

Ethanol steam reforming in a molten carbonate fuel cell: a thermodynamic approach

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Abstract

The economy of the world energy sources is showing interest in the utilization of oxygenated products whose purpose is to improve the storage and the transfer of hydrogen as a non-polluting fuel with a high heat power density. An interesting field of utilization of these products is represented by the fuel cell systems for production of electricity. In this respect, the use of the water/ethanol mixture has been investigated as an alternative fuel for molten carbonate fuel cells. Some thermodynamic calculations have been carried out by a mathematical model to determine the energy and mass balances for a water/ethanol fuelled molten carbonate fuel cell. The thermodynamic efficiencies determined for this system have been correlated with the main operative parameters that give some interesting findings indicating encouraging aspects on the utilization of these systems to the production of electricity and heat. Lastly, attractive operative conditions have been determined and compared with that of a molten carbonate fuel cell with methane direct internal reforming.

Keywords: Molten carbonate fuel cells; Ethanol; Internal reforming; Mathematical model

1. Introduction

The feasibility of electrical power plants based on molten carbonate fuel cell (MCFC) systems has been extensively explored [1–3]. One of the most interesting fields of application for these systems concerns the production of electricity for remote users (on site applications) [4]. MCFCs, like other kinds of fuel cells, use only pure hydrogen [5], which can be produced from carbonaceous fuels [6] (methane, methanol, etc.) by an external reformer before their oxidation in the cell. However, in the MCFC, the high operative temperature ($T \sim 923$ K) allows the direct conversion of methane into H_2 and CO in situ, i.e. inside the cell (direct internal reforming configuration), with a significant improvement of the system performance.

In this respect, extensive research efforts have been made to develop a technology using methane [7–9] based on the steam reforming process; different configurations have been analysed and their performance determined for different operative cell conditions [10–12].

However, the evolution of the world energy demand will lead R&D to the field of the use of alternative fuels, such as heavy hydrocarbons or alcohols (methanol or ethanol), since some practical applications are privileged by the use of raw

fuels locally available or that can be transported and reformed more easily compared with methane [13].

A future industrial economy, based upon the use of diversified raw material fuels, may also find advantageous the production of hydrogen from ethanol. In particular, the technological applications on MCFCs are strictly related to the utilization of fuels that can easily be reformed into hydrogen. Thus, it seems to be interesting to investigate the use of alternative raw fuels, with particular attention to the water/ethanol mixture, in a MCFC system for production of electricity and heat.

Literature reports only few data on the thermodynamic of ethanol conversion [14] and on the kinetic findings of some kinds of catalyst [15] for the ethanol reforming reaction



Based on these preliminary studies, a mathematical model has been developed to verify if the use of water/ethanol mixture in a molten carbonate fuel cell should be convenient, from now on, as an attractive alternative to the methane direct internal reforming configuration. The aim of this paper is to describe the most indicative results, obtained through this model, based on a thermodynamic calculation when the use of water/ethanol mixture for a molten carbonate fuel cell is considered.

2. Thermodynamics

The ethanol reforming reaction (1) can be well represented by the following partial reactions



As reported in Ref. [14], the reaction of steam reforming of methane will take place simultaneously to these reactions, even if it could be depressed by the presence of catalysts. Anyway, it has been taken into account in the overall thermodynamic balance, considering also the reaction



Based on analogous literature models [14,16] and on our previous studies [15], reactions (2)–(4) are mathematically represented by a system of equations

$$K_1 = \frac{x_{CO}^2 x_{H_2}^4}{x_{EtOH} x_{H_2O}} P^{-4} \quad (5)$$

$$K_2 = \frac{x_{CO_2} x_{H_2}}{x_{CO} x_{H_2O}} \quad (6)$$

$$K_3 = \frac{x_{CH_4} x_{H_2O}}{x_{CO} x_{H_2}^3} P^{-2} \quad (7)$$

where K_1 , K_2 and K_3 represent the equilibrium constants associated to the reactions (2)–(4), respectively, x_i 's are the molar fractions of the gaseous components and P is the total pressure.

The equilibrium constants are related to the free energies of each molecule involved in the equilibrium reactions and can be determined once the absolute temperature is specified.

