Short communication

Thermodynamic analysis of carbon formation in a solid oxide fuel cell with a direct internal reformer fuelled by methanol

S. Assabumrungrat[a,*], N. Laosiripojana[b], V. Pavarajarn[a], W. Sangtongkitcharoen[a],
A. Tangjitmatee[a], P. Praserthdam[a]

[a] *Department of Chemical Engineering, Center of Excellence on Catalysis and Catalytic Reaction Engineering,
Chulalongkorn University, Bangkok 10330, Thailand*
[b] *The Joint Graduate School of Energy and Environment, King Mongkut's University of Technology Thonburi, Bangkok 10140, Thailand*

Abstract

A detailed thermodynamic analysis is undertaken for carbon formation in a solid oxide fuel cell (SOFC) with a direct internal reformer (DIR) fuelled by methanol. Two types of fuel cell electrolyte, i.e. oxygen- and hydrogen-conducting, are considered. Equilibrium calculations are performed to find the range of inlet steam methanol (H_2O:MeOH) ratio where carbon formation is thermodynamically unfavourable in the temperature range of 500 to 1200 K. The key parameters that determine the boundary of carbon formation are temperature, type of solid electrolyte, and the extent of the electrochemical reaction of hydrogen. The minimum H_2O:MeOH ratio for which carbon formation is thermodynamically unfavoured decreases with increasing temperature. Comparison between the two types of electrolyte reveals that the hydrogen-conducting electrolyte is impractical for use given the tendency for carbon formation. This is mainly due to the water formed by the electrochemical reaction at the electrodes.
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1. Introduction

Fuel cells are more efficient and cleaner alternative methods of electricity generation than conventional heat engines, steam and gas turbines, and combined cycles. Among the various types of fuel cell, the solid oxide fuel cell (SOFC) has attracted considerable interest as it offers the widest range of applications, flexibility in the choice of fuel, high-system efficiency, and the possibility of operation with an internal reformer. The waste heat at high temperature can be utilized in co-generation applications and bottoming cycles. Moreover, unlike the situation in low-temperature fuel cells, the SOFC anode is not affected by carbon monoxide poisoning.

Hydrogen, which is produced on large scale by the steam reforming of methane in an externally heated fixed-bed re-

actor and on a small scale by the electrolysis of water, is the major fuel for fuel cells. Nevertheless, the use of other fuels such as methanol, ethanol, gasoline and other oil derivatives is also possible. Douvartizide et al. [1] applied a thermodynamic analysis to evaluate the feasibility of different fuels, i.e., methane, methanol, ethanol and gasoline, for SOFCs. The results obtained in terms of electromotive force output and efficiency show that ethanol and methanol are very promising alternatives to hydrogen. Among them, methanol is favourable due to its ready availability, high-specific energy and storage transportation convenience [2,3].

Although the steam reforming of methanol for hydrogen production is feasible from a thermodynamic point of view, a major consideration is carbon formation in the system. Appropriate operating conditions must employed to avoid damage from carbon deposition such as catalyst deactivation in the reformer or anode deactivation in a SOFC with an internal reformer. The formation of carbon

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Nomenclature

a	inlet moles of methanol (mol)
b	inlet moles of steam (mol)
c	extent of the electrochemical reaction of hydrogen (mol)
K_1	equilibrium constant of reaction (11) (kPa^{-1})
K_2	equilibrium constant of reaction (12) (kPa)
n_i	number of moles of component i (mol)
p_i	partial pressure of component i (kPa)
x	converted moles associated with reaction (1) (mol)
y	converted moles associated with reaction (2) (mol)
z	converted moles associated with reaction (3) (mol)

Greek letter

α_C	carbon activity

leads to loss of system performance and poor durability [4].

