Determination of the boundary of carbon formation for dry reforming of methane in a solid oxide fuel cell

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Abstract

The boundary of carbon formation for the dry reforming of methane in direct internal reforming solid oxide fuel cells (DIR-SOFCs) with different types of electrolyte (i.e., an oxygen ion-conducting electrolyte (SOFC-O^{2-}) and a proton-conducting electrolyte (SOFC-H^+)) was determined by employing detailed thermodynamic analysis. It was found that the required CO_2/CH_4 ratio decreased with increasing temperature. The type of electrolyte influenced the boundary of carbon formation because it determined the location of water formed by the electrochemical reaction. The extent of the electrochemical reaction also played an important role in the boundary of carbon formation. For SOFC-O^{2-}, the required CO_2/CH_4 ratio decreased with the increasing extent of the electrochemical reaction due to the presence of electrochemical water in the anode chamber. Although for SOFC-H^+ the required CO_2/CH_4 ratio increased with the increasing extent of the electrochemical reaction at high operating temperature ($T > 1000$ K) following the trend previously reported for the case of steam reforming of methane with addition of water as a carbon suppresser, an unusual opposite trend was observed at lower operating temperature. The study also considered the use of water or air as an alternative carbon suppresser for the system. The required H_2O/CH_4 ratio and air/CH_4 ratio were determined for various inlet CO_2/CH_4 ratios. Even air is a less attractive choice compared to water due to the higher required air/CH_4 ratio than the H_2O/CH_4 ratio; however, the integration of exothermic oxidation and the endothermic reforming reactions may make the use of air attractive. Water was found to be more effective than carbon dioxide in suppressing the carbon formation at low temperatures but their effect was comparable at high temperatures. Although the results from the study were based on calculations of the SOFCs with different electrolytes, they are also useful for selecting suitable feed compositions for other reactors; including conventional reformers and membrane reactors with hydrogen removal.
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Keywords: Solid oxide fuel cell; Carbon formation; Thermodynamic analysis; Dry reforming of methane

1. Introduction

A solid oxide fuel cell (SOFC) is a more efficient electrical power generator than many conventional processes. Due to its high operating temperature, it offers wide potential applications, flexibility of fuel choices, possibility for operation with an internal reformer and a high system efficiency. Recent developments on SOFCs seem to move towards to two main issues: intermediate temperature operation and the use of other fuels instead of hydrogen. The uses of various alternative fuels; e.g., natural gas, bio-ethanol, coal, biomass, biogas, methanol, gaso-

line and other oil derivatives, in SOFCs have been investigated [1–3]. As SOFCs are operated at high temperatures, these fuels can be internally reformed at the anode side of SOFCs producing a H_2-CO rich gas, which is eventually used to generate the electrical energy and heat. This operation is called a direct internal reforming (hence, DIR-SOFCs). Regarding the global environmental problems and current fossil fuel concerns, the development of SOFCs fed by renewable fuels attract more attention as an alternative method for power generation in the near future. Among renewable sources, biogas is a promising candidate, since it is produced readily from the fermentation of biomasses and agricultural wastes. Typically, biogas consists mainly of methane and carbon dioxide. Due to the rich CO_2 in biogas, carbon dioxide (or dry) reforming reaction would be one of the most suitable processes to convert biogas to hydrogen or

Nomenclature

a	inlet moles of methane (mol)
b	inlet moles of carbon dioxide (mol)
c	inlet moles of steam (mol)
d	inlet moles of inert (mol)
e	extent of the electrochemical reaction of hydrogen (mol)
K_1	equilibrium constant of reaction (16) (kPa)
K_2	equilibrium constant of reaction (17) (kPa)
K_3	equilibrium constant of reaction (18) (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

synthesis gas (CO and H_2) for later utilization in SOFCs or other processes.

However, in order to operate SOFCs on the direct feed of alternative fuels (i.e., biogas) rather than hydrogen, several major problems remain to be solved. One of them is the problem of carbon deposition on the anode, causing loss of active sites and cell performance as well as poor durability. The growth of carbon filaments attached to the anode crystallites can generate massive forces within the electrode structure leading to rapid breakdown [4]. A number of efforts have been carried out to alleviate this problem. One approach is to search for appropriate anode formulations and operating conditions. A number of additives were added to the anode to lower the rate of carbon formation. For example, the addition of molybdenum and cerium metal oxides to the Ni-based anode was reported to reduce carbon deposition, and in some cases, to increase fuel conversion [5,6]. The addition of alkalis such as potassium can accelerate the reaction of carbon with steam and also neutralize the acidity of the catalyst support, hence reducing carbon deposition [7].

Another conventional approach to avoid carbon deposition is the addition of extra oxidant to the feed. According to the dry reforming of methane, it was suggested that the use of excess carbon dioxide in the dry reforming reaction could avoid carbon formation [8]. Experimental studies on dry reforming using an excess of carbon dioxide with carbon dioxide to methane (CO_2/CH_4) ratios of 3/1 and 5/1 over a nickel catalyst supported on alumina were carried out. It was reported that the rate of disintegration is smaller for the case with higher ratio. Selection of a suitable CO_2/CH_4 ratio is therefore an important issue [9,10]. Carbon formation can occur when the SOFCs are operated at low CO_2/CH_4 ratios. However, use of high CO_2/CH_4 ratios is

unattractive as it lowers the electrical efficiency of the SOFCs by the dilution of fuel, the yield of hydrogen production and the system efficiency. Consequently, it is necessary to find the CO_2/CH_4 ratio at the boundary of carbon formation at which represents the minimum ratio required to operate the SOFCs in a carbon-free condition.

In this paper, a detailed thermodynamic analysis is carried out to predict the boundary of carbon formation for DIR-SOFCs fueled by mixtures of methane and carbon dioxide. The effects of electrolyte type (i.e., oxygen ion-conducting and proton-conducting electrolytes), operating temperature, and extent of electrochemical reaction on the required CO_2/CH_4 ratio have been investigated. Our previous work employed thermodynamic calculations to predict the required H_2O/fuel ratio for SOFCs fed by methane [11] and methanol [12]. It was found that the SOFCs with an oxygen-conducting electrolyte (SOFC-O^{2-}) require less H_2O/fuel ratio than those with a hydrogen-conducting electrolyte (SOFC-H^+) because extra water generated from the electrochemical reaction is available for use in the anode chamber. In this present work, alternative methods to alleviate the carbon formation by adding water or air to the system were considered as it is practical to add these components along with methane and carbon dioxide in the feed to reduce the degree of carbon deposition.