The moles of each component are given by the following expressions

$$n_{EtOH} = a - x \quad (8)$$

$$n_{CH_4} = z \quad (9)$$

$$n_{CO} = 2x - y - z \quad (10)$$

$$n_{CO_2} = y + b \quad (11)$$

$$n_{H_2} = 4x + y - 3z - b \quad (12)$$

$$n_{H_2O} = b + c - x - y \quad (13)$$

$$n_{tot} = \sum_{i=1}^6 n_i \quad (14)$$

where a represents the inlet moles of ethanol, b the moles of hydrogen electrochemically converted by the cell, c the inlet moles of steam, and x , y , z the converted moles associated to the reactions (2)–(4), respectively.

Because of the complexity of the analytical solution, a mathematical model based on an iterative approach has been used to solve the system of non-linear Eqs. (5)–(14). Starting from an initial approximation for the reaction conversion

and from the equilibrium constants of the reactions (2)–(4), which depend on the temperature, a multidimensional globally convergent method [17] for non-linear system of equations have been used to calculate the outlet gas composition.

In addition, the model realized in Fortran has been supplied with a subroutine able to take into account the progressive catalyst de-activation [18] that can be produced in the cell or caused by a leakage of the catalyst in order to obtain the full thermodynamic equilibrium.

The equilibrium potential, V , has been determined by the Nernst equation

$$V = V_0 + \frac{RT}{2F} \ln \frac{(P_{H_2} P_{O_2}^{1/2} P_{CO_2,c})}{(P_{H_2O} P_{CO_2,a})} \quad (15)$$

where V_0 is the standard potential, P_i 's are the gas partial pressures, R is the universal gas constant and F the Faraday constant.

When the cell is operating with production of electricity, the corresponding potential is affected by losses due to the electrode overpotentials and to the cell resistance. In this case, the potential, V_{eff} , has been determined by the following expression

$$V_{eff} = V - (\mu_a + \mu_c) - IR_i \quad (16)$$

where μ_c and μ_a are the cathodic and anodic overpotentials, I is the current density and R_i is the specific internal resistance.

Then, both the electrical and the thermal power contributions have been determined as well as the efficiencies of the systems. The energy balances for these systems at steady-state conditions can be represented by Eq. (17), that expresses the equality between the inlet energy (fuel + oxidant) and the total output electrical and thermal energy (useful + waste)

$$m_f h_f + m_o h_o = W + Q_u + \sum_w Q_w + \sum_w m_w h_w \quad (17)$$

where m is the mass flow, h the enthalpy, W the electrical power released by the cell, Q the thermal power and the subscripts f , o , u , w refer to the fuel, oxidant, useful and waste, respectively.

In practice, the energy efficiencies have been calculated, taking into account that only a fraction (f) of the waste energy can be usefully recovered, by the expression

$$\eta = \frac{W + Q_u}{m_f h_f} = \frac{W + f Q_p}{m_f h_f} \quad (18)$$

where f is the useful heat fraction equal to Q_u/Q_p and the subscript p stands for produced.

3. Results and discussion

The analysis starts from the selection of the most indicative parameters in order to evaluate their influence on the system performance and the feasibility of the examined system to

produce electrical energy. Initially, the influence of the operative temperature on the cell voltage has been evaluated, determining the polarization curves as a function of the current density (Fig. 1). The cell voltage of the MCFC system fed by a mixture of water/ethanol has been calculated at three different values of the cell temperature (873, 923 and 973 K), which wholly cover the range of temperatures typical for these cells. The potentials at open-circuit voltage (OCV) conditions decrease when the temperature is decreased (1115.5 mV at 973 K versus 1082.7 mV at 873 K). This decrease in potential depends on the reduction of the H_2 available at the anode from the reforming reaction, which is influenced by the cell temperature. In fact, the percentage of hydrogen in the reformed gas ranges from 46.8 to 58.9%, when the temperature varies from 873 to 973 K.

The cell temperature influences also the overpotentials and the ohmic losses, which is, at a fixed current density, higher when the temperature is lower. On the contrary, the cell limiting current is not affected by the relatively poor availability of the hydrogen. In fact, it results approximately equal to 280 mA/cm², independently from temperature and pressure.