Thermodynamic analyses of the steam reforming of methanol have been undertaken in either reformer [5–7] or a fuel-cell system [1,8]. Amphlett et al. [5] examined thermodynamics of reaction based on widely-accepted decomposition-shift mechanisms at different temperatures, pressures and feed ratios. Prior to this study, thermodynamic analyses were based mostly on the overall reaction of methanol steam forming to form carbon dioxide and water. Lwin et al. [6] re-examined the steam reforming of methanol by the method of direct minimization of Gibbs free energy at temperatures in the range of 360 to 573 K and a H_2O:MeOH feed ratio of 0 to 1.5. It was found that the formation of carbon and methane was thermodynamically favoured and reduced both the quantity and the quality of the hydrogen produced. Undesired products such as dimethyl ether occurred at low temperatures and low H_2O:MeOH feed ratios. Brown [7] compared seven types of fuel for on-board hydrogen production for a proton-exchange-membrane fuel cell. It was found that the theoretical input energies did not differ markedly among the different types of fuel. Maggio et al. [8] conducted comparative studies on the internal steam reforming of methane, methanol and ethanol in a molten carbonate fuel cell. Carbon formation was not however considered in the calculations.

The present study aims to find a suitable range of operating conditions under which carbon formation in a SOFC with a direct internal reformer (DIR) is not feasible. This is necessary due to the fact that carbon deposition over the anode results in the growth of carbon filaments that are attached to anode crystallites generate massive forces within the electrode structure and, thereby, result in its rapid break-

down [9]. The calculation is more complicated than that for conventional reformers as the disappearance of hydrogen and the generation water from the electrochemical reaction must be taken into account. SOFCs with both oxygen- and hydrogen-conducting electrolytes are investigated in this work.

2. Theory

The reactions involved in the production of hydrogen from the steam reforming of methanol can be represented by the widely accepted decomposition-shift mechanisms [5]:

$$CH_3OH = 2H_2 + CO \tag{1}$$

$$CO + H_2O = H_2 + CO_2 \tag{2}$$

Early studies [10,11] showed that when in thermodynamic equilibrium the system contains only five species with noticeable concentration, namely: methanol, carbon monoxide, carbon dioxide, hydrogen and water. Recent work by Lwin et al. [6] also confirmed that the equilibrium composition of other higher molecular weight compounds such as formaldehyde, methyl formate and formic acid are negligible. It was revealed, however, that methane formation according to Eq. (3) needed to be included in the calculation.

$$CO + 3H_2 = CH_4 + H_2O \tag{3}$$

When the SOFC is operated with an internal reformer, part of the hydrogen produced is consumed by the electrochemical reaction with oxygen producing water and electricity. Two types of solid electrolyte can be employed in SOFC operation, viz., oxygen- and hydrogen-conducting electrolytes. An oxygen-conducting electrolyte is common for the use in SOFCs, while a hydrogen-conducting electrolyte is normally used in low-temperature fuel cells (e.g., PEM and PAFC). It should be noted that some types of hydrogen-conducting electrolyte are not classified as solid oxides and the term 'ceramic fuel cell' is more preferable in these cases. The difference between both types of electrolyte is the location at which the water is produced. With an oxygen-conducting electrolyte, water is produced in the reaction mixture in the anode chamber. By contrast, with a hydrogen-conducting electrolyte, water appears on the cathode side. In this work, a SOFC with a hydrogen-conducting electrolyte is studied as an alternative approach and is used for comparison purposes. The number of moles of each component is given by the following expressions:

$$n_{MeOH} = a - x \tag{4}$$

$$n_{CH_4} = z \tag{5}$$

$$n_{CO} = x - y - z \tag{6}$$

$$n_{CO_2} = y \tag{7}$$

$$n_{H_2} = 2x + y - 3z - c \quad \text{(for oxygen-conducting electrolyte)}$$
$$n_{H_2} = 2x + y - 3z - c \quad \text{(for hydrogen-conducting electrolyte)}$$

(8)

$$n_{H_2O} = b + c - y + z \quad \text{(for oxygen-conducting electrolyte)}$$
$$n_{H_2O} = b - y + z \quad \text{(for hydrogen-conducting electrolyte)}$$

(9)

$$n_{tot} = \sum_{i-1}^{6} n_i \tag{10}$$

where a and b represent the inlet moles of methanol and water, respectively; c is the extent of electrochemical reaction of hydrogen; x, y and z are converted moles associated with the reactions (1) to (3), respectively. It should be noted that only hydrogen is assumed to react electrochemically with the oxygen supplied from the cathode side.

