

# Syngas and electricity production by an integrated autothermal reforming/molten carbonate fuel cell system

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## Abstract

The feasibility and the overall process economy of an integrated system of molten carbonate fuel cell (MCFC) and autothermal reformer (ATR) have been studied. The ATR–MCFC performance has been evaluated in terms of pressure, inlet rates of oxygen and steam, current density and cell configuration (indirect or direct). The process, carried out close to the MCFC basic conditions ( $T = 923$  K), can be alternatively addressed to the main production of syngas or electricity by means of the inlet operative parameters that strongly influence the outlet composition and the overall thermal balance. A better heat compensation (but a small syngas/electricity production) corresponds to a greater oxygen content in the inlet stream ( $O_2/H_2O/CH_4 = 0.6/2/6/1$ ), while the  $H_2$  residual is a complex function of the current density and of the  $O_2/H_2O/CH_4$  relative ratios. A total gases pressure in the ATR compartment higher as that into the anodic housing can be hypothesised for a direct ATR–MCFC equipped with a ceramic membrane that strongly improves the cell performance. © 1998 Elsevier Science S.A. All rights reserved.

*Keywords:* Molten carbonate fuel cells; Hydrogen; Reforming; Autothermal reforming; Syngas

## 1. Introduction

The molten carbonate fuel cells, as well as other types of fuel cells, directly convert hydrogen and oxygen to water and electricity. Thus, the molten carbonate fuel cell plants must be connected with a plant for the treatment of the raw fuel and the production of hydrogen-rich mixtures. One of the most important sources of hydrogen is represented by the hydrocarbon compounds, and several processes have been proposed for the production of hydrogen from hydrocarbons, like the catalytic steam reforming.

Great attention has been paid to the fuels and the processes to be integrated with the molten carbonate fuel cells. Several authors [1,2] have proposed methane as the source of hydrogen. The use of the methane appears to be very promising because it is clean, largely available and easily processed. The steam reforming of methane has been widely investigated, suitable catalysts for this reaction have been developed and different configurations for a reformer to be integrated with the molten carbonate fuel

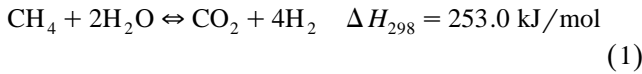
cells have been proposed [3]. Some of these configurations have been designed for in situ production of the hydrogen within the reformer integrated in the hardware of the cell, even if problems of interaction between the electrolyte vapours and the catalyst can arise. More recently, the possibility of using less endothermic reactions related to that of the methane steam reforming has been theoretically examined [4]. Our attention has been addressed towards processes like the indirect internal reforming [5], the ethanol steam reforming [6], the methanol steam reforming and the partial oxidation of the methane [7]. The steam reforming of oxygenate products seems to be thermodynamically acceptable but the high price of the raw fuel requires some investigation on the effective economic convenience. The partial oxidation of the methane could be a suitable answer to develop a reformer system integrated with the cell. Furthermore this process has the advantage of producing, at opportune conditions like low temperature, products of commercial interest like formaldehyde [8] or acetaldehyde [9]. The coupling reaction products (ethane/ethylene) can be also formed in the same molten carbonate eutectic mixture used as electrolyte [10–12]. We have continued this investigation towards the use of steam in addition to

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the catalytic partial oxidation of methane [7] in order to optimize the conditions for autothermal reforming (ATR) and to verify the yields of hydrogen and heat production in the molten carbonate fuel cell (MCFC) working conditions.

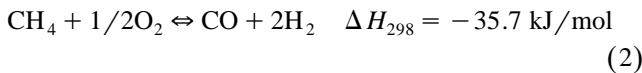
## 2. Theoretical approach

The most acknowledged process for the generation of hydrogen, for molten carbonate fuel cell applications, is the steam reforming of methane (SRM). It can be carried out outside of the cell stack [external reformers (ER)] or in small reactors, located inside the anodic housings [direct internal reformer (DIR)] or inside the connecting pipes [indirect internal reformer (IIR)]. The steam reforming reaction is strongly endothermic and its thermodynamic balance is globally represented by:

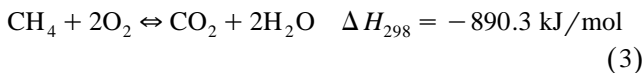


Also at the MCFC's operative conditions, the equilibrium constant is rather unfavourable (e.g.,  $K \cong 1$  at 1000 K), and side reactions, including the water gas shift reaction, result in a product containing substantial proportions of  $\text{H}_2$ ,  $\text{CO}_2$ , water, and unconverted  $\text{CH}_4$ . Moreover is not very easy to apply this process to a small scale size which, at contrary, is highly desirable for 'on site' applications.