2. Theory

The main reaction involved in the production of hydrogen from methane and carbon dioxide is the dry reforming of methane (Eq. (1)). When the SOFC is operated using an oxygen ion-conducting electrolyte, water is also generated by the electrochemical reaction of hydrogen and oxygen ion, and therefore, the steam reforming of methane (Eq. (2)) and the water gas shift reaction (WGS) (Eq. (3)) also take place.

$$CH_4 + CO_2 = 2H_2 + 2CO \tag{1}$$

$$CH_4 + H_2O = 3H_2 + CO \tag{2}$$

$$CO + H_2O = H_2 + CO_2 \tag{3}$$

The dry and steam reforming reactions are strongly endothermic while the WGS is mildly exothermic. Both steam and dry reforming reactions have similar thermodynamic characteristics except that the carbon formation in the dry reforming is more severe than in the steam reforming due to the lower H/C ratio of this reaction [13]. The activities toward steam and dry reforming over several catalysts were investigated [14]. It was observed that replacing water with carbon dioxide gave similar activation energies, which indicated a similar rate-determining step in these two reactions. Nickel and cobalt are usually applied as the catalysts for this reaction. The dry reforming reaction with a stoichiometric feed ratio over several catalysts was studied [15]. It was found that Ni/SiO_2 exhibited this reaction near equilibrium and had high selectivity to carbon monoxide. The activity of the catalyst over other supports was found to be deactivated rapidly due to carbon deposition.

When a SOFC is operated with an internal reformer, hydrogen produced from the reforming process is consumed simultaneously by the electrochemical reaction generating electricity. Theoretically, two types of solid electrolytes can be employed in the SOFC: oxygen ion- and proton-conducting electrolytes. The reactions taking place in the anode and the cathode can be summarized as follows:
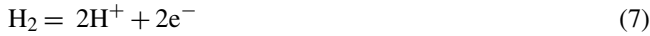
Oxygen ion-conducting electrolyte:
Anode:

$$H_2 + O^{2-} = H_2O + 2e^- \tag{4}$$

$$CO + O^{2-} = CO_2 + 2e^- \tag{5}$$

Cathode:

$$O_2 + 4e^- = 2O^{2-} \tag{6}$$

Proton-conducting electrolyte:
Anode:

$$H_2 = 2H^+ + 2e^- \tag{7}$$

Cathode:

$$2H^+ + \tfrac{1}{2}O_2 + 2e^- = H_2O \tag{8}$$

The difference between the SOFCs with the two electrolyte types is the location of the water produced. For the SOFC with the oxygen ion-conducting electrolyte (SOFC-O^{2-}), water is produced in the anode chamber whereas it appears in the cathode chamber for the SOFC with the proton-conducting electrolyte (SOFC-H^+). It should be noted that for the SOFC-H^+, carbon monoxide cannot be electrochemically consumed. It is, therefore, not so practical to use only the dry reforming of methane in the SOFC-H^+ unless water is included in the feed to enhance the hydrogen production by steam reforming (Eq. (2)) and WGS (Eq. (3)). For the SOFC-O^{2-}, both hydrogen and carbon monoxide can electrochemically react with oxygen. However, the electrochemical reaction of hydrogen is much faster than that of CO [16]. Therefore, in this study it was assumed that only hydrogen reacts electrochemically with oxygen supplied from the cathode side. For comparative purpose between the SOFCs with different electrolytes, only the range of possible electrochemical reaction from hydrogen in the SOFC-H^+ was considered in the study.

The number of moles of each component in the anode gas mixture is given by the following expressions:

$$n_{CH_4} = a - x - y \tag{9}$$

$$n_{CO_2} = b - x + z \tag{10}$$

$$n_{CO} = 2x + y - z \tag{11}$$

$$n_{H_2} = 2x + 3y + z - e \tag{12}$$

$n_{H_2O} = c - y - z + e$ (for oxygen ion-conducting electrolyte)

$n_{H_2O} = c - y - z$ (for proton-conducting electrolyte) (13)
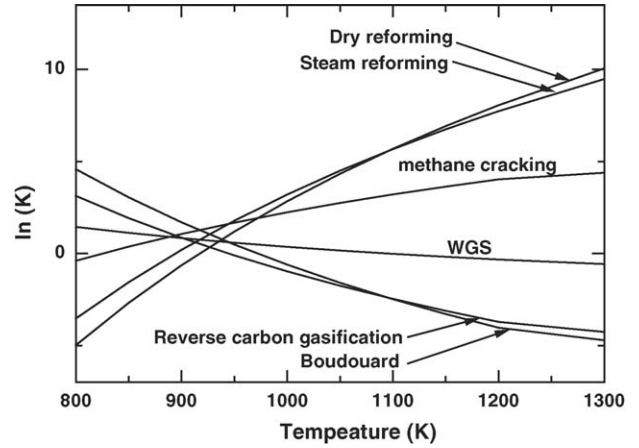

Fig. 1. Values of the equilibrium constants.

$$n_{inert} = d \tag{14}$$

$$n_{total} = \sum_{i-1}^{6} n_i \tag{15}$$

where a, b, c and d represent the inlet moles of methane, carbon dioxide, steam and inert respectively, e the extent of the electrochemical reaction of hydrogen, and x, y and z represent the converted moles associated to the reactions (1)–(3), respectively. The thermodynamic equilibrium composition can be determined by solving a system of nonlinear equations relating the moles of each component to the equilibrium constants of the reactions whose values are given in Fig. 1.