Calculations of the thermodynamic equilibrium composition are accomplished by solving a system of non-linear equations that relate the moles of each component to the equilibrium constants of the reactions.

The following reactions are the most probable reactions that lead to carbon formation:

$$2CO = CO_2 + C \tag{11}$$

$$CH_4 = 2H_2 + C \tag{12}$$

$$CO + H_2 = H_2O + C \tag{13}$$

$$CO_2 + 2H_2 = 2H_2O + C \tag{14}$$

$$CH_3OCH_3 = 2C + H_2O + 2H_2 \tag{15}$$
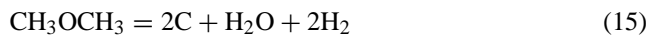
At low temperature, reactions (13–15) are favourable while reaction (12) is thermodynamically unfavoured [6]. The Boudard reaction (Eq. (11)) and the decomposition of methane (Eq. (12)) are the major pathways for carbon formation at high temperature as they show the largest change in Gibbs energy [12]. It should be noted that due to the exothermic nature of the water–gas shift reaction (Eq. (2)) and the methanation reaction (Eq. (3)) amount of CO becomes significant at high temperature [7]. The reactions given by Eqs. (11) and (12) are employed to examine the thermodynamic possibility of carbon formation. The carbon activities, defined in Eqs. (16) and (17), are used to determine the possibility of carbon formation.

$$\alpha_{C,CO} = \frac{K_1 p_{CO}{}^2}{p_{CO_2}} \tag{16}$$

$$\alpha_{C,CH_4} = \frac{K_2 p_{CH_4}}{p_{H_2}{}^2} \tag{17}$$

where K_1 and K_2 represent the equilibrium constant of reactions (11) and (12), respectively, and p_i is the partial pressure of component i. When $\alpha_C > 1$, the system is not in equilibrium and carbon formation is observed. The system is at equilibrium when $\alpha_C = 1$. Finally, when $\alpha_C < 1$, carbon formation is thermodynamically impossible. It is noted that the amount of carbon in the system cannot be directly interpreted from the

carbon activities. The latter are employed only as indicators of carbon formation.

To find the range of SOFC operation that does not suffer from the formation of carbon, the operating temperature and the extent of the electrochemical reaction of hydrogen (c) are specified. Then, the initial value of the H_2O:MeOH ratio is varied and the corresponding value of α_C are calculated. The boundary of carbon formation is defined as the H_2O:MeOH that has a value of $(1-\alpha_C)$ close to zero. This value represents the minimum H_2O:MeOH mole ratio in the initial system at which carbon formation in the equilibrium mixture is thermodynamically impossible. It should be noted that other factors such as mass and heat transfer or the rate of reactions may also affect the prediction of the carbon formation boundary. Local compositions that allow carbon formation may exist, although such formation is unfavourable according to the calculation based on the equilibrium bulk compositions. Moreover, carbon species may form via other chemical reactions such as the thermal cracking of hydrocarbons. In addition, it should be noted that although recent investigators estimated the carbon concentration in steam reforming reactions by the method of Gibbs energy minimization, the simple principle of equilibrated gas to predict carbon formation used in this study is still meaningful. This is because the calculation is carried out to find the boundary of carbon formation where the carbon just begins to form.

In practice, the SOFC should be operated at a H_2O:MeOH ratio that is higher than the theoretical value to avoid the deactivation of the anode by carbon formation. Excessive water in the feed mixture is not favoured, however, because the exothermic heat produced by the SOFC electrochemical section may not satisfy the endothermic heat of the steam reforming reaction, and particularly the enthalpy requirement for water evaporation [13]. This subject will be discussed in more detail in a future communication that deals with the efficiency of the overall SOFC system.