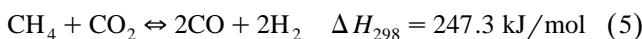
An alternative process for hydrogen production, but with a lower  $\text{H}_2$  yield, is represented by the reaction of methane with sub-stoichiometric  $\text{O}_2$  or air to produce syngas:



The main features of this process are the higher specific feed consumption, the slight exothermicity and it operates at contact times that are about two orders of magnitude lower than that of the SRM. The oxyreforming gas-phase reaction needs a stoichiometric defect of oxygen ( $\text{CH}_4/\text{O}_2$  ratio ranges from 1.8 to 1.9), and in the first reaction step, there is the combustion of a small fraction of methane with a full consumption of the oxygen and the adiabatic temperature rises, according to the following equation:

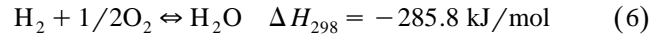


In a second step, the remaining  $\text{CH}_4$  is reformed by both  $\text{H}_2\text{O}$  and  $\text{CO}_2$  according to the endothermic reactions:



The industrial process, carried out by uncatalysed gas phase reaction at very high temperature (1400–1700 K)

and pressure (up to 150 atm), called autothermal partial oxidation (POX), cannot be used in MCFC applications. When this process is integrated with the steam reforming, it is defined autothermal reforming (ATR). In this case, it presents the advantage of lower temperature and pressure, because it can be catalysed by the same SRM catalyst, and the final products and energy balance can be conveniently addressed. Accounting also the exothermic cell reaction:



the overall process becomes almost isothermal and easy suitable at MCFC's conditions. Following the above, we developed a mathematical model to study the behaviour of an MCFC supported by an internal ATR reactor operating both in direct and indirect configuration.

In accordance with previous works aimed to verify the behaviour of  $\text{H}_2$  reactions in the anode compartment of an MCFC [5–7], the outlet concentration of each gas is obtained by solving of a wide set of equations derived from the above equilibria. A multidimensional globally convergent method for non-linear system of equations, supported by 'Mathematica 3.0' (Wolfram research Ed.), has been used. The cell voltage under load is obtained with the inclusion of the electrode overpotentials ( $\eta_a + \eta_c$ ) and the specific internal resistance ( $R_i$ ):

$$V_o = V_n - (\eta_a + \eta_c) - I \cdot R_i \cdot S_o \quad (7)$$

The values of the overpotentials and of the specific internal resistance typical of MCFC monocell, have been used in our analysis. Consequently, the output electric power ( $W = I \cdot V$ ), the thermal energy generated by the cell ( $Q_c$ ) and the available energy from the unreacted fuel ( $Q_{\text{com}}$ ) have been computed.

The energy efficiency ( $h$ ) has been calculated as:

$$h = (W + Q_u) / Q = (W + f \cdot Q_p) / Q \quad (8)$$

where  $Q$  is the flow heat of the combustion of methane supplied in the anode compartment of MCFC. Furthermore, the mass balance, at closed circuit conditions, is given by the following equations.

