

Hydrogen production aided solid oxide electrochemical reformer fed with octane: A theoretical analysis

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Abstract

In the present work the possibility of pure hydrogen production by a solid oxide electrochemical reformer (SOER) is examined. Initial reagents are water steam, flowing into the cathode channel and octane flowing into the anode channel. Three modes of reforming are considered: (i) steam reforming (SR-mode), (ii) preliminary octane partial oxidation (PO-mode) and (iii) preliminary octane reforming by exhaust anode gas recycling (EAGR-mode). A parametric analysis is carried out that can be easily applied for various hydrocarbons. It was found that the electromotive force (EMF) value depends mainly on the ratio of steam moles' number supplied to the cathode space to the number of hydrogen output moles (k -parameter). It was also found that EMF increases with k increase, while is weakly affected from the temperature and the heat losses amount. Moreover, the EMF average value under the PO-mode is lower than that under the SR-mode. Finally, it is shown that the SOER optimum characteristics can be reached under the EAGR-mode, since it provides the most favorable combination of the reforming efficiency and the rate of the electrochemical process.

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1. Introduction

Hydrogen can serve both as an energy source and energy carrier. It can be used in almost every sector where energy is required—transport, households and industry. Unlike electricity, it can be stored for long periods without significant losses. Moreover, at the place of end-use, the only product of hydrogen utilization is water vapor. Finally, hydrogen can be produced from a wide variety of resources, including renewable ones, nuclear energy and fossil fuels. There are about 90 hydrogen production routes that can be divided into four categories: biological, chemical, electrochemical (water electrolysis; photoelectrochemical; halide electrolysis, H₂S electrolysis) and thermal technologies [1]. In the medium term however, fossil

fuels are expected to be more relevant for hydrogen production [2].

Large scale steam reforming of natural gas is the principal industrial process for the production of hydrogen; more than half of world hydrogen is produced by this method [3]. The basis of the process is the endothermic reaction of methane with steam at high temperature in the presence of catalysts, producing a mixture of CO, CO₂, H₂, H₂O and un-reacted CH₄, called raw syngas. In a subsequent exothermic water shift reaction, CO reacts with steam producing additional hydrogen and CO₂. Following a separation step, in which the CO₂ is removed by an alkaline-based solution via chemical absorption, a hydrogen-rich gas is produced which is further purified via pressure swing adsorption. In terms of energy content of the reforming of the fuel to hydrogen, efficiencies range between 70% and 80%.

However, hydrogen used to feed low-temperature fuel cells must be characterized by extremely high purity; more precisely, the impurities of carbon monoxide (CO) and carbon dioxide

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Nomenclature

a	the amount of oxygen passed through the membrane
E	electromotive force (EMF)
F	Faraday constant
h	membrane thickness
i	current density
j	mass flux
k	the ratio of number of the steam moles supplied to the cathode space to the number of hydrogen output moles
L	heat of water evaporation
m	H ₂ O/C ₈ H ₁₈ ratio (in the case of steam pre-reforming)
n	theoretical output
p	partial pressure
Q	heat
R	gas constant
T	temperature
w	index of heat losses in the SOER
z	the re-cycling factor

Greek letters

η	efficiency
σ	conductivity

Subscripts

e	electronic
hydr/H ₂	hydrogen
H ₂ O	steam
i	ionic
O ₂	oxygen

(CO₂) should not exceed 10 ppm for polymer electrolyte membrane fuel cells (PEMFCs) and alkaline fuel cells (AFCs), respectively. On the other hand, hydrogen, produced by the above-mentioned methods contains significant amounts of CO and CO₂. Effective means of purifying hydrogen are either its filtration through palladium membranes or its production through water electrolysis. In view of economical requirements, low temperature water electrolysis has not had a significant commercial impact because it has not been cost-effective, due to the high electricity consumption, although it is technologically very simple and delivers very clean gases. The minimum specific power inputs for the low temperature water electrolysis is 4.1 kWh N⁻¹ m⁻³ of H₂, which corresponds to an efficiency of electrical energy to chemical energy transformation of 87%. Considering the fact that the production of electricity from fossil fuels has an average efficiency of ~40% with respect to primary energy, the overall efficiency of the electrolyzer is generally below 35%. Recently, some attempts have been made to reduce energy consumption in the electrolytic hydrogen production by using ionic activators [4], geothermal heat [5] and polymer electrolyte membranes [6].

The high temperature electrolysis (HTE) of water with the use of solid electrolytes is characterized by low specific electrical power inputs (≤ 2.4 kWh N⁻¹ m⁻³ of H₂) [7]. The theoretical energy required for hydrogen production is 3.54 kWh N⁻¹ m⁻³ of H₂ and the deficient amount of energy can be supplied to the HTE in the form of heat; for example, from the high-temperature gas-cooled reactor (HTGR). The power inputs can be decreased by using a gas fuel assisted electrolysis (see, for instance [8]) which leads to a significant decrease of the cell voltage and hence of the power inputs. Under this mode of the HTE operation, its anode compartment is supplied by a gas fuel, thus decreasing the applied voltage. In fact, the HTE uses both the electrical energy and the fuel chemical energy for hydrogen production. It is possible to exclude completely the utilization of the electrical energy in the electrochemical device for hydrogen production. The theoretical base of this process called “electrochemical reforming” was developed by Korovin et al. [9].

