

Thermodynamic analysis of a solid oxide fuel cell system fuelled by ethanol

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Abstract

In the present study, a detailed thermodynamic analysis has been carried out in order to provide useful information concerning ethanol utilization as alternative fuel in solid oxide fuel cells (SOFCs) by using different oxidants for preliminary fuel reforming. The SOFC was considered being fed with the thermodynamic equilibrium products of ethanol, (a) steam reforming, (b) reforming with CO₂ and (c) partial oxidation with air. Equilibrium calculations were performed in the region where carbon formation is thermodynamically impossible, in the temperature range between 800 and 1200 K assuming different oxidant/ethanol ratios of the initial system.

It was found that the maximum SOFC system efficiency at $T < 950$ and >1100 K is achieved when the SOFC electrochemical section is fed by the products of ethanol steam reforming, whereas at the intermediate temperature region it seems more preferable to feed the SOFC electrochemical section with the products of ethanol reforming with carbon dioxide. Maximum obtainable SOFC system efficiency if the products of ethanol partial oxidation feed the SOFC electrochemical section is about 20% less compared to the maximum SOFC system efficiency in the previous cases. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

It is well known that the most promising technology of chemical to electrical energy conversion during the 21st century is the technology of fuel cells, which have attracted considerable interest during the past decade as highly effective and environmentally acceptable systems for chemical to electrical energy conversion. Among fuel cells it is known that solid oxide fuel cells can offer the widest potential range of applications and high system efficiency, also achievable by use of waste heat released at high temperature level in cogeneration applications and bottoming cycles [1].

On the other hand, ethanol has been proposed as raw material for many applications, such as the production of useful chemicals and/or electrical power. The basic difference of ethanol in comparison with other alternative fuels is the feasibility of its production from biomass with biochemical processes [2]. In this respect, ethanol can be considered as an economically attractive alternative green power source

promising low pollutant emissions and controlled combustion. Furthermore, by considering its high heating value and its high hydrogen atom content, ethanol has been the subject of several works aiming at both the production of hydrogen through steam reforming processes and the evaluation of the feasibility of its utilization in fuel cells [3–7].

In particular, Vasudeva et al. [3] accomplished the thermodynamic analysis of ethanol steam reforming for hydrogen production in the temperature range between 800 and 1200 K and for a wide range of steam/ethanol inlet mole ratios (0–80). Garcia and Laborde [4] have also examined the same process by estimation of the thermodynamic equilibrium composition at low temperatures (400–800 K) and for three steam/ethanol ratios equal to 0.1, 1 and 10. From a practical point of view, a steam/ethanol ratio equal to 0.1 is too low for SOFC operation, while a ratio equal to 10 corresponds to extremely impure ethanol, that cannot be useful for actual applications. Moreover, the conditions selected did not prohibit carbon formation and carbon was not included as component of the equilibrium mixture. However, both the above-mentioned works agree that at thermodynamic equilibrium only H₂, CO, CO₂, CH₄, H₂O and C can be present in practically significant concentrations.

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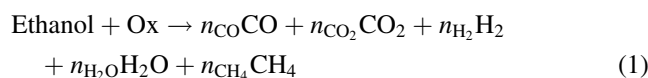
Although the results of these works are useful in understanding the thermodynamics of hydrogen production from ethanol reforming, a similar analysis for ethanol utilization in fuel cells should especially examine low steam/ethanol inlet ratios (1–5) and high temperatures in the range between 800 and 1200 K.

Concerning ethanol utilization in fuel cells, the comparative study of Maggio et al. [5] between ethanol, methanol and methane fueled molten carbonate fuel cells, revealed that ethanol exhibits better electrochemical characteristics, such as (a) higher power density for every inlet fuel flow rate, (b) higher electromotive force at each current density (at the same fuel flow rate and operation conditions) and (c) significantly higher electrical output. It is shown that ethanol can also be considered as a good candidate fuel for the production of electrical power by using solid oxide fuel cells (SOFCs).