C balance:

$$F^\circ \cdot X_{i\text{CH}_4} = F_{\text{out}} (X_{\text{CH}_4} + X_{\text{CO}} + X_{\text{CO}_2}) - (S_o \cdot I / 2F) \cdot 3600 \quad (9)$$

$\text{O}_2$  balance:

$$2F^\circ \cdot X_{i\text{O}_2} = F_{\text{out}} (2X_{\text{O}_2} + X_{\text{CO}} + X_{\text{H}_2\text{O}} + 2X_{\text{CO}_2}) - (3S_o \cdot I / 2F) \cdot 3600 \quad (10)$$

$\text{H}_2$  balance:

$$4F^\circ \cdot X_{i\text{CH}_4} = F_{\text{out}} (2X_{\text{H}_2\text{O}} + 2X_{\text{H}_2} + 4X_{\text{CH}_4}) \quad (11)$$

Diluted balance:

$$F^\circ \cdot X_{i\text{d}} = F_{\text{out}} \cdot X_{\text{d}} \quad (12)$$

Table 1  
Selected catalysts for partial oxidation and autothermal steam reforming of methane

Catalysts	Reactor	Temperature (K)	Contact time (s)	Oxidant	Other experimental details	Conversion of CH <sub>4</sub>	Selectivity to H <sub>2</sub>	Selectivity to CO	Main conclusion	Reference
Ln <sub>2</sub> Ru <sub>2</sub> O <sub>7</sub> (Ln = lanthanide)	Labcon microreactor (i.d. 4 mm)	1050	$5-9 \times 10^{-2}$	air/O <sub>2</sub>	–	4–94	≤ 99	40–97	Ru supported is a good catalyst for CPOX	[14]
Trans. Me/ Al <sub>2</sub> O <sub>3</sub> (1 wt.%) CoO/MgO	Labcon microreactor (i.d. 4 mm)	650–1050	$9 \times 10^{-2}$	air/O <sub>2</sub>	$1 \leq P \leq 20$ bar	4–94	≤ 99	0–97	Very high yields to CO and H <sub>2</sub>	[15]
	Quarz microreactor (i.d. 4 mm)	573–1073	$\sim 7 \times 10^{-3}$	O <sub>2</sub>	With steam	16–77.2	70–92	< 92	Mechanism involves methoxide formation at low <i>T</i>	[16]
NiO/Ln <sub>2</sub> O <sub>3</sub> (Ln = lanthanide)	Continuous and pulsed quartz microreactor (i.d. 4 mm)	573–1073	$\sim 7 \times 10^{-3}$	O <sub>2</sub>	CH <sub>4</sub> pulsed alone	68–75	86–93	~ 88	Low <i>T</i> active sites are formed 'in situ' during the reaction. O-lattice reacts with CH <sub>4</sub> in the initial step.	[17]
Me/Al <sub>2</sub> O <sub>3</sub> Me = Ni, Pd, Rh, Ir (1 wt.%)	Tubular silica reactor	1050	$1.5 \times 10^{-2}$	O <sub>2</sub>	Temperat. Progr. Ox. tests	94	99	~ 97	Carbon is formed mainly by the CH <sub>4</sub> decomposition at high <i>T</i>	[18]
Pt, Rh/ $\alpha$ -Al <sub>2</sub> O <sub>3</sub> monolites	Adiabatic quartz microreactor (i.d. 18 mm)	298–1313	$10^{-2} - 10^{-4}$	air/O <sub>2</sub>	$1 < \text{CH}_4/\text{O}_2 < 1.7$	67–98	70–90	82–96	Rh is the best due to its high inertia to form OH bonds	[19]
(Cr, La) Ni/MgO	Continuous quartz microreactor (i.d. 5 mm)	1053	$2 \times 10^{-2}$	O <sub>2</sub>	CH <sub>4</sub> /O <sub>2</sub> = 2.1	89	–	96	The formation of a solid solution improve the coking-resistance.	[20]

and:

$$X_{\text{CH}_4} + X_{\text{H}_2\text{O}} + X_{\text{CO}} + X_{\text{CO}_2} + X_{\text{H}_2} + X_{\text{O}_2} + X_{\text{d}} \\ = X_{\text{iCH}_4} + X_{\text{iO}_2} + X_{\text{id}} = 1 \quad (13)$$

The equilibrium constants expressions are:

$$K_1 = (X_{\text{CO}_2} \cdot X_{\text{H}_2\text{O}}^2) / (X_{\text{CH}_4} \cdot X_{\text{O}_2}^2) \quad (14)$$

$$K_2 = (X_{\text{CO}} \cdot X_{\text{H}_2}^3 \cdot P^2) / (X_{\text{CH}_4} \cdot X_{\text{H}_2\text{O}}) \quad (15)$$

$$K_3 = (X_{\text{CO}_2} \cdot X_{\text{H}_2}) / (X_{\text{CO}} \cdot X_{\text{H}_2\text{O}}) \quad (16)$$

The Eqs. (7)–(16) have been used to calculate the outlet gas compositions from the anode compartment and the cell voltage free of the overpotentials and resistance losses.