The base of a solid oxide electrochemical reformer (SOER) is a solid oxide membrane that provides both high oxygen anion and electronic conductivity at temperatures 1100–1200 K, as well as chemical and structural stability under operating in various oxygen partial pressures and temperatures. In the SOER, fuel containing gas is fed to the anode compartment, while the cathode compartment is fed by steam. Oxygen permeates through the non-porous mixed ionic-electronic conductor (MIEC) membrane from the cathode compartment into the anode one due to the oxygen activity difference across the membrane, whereas the MIEC is impervious to other gas constituents. As a result, the fuel components of the anode gas are oxidized and hydrogen is produced from steam in the cathode compartment. Transfer phenomena in an electrochemical reactor based on a MIEC for hydrogen production have been considered by Demin and Dunyushkina [10].

Iron-doped perovskites of the type CaTi_{1-x}Fe_xO_y, seem to be good candidates for membranes so far, as it has been reported that they are characterized by sufficient long-term stability in reducing atmospheres, as well as by acceptable levels of ionic and electronic conductivity [11]. The electrical conductivity dependence of CaTi_{1-x}Fe_xO_y on the oxygen partial pressure (p_{O_2}) confirms hole and electron conductivity at high and low p_{O_2} , respectively, and a predominant ionic conductivity, independent of p_{O_2} , in a wide region of intermediate oxygen partial pressures. The electronic conductivity is proportional to $p_{O_2}^{1/n}$ for the hole and to $p_{O_2}^{-1/n}$ for the electron carriers, respectively. In reducing atmospheres, the electronic (of n-type) and ionic conductivities are comparable. In this case, both the membrane resistivity and the oxygen permeability are complex functions of p_{O_2} on both sides of the membrane [11].

In the present work the determination of the optimal operating parameters of a SOER fed with octane for pure hydrogen production is carried out. Three cases of reforming are considered: (i) steam reforming (SR-mode), (ii) preliminary octane partial oxidation (PO-mode) and (iii) preliminary octane reforming by exhaust anode gas recycling (EAGR-mode).

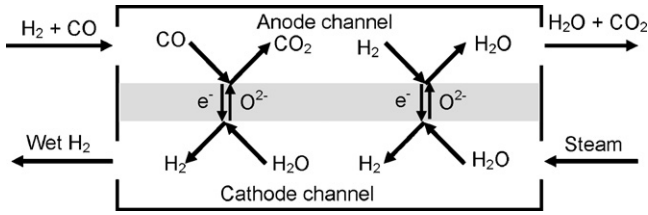


Fig. 1. Schematic illustration of the processes occurring in the SOER.

2. Theory

2.1. SOER operation

The main processes occurring in a SOER are schematically illustrated in Fig. 1. The SOER consists of a membrane having oxygen ion and electron charge carriers which are in contact with two gas channels: the anode and the cathode ones. Initial reagents in the SOER are steam supplied into the cathode channel, and a gas mixture containing H_2 and CO supplied into the anode channel.

At the cathode side of the membrane, the reduction of H_2O occurs according to the following reaction:



The oxygen anions pass through the membrane and reacts with reduced components at the anode side. The reaction of the oxygen ion with a hydrogen molecule at the anode side of the membrane is opposite to reaction (1):



while the reaction of the oxygen anion with CO is as follows:



On the whole, the anode gas mixture contains four components (reformats): H_2 , CO , H_2O and CO_2 . As the gas mixture flows along the anode channel from the inlet to the outlet side (Eqs. (2) and (3)), the concentration of the reducing components (Red-components), i.e. H_2 and CO decreases; accordingly, the concentration of the oxidized components (Ox-components), i.e. H_2O and CO_2 increases. At the same time, as the water vapor flows from the inlet to the outlet side of the cathode channel its amount decreases, while hydrogen concentration increases (Eq. (1)).

The rate of the electrochemical process depends on the membrane parameters (thickness and ionic and electronic conductivities). The ionic current density in the membrane obeys to the following equation:

$$i = \frac{\sigma_i \sigma_e E}{(\sigma_i + \sigma_e)h} \quad (4)$$

where σ_i and σ_e stands for ionic and electronic conductivity, respectively, E is the electromotive force, EMF, and h the membrane thickness. The electromotive force is calculated as follows:

$$E = \frac{RT}{4F} \ln \frac{p_{O_2}(c)}{p_{O_2}(a)} \quad (5)$$

where R is the gas constant, T is the temperature (K), F is the Faraday constant and p_{O_2} is the oxygen partial pressure; "a" and "c" in the brackets denote the anode and cathode side of the membrane, respectively. Eq. (5) can be rewritten in the following form:

$$E = \frac{RT}{2F} \ln \frac{p_{H_2}(a) p_{H_2O}(c)}{p_{H_2O}(a) p_{H_2}(c)} \quad (6)$$

where p_{H_2} and p_{H_2O} are the partial pressures of hydrogen and steam, respectively. It is obvious that the EMF value will increase with the increase of the p_{H_2}/p_{H_2O} ratio at the anode side of the membrane and the decrease of such a ratio at the cathode side.

The flux of hydrogen which springs up at the anode side of the membrane is as follows:

$$j = \frac{i}{2F} \quad (7)$$

The schemes of the processes in the SOER system are shown in Fig. 2. In the general case, the SOER system consists of an electrochemical section (the proper SOER), a pre-reformer, an afterburner, a heat exchanger, an evaporator, and includes at least one condenser for steam separation from the produced hydrogen; the second condenser can be used for the reduction of water flow fed to the evaporator.

