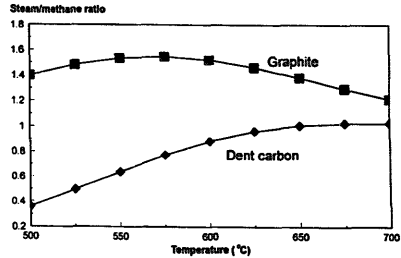


Fig. 5. Steam/methane ratio limit for carbon formation at equilibrium at 1 bar.

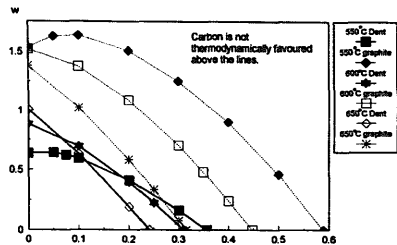


Fig. 6. Carbon formation limits at three temperatures for  $CH_4 + 4U_xCO_2 + wH_2O$  at equilibrium (see text Section 6).

not thermodynamically favoured. The corresponding figure for 'Dent' carbon is 0.31. Many of the system calculations reported here have been performed at constant  $U_{in}$  and a value of 0.4 was chosen. This is close to the values calculated from other papers [2,3].

Fig. 5 gives the equilibrium carbon formation limits for the case where  $U_x=0$ . It is therefore applicable to systems that do not employ anode recycle but rely instead on steam addition to ensure carbon-free operation.

Fig. 6 gives the equilibrium carbon formation boundaries on a plot of  $w$  against  $U_x$  for three temperatures. It can be seen from this figure that a combination of both the anode recycle and the steam addition will prevent the lay-down of carbon.

### 7. Parametric analysis

In the following analysis we shall consider the effects of changing the system variables individually. For convenience the feed fuel flow rate has been kept constant throughout.

#### 7.1. Effect of air ratio, S

Fig. 7 shows the influence of air ratio,  $S$ , on the stack performance for a system with anode recycle and no steam

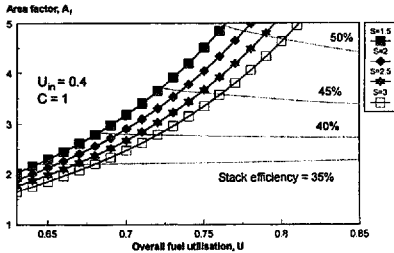


Fig. 7. The effect of air ratio,  $S$ , on stack performance.

injection ( $w=0$ ). There is no cathode recycle ( $C=1$ ) and the inlet oxidation factor is constant ( $U_{in}=0.4$ ). For any particular value of  $S$ , it can be seen that an increase in area factor allows an increase in fuel utilisation,  $U$  (while maintaining the same inlet and exit temperatures). On the same graph are near-horizontal lines calculated for four values of the stack efficiency, which is defined here as the electrical power output of the stack divided by the higher heating value of the feed fuel. It can be seen that an increase in stack size, i.e. an increase in  $A_f$ , results in an increase in efficiency for constant  $S$ . It can also be seen that an increase in  $S$  allows an increase in  $U$  for any given area factor. Although this increase in  $U$  represents an increase in current, there is little, if any increase in efficiency, because of a reduction in voltage. When the power consumption of the blower is accounted for, there can actually be a reduction in net power output when  $S$  is increased while keeping the area factor constant.

7.2. Effect of  $U_{in}$

Fig. 8 shows the effect of  $U_{in}$  on the stack performance for  $S=2$ ,  $C=1$ , and  $w=0$ . For any fixed area factor,  $A_f$ , a high  $U_{in}$  allows a high  $U$ . This is because as  $U_{in}$  is increased the anode recycle goes up resulting in a greater cooling of the stack. The lines of the constant stack efficiency show that for any fixed  $A_f$  the efficiency declines as  $U_{in}$  increases from 0.2 to about 0.5. A further increase in  $U_{in}$  results in a slight increase in stack efficiency but this advantage may be can-

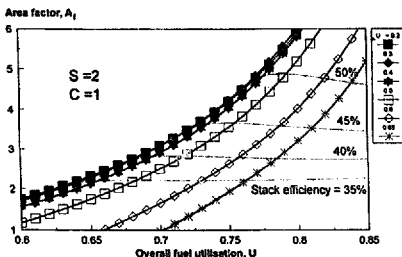


Fig. 8. The effect of  $U_{in}$  on stack performance.

celled out by the increased power consumption of the recycle blower. To minimise the cost of the equipment,  $U_{in}$  (and thus, anode recycle) should be as low as possible while ensuring carbon-free operation.

7.3. Effect of cathode recycle ratio,  $C$

Cathode recycle has often been recommended as a means of increasing the stack cooling that is performed by the cathode gas. Fig. 9 shows the effect of introducing cathode recycle for a fixed  $S$  and a fixed  $U_{in}$ . The lines of constant efficiency given in this figure have taken into account the effect of the power consumption of the cathode recycle blower. It can be seen that the increased cooling produced by the recycle allows an increase in  $U$  for any given  $A_f$ . However, it can be seen that there is no significant improvement in efficiency. This is because of a reduction in voltage, due in part to the fact that the recycled gas is rather depleted in both  $O_2$  and  $CO_2$ .

