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The importance of the fuel choice on the efficiency of a solid oxide fuel cell system

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Abstract

A simplified model has been formulated in order to easily and adequately determines the efficiency of a solid oxide fuel cell (SOFC) stack system, independently on the fuel choice. Simple analytical formulas for the calculation of electromotive force (emf) generated in a SOFC system as well as for the estimation of its efficiency are proposed. It was found that both emf and efficiency are functions of the amount of carbon atoms of the fuel (oxygenated or not) as well as of the operational temperature. The steam to fuel molar ratio, defined as reforming factor, m, for each fuel and temperature has been adjusted to be low enough so as to ensure optimal conditions in the SOFC operation but high enough to avoid carbon formation within the cell. It has been also demonstrated that the efficiency values predicted by the model are of low relative difference compared with the numerical ones and, therefore, the approach presented here can be considered as sufficient enough for practical use.
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1. Introduction

Increasing global energy consumption has had and will continue to have many detrimental effects on the earth's environment. Consequently, the need for highly effective and environmental friendly power generation systems is nowadays more than obvious. In this direction, fuel cell (FC) technology offers many advantages over conventional methods of power generation, including higher efficiencies and negligible emissions [1–4].

Solid oxide fuel cells (SOFCs) present special interest because of their high operation temperature, which allows flexibility in fuel choice [5]. Various fuel options such as methane, methanol, ethanol and gasoline are considered feasible for SOFC operation, offering in fact a very significant ecological dimension in the problem of effective energy conversion [6–8]. The electrochemically combustible species are usually H_2, CO and CH_4 provided by external steam-reforming of each raw fuel, but, it is common system analysis practice to assume that only H_2 contributes to power generation while CO and CH_4 are converted through in situ steam-reforming providing additional amounts of H_2 [9].

It is well known that the fuel cell efficiency (FCE) is one of the most critical parameters for the fuel choice. FCE is defined as the ratio of the electric power produced by the cell to the total chemical energy of the fuel. Even for the simplest case of a single planar SOFC, at least one integration of the local value of the electromotive force (emf) along the length of the cell is necessary for the calculation of the efficiency and, thus, numerical techniques are normally used to this purpose. This represents obviously a disadvantage for the method, especially in the case of the necessity for a critical decision about the eligibility of each fuel.

In the present work, simple analytical formulas for the calculation of the electromotive force generated and, consequently, for the estimation of the overall efficiency of a SOFC system are proposed as functions of the number of carbon atoms of the fuel (oxygenated or not) and of the operational temperature. The results are also a function of the steam to fuel mole ratio, defined as reforming factor, m, and on the operational temperature. It has been also demonstrated that the agreement between analytical data presented here with the numerical ones obtained by previous work [10] is very accurate presenting relative differences in the estimation of both emf and efficiency lower than 3% for any temperature value and fuel type.

It is important to note that at least one analytical approach has already been used in the relative bibliography [11] but

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Nomenclature

a, c	indicators for the anode and the cathode of the SOFC, respectively
E	electromotive force
$\bar{E}$	overall electromotive force defined by Eq. (6)
F	Faradays' constant (96,484 J/(mol V))
$K, K(T)$	equilibrium constant of reaction (1)
L	length of the cell stack
m	steam to fuel ratio (reforming factor)
$n_{CO}, n_{CO_2},$ $n_{H_2},$ n_{H_2O}, n_{CH_4}	coefficients of each species in Eq. (1)
n	number of carbon atoms of the hydrocarbon
p	index of the hydrocarbon (1 = oxygenated, 0 = non-oxygenated)
$p_{H_2O}(x),$ $p_{H_2}(x),$ $p_{O_2}(x)$	partial pressure at position x of steam, hydrogen and oxygen, respectively
q	electrical charge
R	universal gas constant (8.314 J/(mol K))
T	cell temperature
U	hydrogen utilization factor
x	spatial position
$y_{CO}, y_{CO_2},$ $y_{H_2}, y_{H_2O},$ y_{CH_4}	molar fractions of carbon monoxide and dioxide, hydrogen, water and methane, respectively

Greek letters

$-\Delta H^0$	lower heating value (enthalpy of combustion) of fuel at standard conditions
η	efficiency of the cell, defined by Eq. (7)

it deals with completely different points of the cell power cycle such as the reforming reaction and the consequent hydrogen production. Furthermore, they avoid considering the possibility of carbon deposition in the gaseous equilibrium system and, therefore to limit the reforming factor values in such a range that carbon deposition is thermodynamically impossible [12].