In the present study, the thermodynamic analysis of ethanol utilization in a SOFC system was carried out considering the reactions of (a) ethanol steam reforming, (b) ethanol reforming with CO₂ and (c) ethanol partial oxidation as separate possible ways for preliminary fuel reforming. It was assumed that the preliminary fuel reforming occurred in an internal reformer, which consumed heat produced by a SOFC electrochemical section. In each case, the calculation of the thermodynamic equilibrium compositions and maximum obtainable electrical power was theoretically accomplished in the region where carbon formation is thermodynamically impossible. Moreover it must be stressed that the analysis in each case was done considering both absolute (dry) ethanol and ethanol containing an inevitable (for practical reasons) portion of steam.

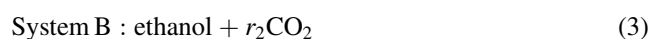
2. Theory

As it follows from previous works describing gas compositions derived from ethanol reaction with oxidants [3–5], the thermodynamic equilibrium gas mixture contains only five components of noticeable concentration: carbon monoxide, carbon dioxide, hydrogen, steam and methane. Therefore, the full transformation of the initial ethanol–oxidant system into the equilibrium mixture can be expressed as follows



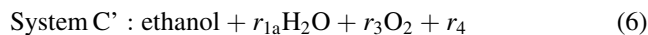
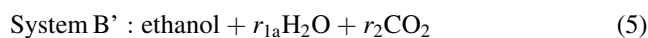
where Ox represents anyone of possible oxidants or their mixture.

The simplest and at the same time the most accessible oxidants for ethanol oxidation are steam, carbon dioxide and oxygen. Initially, three systems were considered



where r_i represents the corresponding oxidant to ethanol mole ratio.

It is clear that the two latter systems (3 and 4) are interesting only from a theoretical point of view, because it is senseless to use in practice both absolute ethanol as a fuel and pure oxygen as an oxidant. It seems plausible that the following systems, as well as the system A, can be of interest from a practical point of view



where r_{1a} is the water/ethanol mole ratio in azeotropic ethanol and r_4 represents all air components except oxygen. Taking into account that azeotropic ethanol contains 96 vol.% of ethanol and that the oxygen mole fraction in air is 0.209, one can obtain that $r_{1a} = 0.135$ and $r_4 = 3.785r_3$.

The calculation of the thermodynamic equilibrium composition derived from ethanol reaction with steam, CO₂ or O₂ was accomplished using the method of the direct minimization of the free energy, which has been discussed in detail in many literature sources [4,8].

The most probable reactions that can lead to carbon formation in the mixture obtained from the initial systems are as follows



This analysis was evidently necessary since the possibility of carbon formation must be excluded during the SOFC operation. It is well known that carbon deposition over the SOFC anode (commonly nickel) results in the growth of carbon filaments attached to anode crystallites that generate massive forces within the electrode structure leading to its rapid breakdown [9].

The thermodynamic possibility of carbon formation was examined by considering the reaction (7) through the value of carbon activity, α_c , which shows if the system is in equilibrium from the point of view of possibility of carbon formation. This value is expressed by the following equation

$$\alpha_c = \frac{K_1 p_{\text{CO}}^2}{p_{\text{CO}_2}} \quad (10)$$

where K_1 represents the equilibrium constant of reaction (7) and p_i the partial pressure of component i . When $\alpha_c > 1$, the system is not in equilibrium and carbon formation is occurring. If $\alpha_c = 1$ the system is in equilibrium but it is unknown how much carbon the system contains. Finally, when $\alpha_c < 1$, carbon formation in the system is thermodynamically impossible.

It is clear that it is sufficient to consider only one of the possible reactions that can lead to carbon formation in order to judge on the possibility of carbonization in the system. Carbon activity is the characteristic of the equilibrium system and it does not matter which equation is used for its calculation.

For the characterization of the initial (ethanol + oxidant) system with regard to possibility of carbon formation at equilibrium, the term “boundary of carbonization” is used. This boundary represents the minimum oxidant/ethanol mole ratio, in the initial system, at which carbon formation in the equilibrium mixture is thermodynamically impossible. For simplifying, this value can be indicated as “border mole ratio (BMR)”. The BMR values associated with each oxidant were calculated assuming that