The anode channel of the SOER is fed with synthesis-gas produced via hydrocarbons reforming. In this work, the octane is considered as one of the possible primary fuel for hydrogen production. The results can be easily generalized to other hydrocarbons.

Three variants of the octane preliminary reforming (pre-reforming) are considered: steam reforming (Fig. 2(a)), partial oxidation (Fig. 2(b)) and reforming by exhaust anode gas recycling (EAGR) (Fig. 2(c)). When the oxygen activity at the anode side of the membrane is less than at the cathode side, the electrochemical reforming process in the SOER takes place spontaneously (without an external electrical power supply). In the SOER, the supply is provided by the reagents (steam and synthesis-gas) in a counter-flow mode. In general, all the processes that take place in the SOER (as well as the maintenance of thermal regime) consume the initial energy of the fuel.

The theoretical output of hydrogen (number of moles of the produced hydrogen per one mole of the initial fuel) can be calculated by using the heat balance equation. In the SOER the octane's chemical energy is transformed partially in hydrogen chemical energy and partially in heat. It is supposed that the produced heat is mainly supplied to the evaporator and only a small part is wasted (losses). In the frame of this consideration, it is accepted that the above-mentioned part, w , is equal to 0.1 or 0.2. Accordingly, the simplest form of the heat balance equation is as follows:

$$Q_{oct} = n_{hydr} Q_{hydr} + \frac{(m + kn_{hydr})L}{1 - w} \quad (8)$$

where Q_{oct} and Q_{hydr} represent the heats of octane and hydrogen combustion, respectively, L the heat of water evaporation, m the H_2O/C_8H_{18} ratio (in the case of steam pre-reforming), k the ratio of number of the steam moles supplied to the cathode space to

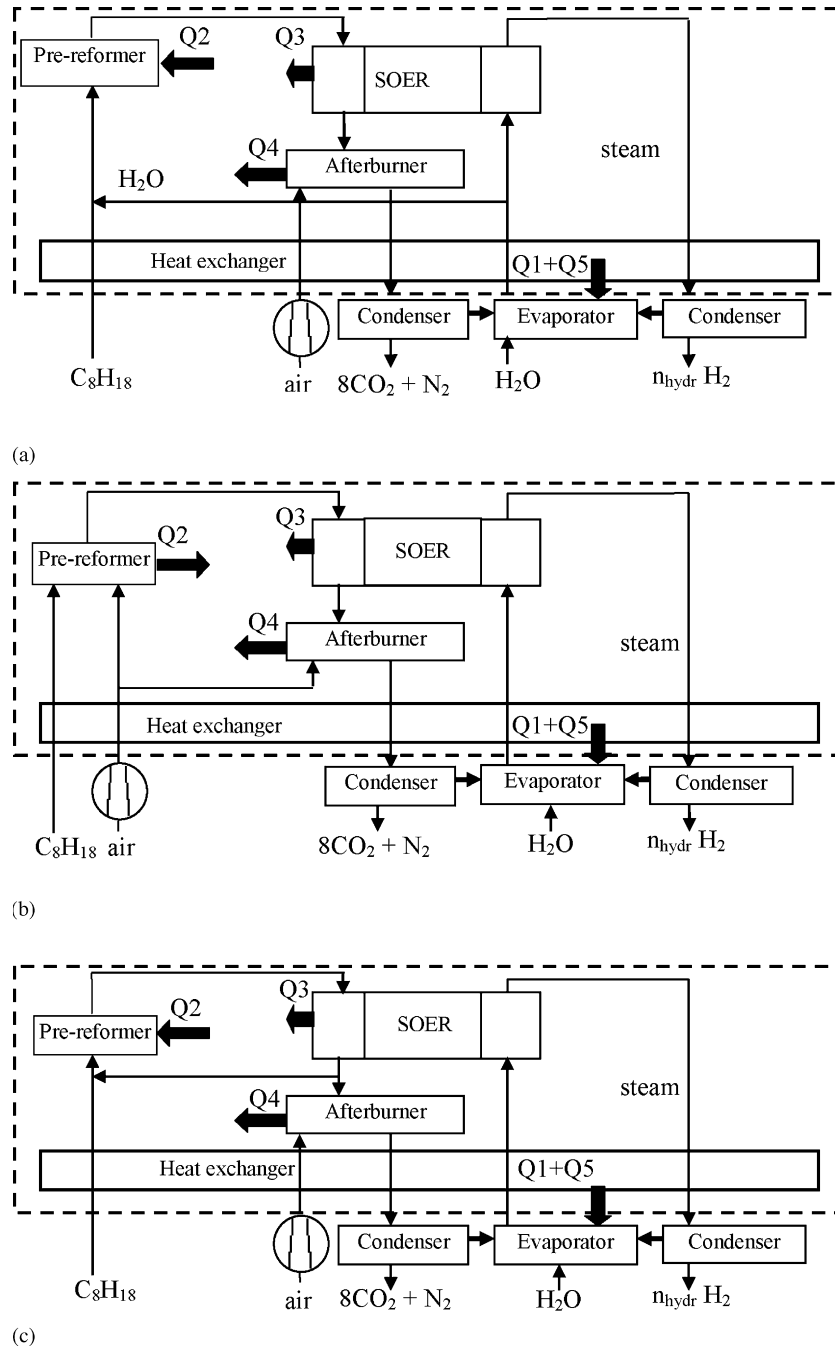


Fig. 2. SOER system for hydrogen production with: (a) preliminary steam octane reforming (SR-mode), (b) preliminary octane partial oxidation (PO-mode) and (c) preliminary octane reforming by exhaust anode mixture (EAGR-mode). The values of thermal flows are calculated for $T = 1200\text{K}$, $w = 0.1$, $k = 1.7$.

the number of hydrogen output moles and w an index of heat losses in the SOER.