2. Theory

The hydrogen rich gas mixture feeding fuel cells is typically generated in a fuel processor by means of the steam-reforming reaction. According to the acquired knowledge on the thermodynamics of the steam-reforming so far,

the equilibrium gas mixture might contain only five components of noticeable concentration: carbon monoxide, carbon dioxide, hydrogen, steam and methane. Therefore, the full transformation of the initial fuel–oxidant system into the equilibrium mixture has been expressed as [13]

$$\text{Fuel} + m_{H_2O} \rightarrow n_{CO}CO + n_{CO_2}CO_2 + n_{H_2}H_2 + n_{H_2O}H_2O + n_{CH_4}CH_4 \qquad (1)$$
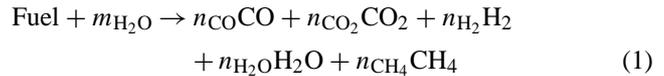
where m represents the steam to fuel mole ratio. The thermodynamic equilibrium composition derived from the fuel steam-reforming was described by a non-linear system where the unknown molar fractions y_{CO}, y_{CO_2}, y_{H_2O}, y_{CH_4} and y_{H_2} are derived numerically. However, it can be considered that both CH_4 and CO further react with water producing CO_2 and H_2. Therefore, Eq. (1) for saturated hydrocarbons, can be written as

$$C_nH_{2n+2}O_p + mH_2O \rightarrow nCO_2 + (3n+1-p)H_2 + (m-2n+p)H_2O \qquad (2)$$
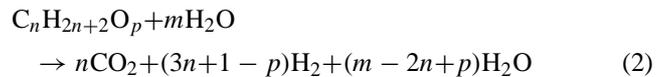
where p equals to 1 or 0 for the case of saturated hydrocarbons, oxygenated or not, respectively. The coefficients in the right-hand side represent the molar fractions of y_{CO_2}, y_{H_2O} and y_{H_2}. Therefore, the electromotive force can be calculated according to the Nernst equation [14]:

$$E = \frac{RT}{4F} \ln \frac{p_{O_2}(c)}{p_{O_2}(a)} \qquad (3)$$

where R is the universal gas constant, T the absolute temperature, F the Faraday constant, $p_{O_2}(c) = 0.209$ is the partial pressure of oxygen when exposed to the atmospheric
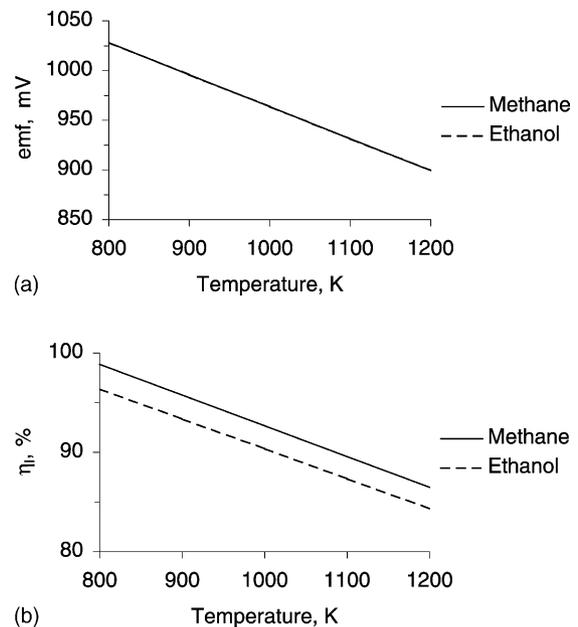
Fig. 1. SOFC electromotive force (a) and efficiency (b) dependence on the temperature of the fuel cell for optimal values of reforming factor ($m = 2n - p$).