### 3. Catalysts

Though in a developmental stage, the reaction of interest has been sufficiently investigated on a laboratory scale by using a great variety of catalysts mainly based upon Ni supported on different oxides, lanthanide or transition metal catalysts and noble metals supported on different oxides or monoliths. Main available catalysts and related conditions are reported in Table 1. Regarding to the general mechanism, a set of the elementary involved reactions has been listed by Mackie [13].

### 4. Results and discussion

The ATR–MCFC performance has been evaluated in terms of power and syngas production as a function of some operative parameters. For comparative purposes to

previous papers [4,21] the temperature was prefixed at  $T = 923$  K and only for the  $\text{H}_2\text{O}/\text{CH}_4$  (from 2 to 6) and  $\text{O}_2/\text{CH}_4$  (from 0 to 0.6) inlet ratios, the pressure (from 1 to 4 bar) and the current density (from 0 to  $150 \text{ mA}/\text{cm}^2$ ) mutual variations have been accounted. The ATR–MCFC feasibility has been evaluated in terms of outlet composition and thermal balance, because both these parameters are indicative of the efficiency of the process to produce syngas and electricity (lower residual  $\text{H}_2 \rightarrow$  higher current). Particularly, the hydrogen produced by each mole of methane, the  $\text{CO}/\text{H}_2$  and the residual content of methane represent the most significant chemical parameters if the outlet stream will be used to feed a chemical process (i.e., methanol synthesis, hydrogenation, etc.).

The  $\text{H}_2\text{O}/\text{CH}_4$  and  $\text{O}_2/\text{CH}_4$  ratios strongly influence both the outlet composition and the thermal balance of the system. As reported in Figs. 1 and 2, the residual hydrogen increases with the  $\text{H}_2\text{O}/\text{CH}_4$  ratio at any operating condition and nearly independent of cell configuration, while the  $\text{CO}/\text{H}_2$  ratio presents an inverse behaviour. Moreover, depending upon the  $\text{O}_2$  inlet amount, more or less  $\text{H}_2$  is produced and an outlet gas poor in  $\text{H}_2$  is obtained if too much  $\text{O}_2$  is used for the partial combustion reaction. The  $\text{CO}/\text{H}_2$  ratio seems to be independent from the inlet  $\text{O}_2$  (see Fig. 2). Obviously, the  $\text{H}_2$  residual can also be related to  $\text{H}_2$  consumed in the cell reaction and a richer outlet is obtained if the MCFC works at a lower current density. If no current flows through the cell (OC condition), the  $\text{H}_2$  outlet is 3.5 times the  $\text{CH}_4$  inlet stream (SRM reaction) with a  $\text{CO}/\text{H}_2$  ratio lower than 0.1. If the direct configuration is adopted, the outlet composition looks more stable, at current density higher than 0, as in the indirect case; a better utilisation of the  $\text{CH}_4$  is obtained (see below) and a syngas fed plant (i.e., for  $\text{CH}_3\text{OH}$  production) can be