3. Results

For the SOFC with DIR operation in this study, methanol is reformed at the anode. Due to the presence of the electrochemical reaction, calculations need to take into account disappearance of hydrogen as well as steam generation by the electrochemical reaction. As mentioned earlier, both oxygen- and hydrogen-conducting electrolytes are investigated and compared. The study includes the effects of the extent of the electrochemical reaction of hydrogen, the inlet H_2O:MeOH ratio, the operating temperature and the pressure on the
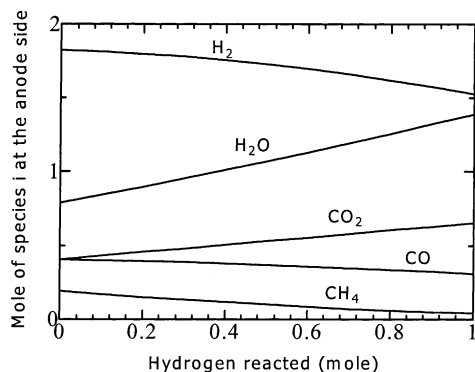
Fig. 1. Influence of extent of electrochemical reaction of hydrogen on moles of components at anode side (oxygen-conducting electrolyte, $a = 1$ mol, $b = 1$ mol, $P = 101.3$ kPa, $T = 1173$ K).

chemical species in the anode side, e.g. CO, CO_2 and H_2O. Carbon formation at various operating conditions is also predicted. The results obtained and their discussions are illustrated as follows.

3.1. Effect of extent of hydrogen consumption on anode components

In the DIR operation, hydrogen produced from the reforming reactions electrochemically reacts with oxygen ion from supplied air and products steam. This reaction is an important element in electricity production from the fuel cell. In this section, the effects of the extent of hydrogen consumption via this electrochemical reaction, c, on each component at the anode are discussed. The results for the fuel cell with the oxygen- and hydrogen-conducting electrolytes are presented in Figs. 1 and 2, respectively.

For all the operating conditions investigated, the number of moles of methanol is close to zero. This is due to the strong endothermic decomposition reaction (Eq. (1)) that is favoured at the high-operating temperature of SOFCs. For other species, it can be seen from Figs. 1 and 2 that the consumption of hydrogen by the electrochemical reaction affects their equilibrium concentrations. Con-
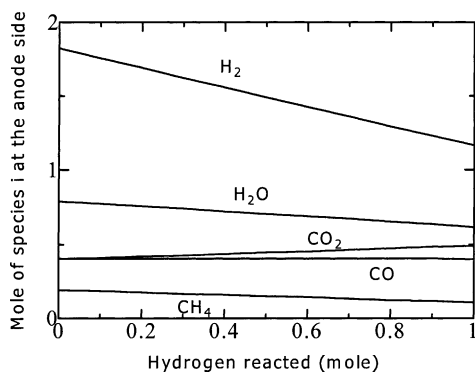

Fig. 2. Influence of extent of electrochemical reaction of hydrogen on moles of components at anode side (hydrogen-conducting electrolyte, $a = 1$ mol, $b = 1$ mol, $P = 101.3$ kPa, $T = 1173$ K).

stant removal of H_2 from the system via the electrochemical reaction shifts the equilibrium reactions of Eqs. (1) and (2) in a forward direction and the reaction of Eq. (3) in a backward direction. Therefore, the carbon dioxide concentration increases whereas the carbon monoxide and methane concentrations decrease with the increase in the amount of hydrogen consumed. It should be noted that the changes in the concentrations of those species with the amount of hydrogen consumed for the hydrogen-conducting electrolyte system are less pronounced than those for the oxygen-conducting electrolyte system. The main difference between the use of oxygen- and hydrogen-conducting electrolytes in SOFCs is the location where the electrochemical reaction mentioned above takes place. For the oxygen-conducting electrolyte system, the reaction occurs at the anode side. Therefore, the partial pressure of steam, which is the main product from the reaction, at the anode increases with greater consumption of hydrogen, as shown in Fig. 1. On the other hand, by using the hydrogen-conducting electrolyte, steam is generated at the cathode side. The amount of steam in the anode slightly decreases with increased hydrogen consumption, as shown in Fig. 2, because the disappearance of hydrogen in the anode shifts the reactions that consume steam in a forward direction.