air cathode and $p_{O_2}(a) = (p_{H_2O}(a)/Kp_{H_2}(a))^2$ is the partial pressure of oxygen in the anode depended on the hydrogen and steam partial pressures, respectively. The parameter $K = K(T)$ denotes the equilibrium constant of the reaction:

$$H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O \tag{4}$$
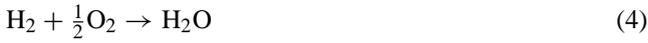
that takes place in the SOFC. By supposing that the cathode surface of the SOFC is fed by air and by assuming

one-dimensional flow, Eq. (3) can be written as follows:

$$E(x) = \frac{RT}{2F}\left(\ln\frac{m - 2n + p + Ux}{U - Ux} - K(T) + 0.7827\right) \tag{5}$$

where $U = 3n + 1 - p$ represents the hydrogen utilization in the dimensionless distance x, and thus, the overall electromotive force of the multi-cell stack can be calculated by
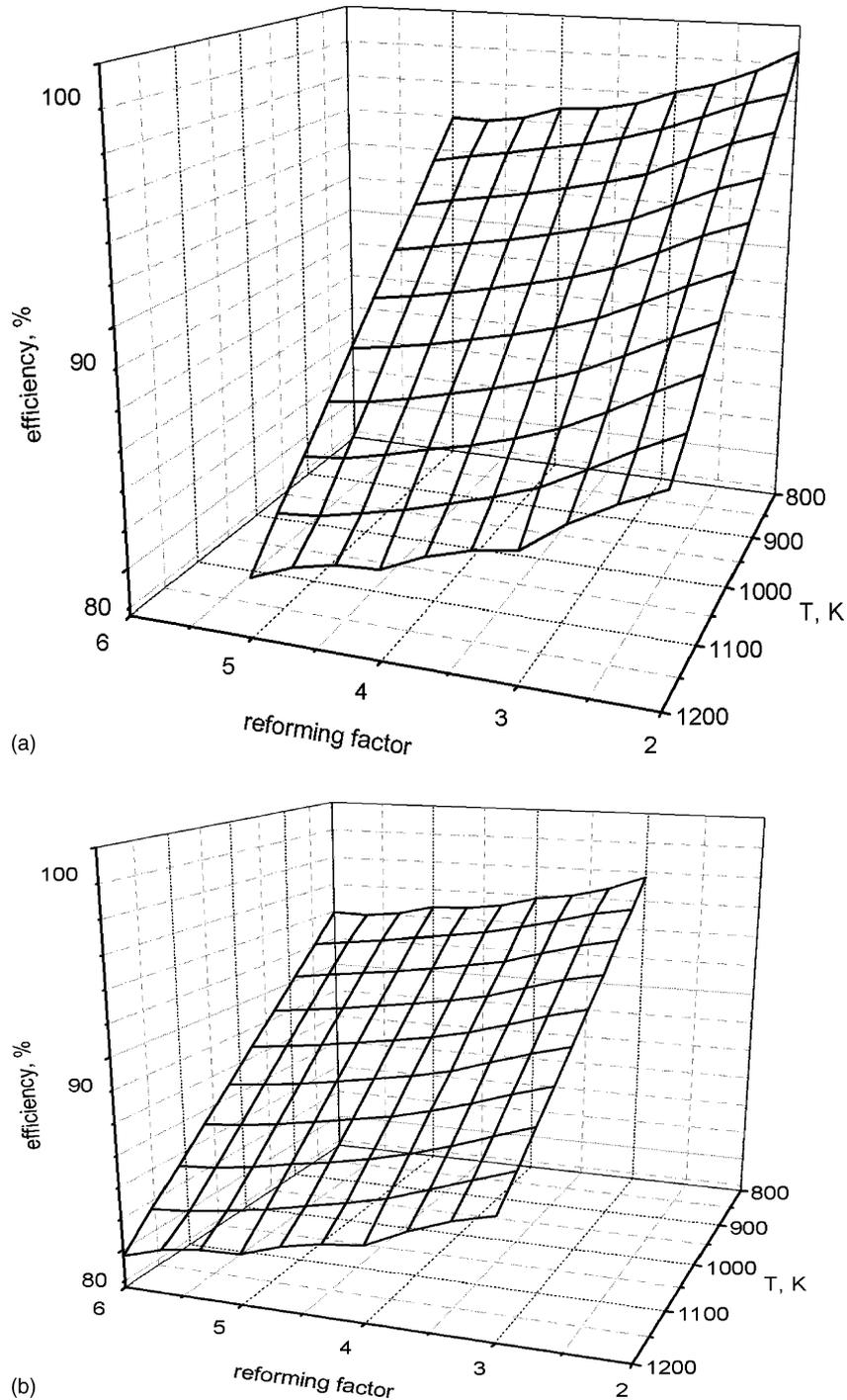
Fig. 2. Dependence of the efficiency of SOFC on the operational temperature of the fuel cell and on the reforming factor for methane (a) and for ethanol (b).