The efficiency of the electrochemical reforming is defined as the ratio of the chemical energy of the produced hydrogen to the chemical energy of the consumed octane and can be presented as follows:

$$\eta = \frac{n_{\text{hydr}} Q_{\text{hydr}}}{Q_{\text{oct}}} \quad (9)$$

Consequently, the reforming efficiency is proportional to the hydrogen output.

3. Results and discussion

3.1. The case of steam reforming (SR-mode)

In the case of the steam pre-reforming of octane, the pre-reformer is fed with an octane/steam mixture (Fig. 2(a)). Since chemical octane reforming is an endothermic process it is necessary to use additional heat for the maintenance of the pre-reformer thermal conditions. In the present case it is possible to use the heat produced by burning residual fuel components in the outlet of the anode gas mixture.

Table 1
Heat fluxes into the SOER system

The kind of pre-conversion	$Q1 + Q5$ (kJ)	$Q2$ (kJ)	$Q3$ (kJ)	$Q4$ (kJ)
SR-mode	-1682	-1431	253	2860
PO-mode	-1329	791	309	229
EAGR-mode	-1354	-1522	400	2476

The amount of heat necessary for evaporation of water which is supplied to the cathode compartment and to the reformer ($Q1$ and $Q5$, respectively (Table 1)) was calculated taking into account the heat of water evaporation ($L = -44 \text{ kJ mol}^{-1}$).

The reforming thermal effect ($Q3$) was calculated as the difference between the combustion heat values of octane and the reformates (reforming products). The electrochemical reforming thermal effect ($Q2$) was calculated from the difference between the combustion heat of the fuel components contained in the anode and cathode inlet streams and the combustion heat of the fuel components contained in the respective outlet streams.

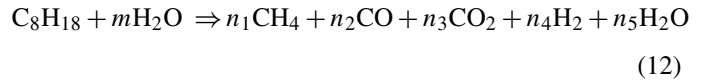
Finally, the produced heat from the afterburning of the exhaust anode gas ($Q4$) was calculated as the sum of the combustion heat of hydrogen and carbon monoxide in the gas mixture fed to the afterburner. It was supposed earlier that heat losses correlate with heat supplied to the evaporator. Therefore, the above-mentioned amounts of heat must obey the following equation:

$$\frac{(Q1 + Q5)}{(1 - w)} + Q2 + Q3 + Q4 = 0 \quad (10)$$

The stoichiometric reaction of octane steam reforming is as follows:



However this amount of steam is insufficient for the formation of the equilibrium reformates mixture due to unavoidable coking. In order to avoid carbon formation, it is necessary to increase the ratio $m = \text{H}_2\text{O}/\text{C}_8\text{H}_{18}$. In the real conditions, at appropriate m value, the octane–steam mixture transforms to five-component equilibrium gas mixture:



The coefficients n_i depend on both the m value and temperature. For unification, in the frame of this consideration, it is accepted that the part of the reducing components, i.e. H_2 and CO (Red-components) in equilibrium is 0.95, which corresponds to the impossibility of the carbon formation from the thermodynamic point of view.

Before the pre-reformer, octane is mixed with steam in a ratio $m = \text{H}_2\text{O}/\text{C}_8\text{H}_{18}$. In the pre-reformer, the equilibrium mixture of the reformat is considered to be formed according to Eq. (12). This mixture is supplied to the anode inlet channel.

Due to transport of oxygen through the membrane, the gas mixtures in the cathode and anode channels change while they are flowing. The partial pressure of the reducing components along the anode flow decreases – from the inlet to the outlet – due to their oxidation by oxygen ions according to reactions (2) and (3). Simultaneously, the hydrogen partial pressure along the cathode flow increases from the inlet to the outlet, due to steam decomposition according to reaction (1). Spontaneous transport of oxygen ions from the cathode side of the membrane to the anode side occurs in the case where the oxygen partial pressure at the cathode side of the membrane is higher than at the anode side. In order to provide such conditions it is necessary to supply the reactants to the SOER in a counter-flow mode. Below, it is