$$1 - \alpha_c \rightarrow 0 \quad (11)$$

In the present work, all calculations concerning SOFC electromotive force and efficiency were done for systems A, B' and C'. Under this consideration, the distribution of molar fractions of the equilibrium mixtures along the anode was also calculated. It was assumed that an inlet gas into the SOFC anode channel is an equilibrium mixture at or above (for high amount of oxidants) boundary of carbonization. When this mixture is passing along the anode both hydrogen and carbon monoxide are gradually oxidized electrochemically by oxygen spontaneously supplied through the solid electrolyte and the oxidation products concentration is increasing. The inlet gases, especially those derived from the system A at the boundary of carbonization, contain also some amount of methane. The latter very likely does not take part in the reaction of electrochemical oxidation. Nevertheless methane is disappearing in the inlet part of the channel due to its reforming by arising oxidants. Within the rest part of the channel, methane concentration is negligible. Finally, at the end of the channel, the fuel components disappear at all and only oxidants (and “nitrogen” for the systems C and C') remain.

For the calculation of the emf distribution along the channel, it was supposed that oxygen anions flux through the electrolyte is uniform. As it was demonstrated [10] this assumption is true for multi-cell SOFCs. Emf was then calculated according to the Nernst equation

$$E = \frac{RT}{4F} \ln \frac{p_{O_2}(c)}{p_{O_2}(a)} \quad (12)$$

where R represents the universal gas constant, T the absolute temperature, F the Faraday's constant and “a” and “c” stand for anode and cathode, respectively. It was supposed that the SOFC cathode space is fed by air and therefore $p_{O_2}(c) = 0.209$. Oxygen partial pressure at the anode was calculated by the following equation

$$p_{O_2}(a) = \left(\frac{p_{H_2O}}{K_2 p_{H_2}} \right)^2 \quad (13)$$

where K_2 is the equilibrium constant of the reaction of hydrogen oxidation. From Eqs. (12) and (13) one can obtain the following equation for the emf calculation

$$E = \frac{RT}{2F} \left(\ln \frac{0.457 p_{H_2} K_2}{p_{H_2O}} \right) \quad (14)$$

It has been previously shown [10], a multi-cell SOFC presents higher efficiency comparing to a single-cell SOFC. For the multi-cell SOFC, it is possible to calculate the produced work using the following equation

$$W = q\bar{U} \quad (15)$$

where q is an electrical charge passing through the electrolyte and \bar{U} is the average voltage of the SOFCs. In the frame of thermodynamical analysis it is possible to assume that all processes in the SOFC occur under reversible conditions, in particular, at $I \rightarrow 0$. The latter means that $\bar{U} \rightarrow \bar{E}$ and therefore the equation for the maximum work produced by SOFC can be presented as

$$W = q\bar{E} \quad (16)$$

The average emf was calculated by means of numerical integration.

Fuel components can be, in principle, fully utilized in the SOFC [11]. Oxidation of the fuel components in the products of ethanol reforming requires 3 mole of oxygen per mole of ethanol. Therefore, for the cases A, B and B', $q = 12F$. The products of ethanol partial oxidation contain fewer amounts of fuel components and only $(3 - r_3)$ moles of oxygen per mole of ethanol are required for their electrochemical oxidation. Therefore, for the cases C and C', one can write

$$q = (12 - 4r_3)F \quad (17)$$

The SOFC system efficiency is defined as the ratio of electrical work produced by the SOFC to the chemical energy of fuel spent in the SOFC system. Therefore, the maximum SOFC system efficiency was calculated by using the following equation

$$\eta = \frac{q\bar{E}}{-\Delta H^0} \quad (18)$$

where $-\Delta H^0 = 1235$ kJ/mol and represents the lower heating value of ethanol at the standard conditions.

3. Results and discussions

The BMRs were calculated for each combination of oxidants and for both dry and azeotropic ethanol. The results of these calculations are shown in Fig. 1. Fig. 1a illustrates the temperature dependencies of the BMR values of the main oxidants for the cases of utilization of dry (dashed lines) and azeotropic ethanol (solid lines). The main oxidants in cases B' and C' are CO₂ and oxygen, respectively