The following reactions are the most probable carbon formation reactions in the system [17]:
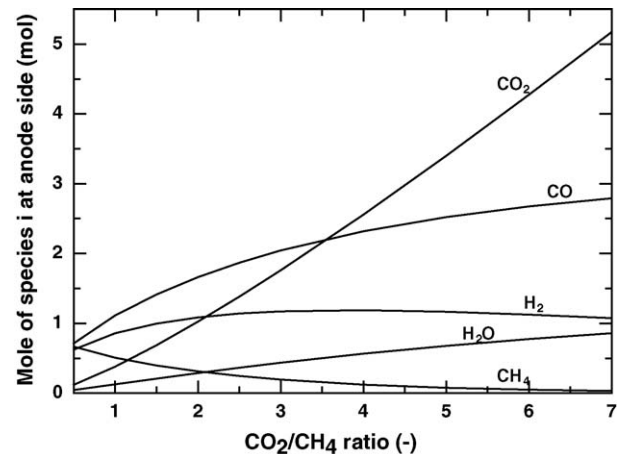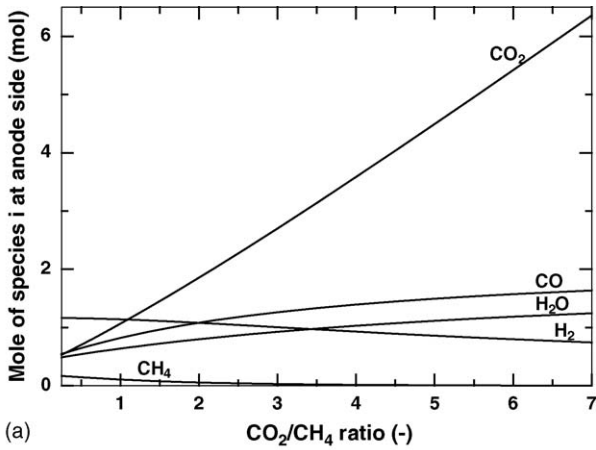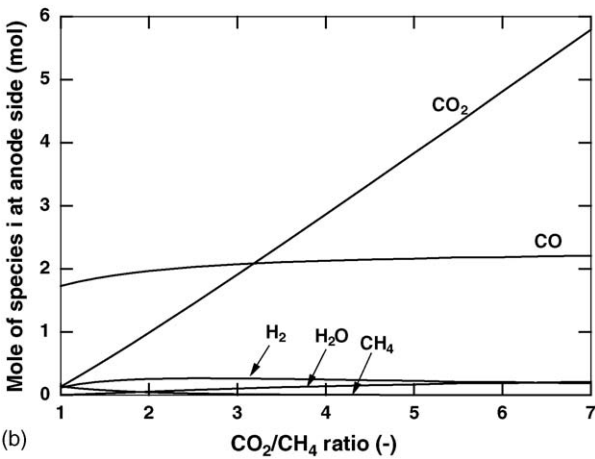
$$2CO = CO_2 + C \tag{16}$$

$$CH_4 = 2H_2 + C \tag{17}$$

$$CO + H_2 = H_2O + C \tag{18}$$

Fig. 2. Effect of inlet CO_2/CH_4 ratio on the moles of each component in a conventional reformer ($a = 1$ mol, $P = 101.3$ kPa and $T = 900$ K).

(a)

(b)

Fig. 3. Effect of inlet CO_2/CH_4 ratio on the moles of each component: (a) SOFC-O^{2-} and (b) SOFC-H^+ ($a = 1$ mol, $e = 1.6$ mol, $P = 101.3$ kPa and $T = 900$ K).
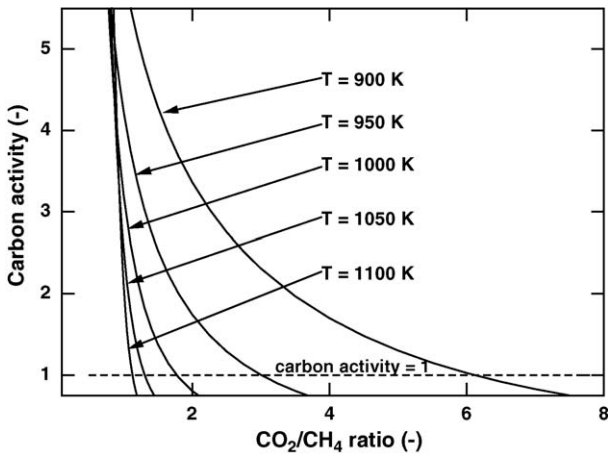
Fig. 4. Effect of inlet CO_2/CH_4 ratio on carbon activity ($a = 1$ mol, $e = 1.6$ mol, $P = 101.3$ kPa and $T = 900$ K).

It should be noted that due to the endothermic nature of the dry reforming of methane (Eq. (1)) and the mildly exothermic nature of the WGS reaction (Eq. (3)), the amount of CO becomes significant at high operating temperatures [18]. All reactions are employed to examine the thermodynamic possibility of carbon formation by calculating the values of their carbon activities (α_c)
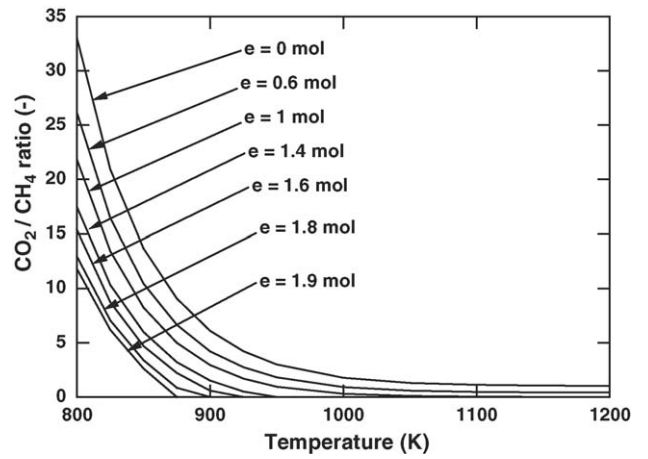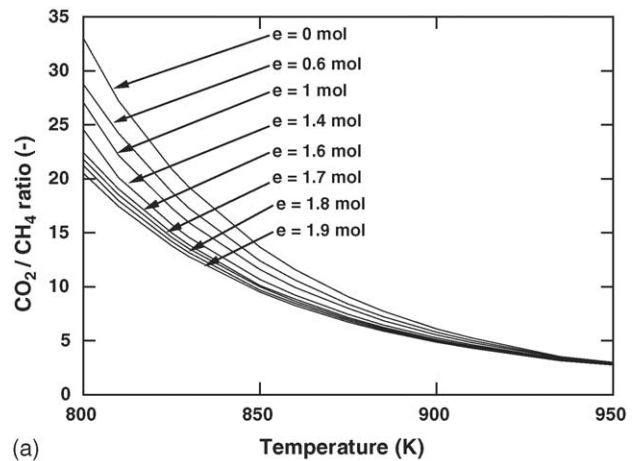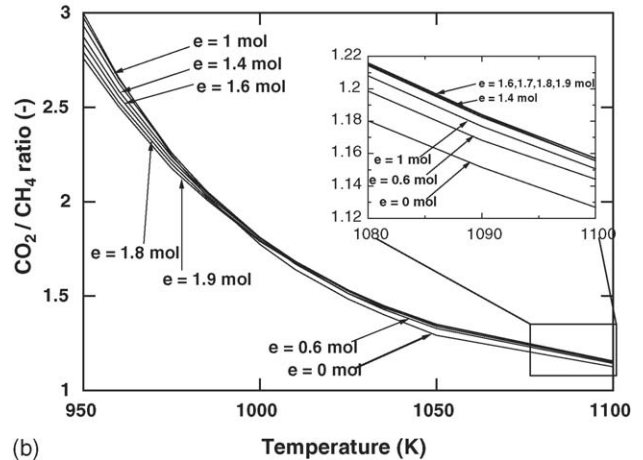