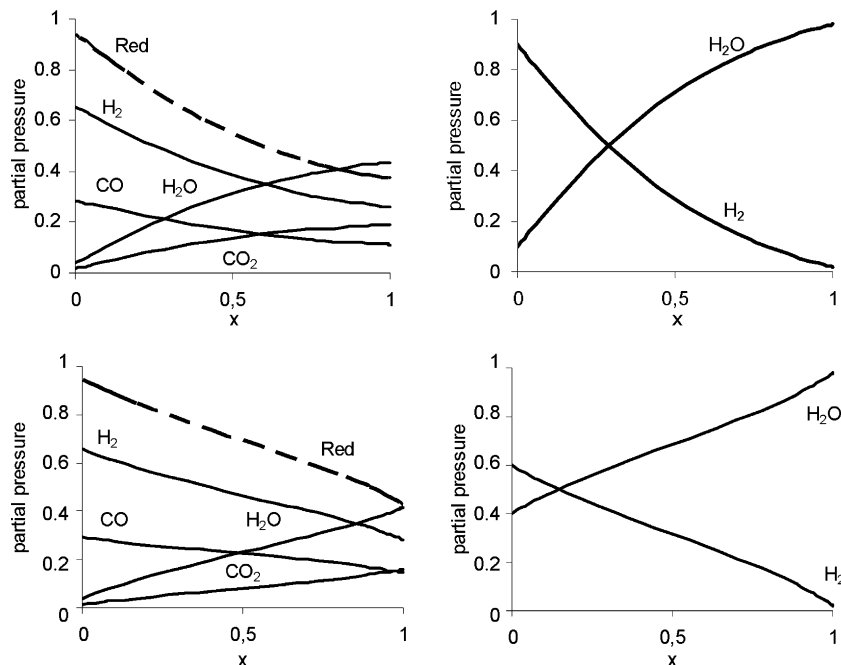


Fig. 3. Distribution of partial pressures of the gas mixture components along the SOER in the anode (left) and cathode (right) channels at 1200 K. $k = 1.1$ (top) and $k = 1.7$ (bottom). The SR-mode.

assumed that the positive direction of the x -axis in the SOER is the direction of the anode flow.

In Fig. 3 the change of the gas mixture composition along the SOER electrochemical section is depicted for $k = 1.1$ and $k = 1.7$, $w = 0.1$ and $T = 1200$ K. One can see that the partial pressures of hydrogen and carbon monoxide decrease monotonously along the anode channel. For the case of lower k value, in each membrane cross-section, the hydrogen partial pressure in the cathode channel is higher than that in the anode one. However in each membrane cross-section, the hydrogen partial pressure in the cathode channel is lower than the total partial pressure of the Red-components in the anode channel, thus providing the appropriate conditions for oxygen anions' transport from the membrane cathode side to its anode side. In the case of higher k value, the hydrogen partial pressure in the anode channel is higher than that in the cathode channel in each membrane cross-section. It was found that the effect of w and T parameters on the gas components distribution is very small: the corresponding lines practically interflow in the diagrams.

The EMF distribution corresponding to the gas mixtures distributions in the anode and cathode channels are illustrated in Fig. 4. The EMF value depends mainly on the k -parameter. As someone can observe, at higher k values, higher EMF values are obtained. The EMF is practically independent of the temperature for the examined conditions; the EMF values at 1200 K are slightly higher in comparison with the ones at 1100 K. Consequently, the EMF dependence on the level of heat losses is insignificant.

The most important parameter for practical applications is the EMF average value within the SOER, which can be calculated from the EMF distribution by its numerical integration. In Fig. 5 the dependence of the EMF average value on the k -parameter is illustrated for various w and T values. It can easily be distinguished that the EMF average value increases almost by the same amount when temperature increases by 100 K or w -parameter grows by 0.1.

The theoretical output of hydrogen derived from Eq. (8), for the case of the preliminary steam reforming is as follows:

$$n_{\text{hydr}} = \frac{(1-w)Q_{\text{Oct}} - mL}{(1-w)Q_{\text{H}_2} + kL} \quad (13)$$

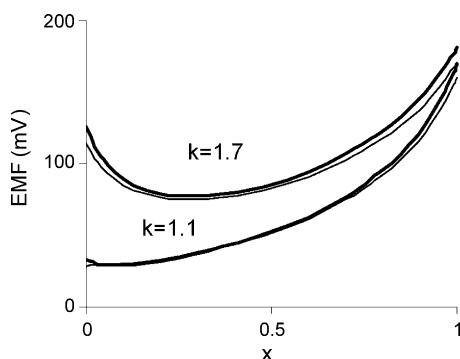


Fig. 4. EMF distribution along the SOER. $T = 1100$ K (thin lines), $T = 1200$ K (bold lines). The SR-mode.

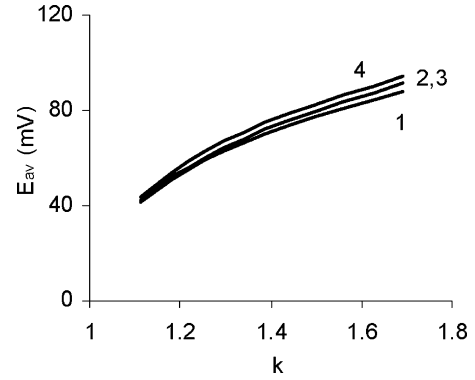


Fig. 5. Dependence of the average EMF value on the k -parameter. $T = 1100$ K (1, 2) and 1200 K (3, 4). $w = 0.1$ (1, 3) and 0.2 (2, 4). The SR-mode.

It is obvious that the hydrogen output decreases with: (a) the heat losses increase, (b) the increase of the amount of steam utilized for the steam pre-reforming and (c) the increase of k -parameter. As it was earlier reported the Red-components (CO , H_2) partial pressure was assumed to be 0.95. This corresponds to $m = 9.32$. It is necessary to point out that the increase of m value leads not only to the hydrogen output decrease, but also to the EMF decrease due to the decrease of $\text{H}_2/\text{H}_2\text{O}$ ratio in the anode mixture and the concomitant reduction of the electrochemical reforming process rate. Therefore it is undesirable to use higher amounts of reforming agents (steam or air).