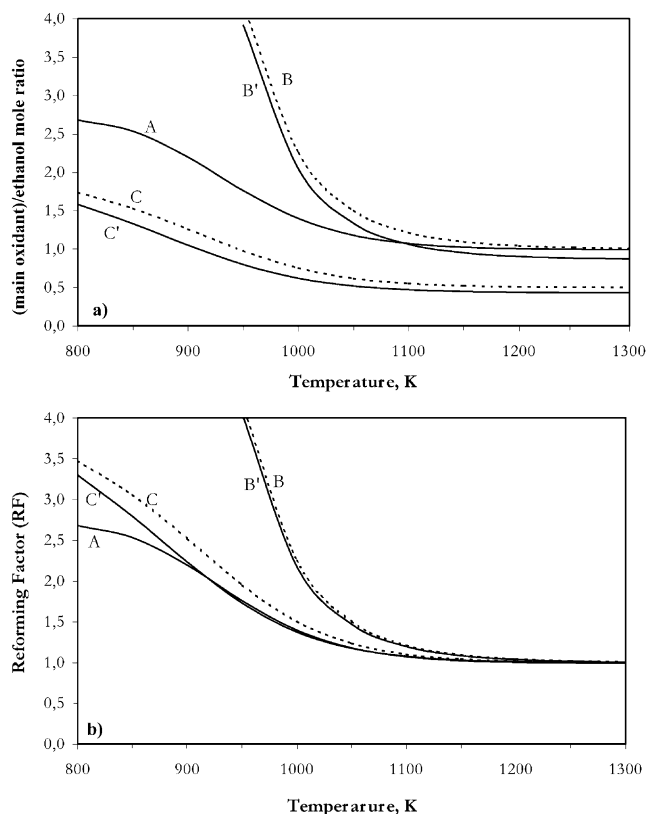


Fig. 1. Effect of temperature on the boundary of carbonization: (a) (main oxidant)/(ethanol mole ratio); (b) RF. Labels A, B, B', C, C' are explained in the text.

(Eqs. (5) and (6)). As one can observe, the region of the temperature and initial system conditions, where carbon formation is thermodynamically possible, increases from the case of partial oxidation to the case of CO_2 reforming. It is obvious that oxygen has the highest oxidative force and the BMR value for oxygen is less than the BMR values for steam and carbon dioxide in the corresponding systems. On the other hand, it is also obvious that carbon dioxide brings to the system additional carbon and the BMR value for carbon dioxide in the system B must be higher than the BMR value for steam in the system A. It is clear that for azeotropic ethanol that contains 4 vol.% water, the BMR values for the main oxidants are less than the corresponding BMR values for the systems with dry ethanol. That is why the dashed lines for systems “azeotropic ethanol + carbon dioxide” and “azeotropic ethanol + oxygen” lie significantly lower than solid lines of the corresponding systems with dry ethanol. It can be seen that the use of values “oxidant/ethanol BMR” is not convenient for the comparison of different oxidants regarding their ability for ethanol trans-formation.

It has been previously proposed [12], to use for this purpose a parameter called “reforming factor” (RF). This parameter is equal to the number of oxygen atoms of the oxidant in Eq. (1) that are able to oxidize ethanol. Thus, an oxygen molecule contains two such atoms and a steam

molecule contains one such atom. Although a carbon dioxide molecule contains two oxygen atoms, only one of them is capable for ethanol oxidation. By taking into account Eqs. (2)–(6), the expression for the RF is as follows

$$\text{RF} = r_1 + r_2 + 2r_3 \quad (19)$$

Below, the term “border reforming factor” (BRF) is used for the RF, which corresponds to the boundary of carbonization.

Fig. 1b illustrates that at temperature values higher than 1150 K the BRF values of all considered systems are practically the same. The BRF values for the systems B and B' are very close to each other in all temperature regions. On the whole, the BRF values of these systems are significantly higher than those for other systems at temperatures below 1100 K. If the oxidant does not contain carbon (systems A, C and C') the BRF values are almost identical at temperatures higher than 1050 K. It is very interesting to point out that the BRF values of the systems A and C' are indistinguishable at temperatures higher than 900 K.

The effect of temperature on the thermodynamic equilibrium composition at the boundary of carbonization for both dry and azeotropic ethanol is shown in Fig. 2. Practically, for all systems above 1100 K no significant differences were observed. This behavior can be explained by the insignificant change of the RF in the same temperature region (Fig. 1). As one can see in Fig. 2c, d and e, only traces (with no practical interest) of methane, water and carbon dioxide can be present in the above mentioned temperature region. The above compositions have been used (Eqs. (12)–(15)) for the calculation of the initial emf values.