Fig. 5. Influence of the extent of the electrochemical reaction of H_2 on the requirement of the inlet CO_2/CH_4 ratio at different operating temperature (SOFC-O^{2-}, $a = 1$ mol and $P = 101.3$ kPa).

as defined in Eqs. (19)–(21).

$$\alpha_{c,CO} = \frac{K_1 p_{CO}^2}{p_{CO_2}} \tag{19}$$

(a)

(b)

Fig. 6. Influence of the extent of electrochemical reaction of H_2 on the requirement of inlet CO_2/CH_4 ratio at different operating temperature: (a) $T = 800$–950 K and (b) 950–1100 K (SOFC-H^+, $a = 1$ mol and $P = 101.3$ kPa).

$$\alpha_{c,CH_4} = \frac{K_2 p_{CH_4}}{p_{H_2}^2} \tag{20}$$

$$\alpha_{c,CO-H_2} = \frac{K_3 p_{CO} p_{H_2}}{p_{H_2O}} \tag{21}$$

where K_1, K_2 and K_3 represent the equilibrium constants of the reactions (16)–(18), respectively, and p_i represents 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 $\alpha_c = 1$. It is noted that the carbon activity is only the indicator for the presence of carbon in the system. It does not give the information regarding the amount of carbon formed. Finally, when $\alpha_c < 1$, carbon formation is thermodynamically impossible.

To find the range of SOFC operation which does not suffer from the carbon formation, the operating temperature and the extent of the electrochemical reaction of hydrogen are specified. Then, the initial value of the CO_2/CH_4 ratio is varied and the corresponding values of α_c are calculated. The carbon formation boundary is defined as the value of CO_2/CH_4 ratio whose value of $(1 - \alpha_c)$ is approaching zero. This value represents the minimum inlet CO_2/CH_4 ratio at which carbon formation in the equilibrium mixture is thermodynamically impossible. When

the inlet CO_2/CH_4 ratio is fixed at a certain value and water is added to the feed for the purpose of suppressing the carbon formation, the same calculation procedure can be applied to find the value of H_2O/CH_4 ratio whose value of $(1 - \alpha_c)$ is approaching zero. When air is employed instead of water, the calculation is carried out by assuming the complete combustion of oxygen in air with methane to yield water and carbon dioxide. Then the obtained feed composition is used to calculate the carbon activity. The value of air/CH_4 ratio is varied until the value of $(1 - \alpha_c)$ approaching zero is obtained.

It should be noted that although recent investigators have estimated the carbon concentration in the reforming reactions by the method of Gibbs energy minimization [19], the principle of equilibrated gas to predict the carbon formation in this study is still meaningful since the calculations are carried to find the carbon formation boundary where the carbon just begins to form. In addition, other factors such as mass and heat transfer or rate of reactions may also affect the prediction of the carbon formation boundary. Local compositions which allow the local carbon formation may exist, although the carbon formation is unfavorable according to the calculations based on equilibrium bulk compositions. Moreover, other forms of carbonaceous compounds such as C_nH_m may be formed and result in comparable damages.
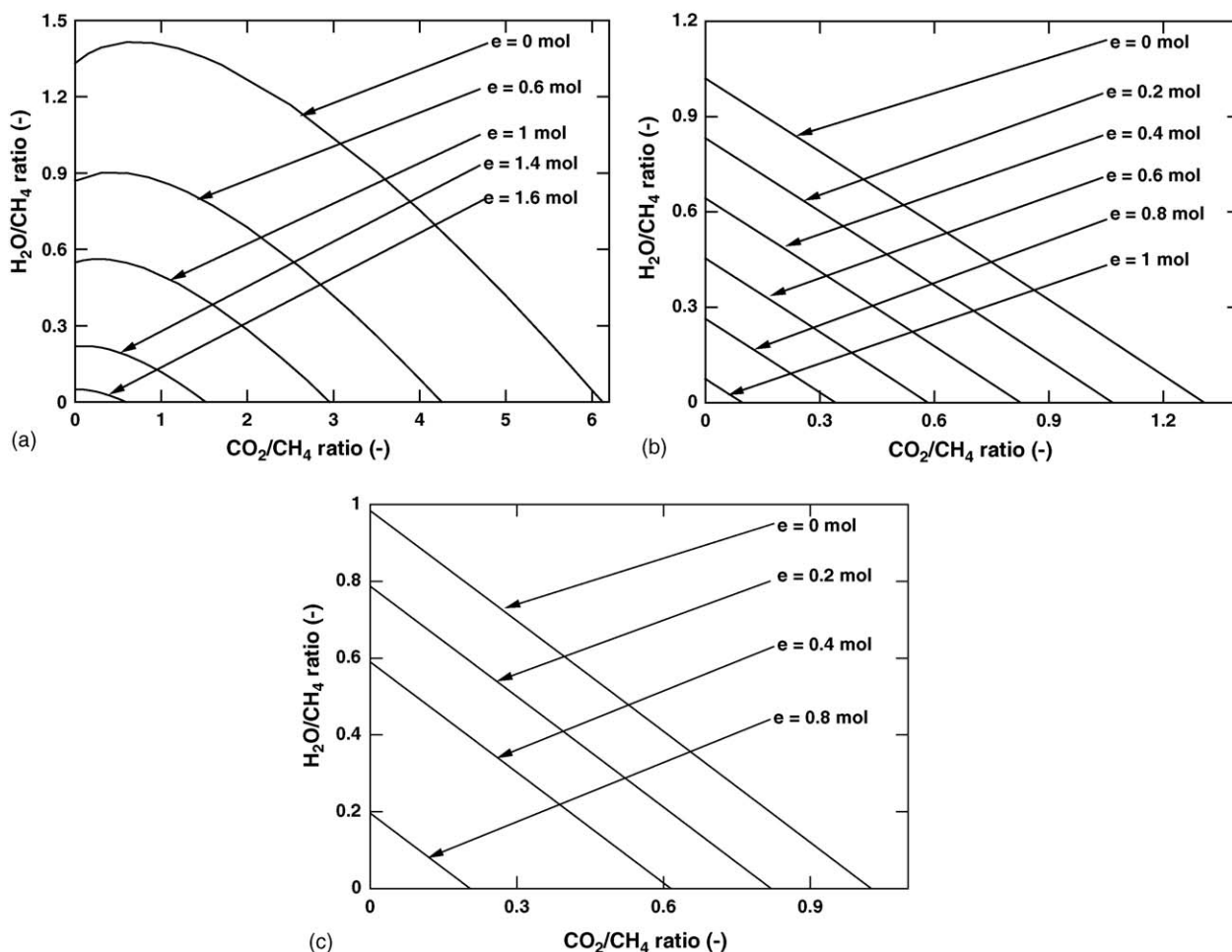