3.2. Effect of hydrogen consumption on carbon formation

Theoretically, the excess inlet steam reacts with carbon monoxide to form carbon dioxide according to the water–gas shift reaction (Eq. (2)). In addition, it helps to prevent the formation of methane (Eq. (3)). The increase in carbon dioxide concentration and the decrease in methane concentration subsequently prevent possible carbon formation by the Boudard reaction (Eq. (11)) and by the decomposition of methane (Eq. (12)), respectively. Therefore, the formation of carbon is less likely in the oxygen-conducting electrolyte system because of the extra steam generated from the electrochemical reaction between hydrogen and oxygen ions at the anode side. The amount of each species in the anode side when the oxygen-conducting electrolyte is employed with $c = 0$ and 1.5 mol is shown in Fig. 3(a) and (b), respectively. It is evident, especially for the case of $c = 0$, that more carbon monoxide is converted to carbon dioxide when a greater amount of steam is supplied to the system. Moreover, a higher concentration of carbon dioxide is observed when the extent of hydrogen consumption (c) is increased. The extra steam produced from the electrochemical reaction between hydrogen and oxygen ions enhances the water–gas shift reaction and retards the methanaation reaction. Therefore, increasing the inlet H_2O:MeOH ratio in such a system (i.e., when $c = 1.5$) decreases the amounts of carbon monoxide and methane.

The boundary of carbon formation, i.e., the minimum inlet H_2O:MeOH ratio at which the formation of carbon is thermodynamically unfavoured, is better represented in Figs. 4 and 5. The lines in the plots indicate the system in which carbon is in equilibrium with other species. In the region above the
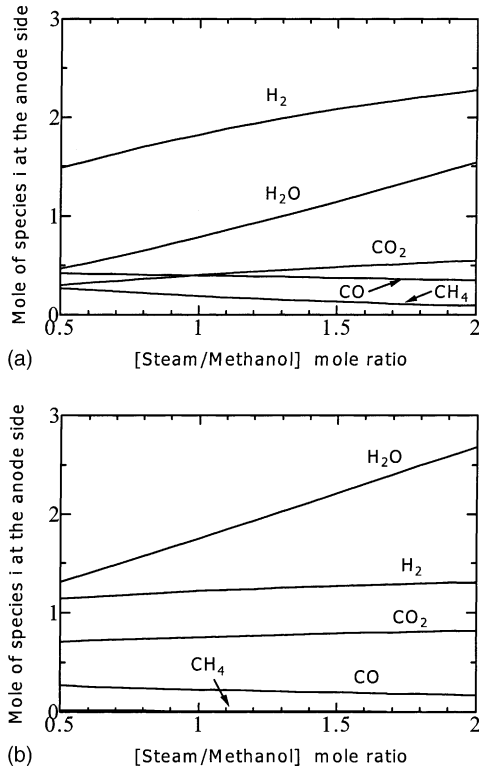
(a)

[Steam/Methanol] mole ratio

(b)

[Steam/Methanol] mole ratio

Fig. 3. Effect of inlet H_2O:MeOH ratio on each component mole at anode side (oxygen conducting electrolyte $a = 1$ mol, $P = 101.3$ KPa, $T = 1173$ K): (a) $c = 0$ mol and (b) $c = 1.5$ mol.