Fig. 3a, b and c illustrate the emf distribution along the SOFC channel dimensionless length for the cases A, B' and C', respectively. In all cases it is assumed that the inlet mixture is at the boundary of carbonization. The examined range of BFR values was chosen taking into account practical aspects (Eq. (19)). For example, it is senseless to consider the system B' if its RF is >5 because, at higher reforming factors, too much oxidant is necessary, which is unacceptable from technical point of view. It is also clear that it is of no use to consider the system C' when its RF is >2.4 because in this case 40% of ethanol is lost in non-electrochemical combustion (gas phase combustion). Based on the above reasoning, the lower temperature for the systems B' and C' was chosen as 900 K. This choice seems quite logical also because the molar fractions of the fuel components at low temperature for these systems are very low (Fig. 2) $\sim 10\%$ for system B' $\sim 20\%$ for system C' compared to $\sim 40\%$ for system A.

On the whole, the range of emf values along the anode becomes wider as temperature increases. At low temperatures, emf varies strongly only very close to the channel outlet, whereas at high temperatures emf varies very strongly both at the inlet and at the outlet. Finally, within the wide middle part of the channel, emf varies only slightly at all temperatures examined.

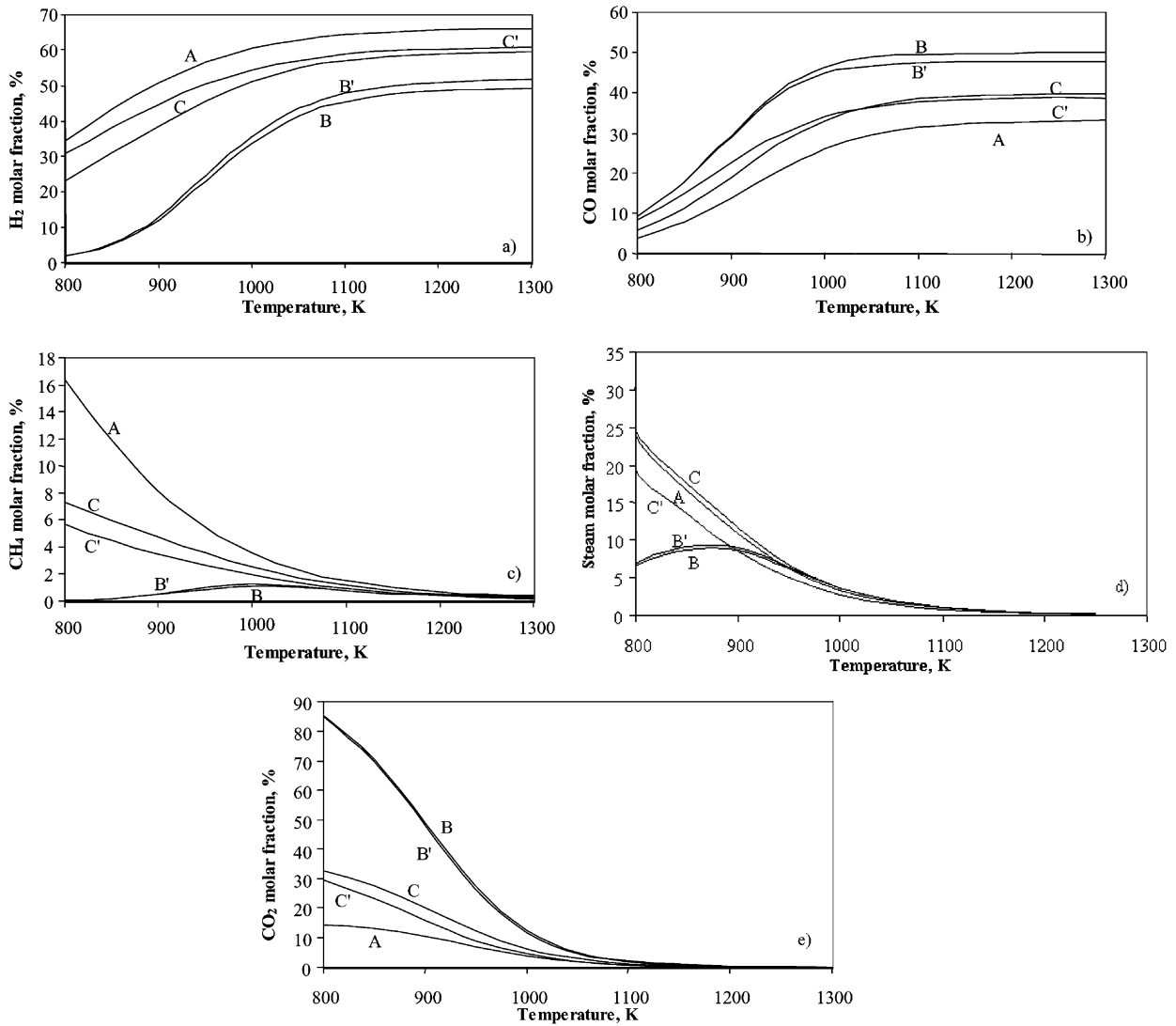


Fig. 2. Effect of temperature on the thermodynamic equilibrium composition at the boundary of carbonization: (a) H₂; (b) CO; (c) CH₄; (d) H₂O; (e) CO₂.