Fig. 7. Required inlet H_2O/CH_4 ratio at different inlet CO_2/CH_4 ratios: (a) $T = 900$ K, (b) $T = 1050$ K and (c) $T = 1200$ K (SOFC-O^{2-}, $a = 1$ mol and $P = 101.3$ kPa).

3. Results and discussion

The influences of the inlet CO_2/CH_4 ratio on equilibrium composition of the dry reforming reaction in a conventional reactor at the isothermal condition ($T = 900$ K) are shown in Fig. 2. It was found that the amounts of carbon monoxide and hydrogen increased with increasing moles of carbon dioxide in the feed, and that some hydrogen was converted to water particularly at high CO_2/CH_4 ratios due to the reverse water gas shift reaction (RWGS) and methanation reaction (reverse steam reforming of methane). However, at higher operating temperatures, the contribution of the methanation reaction was much less pronounced due to the high value of the equilibrium constant of the steam reforming of methane as shown in Fig. 1. It should be noted that some methane still existed even with high CO_2/CH_4 ratios at a moderate temperature of 900 K. For SOFC-O^{2-} operation, hydrogen was electrochemically consumed and water was generated in the anode chamber. It is shown in Fig. 3(a) that negligible amount of methane was observed because the consumption of hydrogen moved the dry reforming of methane forward and, in addition, the steam reforming of methane promoted the methane consumption. When the extent of carbon dioxide in the feed was increased, a lower amount of hydro-

gen and a higher amount of water were observed according to the RWGS reaction. For SOFC-H^+ operation, hydrogen was also electrochemically consumed; however, the electrochemical water appeared in the cathode chamber and played no role in the anode reactions unlike in the SOFC-O^{2-}. It should be noted that the SOFC-H^+ behaved quite similarly to a membrane reactor in which the forward reaction is enhanced by removing some products (e.g., hydrogen) from the reaction zone. From Fig. 3(b), it was observed that the amounts of hydrogen and water involved in the SOFC-H^+ were much less than those in the SOFC-O^{2-}. Moreover, when higher amount of carbon dioxide was added in the feed, more hydrogen was converted to water and a slight increase of carbon monoxide was observed.