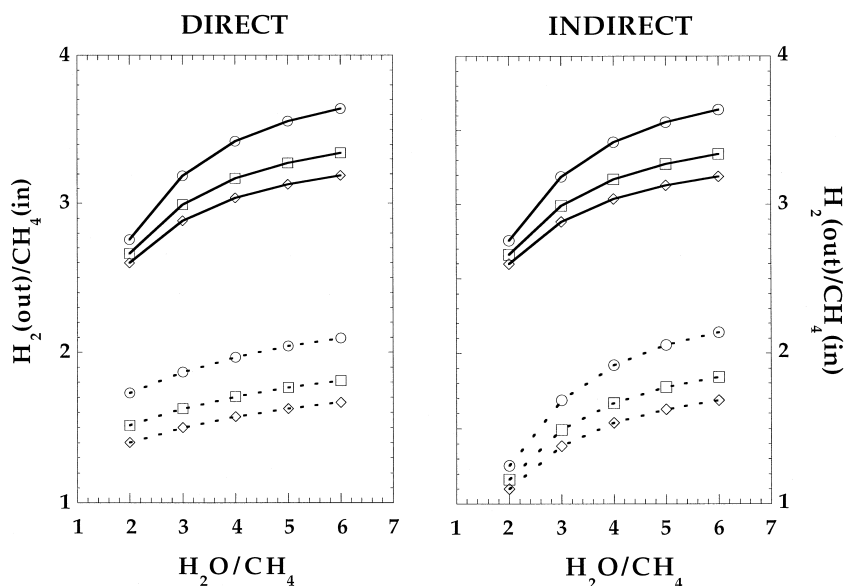


Fig. 1. Hydrogen production in a MCFC fuelled with ATR as a function of the water content in the feeding stream: OC (dotted lines);  $I = 100 \text{ mA}/\text{cm}^2$  (solid lines);  $\text{O}_2/\text{CH}_4$  inlet ratio = 0 ( $\circ$ ); = 0.175 ( $\square$ ); = 0.262 ( $\diamond$ ).

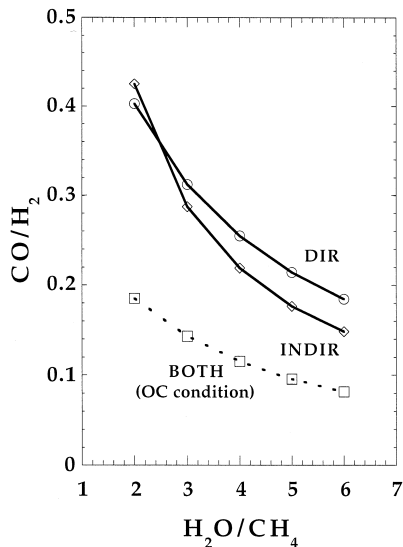


Fig. 2. Syngas composition ( $\text{CO}/\text{H}_2$ ) ATR as a function of the water content in the feeding stream: OCV (dotted line);  $I = 100 \text{ mA}/\text{cm}^2$  (solid lines);  $\text{O}_2/\text{CH}_4$  inlet ratio = 0–0.262.

conveniently hypothesised to improve the overall process economy.

As reported in Fig. 3, the thermal power of the system is little influenced by the  $\text{H}_2\text{O}$  inlet, but it is strongly depending upon the  $\text{O}_2/\text{CH}_4$  ratio. In fact, an increase of  $\text{H}_2\text{O}$  moves all equilibria with a ‘buffer’ effect on the final composition, while the  $\text{O}_2$  selectively acts only on the exothermic reaction of combustion.

The influence of the  $\text{O}_2/\text{CH}_4$  inlet ratio on the overall outlet composition is fully represented in Figs. 4 and 5, for baseline conditions ( $S/C = 2$ ,  $P = 1 \text{ bar}$  and  $I = 100 \text{ mA}/\text{cm}^2$ ). Some residual  $\text{CH}_4$  can be expected both for the direct and indirect configurations. For the indirect configuration this drops to 0.25% at  $\text{O}_2/\text{CH}_4 > 0.5$ , while for the direct configuration this is  $\gg 10$  times less. The