integrating Eq. (5) as follows:

$$\bar{E} = \int_0^1 E(x)\,dx \tag{6}$$

and the overall efficiency of the SOFC can be estimated by using the formula:

$$\eta = \frac{q\bar{E}}{-\Delta H^0} \tag{7}$$

where $-\Delta H^0$ is the lower heating value (LHV) of the fuel at the standard conditions, and q is the electrical charge passing through the electrolyte. According to the general reaction:

$$C_nH_{2n+2}O_p + \frac{3n+1-p}{2}O_2 \rightarrow nCO_2 + (n+1)H_2O \tag{8}$$

(a)

(b)
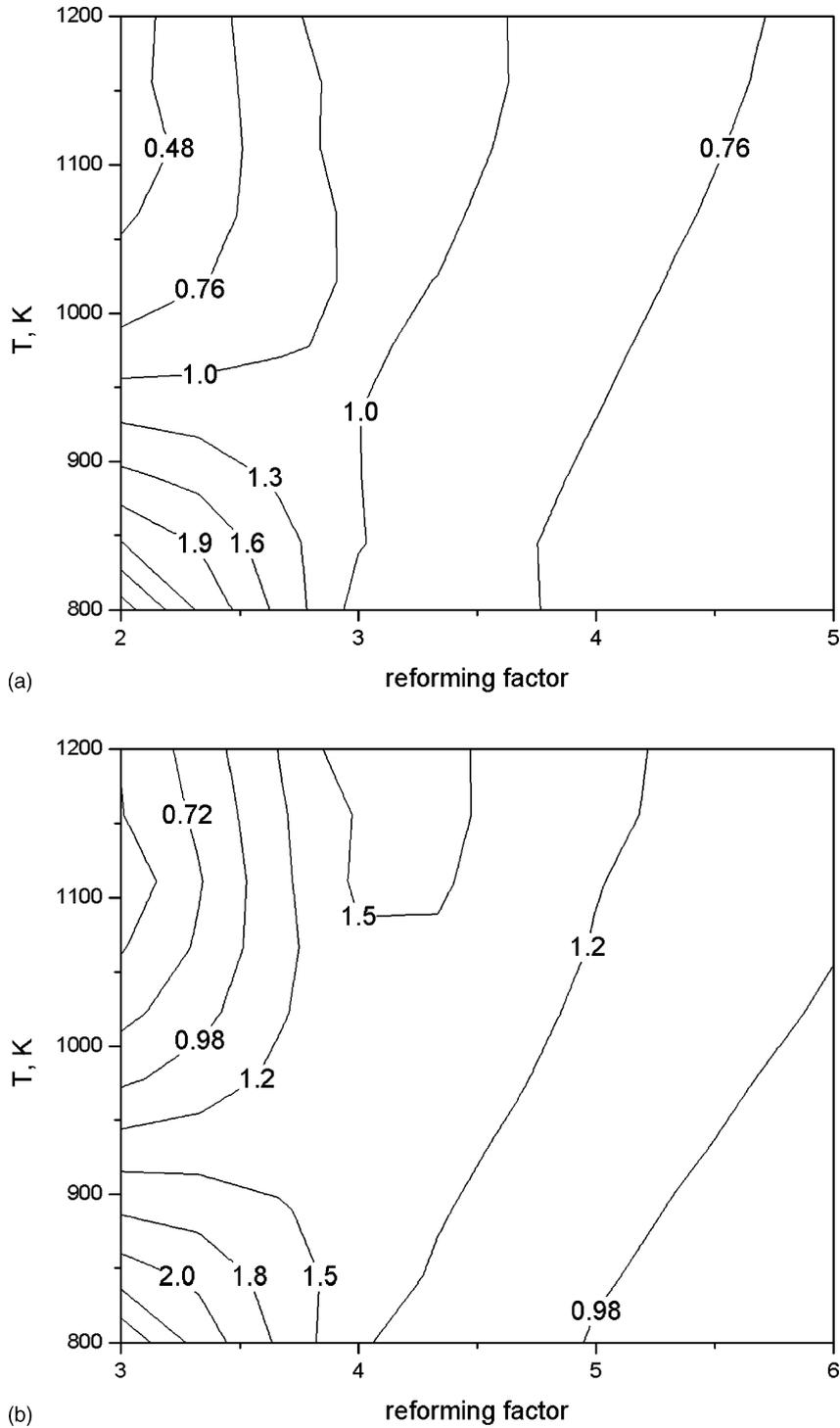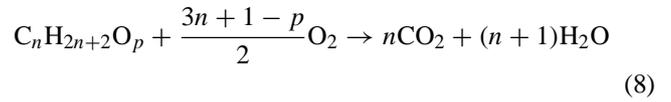
Fig. 3. Relative difference in the estimation of efficiency for the cases of methane (a) and ethanol (b) ($m = 2n-p$).