When the k -parameter change from 1.1 to 1.7 and $w = 0.1$, the hydrogen output reduces from 15.2 to 13.8 (Fig. 6). This corresponds to an efficiency of the chemical energy transformation (reforming efficiency) of 71.8% and 65.2%, respectively. The increase of the heat losses leads to the decrease of both the hydrogen output and the reforming efficiency. Therefore the elimination of the heat losses is a very important task.

3.2. The case of preliminary octane partial oxidation (PO-mode)

In this case the pre-reformer is fed with a mixture of octane and air (Fig. 2(b)). The equation of heat transport calculation in this case is the same as in the case of the octane steam reforming. The equation of the octane partial oxidation reaction can

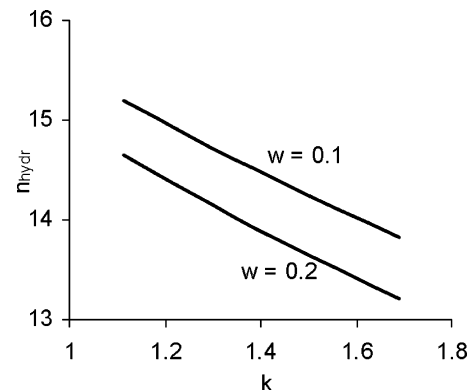


Fig. 6. Dependence of the hydrogen output on k -parameter for various values of w . The SR-mode.

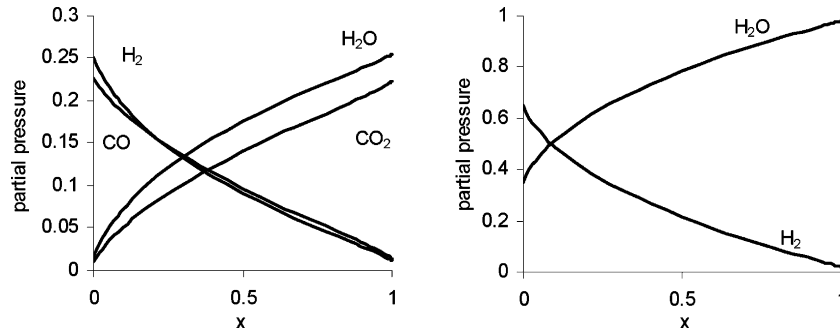


Fig. 7. Distribution of partial pressures of the gas mixture components along the SOER in the anode (left) and cathode (right) channels. $T = 1200$ K, $w = 0.1$, $k = 1.7$. The SR-mode.

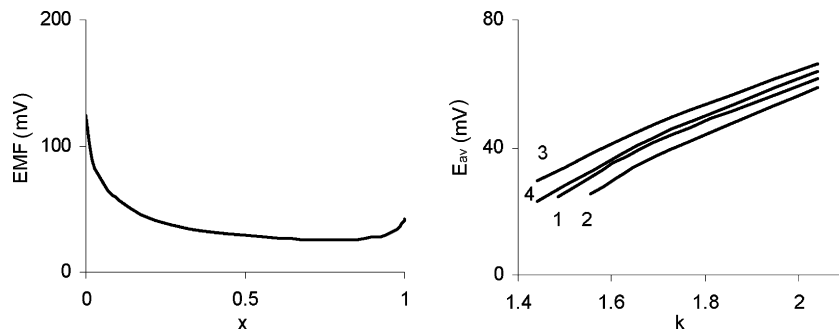
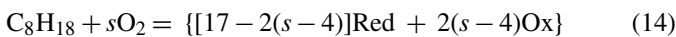


Fig. 8. EMF distribution along the SOER. $T = 1200$ K, $w = 0.1$, $k = 1.7$ (left) and the average EMF dependence on k -parameter; $T = 1100$ K (1, 2) and 1200 K (3, 4). $w = 0.1$ (1, 3) and 0.2 (2, 4) (right). The SR-mode.

be presented in the following conditional form (unchangeable components are not shown):



This form means that the expression in braces corresponds to the equilibrium gas mixture formed as the result of a reaction between reagents written in the left part of the equation. Similarly, as assumed before for the case of steam reforming, it is assumed that the ratio Red/Ox = 95/5 in the reformat (products) mixture.

The distribution of the components partial pressures along the SOER at $T = 1200$ K and $k = 1.7$ is plotted in Fig. 7. One can see that the partial pressures of the Red-components in the anode channel are significantly lower than that in the cathode channel due to dilution of the synthesis-gas by nitrogen. However, the ratio Red/Ox in the anode channel is higher than that in the cathode channel, providing higher oxygen partial pressure for the latter and consequently provoking the oxygen anions transfer from the cathode to the anode.

The EMF average value under the PO-mode is affected mainly by the k -parameter; the influence of temperature value and heat losses is not considerable (Fig. 8). It is worth mentioning that on the whole the EMF average value under the PO-mode is visibly lower than that under the SR-mode. Moreover, the lower level of the k -parameter is in the range from 1.2 for $T = 1200$ K and $w = 0.1$, to 1.3 for $T = 1100$ K and $w = 0.2$, because for lower k -parameter values the EMF becomes negative.

The theoretical output of hydrogen calculated from the heat balance Equation (8) as applied to the PO-mode and taking into account that steam is not supplied to the pre-reformer ($m = 0$) is

as follows:

$$n_{\text{hydr}} = \frac{Q_{\text{okt}}(1 - w)}{Q_{\text{H}_2}(1 - w) + kL} \quad (15)$$

Under the k -parameter change from 1.5 to 2.04 and $w = 0.1$, the hydrogen output reduces from 15.9 to 14.7 (Fig. 9), which corresponds to an efficiency of the chemical energy transformation of 75.1% and 69.5%, respectively.