The temperature dependence of the maximum efficiency of the ethanol fueled SOFC system is illustrated in Fig. 4. For systems A and B' at the boundary of carbonization, the maximum SOFC system efficiency is very high in the entire temperature region and increases as the temperature decreases. On the whole, the SOFC system efficiency in the case of ethanol steam reforming is higher than in the case of ethanol CO₂ reforming and exceeds 93% at 800 K, whereas the efficiency in the latter case does not exceed 90%. As to the efficiency in the case of ethanol partial oxidation C' (ethanol-air feed), it is significantly less than in the previous cases. The temperature dependence of the efficiency in this case presents a maximum at about 1080 K and decreases strongly with the temperature decrease. The low SOFC system efficiency in this case is connected with a waste of significant amount of fuel due to non-electrochemical combustion of ethanol which becomes more important with decreasing temperature.

It is clear that in practice it is necessary to use gas compositions above the boundary of carbonization, i.e. systems with a RF higher than BR_F. Fig. 5 represents the dependence of maximum thermodynamic efficiency on the RF for the SOFC system fueled by azeotropic ethanol (Fig. 5a for systems A (solid lines) and B' (dashed lines), and Fig. 5b for system C'). As it was mentioned above, it was assumed that the RF is <5 for systems A and B' and <2.4 for system C'.

As one can observe in Fig. 5, the SOFC system efficiency increases with decreasing temperature and RF. For the systems A and B', the SOFC system efficiency is very high in all temperature and RF regions (Fig. 5a). Influence of the temperature decreasing on the maximum efficiency is more essential than influence of the RF decreasing. On the whole maximum reachable efficiency lies in the region of low temperature and relatively high RF. It can be seen, that within temperature interval 950–1100 K and at RF > BR_F,