the electrical charge, q, passing through the electrolyte, can be expressed as

$$q = 2(3n + 1 - p)F = 2UF \qquad (9)$$

The above-mentioned procedure can also be applied for the case of unsaturated hydrocarbons of the form $C_nH_{2n}O_p$ and $C_nH_{2n-2}O_p$ where $U' = 3n - p$ and $U'' = 3n - 1 - p$, respectively.

3. Results and discussion

Fig. 1a shows the maximum $\bar{E}$ obtained by Eq. (6) for different temperatures and fuel options. The reforming factor, m, has been chosen for each fuel and temperature to be the stoichiometric one defined by reaction (2). It has already been observed that the reforming factor is an unfavorable parameter for both emf and efficiency as they present their maximum values for the lower m values [13]. However, the reforming factor should not be lower than a critical value dependent on the temperature, in order to avoid carbon formation within the cell [10]. This critical value of m can be calculated by assuming that reaction (2) occurs completely and thus, $m = 2n - p$, which predicts an emf value as follows:

$$\bar{E}|_{m=2n-p} = \frac{RT}{2F}(0.7827 - K(T) - 1) \qquad (10)$$

It should be stressed that this emf value is independent of the fuel choice because the stoichiometric value of m corre-sponds to the complete utilization of the available hydrogen. Under this respect, all the fuels present the same optimum emf outputs that decrease as the temperature increases.

The efficiency produced by Eq. (7) for various tempera-tures is shown in Fig. 1b for the same fuels and conditions as in Fig. 1a. As the efficiency is linearly related to the max-imum overall emf, it also decreases with temperature incre-ment. Moreover, it is worth noticing that the lower absolute value observed for any fuel and temperature is high enough (>80%) for almost any practical use.

In Fig. 2, is reported the dependence of the efficiency on the reforming factor for methane (a) and ethanol (b). An in-crement in the reforming factor results decrement of the effi-ciency. At the same time the molar fraction of the produced H_2 decreases due to the increment of the steam that has not reacted. Thus, the emf produced lowers and the efficiency also decreases. Furthermore, one can distinguish once more the negative impact of temperature on the efficiency, as it has been already observed in Fig. 1.