The second series of curves (Fig. 2(a)–(c)) gives the variation of the anodic gas composition as a function of the current density at different temperatures (873, 923 and 973 K). From these diagrams, it is evident that, from a thermodynamic point of view, the production of methane associated to reaction (4) is not negligible, mainly at a low temperature. Thus, at OCV conditions, the methane concentration in the outlet anodic gas composition is 12.1% at 873 K and decreases to 6.4% at 923 K and to 2.6% at 973 K. In addition, the amount of methane slightly decreases when the current density increases, and a complete conversion of methane is obtained at current densities greater than 150 mA/cm².

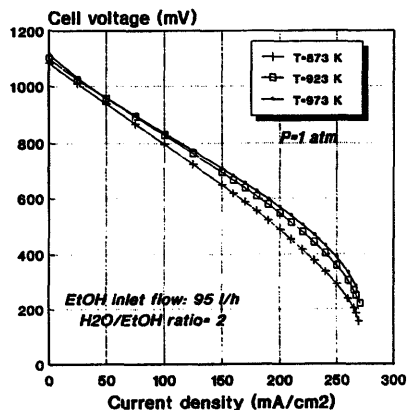


Fig. 1. Cell voltage vs. current density at 1 atm and 873, 923 and 973 K.

Reaction (2), which regulates the CO production, is on the contrary favoured by a high temperature; thus, the amount of CO in the outlet anodic composition, at OCV conditions, increases from 11.2% at 873 K to 20.9% at 973 K. At a low

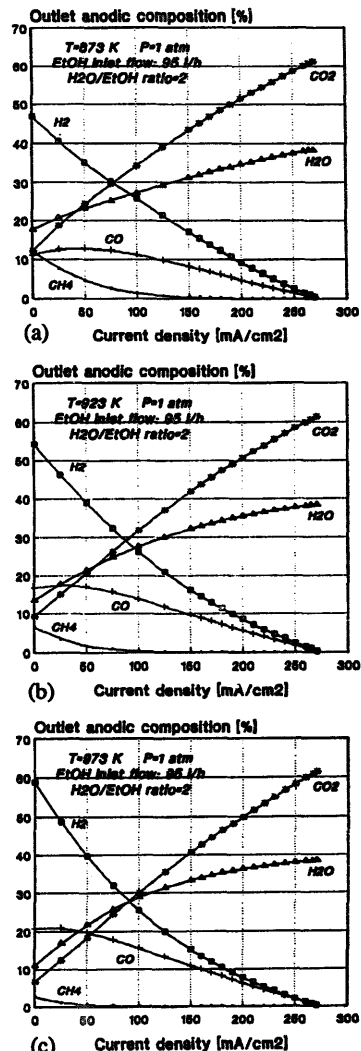


Fig. 2. Outlet anode composition vs. current density at 1 atm: (a) 873 K, (b) 923 K, and (c) 973 K.

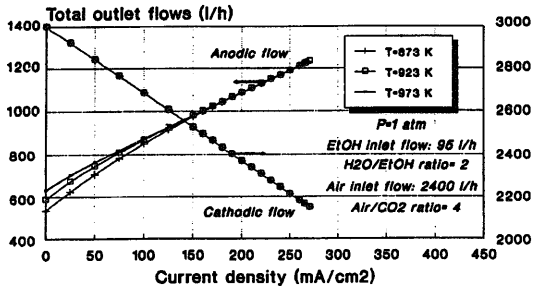


Fig. 3. Total outlet flows vs. current density at 1 atm and 873, 923 and 973 K.

temperature the CO percentage shows a peak localized at current densities close to 50 mA/cm², decreasing for higher current densities.

The steam and CO₂ concentrations in the exhaust anodic gas reveal an analogous behaviour: H₂O and CO₂ monotonically increase with the current density, because both are products of the electrochemical activity of the cell.

Furthermore, at high current densities CO₂ is the main component of the exhaust gases. For instance, at 260 mA/cm² there is about 60% of CO₂ in the exhaust anode gas, when standard conditions ($T=923$ K and $P=1$ atm) are taken into consideration.

The percentage H₂ produced by the ethanol reforming is significantly influenced by the temperature: at OCV conditions the H₂ in the exhaust gases is only 46.8% at 873 K, but a remarkable increase is observable at higher temperatures (58.9% at 973 K). This different H₂ content practically results in the possibility to have a higher current density that allows the reduction of the electrode surface and improves the weight factor of the system, which is defined as the ratio between the stack weight and the surface of the electrodes [19].