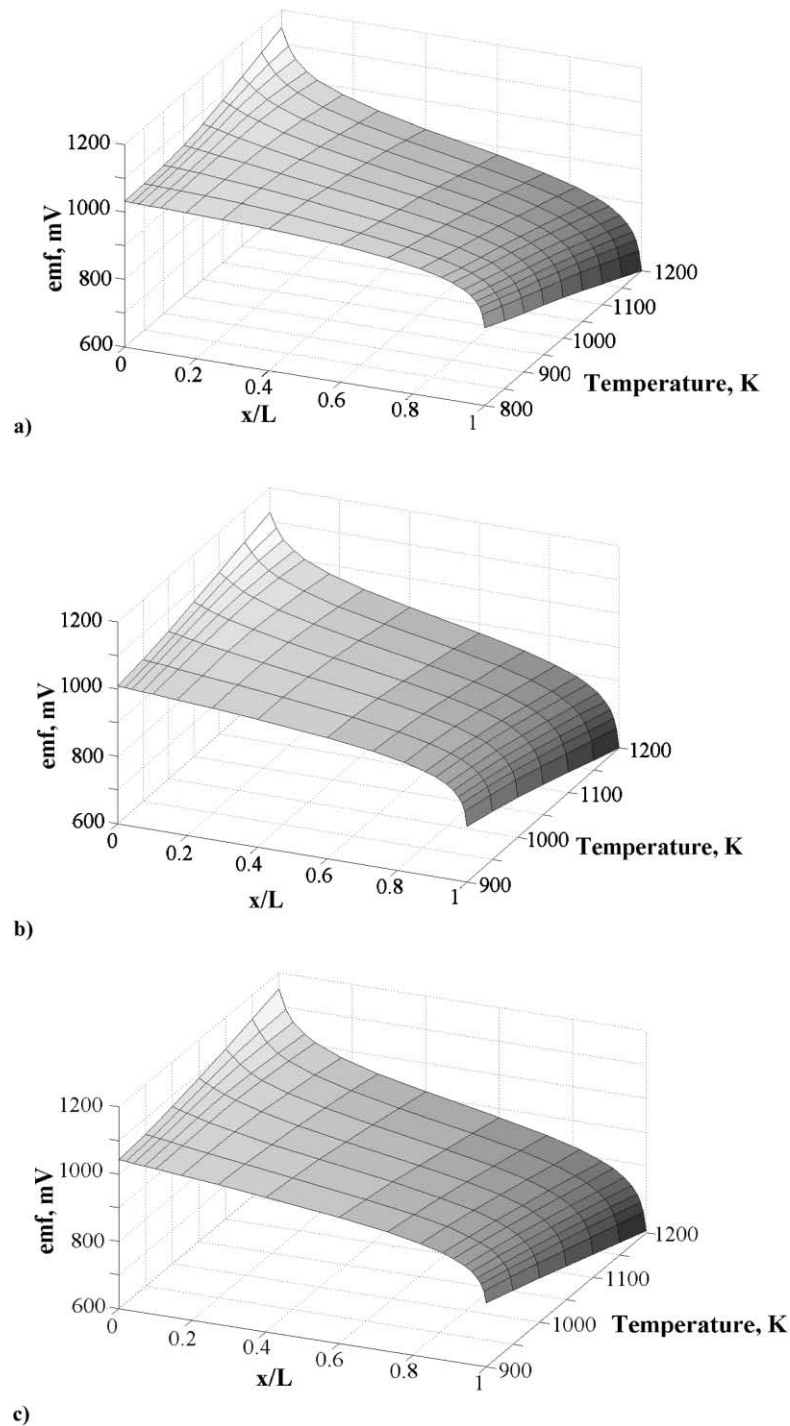


Fig. 3. Effect of temperature on the emf distribution along the SOFC length for: (a) system A; (b) system B'; (c) system C'. The inlet mixture corresponds to the boundary of carbonization.

the efficiency in the case of ethanol CO_2 reforming is higher than in the case of ethanol steam reforming, while under other conditions the SOFC system efficiency is higher in the latter case.

As it is shown in Fig. 5b, the highest SOFC system efficiency in the case of system C' corresponds to the RF of 1.1. Decrease in efficiency with decrease of the RF down

to 1.1 is connected with increase of temperature and consequent decrease in the emf for the mixtures corresponding to the thermodynamically possible RFs.

It should be finally stressed out that the results of SOFC system efficiency with the systems A and B are based on the assumption of heat transfer from the electrochemical section to the reforming section to account for the endothermicity of

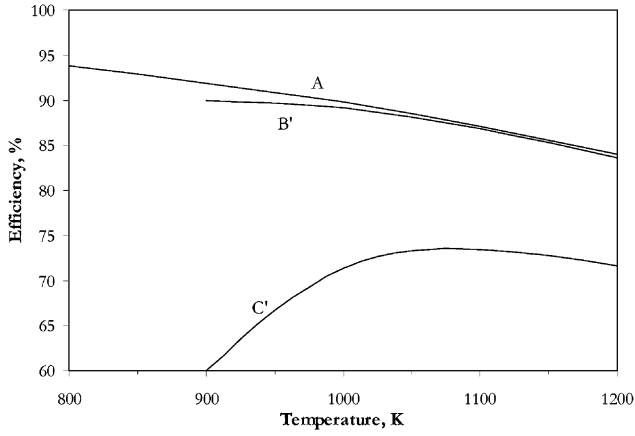


Fig. 4. Temperature dependence of the maximum thermodynamic efficiency of the ethanol fueled SOFC for systems A, B' and C'.

the reforming step. Such an assumption is not necessary for system C, which is generally exothermic because of the use of oxygen as an oxidant.