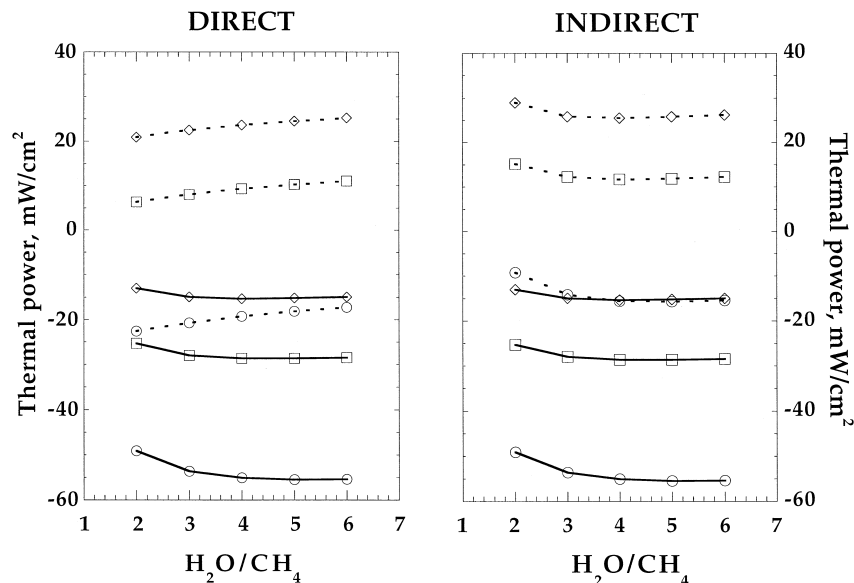


Fig. 3. Overall thermal balance of a MCFC fuelled with ATR as a function of the water content in the feeding stream (for legend see Fig. 1).

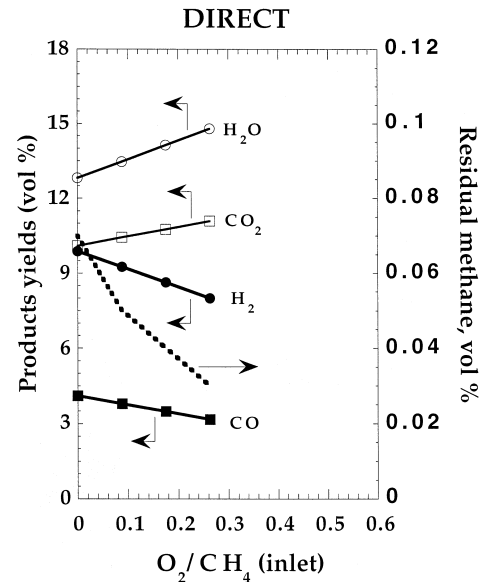


Fig. 4. Outlet composition as a function of the inlet  $\text{O}_2/\text{CH}_4$  ratio ( $P = 1 \text{ bar}$ ,  $I = 100 \text{ mA}/\text{cm}^2$ ,  $\text{H}_2\text{O}/\text{CH}_4$  (in) = 2.0. Direct ATR).

‘DIR–ATR’ configuration, in fact, presents the great advantage that the  $\text{H}_2$  produced is quickly burned ‘in situ’ by the reaction 6), so that the equilibrium moves to the highest  $\text{CH}_4$  conversion. The only limiting factor is thus the current density of the MCFC and all the  $\text{CH}_4$  can, in principle, be converted by the steam.

With regard to the reaction products, the same general behaviour of it is expected for both the ‘DIR–ATR’ and ‘IIR–ATR’ configuration. As shown in Figs. 4 and 5, by increasing the  $\text{O}_2$  in the inlet stream, the final combustion products ( $\text{H}_2\text{O}$  and  $\text{CO}_2$ ) are favoured and less  $\text{CO}$  and  $\text{H}_2$  can be recovered.

When a ceramic or metallic membrane [22] is interposed to avoid the catalyst poisoning and to move the

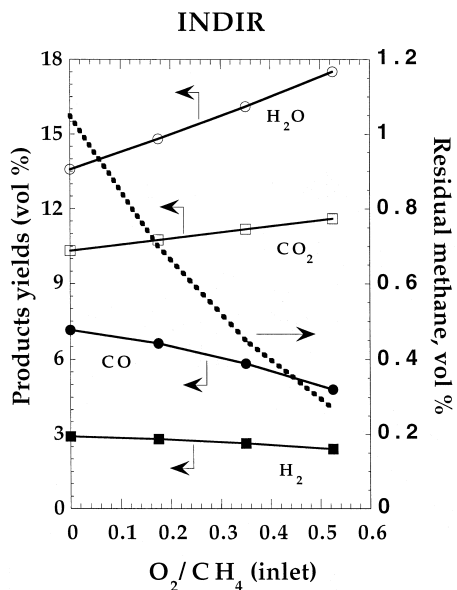


Fig. 5. Outlet composition as a function of the inlet  $O_2/CH_4$  ratio ( $P = 1$  bar,  $I = 100$  mA/cm<sup>2</sup>,  $H_2O/CH_4$  (in) = 2.0. Indirect ATR).