The optimization of such a system involves also the determination of the behaviour of the anodic and cathodic outlet flows. These parameters are paramount to dimension the auxiliary plant components [20], such as blowers and condensers, devoted to the treatment of the recycled anode off-gas. In fact, the outlet anodic gas should be cooled and its content of water condensed, in order to raise the gas heating value before it is burned. The condensed water will be used to produce steam for the reforming reaction and the burned gas provides CO₂ to the cathode.

In Fig. 3, the outlet flows versus current density are shown. From this figure it is evident that the outlet anodic flow increases with the temperature (at OCV is equal to 535.4, 589.3 and 632.1 l/h at 873, 923 and 973 K, respectively) and with the current density, reaching a value of about 1000 l/h (44.6 mol/h) at 160 mA/cm², becoming independent of the temperature at current densities higher than this value.

Another parameter analysed in the course of this study is the fuel utilization. The choice of the most convenient value

at which the system should operate is important to establish the overall stack size. In fact, when the operative cell conditions require a high degree of fuel utilization, the system provides higher current densities, even if the efficiency is lower. In this case the surface of the electrodes and consequently the dimension of the hardware structures of the stack can be reduced. On the contrary, a low degree of fuel utilization, that requires larger stack size, is necessary when a high system efficiency needs to be obtained.

In this case a compromise between these two extreme solutions seems to be possible choosing current densities close to 190 mA/cm². At this current density value the maximum of the fuel utilization matches with the higher electrical efficiency, and their values are significant for practical applications.

The fuel and oxidant utilization coefficients, determined in the examined case, are shown in Fig. 4. In particular, a fuel utilization equal to about 70% is obtained at 190 mA/cm²; the complete fuel utilization (100%) corresponds to the limiting current density (~ 280 mA/cm²).

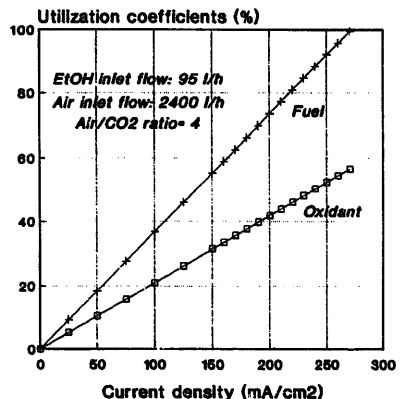


Fig. 4. Fuel and oxidant utilization coefficients vs. current density at 923 K and 1 atm.

The degree of reliability of a power plant for production of electricity clearly appears from the analysis of the curves representing the electrical power released as a function of the current density (Fig. 5). Thus, the electrical power presents a volcano-shaped behaviour with a maximum localized at about 190 mA/cm^2 ($99.8, 109.8$ and 113.7 mW/cm^2 at $873, 923$ and 973 K , respectively), but these curves are limited in the region characterized by high values of current density because of a lack of hydrogen. A specular behaviour is evidenced in Fig. 5 for the thermal power densities, calculated assuming that 50% of the waste energy (uncombusted fuel and sensible heat) is recovered ($f=0.5$).

In Fig. 6, the curves representing the values of the electrical efficiency calculated as a function of fuel utilization are reported. The trend of these curves is similar to that of the electrical power, with maximum values at about 70% of fuel utilization (30.9, 34.2 and 35.4% at $823, 923$ and 973 K , respectively). The electrical efficiencies determined as a function of the current density, for three different temperatures (873, 893 and 923 K), are shown in Fig. 7, along with the overall efficiencies calculated for $f=0.5$.

It appears obvious that, in the range of operative temperatures explored, the system can reach levels of efficiency interesting for practical applications. So, an overall efficiency of 65.1% (31.1% is the corresponding electrical efficiency) can be obtained at 170 mA/cm^2 for the cell operating at 873 K , and this value increases up to 67.8% (electrical efficiency $\sim 35\%$) at 973 K .