4. Summary

The thermodynamic analysis showed that theoretical maximum of the ethanol fueled SOFC system efficiency is very high in the temperature interval between 800 and 1200 K. From a thermodynamical point of view, the most attractive method of ethanol preliminary transformation is steam reforming. It was found that the theoretical efficiency obtainable in the SOFC system using ethanol steam reforming varies between 83.9 and 93.8% at the examined conditions. As a matter of fact, ethanol steam reforming allows the additional advantage of utilization of under-azeotropic ethanol obtained directly from biomass fermentation. Theoretical maximum of SOFC system efficiency with reforming of

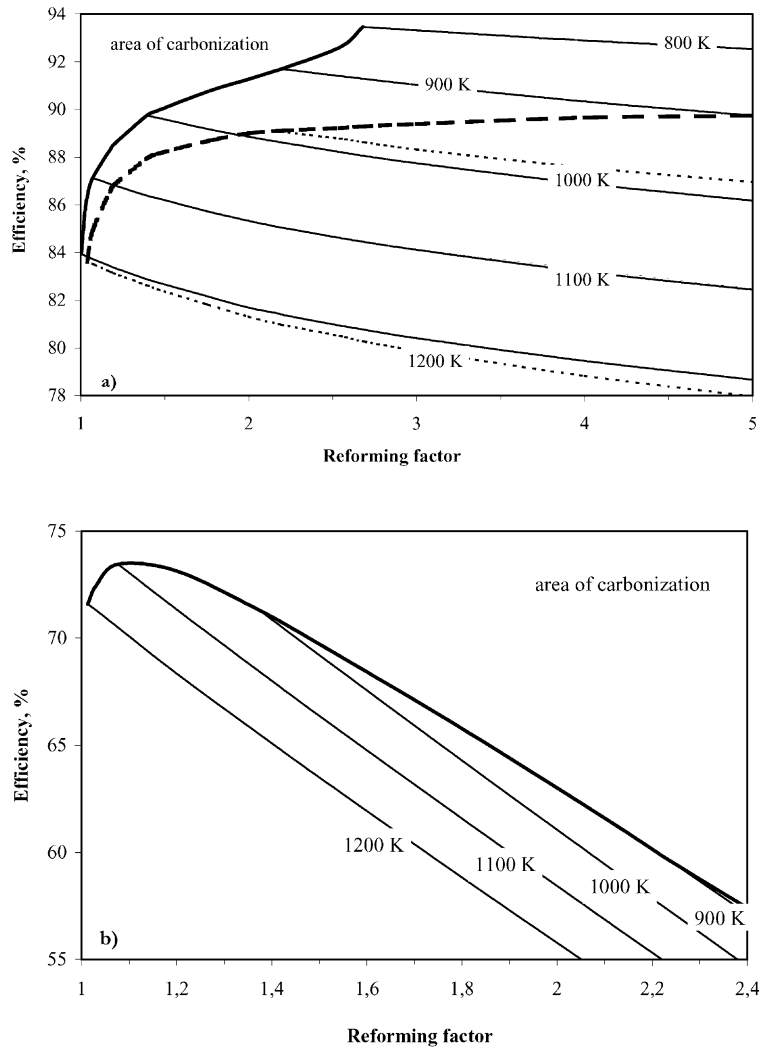


Fig. 5. Dependence of the maximum thermodynamic efficiency of the ethanol fueled SOFC on the RF for systems: (a) A (solid lines) and B' (dashed lines); (b) C'. The thick dashed line in Fig. 5a represents the boundary of carbonization for system B'.

ethanol with CO₂ was calculated in the temperature range between 900 and 1200 K and was found to vary between 83.6 and 89.9%. When RFs higher than BRF are assumed, reforming of ethanol with CO₂ results in higher efficiency in the temperature region of 950–1100 K. Partial oxidation of ethanol was found to lead to relatively low SOFC system efficiency values with a maximum of 73.5% at about 1060 K.

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