equilibrium line, carbon formation is thermodynamically impossible. Generally, the higher the temperature, the lower is the boundary of carbon formation. This is due to a decrease in $\alpha_{C,CO}$ at high-operating temperature, as the Boudard reaction (Eq. (11)) is exothermic. Moreover, the methane concentration at high temperature is small because of the strong exothermic methanation reaction. Therefore, increasing the SOFC-operating temperature is one possibility to prevent carbon formation at the anode, but the cost of high-temperature materials and the problem of cell sealing must also be considered.
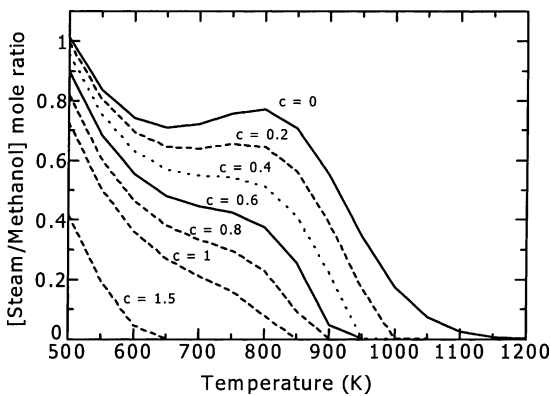

Fig. 4. Influence of extent of electrochemical reaction of hydrogen on requirement of inlet H_2O:MeOH ratio at different operating temperature (oxygen-conducting electrolyte, $a = 1$ mol, $P = 101.3$ kPa).
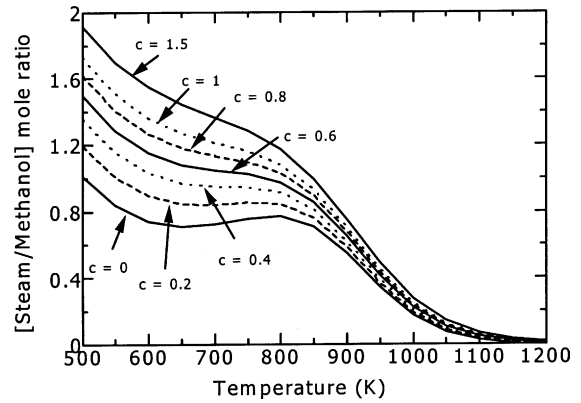

Fig. 5. Influence of extent of electrochemical reaction of hydrogen on requirement of inlet H_2O:MeOH ratio at different operating temperatures (hydrogen-conducting electrolyte, $a = 1$ mol, $P = 101.3$ kPa).

For the oxygen-conducting electrolyte system, higher hydrogen consumption (i.e., increasing c) results in a decrease in the carbon formation boundary, as shown in Fig. 4. This results from the presence of extra steam from the electrochemical reaction as discussed earlier. It can be seen that the extent of this electrochemical reaction significantly affects the boundary of carbon formation. By using the same inlet H_2O:MeOH ratio, the system can be operated without carbon formation at an appreciably lower temperature when the extent of hydrogen consumption is slightly increased. In the other words, the possibility of carbon formation on the anode of the SOFCs with the oxygen-conducting electrolyte is dramatically decreased if the electrochemical reaction between the generated hydrogen and the supplied oxygen is maintained.

On the other hand, for the hydrogen-conducting electrolyte system, a higher inlet H_2O:MeOH ratio is required to prevent possible carbon formation, as shown in Fig. 5. Higher amounts of carbon monoxide and methane reside in the system, while less carbon dioxide is produced from the water–gas shift reaction, when the hydrogen-conducting electrolyte is used, as shown earlier in Fig. 2. For the hydrogen-conducting electrolyte, an increase in the extent of the electrochemical reaction of hydrogen (c) significantly demands a higher inlet H_2O:MeOH ratio to prevent carbon formation, especially at low-operating temperatures. This effect diminishes when the operating temperature is higher than 1173 K. Nevertheless, it is obvious that the oxygen-conducting electrolyte is preferable due to less tendency for carbon formation.

3.3. Effect of pressure on carbon formation

According to our calculations, the influence of the operating pressure on the boundary of carbon formation is negligible for both the oxygen- and hydrogen-conducting electrolyte operations and, hence, the results are not shown.