The relative difference between the efficiency calculated by Eq. (7) for the case of methane and ethanol compared with that estimated numerically for the same fuels and conditions in previously published work [10] is presented in Fig. 3. As one can observe, the agreement with numerical data is very good as relative differences are for all the fuels in a range of 0.09–2.9% depending on temperature and reforming factor. Generally speaking, the lower the values of temperature and reforming factor, the higher the differences that have been calculated. These divergences are mainly produced due to the integral in Eq. (6), which presents a singularity in its
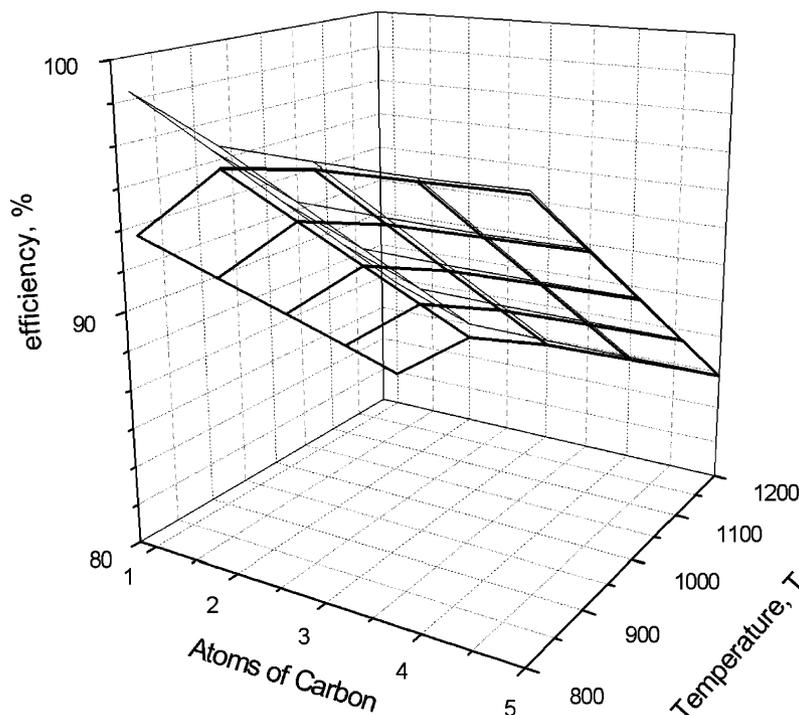
Fig. 4. Dependence of the electromotive force (a) and efficiency (b) of SOFC on the carbon atoms of the fuel for optimum reforming factor.

lower bound $x = 0$. Furthermore, the absence of carbon monoxide and methane in the consideration for the products of the reaction (2) is also a significant factor for the production of this relative difference.

The dependence of maximum efficiency on the carbon atoms is given in Fig. 4 for saturated hydrocarbons either oxygenated or not. In all cases, the absence of oxygen from the fuel ($p = 0$) leads to higher efficiency values than those predicted for the oxygenated ones ($p = 1$). From mathematical point of view it can be considered as an expected result as all the numerators in Eq. (7), as a result of the combination of Eqs. (5) and (6) with Eq. (9), become higher and all denominators become lower in the case of saturated non-oxygenated hydrocarbons with respect to that of oxygenated ones. When $p = 0$, the ratio of carbon to hydrogen atoms becomes lower as n increases and thus, the trend for hydrogen utilization of the fuel (i.e. the efficiency) decreases. On the other hand, oxygenated fuels allow reforming factor to attain lower values. Therefore, the oxygenated fuels can be considered as an extension of the non-oxygenated ones, in otherwise unattainable ranges of reforming factor's values.

4. Conclusions

A mathematical model has been developed in order to adequately calculate both the electromotive force (emf) and the efficiency of a SOFC stack system, independently on the fuel choice. Simple analytical formulas for the calculation of emf produced by a SOFC system as well as for the estimation of its efficiency are proposed. It was found that both emf and efficiency are functions of the fuel type (oxygenated or not) and its carbon atoms as well as of the operational temperature. The reforming factor has been ad-

justed for each fuel and temperature to be low enough so as to ensure optimal conditions in the SOFC operation but high enough to avoid carbon formation within the cell. It was proved that the agreement between numerical and analytical data is generally very good presenting relative differences in the estimation of the efficiency lower than 3% for any temperature and fuel. The model has also predicted that oxygenated hydrocarbons are less effective fuels than non-oxygenated ones in terms of both emf production and system efficiency.

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