The effect of the inlet CO_2/CH_4 ratio on the carbon activity for the conventional reformer is shown in Fig. 4. The carbon activity decreased dramatically with increasing CO_2/CH_4 ratio and operating temperature, implying that the chance of carbon formation can be rapidly decreased by adding CO_2 to the system or operating the system at a high temperature. Increasing the amount of CO_2 in the feed promoted the consumption of methane and generation of water, which reduced the possibility of carbon formation. Because the Boudard (Eq. (16)) and reverse carbon gasification (Eq. (18)) reactions are exothermic,
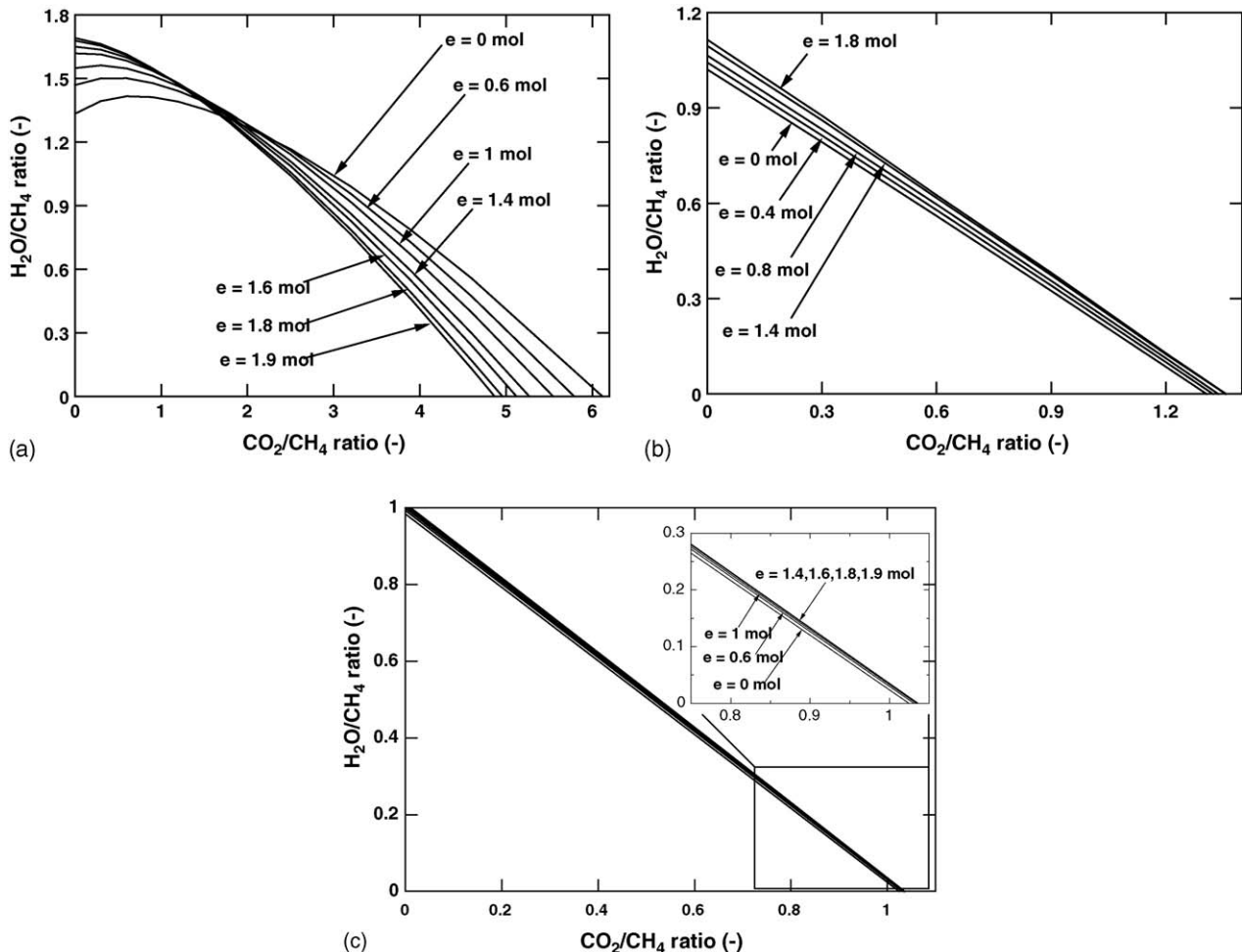

Fig. 8. Required inlet H_2O/CH_4 ratio at different inlet CO_2/CH_4 ratios: (a) $T = 900$ K, (b) $T = 1050$ K and (c) $T = 1200$ K (SOFC-H^+, $a = 1$ mol and $P = 101.3$ kPa).

the carbon activity was significantly reduced at high operating temperatures. Although the carbon formation from methane cracking (Eq. (17)) should be more significant at high temperature, the much higher values of the equilibrium constants of the dry and steam reforming reactions compared to that of the methane cracking make it become less likely at high operating temperatures (see Fig. 1). It should be noted that the carbon activity calculated from Eqs. (19)–(21) yield the same value, which is in good agreement with previous literature [11,20]. Fig. 5 shows the required CO_2/CH_4 ratio at the boundary of carbon formation for the SOFC-O^{2-} at different temperatures and extent of electrochemical reaction of hydrogen (e). Lower CO_2/CH_4 is required for the SOFC-O^{2-} compared to that of the conventional reformer due to the presence of electrochemical water in the anode chamber. The difference was particularly pronounced at for a higher extent of the electrochemical reaction. For the SOFC-H^+, at moderate operating temperatures (T = 800–1000 K) when the extent of the electrochemical reaction (e) was increased, the lower CO_2/CH_4 ratio was sufficient to alleviate carbon formation as shown in Fig. 6(a). However, the opposite trend was observed at higher operating temperatures (T > 1000 K) as shown in Fig. 6(b). The trend at lower operating temperatures was quite unusual as it has been reported

earlier for the systems of the steam reforming of methane [11] and methanol [12] that a higher H_2O/fuel ratio was required at the higher extent of electrochemical reaction because hydrogen was consumed and no benefit of electrochemical water was realized in the anode gas mixture in the SOFC-H^+. In addition, there was a general concern in using a membrane reactor for dehydrogenation reactions where the carbon formation problem could be more severe due to the removal of hydrogen from the reaction system. Therefore, it is likely that for the SOFC-H^+, more carbon dioxide would be needed when the extent of the electrochemical reaction is higher in the dry reforming system.