3.3. The case of preliminary octane reforming by exhaust anode gas (EAGR-mode)

The anode exhaust gas contains high amounts of the Ox-components (CO_2 , H_2O) that can be utilized as reforming agents. So it is possible to apply recycling of the anode gas (Fig. 2(c)).

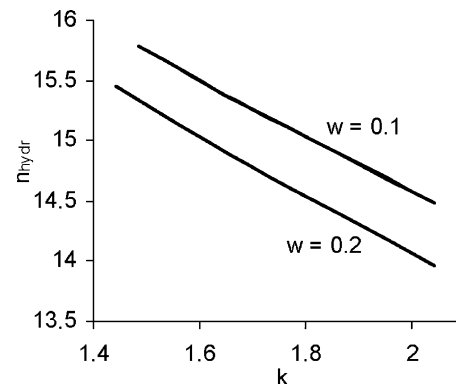


Fig. 9. Dependence of the hydrogen output on k -parameter for various values of w . The PO-mode.

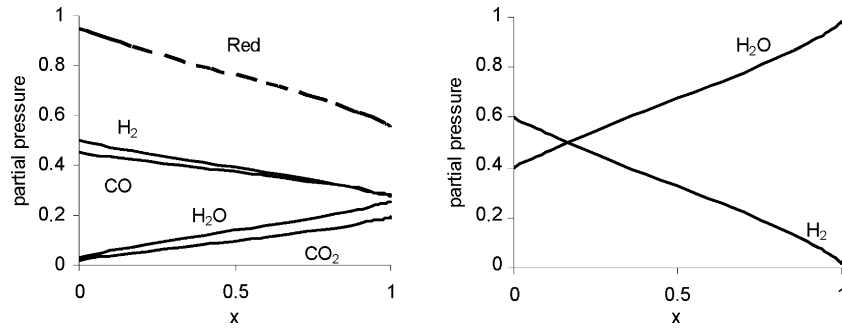


Fig. 10. Distribution of partial pressures of the gas mixture components along the SOER in the anode (left) and cathode (right) channels. $T=1200\text{ K}$, $w = 0.1$, $k = 1.7$. The EAGR-mode.

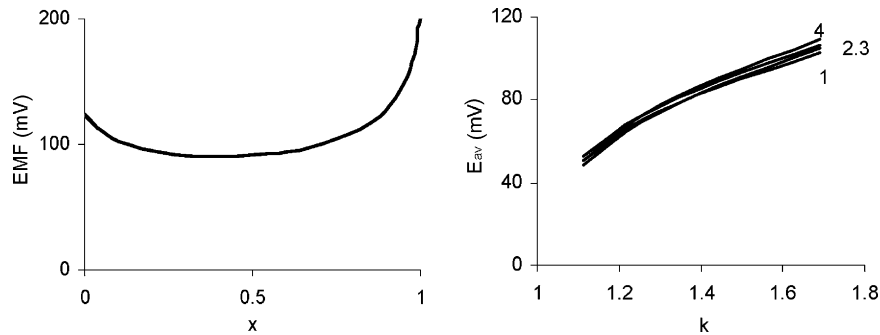
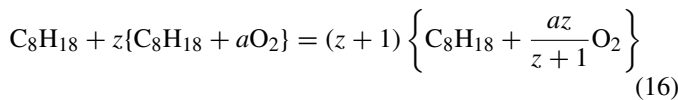


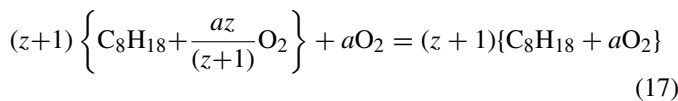
Fig. 11. EMF distribution along the SOER. $T=1200\text{ K}$, $w = 0.1$, $k = 1.7$ (left) and the average EMF dependence on k -parameter; $T=1100\text{ K}$ (1, 2) and 1200 K (3, 4). $w = 0.1$ (1, 3) and 0.2 (2, 4) (right). The EAGR-mode.

Under the assumption that the pre-reformer is fed by 1 mole of octane and z moles of the output anode gas, the reaction in the pre-reformer can be written as follows:



where z is the cycling factor and a is a coefficient which is explained below.

In the anode channel, the reformat is oxidized with the oxygen anions passed through the membrane, according to the following reaction:



The outgoing anodic mixture is divided in a special separator into two parts. $\{C_8H_{18} + aO_2\}$ goes into the burner and $z\{C_8H_{18} + aO_2\}$ goes into the pre-reformer.

The only source of oxygen for octane oxidation in the SOER is the oxygen passed through the membrane. The amount of this oxygen is twice less than the amount of the produced hydrogen (n_{hydr}); therefore in the mixture $\{C_8H_{18} + aO_2\}$ the coefficient $a = n_{hydr}/2$.

The relation $O_2/C_8H_8 = za/(z + 1) = zn_{hydr}/2(z + 1) = b$ in the reformed mixture is analogically determined by the reduced components' partial pressure value that is chosen as it is

mentioned above from the condition for the thermodynamical stability of gas mixture.