Lastly, the performance of an ethanol direct internal reforming MCFC has been compared with that of a methane direct internal reforming MCFC, operating under similar conditions (923 K , 1 atm and a steam/raw fuel molar ratio of 2.0). The results of this comparison are summarized in Table 1 (at OCV and 190 mA/cm^2) and in Table 2, where in particular, the cell voltages determined for the two cell configurations are reported. A methane inlet flow equal to 142.5 l/h (95 l/h is the ethanol inlet flow) has been considered in order to have the same fuel utilization at any fixed current density and to perform a rational comparison.

The analysis of these data indicates that the ethanol direct internal reforming configuration gives higher OCV (1099.9

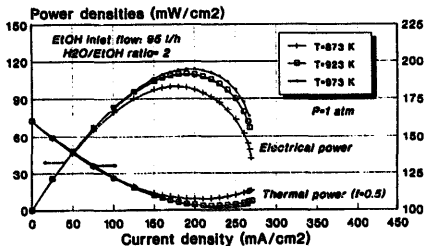


Fig. 5. Thermal power density (for $f=0.5$) and electrical power density vs. current density at 1 atm and $873, 923$ and 973 K .

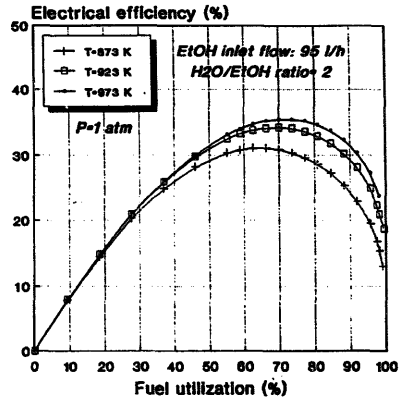


Fig. 6. Electrical efficiency vs. fuel utilization at 1 atm and $873, 923$ and 973 K .

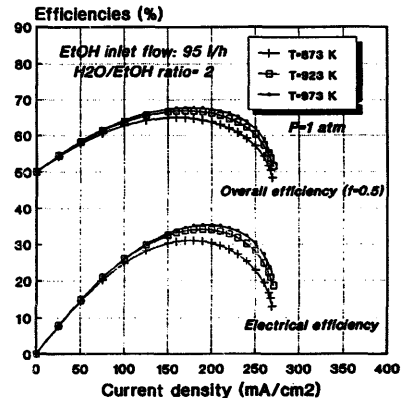


Fig. 7. Overall efficiency (for $f=0.5$) and electrical efficiency vs. current density at 1 atm and $873, 923$ and 973 K .

mV against 1073.6 mV) and cell potentials (578.0 mV against 526.9 mV at 190 mA/cm^2). This is due to the low utilization of CO and methane that is produced in the ethanol cell. Besides, the electrical and the overall efficiencies are higher in the ethanol cell and are respectively equal to 34.2 and 66.6% at 190 mA/cm^2 (31.9 and 63.8% are the values corresponding to the methane fuelled cell).

4. Conclusions

The theoretical calculations, carried out by a mathematical model, gave clear correlations between the main operational

Table 1
Comparison between results of ethanol and methane fuelled direct internal reforming (DIR) MCFC obtained at OCV and 190 mA/cm²

Parameter	Units	CH ₄ DIR MCFC		EtOH DIR MCFC	
a) Input data					
Temperature	K	923		923	
Pressure	atm	1.0		1.0	
Fuel (CH ₄ or EtOH) inlet flow	l/h	142.5		95.0	
H ₂ O/(raw fuel) mole ratio		2.0		2.0	
Cell resistance	Ω cm ²	0.80		0.80	
Current density	mA/cm ²	0	190	0	190
b) Results					
Fuel utilization	%	0.0	69.9	0.0	69.9
Oxidant utilization	%	0.0	39.7	0.0	39.7
Raw fuel conversion	%	81.6	100.0	100.0	100.0
Electrical efficiency	%	0.0	31.9	0.0	34.2
Overall efficiency (f=0.5)	%	50.0	63.8	50.0	66.6
Cell voltage	mV	1073.6	526.9	1099.9	578.0
c) Anodic outlet composition:					
EtOH	%			0.0	0.0
CH ₄	%	4.0	0.0	6.4	0.0
CO	%	10.5	5.1	16.8	6.3
CO ₂	%	7.1	43.6	9.1	49.0
H ₂	%	59.9	10.3	54.3	9.8
H ₂ O	%	18.5	41.0	13.5	34.9