equilibria to the  $H_2$  production, a pressure drop is needed. Pressure is an important parameter that plays a role in the reaction pattern and strongly influences the outlet composition. As reported in Fig. 6, the highest  $H_2$  residual and the lowest  $CO/H_2$  ratio is obtained for OC conditions and pressure increase reduces both. This is due to the fact that among the overall reaction set, only the steam reforming reaction (Eq. (4)) is influenced (negatively) by the pressure. In fact, this reaction produces an increase of the mole number and an increase of the pressure moves the equilibrium to the left and the  $CH_4$  is not fully converted. Obviously, in the OC condition, no difference between the

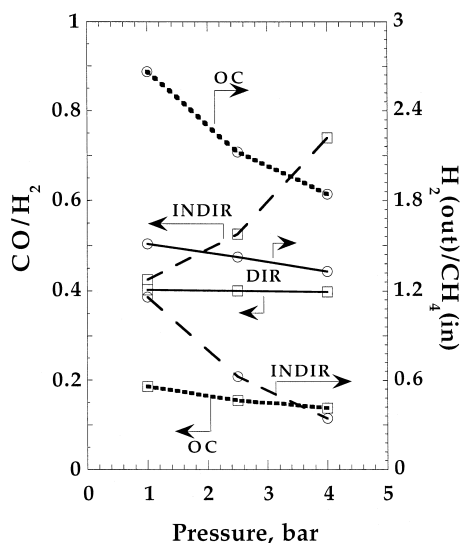


Fig. 6. Pressure influence on the outlet syngas composition in terms of  $CO/H_2$  ( $\square$ ) and  $H_{2(out)}/CH_{4(in)}$  ( $\circ$ ). Current density  $I = 100$  mA/cm<sup>2</sup> (direct = solid; indirect = dashed lines). OC condition (dotted lines).

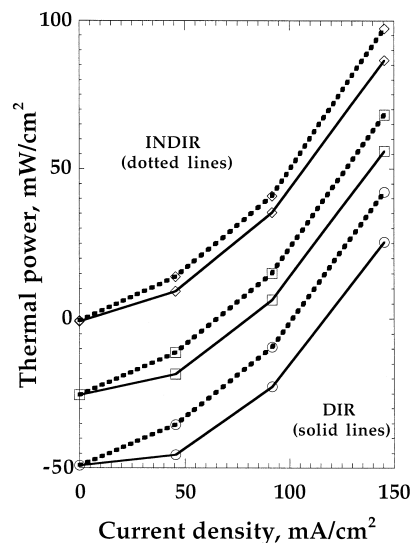


Fig. 7. Current density influence on the thermal balance of the MCFC:  $O_2/CH_4$  inlet ratio = 0 ( $\circ$ ); = 0.175 ( $\square$ ); = 0.262 ( $\diamond$ ); direct = solid lines; indirect: dotted lines.

direct and the indirect configurations can be observed. But when a current density of 100 mA/cm<sup>2</sup> is produced by the cell, a great difference between the two configurations is observed and the 'DIR-ATR' gives a more stable outlet composition. The direct configuration looks to be the most stable also from the point of view of the thermal balance. As shown in Fig. 7, when the current density increases from OC conditions to its highest value (the limit current is close to 150 mA/cm<sup>2</sup>), the exothermic cell reaction (Eq. (6)) becomes predominant with a positive thermal balance. A similar effect (to be added to the first one) can be produced by increasing the percentage of inlet oxygen and burning more methane in the initial reaction step. In any case, the curves related to the DIR-ATR configuration (solid lines) look to be the flattest and the two effects, if properly combined, can be used to a better regulation of the heat balance of the process.