7.4. Effect of steam injection ratio,  $w$

For single pass anode systems it is necessary to add steam to the fuel. The steam prevents the deposition of carbon but causes a reduction in the Nernst voltage as shown in Fig. 6. Fig. 10 gives the performance of such a single pass system and shows that the addition of steam results in a loss of stack efficiency.

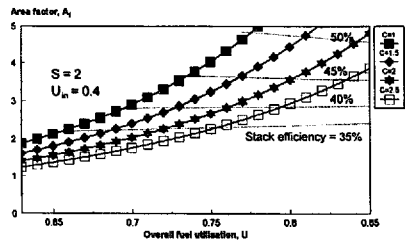


Fig. 9. Effect of cathode recycle on stack performance including the effect of parasitics.

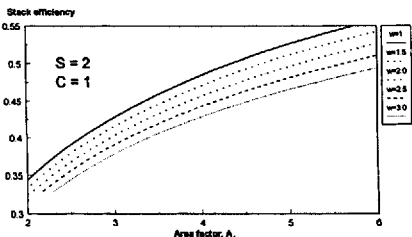


Fig. 10. Steam/methane ratio vs. stack efficiency.

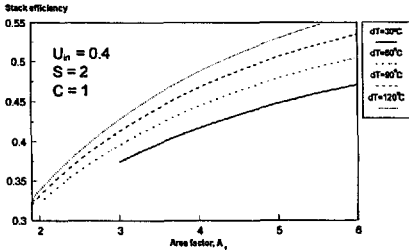


Fig. 11. Stack performance for four stack temperature differences (average temperature constant at 645 °C).

Single pass anode schemes have been compared with anode recycle schemes and it has been shown that these two options give very similar stack efficiencies.

### 7.5. Effect of stack temperature difference

The choice of stack inlet and outlet temperature requires a compromise between system considerations and lifetime and cell resistance issues. A large temperature difference allows the gas flows to perform a large amount of stack cooling and this allows a high fuel utilisation and thus a high efficiency. Fig. 11 plots the performance for four values of temperature difference. In each case the average temperature has been kept at 645 °C. This graph can be used in conjunction with information on the temperature dependence of cell resistance and degradation rates to select the optimum temperature difference.

## 8. Systems selection

Single pass anode schemes require a supply of water. This water can come from outside the system. Alternatively, the water can be condensed from the anode exhaust stream, or possibly from the cathode exhaust stream, making the system self-sufficient in water. Using an external water supply results in a loss of heat output, since the latent heat of the steam is lost. The option of condensing water from one of the gas streams requires a condenser and additional system complexity. For these reasons, anode recycle systems have been selected for the present study.

The analysis presented in Section 7 has shown that there is no significant efficiency advantage in the cathode recycle, so single pass cathode flow has been chosen as the preferred option.

System A, shown in Fig. 12, is extremely simple. No air preheated heat exchanger is necessary. The feed fuel is preheated from the recycle stream. The desulfuriser is a modified ZnO bed operating at about 350 °C. The anode recycle blower has been located so that the anode and cathode inlet pressures are well balanced. The major disadvantage of this system is

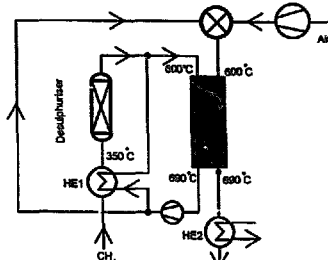


Fig. 12. System A.

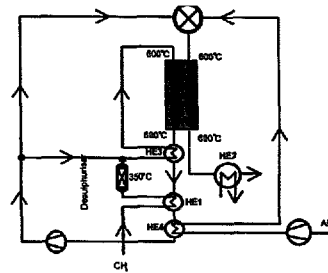


Fig. 13. System B.

that the anode blower is at a high temperature and is therefore expensive.

System B, shown in Fig. 13, is an example of a system that allows a lower anode recycle blower temperature. The anode exit stream is cooled by the feed air in heat exchanger 4. The anode inlet gas is reheated in heat exchanger 3.

Both Systems A and B can satisfy the criterion that the cathode pressure must be higher than the anode pressure. The removal of this constraint would allow many other systems.

## 9. Conclusions

1. The operation of DIR-MCFC systems has been characterised by a few independent system variables. These have been used to provide performance data for generic system types, independent of the total system configurations.
2. The composition of the anode inlet stream can most conveniently be described by its oxidation factor, given by the overall fuel utilisation multiplied by the recycle fraction.
3. In anode recycle schemes, the recycle rate should be as low as possible to minimise plant costs, whilst being sufficient to prevent carbon deposition in the anode stream.
4. Cathode recycle offers no significant advantage in terms of efficiency.
5. The most simple systems employ anode recycle with a high temperature blower.

### Acknowledgements

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