Table 2

Cell voltages (calculated by the model) for ethanol and methane fuelled direct internal reforming (DIR) MCFC

Current density (mA/cm ²)	CH ₄ DIR-MCFC cell voltage (mV)	EtOH DIR-MCFC cell voltage (mV)
OCV	1073.6	1099.9
25	993.3	1022.5
50	926.1	957.4
75	860.5	893.9
100	794.1	829.9
125	725.3	764.1
150	653.2	695.6
160	623.1	667.2
170	592.1	638.3
180	560.1	608.5
190	526.9	578.0
200	492.4	546.4
210	456.2	513.6
220	417.9	479.4
230	376.8	443.2
240	331.6	404.2
250	280.0	360.6
260	215.3	307.1
265	171.1	270.5

and energetic factors that are paramount in the evaluation of the feasibility of an ethanol direct internal reforming molten carbonate fuel cell system to produce electrical energy and heat.

The analysis appears to indicate some restrictions, but also several encouraging aspects on the utilization of these electricity producing systems. So, it is very interesting to note

that the whole reforming of the ethanol is reached at the operational conditions, so that it is not present in the exhaust anode gas.

The methane production is favoured by low reforming temperatures; on the contrary, the hydrogen content decreases when the temperature is lowered, even if this reduction of the hydrogen content is not so drastic to inhibit the achievement of significative values of the current density (~280 mA/cm²) and high fuel utilizations (close to 100%). In practice, however, the most convenient values of current density at which the examined system must operate are close to 190 mA/cm². At this value of current density the maximum of the fuel utilization (~70%) matches with the higher electrical efficiency (34.2% at 923 K and 1 atm) and their values are appreciable for practical applications. Particularly, this condition allows to avoid a disadvantageous increase in overall stack size. If only a low fuel utilization degree can be obtained, larger stack sizes are required and a very large amount of CO and methane will be found in the anode exhaust gas, that must be considered as substantial sources of chemical heat for a thermal recovery cycle.

As expected, no significant variations have been found on the behaviour of the anodic and cathodic outlet flows if compared with traditional direct internal reforming MCFC systems.

In the meantime, the electrical power released by the system is enhanced by the temperature because it improves both the H₂ production and the kinetics of the electrode half-reactions. But, there is also the evidence that the electrical power released by the cell is limited in the region characterized by high values of current density (> 190 mA/cm²) because of

a lack of H_2 , making the practical convenience of low operative temperatures uncertain (at 873 K the maximum electrical power is 99.8 mW/cm²). In this case, the most convenient temperature seems to be 973 K at which the cell produces 113.7 mW/cm² at 190 mA/cm². Unfortunately, this high operative temperature enhances the problems of hardware corrosion and electrolyte vaporization, shortening the cell life time. An acceptable compromise could be represented by the selection of an intermediate operating temperature. Thus, a system operating at 923 K can yield about 109.8 mW/cm² at 190 mA/cm² with a level of life-time limiting problems that are well known in the present state-of-the-art [21].

However, the most important parameter in relation to the reliability degree of the examined system to the heat and electricity production is the value of the electrical efficiency that can be obtained. The case of an ethanol-fed system presents, mainly at intermediate and high temperatures, appreciable values of electrical efficiency (34.2% at 923 K and 35.4% at 973 K versus 31% at 873 K), that should be compared with those of an MCFC traditional system (32.2% at 923 K), and the same goes for the overall efficiency values calculated with the assumption that the 50% of waste heat is recovered (maxima at 923 K are 66.9 and 64.9% for the ethanol and the methane case, respectively).

Again, even if there are no severe restrictions at lower temperatures, it appears evident that operative temperatures equal to 923 K or higher allow more interesting efficiency levels for practical applications.

Further additional indicative factors on the theoretical interest for the application of ethanol direct internal reforming MCFCs is the comparison between this system and that based on the methane direct internal reforming. The results of this comparison indicate that a cell based on the ethanol direct internal reforming configuration, operating at the same fuel utilization of a similar cell fuelled with methane, gives comparable electrical and overall efficiencies that encourage continuing the study of the applications of these systems.

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