To explain the reasons for the unusual behavior of the dry reforming of methane in the SOFC-H^+ at moderate temperatures (800–1000 K), the moles of each species at different CO_2/CH_4 ratios at T = 900 K for the conventional reactor (Fig. 2) and the SOFC-H^+ (Fig. 3(b)) were compared. Note that because the carbon activity of all the possible carbon formation reactions provided the same value when the gas mixtures are at their equilibrium conditions, for simplicity the carbon activity based on the Boudard reaction (Eq. (19)) is considered as an example for understanding the behavior of the system when carbon dioxide is added to the system. From the figures, when hydrogen was electrochemically removed from the anode gas mixture, the dry
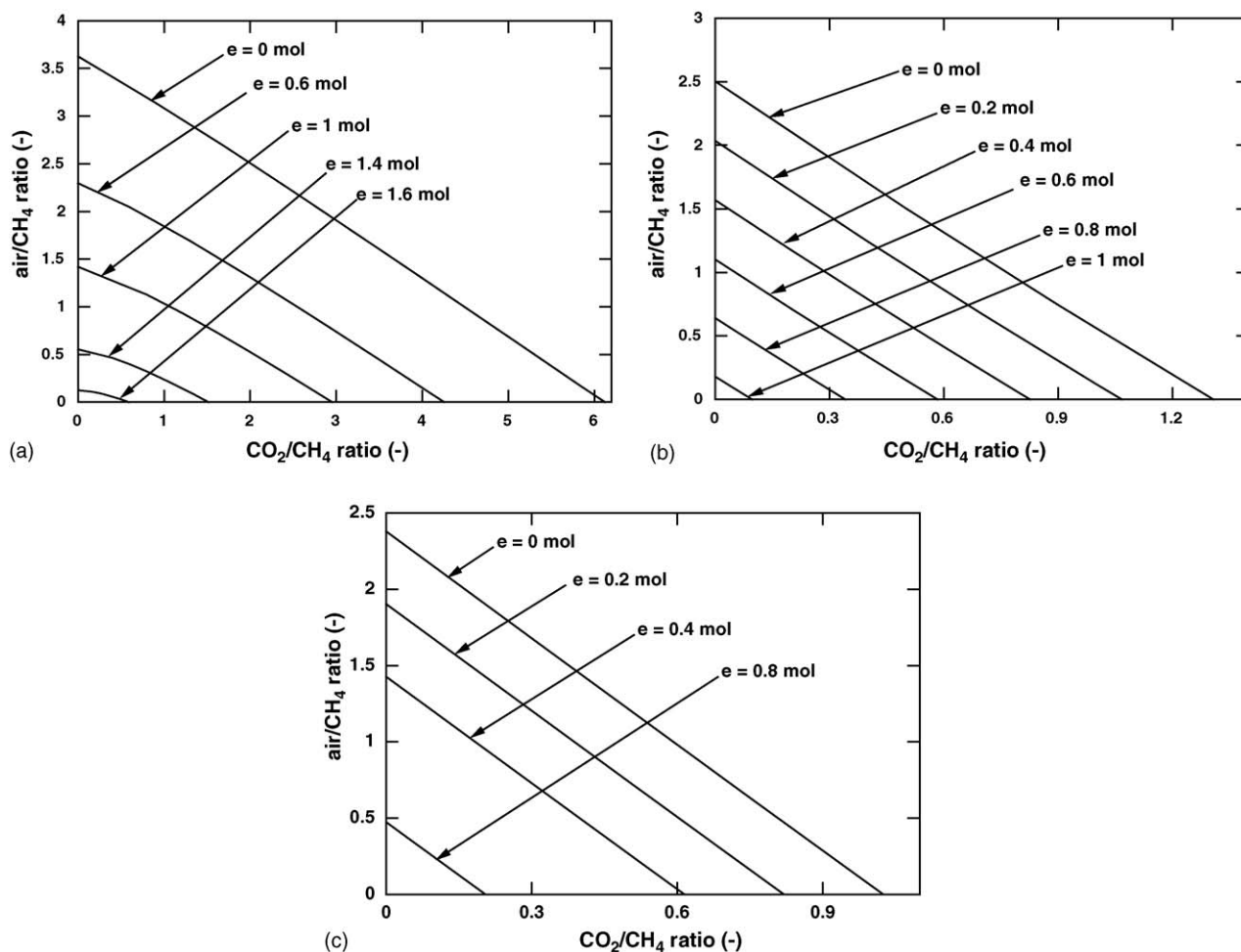

Fig. 9. Required inlet air/CH_4 ratio at different inlet CO_2/CH_4 ratios: (a) T = 900 K, (b) T = 1050 K and (c) T = 1200 K (SOFC-O^{2-}, a = 1 mol and P = 101.3 kPa).

reforming of methane moved forward, resulting in a low content of CH_4 in the gas mixture. It is observed that the moles of CO in the gas mixture for the SOFC-H$^+$ were less dependent on the CO_2/CH_4 ratio than for the conventional reactor because the RWGS played a less significant role when smaller amounts of hydrogen was present in the system. Consequently, the value of the carbon activity ($K_1 p_{CO}^2/p_{CO_2}$) for the SOFC-H$^+$ decreased with increase of the CO_2/CH_4 ratio more rapidly than that for the conventional reactor and, therefore, reached the boundary of carbon formation ($\alpha_c = 1$) at a lower value of CO_2/CH_4 ratios.

In practical operation, carbon dioxide is unlikely to be added to the system to suppress carbon formation. Other components such as water and air are more practical additive choices. The calculations were carried out to find the required H_2O/CH_4 or air/CH_4 ratio for different inlet CO_2/CH_4 ratios, the extent of the electrochemical reaction and the operating temperature. This information is important for selecting a suitable feed composition which avoids the carbon formation problem. Figs. 7 and 8 show the H_2O/CH_4 ratio at the boundary of carbon formation for different CO_2/CH_4 ratios in the feed for SOFC-O^{2-} and SOFC-H$^+$, respectively. It was found that for the SOFC-O^{2-}, the required H_2O/CH_4 ratio decreased with the increases of inlet CO_2/CH_4 ratio, extent of electrochemical reaction and operating temperature. The operation at a high extent of the electrochemi-