## 5. Conclusions

The performance of a molten carbonate fuel cell coupled with autothermal reforming (ATR) has been evaluated as a function of some operative parameters, and their influence on the overall process economy in terms of gas outlet composition and thermal balance.

Among the parameters examined, the  $H_2O/CH_4$  and  $O_2/CH_4$  inlet ratios strongly influence the outlet composition. In fact, the content of hydrogen increases with the  $H_2O/CH_4$  ratio, while it decreases if the inlet  $O_2$  is increased. However the  $CO/H_2$  ratio is reduced by a higher  $H_2O$  inlet and by the current density. Moreover, it is influenced by the cell configuration and it appears to be independent of the  $O_2$  inlet.

Furthermore, the direct configuration appears to be more insensitive, mainly at high values of the current density and a better utilisation of the  $\text{CH}_4$  is obtained.

With regard to the influence of the inlet rate of oxygen, the same general behaviour can be expected both for 'DIR-ATR' and 'IIR-ATR' configurations, because by increasing the  $\text{O}_2$  in the inlet stream, the production of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  is favoured at the expense of  $\text{CO}$  and  $\text{H}_2$ .

The thermal balance of the system is little influenced by the  $\text{H}_2\text{O}$  inlet, but it is strongly influenced by the  $\text{O}_2/\text{CH}_4$  ratio, because  $\text{O}_2$  selectively acts on the exothermic reaction of combustion.

An increase in pressure is mainly felt through its negative effect on the thermodynamic equilibrium of the steam reforming reaction. Thus, at OC conditions (no difference has been encountered between the two configurations) the  $\text{CO}/\text{H}_2$  ratio increases with the pressure, while the content of  $\text{H}_2$  is reduced. At high values of current density a great difference between the two configurations is observed and the 'DIR-ATR' has to be preferred, because  $\text{H}_2$  consumed moves the equilibria to a better fuel utilization.

This system appears to be very flexible about the heat management and the reactions involved in the process can be combined for obtaining an optimal thermal and chemical balance.

## 6. List of symbols

$W$	Output electrical power (kW)
$Q$	Flow heat of the combustion of methane supplied (kW)
$Q_c$	Output thermal power from MCFC (kW)
$Q_{\text{com}}$	Output thermal power from burner (kW)
$Q_u$	Useful thermal power = $f \cdot Q_p$ (kW)
$Q_w$	Waste thermal power (kW)
$Q_p$	Total output thermal power = $Q_c + Q_{\text{com}} = Q_u + Q_w$ (kW)
$f$	Useful heat fraction = $Q_u/Q_p$
$h$	Energy efficiency (%/100)
$K_i$	Equilibrium constant;
$E^\circ$	Standard electrode potential (V)
$R$	Universal gas constant (1.987 cal/K mol)
$T$	Temperature (K)
$P$	Total pressure (Ata)
$P_i$	Partial pressure (Ata)
$F$	Faraday's constant (23.06 kcal/V = 96490 C/equiv.)
$\eta_i$	Electrode overpotential (V)
$R_i$	Specific internal resistance ( $\Omega \text{ cm}^2$ )
$I$	Current density ( $\text{A}/\text{cm}^2$ )
$S_o$	Effective electrodes surface ( $\text{cm}^2$ )
a, c, d	Indices referred to the anode and cathode compartment and to the diluent, respectively

$F^\circ$	Inlet flow rate of gas mixtures in the anode compartment of MCFC (mol/h)
$F_{\text{out}}$	Outlet flow rate of gas mixtures from the anode compartment of MCFC (mol/h)
$\text{Xi}^\circ$	Molar fraction of gas for the inlet gas mixture in the anode compartment of MCFC
$\text{Xi}$	Molar fraction of gas for the outlet gas mixture from the anode compartment of MCFC
$U_f$	Fuel utilisation = $(100 \cdot (I/2 \cdot F) \cdot 3600 \cdot S_o) / (2 \cdot F^\circ \cdot \text{Xi}_{\text{CH}_4})$ (%)
OC	Open circuit
DIR	Direct
INDIR	Indirect

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