4. Discussion

The great benefit of the internal reforming operation is the coupling of the endothermic reforming reaction and the exothermic electrochemical reaction in a single unit. This coupling process is called an autothermal operation, which provides a thermal efficient approach for heat integration in SOFC. Another advantage of the DIR operation is reduction of the inlet steam requirement, as extra steam is supplied from the anode electrochemical reaction. The DIR operation must be carefully controlled during the start-up period, however since the steam generated from the electrochemical reaction is expected to be less. Another advantage of using methanol as the fuel is reduction of the high-operating temperature requirement, because this component is easily reformed at low temperature. Low-temperature operation results in an increase in hydrogen production and also a decrease in carbon monoxide production due to forward moving of the exothermic water–gas shift reaction.

As described above, although direct internal reforming is expected to simplify the overall system design, this operation is not easy to achieve due to local mismatch between the rates of the endothermic and the exothermic reactions. This can lead to a significant reduction in the local temperature close to the entrance of the anode, which can result in possible carbon formation and also in mechanical failure due to thermally induced stresses. Therefore, this difficulty must also be considered as well as the mass transfer and heat transfer problems when using DIR in a SOFC.

The impact of a SOFC-DIR with a hydrogen-conducting electrolyte is comparable with membrane reactor operation in which hydrogen is removed from the system.

Consequently, without careful control, carbon formation can be easily formed and result in possible catalyst or system damage. A higher inlet steam:carbon ratio could reduce this problem, but the additional energy requirement for water evaporation must then be considered.

5. Conclusions

A theoretical thermodynamic analysis has been performed to predict the boundary of carbon formation for a SOFC with direct internal reforming when methanol was used as fuel. The results indicate that carbon formation can be prevented by either increasing the inlet H_2O:MeOH ratio or by increasing the operating temperature. A comparison between the hydrogen- and the oxygen-conducting electrolyte system shows that carbon formation in the latter system is less likely due to the extra steam that is produced from the electrochemical reaction of hydrogen at the anode.

Although the boundary of carbon formation for SOFCs can be predicted according to the thermodynamic calculations presented in this work, it should be realized that carbon may be formed by other mechanisms besides the Boudard reaction and the decomposition of methane. Moreover, other forms of carbonaceous species such as polymeric coke (C_nH_m), which can also result in comparable damage, can exist in the system. Therefore, the results obtained here should be considered only as crude guideline for the operating conditions of a SOFC. Experimental work, including a kinetic study of the rate of carbon formation, should be carried out to determine the most suitable inlet H_2O:MeOH ratio.

References

[1] S.L. Douvartzides, F.A. Coutelieris, K. Demin, P.E. Tsiakaras, AIChE 49 (2003) 248–257.
[2] B. Emonts, J.B. Hansen, S.L. Jorgensen, B. Hohlein, R. Peters, J. Power Sources 71 (1998) 288.
[3] K. Ledjeff-Hey, V. Formanski, T. Kalk, J. Roes, J. Power Sources 71 (1998) 199–207.
[4] A.L. Dicks, J. Power Source 61 (1996) 113–124.
[5] J.C. Amphlett, M.J. Evans, R.A. Jones, R.F. Mann, R.D. Weir, Can. J. Chem. Eng. 59 (1981) 720.
[6] Y. Lwin, W.R.W. Daud, A.B. Mohamad, Z. Yaakob, Int. J. Hydrogen Energy 25 (2000) 47–53.
[7] L.F. Brown, Int. J. Hydrogen Energy 26 (2001) 381–397.
[8] G. Maggio, S. Freni, S. Cavallaro, J. Power Sources 74 (1998) 17–23.
[9] S.H. Clarke, A.L. Dicks, K. Pointon, T.A. Smith, A. Swann, Catal. Today 38 (1997) 411–423.
[10] J.C. Amphlett, R.F. Mann, R.D. Weir, Can. J. Chem. Eng. 66 (1988) 950.
[11] E. Santacesaria, S. Carra, Appl. Catal. A 5 (1983) 363.
[12] J.N. Amor, Appl. Catal. A 176 (1999) 159–176.
[13] T. Ionnides, J. Power Sources 92 (2001) 17–25.