The balanced mixture in the braces in Eq. 16 may be presented in various versions: $\{C_8H_{18} + bO_2\} = \{17\text{ Red} + (b - 4)O_2\} = \{(25 - 2b)\text{Red} + (2b - 8)Ox\}$. The whole quantity of moles in the reformed mixture in the right braces is 17. Therefore the Ox-components partial pressure in the reforming mixture is $p_{ox} = (2b - 8)/17$ and hence $b = 8.5p_{ox} + 4$. So, the z -factor may be calculated by using the following formula:

$$z = \frac{8.5p_{ox} + 4}{0.5n_{hydr} - 8.5p_{ox} - 4} \quad (18)$$

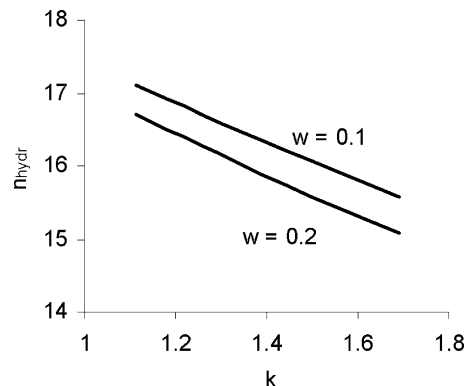


Fig. 12. Dependence of the hydrogen output on k -parameter for various values of w . The EAGR-mode.

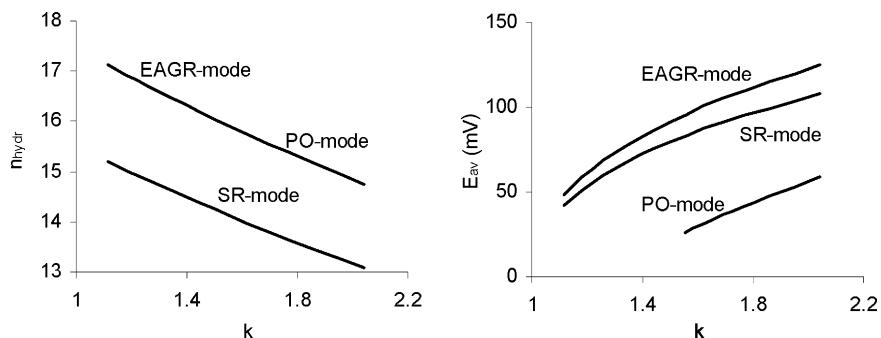


Fig. 13. Dependence of the hydrogen output (left) and the average EMF (right) on k -parameter for various modes of preliminary reforming. $T=1200$ K, $w=0.1$.

In our case it is accepted that $p_{\text{ox}}=0.05$, so the formula (18) can be written as

$$z = \frac{4.425}{0.5n_{\text{hydr}} - 4.425} \quad (19)$$

Consequently, the cycling factor depends only on the hydrogen output. The latter is calculated by using Eq. (15) as for the case of PO-mode.

The distribution of the components' partial pressures along the SOER at $T=1200$ K, $w=0.1$ and $k=1.7$ is shown in Fig. 10. It is interesting that the partial pressures of hydrogen and carbon monoxide are very close.

The EMF value under the EAGR-mode is the highest among the considered modes. Fig. 11 illustrates that the EMF exceeds 100 mV over all SOER cases at $k=1.7$.

During the change of k from 1.1 to 1.7 and $w=0.1$, the hydrogen output reduces from 17.11 to 15.57 (Fig. 12), that corresponds to an efficiency of the chemical energy transformation equal to 80.8% and 73.6%, respectively.

Finally, in Fig. 13 one can compare the hydrogen output and average EMF (right) dependence-forms on k -parameter for the various modes of preliminary reforming. On the one hand, the k -parameter decrease is desirable because of the increase in the hydrogen output; this is a way to save primary fuel. On the other hand, however, the k -parameter increase is desirable because of the increase in the EMF value; this is a way to lessen the SOER size. In practice it is necessary to find the right balance between the value of EMF and energy efficiency.

It is clear that the SOER optimum characteristics can be reached under the EAGR-mode, since it provides the most favorable combination of the reforming efficiency and the rate of the electrochemical process.

4. Conclusions

The operation analysis of a solid oxide electrochemical reformer (SOER) based on a MIEC membrane was investigated. The anode compartment was fed with octane while the cathode with water steam. Three different cases of preliminary octane reforming were taken into consideration: (i) steam reforming (SR-mode), (ii) octane partial oxidation (PO-mode) and (iii)

octane reforming by exhaust anode gas (EAGR-mode). It was found that this method of hydrogen production is characterized by very high efficiency of transformation of the primary fuel chemical energy to the hydrogen chemical energy: the efficiency was 65–72% in the case of SR-mode, 70–75% in the case of PO-mode and 74–81% in the case of EAGR-mode. The obtained theoretical results provide a base for optimization of the input gases parameters and the regime of the SOER operation that can be easily used for various hydrocarbons. For practical applications, the most important parameter is the average value of the EMF within the SOER. This value depends mainly on the ratio of steam moles' number supplied to the cathode space to the number of hydrogen output moles (k -parameter). It was found that EMF increases with k increase, while is weakly affected from the temperature and the heat losses amount. In the case of octane pre-reforming the hydrogen output decreases with the heat losses increase, with the increase of the amount of steam utilized for the steam pre-reforming, and with the increase of k -parameter. Finally, the SOER optimum characteristics can be reached under the EAGR-mode, since it provides the most favorable combination of the reforming efficiency and the rate of the electrochemical process.

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