cal reaction and high temperature significantly reduced the risk of carbon formation. For the SOFC-H$^+$, the required H_2O/CH_4 ratio also decreased with increase of the inlet CO_2/CH_4 ratio and operating temperature. Higher H_2O/CH_4 ratios were required at higher extents of the electrochemical reaction. However, the reverse trend was observed when the system was operated at a moderate operating temperature ($T = 900$ K) with high inlet CO_2/CH_4 ratio (approximately higher than 1.5) which is in good agreement with the previous case in which only carbon dioxide was used as the carbon suppresser. When comparing between the required H_2O/CH_4 ratio for the case with no carbon dioxide present in the inlet feed (CO_2/CH_4 ratio = 0) and the required CO_2/CH_4 of the case without the addition of water for both SOFC-O^{2-} and SOFC-H$^+$, it is clear that water showed a more pronounced influence on inhibiting the carbon formation than carbon dioxide particularly at low operating temperatures. The results also revealed that for the SOFC-H$^+$ the extent of the electrochemical reaction had no significant effect on the required H_2O/CH_4 ratio at high temperatures. It should be noted that when comparing between the dry reforming and the steam reforming of methane with addition of carbon dioxide and water, respectively, as the components for inhibiting the carbon formation, the addition of water always provided a beneficial effect to the system as water reacted with methane to reduce the extent
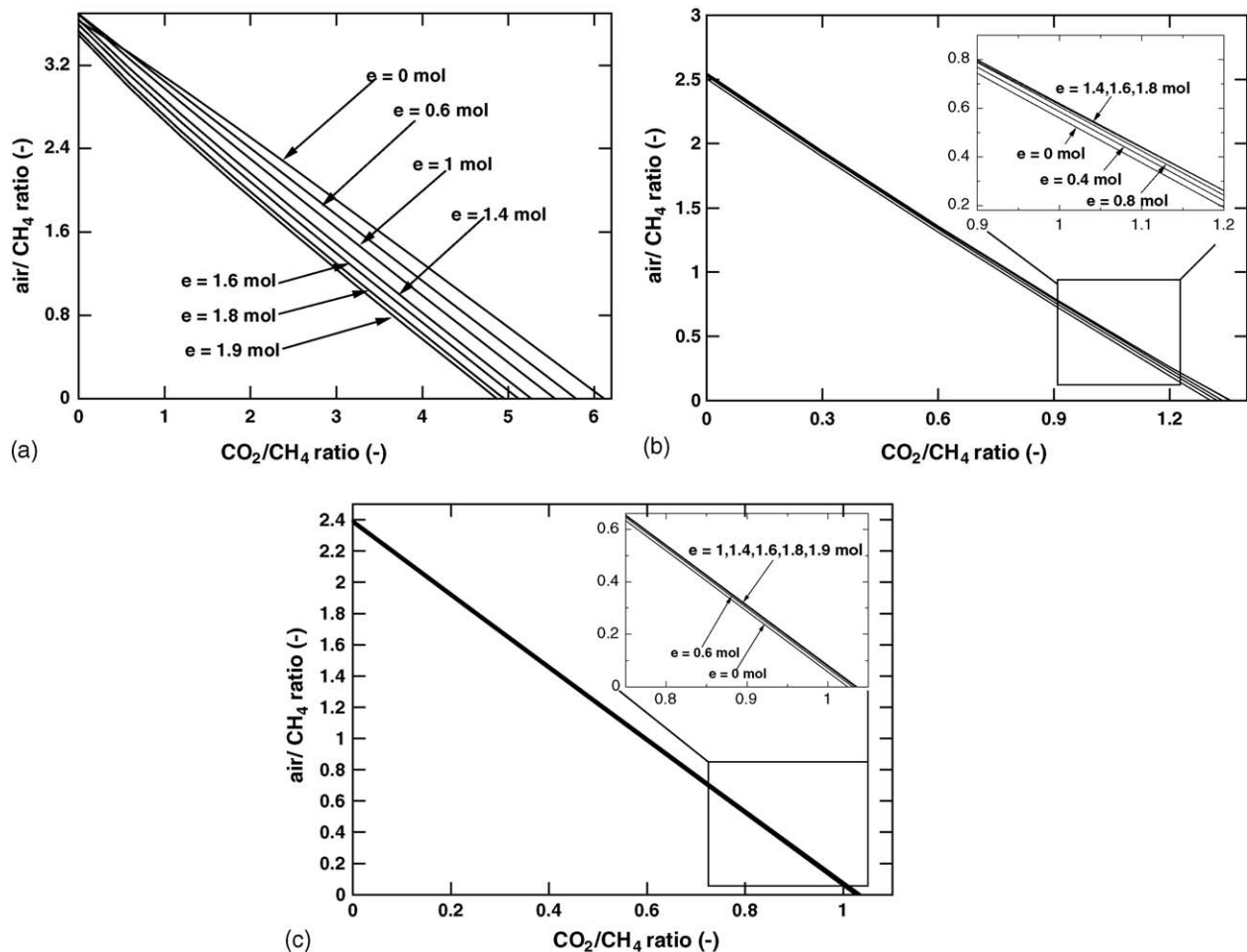

Fig. 10. Required inlet air/CH_4 ratio at different inlet CO_2/CH_4 ratios: (a) $T = 900$ K, (b) $T = 1050$ K and (c) $T = 1200$ K (SOFC-H$^+$, $a = 1$ mol and $P = 101.3$ kPa).

of methane and with carbon monoxide to reduce the extent of carbon monoxide, forming hydrogen and carbon dioxide. The presence of high amounts of carbon dioxide, hydrogen and water was important in preventing the carbon formation in the system. For the case of addition of carbon dioxide, although extra carbon dioxide promoted the consumption of methane from the dry reforming reaction, unlike water, carbon dioxide did not help reduce the extent of carbon monoxide in the system. In addition, more carbon monoxide could be generated by the RWGS reaction.

When air is used as an alternative oxidant for preventing carbon formation, oxygen in air can react with methane, carbon monoxide or hydrogen whose products are beneficial for preventing the carbon formation. Figs. 9 and 10 show the required air/CH_4 ratios for the SOFC-O^{2-} and SOFC-H^+, respectively. It was found that the similar trend as that of the addition of water was observed for both cases. It should be noted that, the advantage of air addition, that although the presence of nitrogen diluted the partial pressure of hydrogen in the anode gas mixture, which resulted in lower fuel cell performance, the exothermic heat from the oxidation reactions was useful for the endothermic dry reforming reaction in the system.

4. Conclusion

Thermodynamic analysis was employed to predict the boundary of carbon formation for DIR-SOFCs. The required CO_2/CH_4 ratio to prevent carbon formation has been determined by varying the operating temperature, electrolyte type and the extent of the electrochemical reaction. Operation at high temperatures dramatically reduced the required inlet CO_2/CH_4 ratio. The benefit of the presence of electrochemical H_2O in the anode chamber on suppression of carbon formation was realized in the SOFC-O^{2-} which resulted in a lower requirement for the CO_2/CH_4 ratio. For the SOFC-H^+, due to the disappearance of H_2 without gaining the benefit of the electrochemical H_2O in the anode chamber, a higher CO_2/CH_4 ratio was necessary. However, at moderate temperatures ($T = 800–1000$ K) an unexpected and opposite trend was observed. The additions of water and air to a feed with a certain inlet CO_2/CH_4 ratio were considered as alternative strategies for suppressing the carbon formation. Water was a more effective choice than CO_2 particularly at low temperatures. Although air is less attractive to water, the benefit of the exothermic heat from the reactions with oxygen may make the system more practical.

It should be noted that although the thermodynamic calculations can be used to predict the boundary of carbon formation, the deactivation of the anode is not solely the result of the deposition of carbon. Deposition of other forms of carbonaceous compounds such as polymeric coke (C_nH_m) may result in comparable damage. Therefore, the results obtained in this study should be considered only as a crude guideline for selecting suitable operating conditions for SOFCs and other related reactors.

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