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Short communication

Comparison of carbon formation boundary in different modes of solid oxide fuel cells fueled by methane

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Abstract

A detailed thermodynamic analysis is employed as a tool for prediction of carbon formation boundary for solid oxide fuel cells (SOFCs) fueled by methane. Three operating modes of SOFCs, i.e. external reforming (ER), indirect internal reforming (IIR) and direct internal reforming (DIR), are considered. The carbon formation boundary is determined by finding the value of inlet steam/methane (H_2O/CH_4) ratio whose equilibrium gas composition provides the value of carbon activity of one. It was found that the minimum H_2O/CH_4 ratio requirement for which the carbon formation is thermodynamically unfavorable decreases with increasing temperature. For SOFCs with the oxygen-conducting electrolyte, ER-SOFC and IIR-SOFC show the same values of H_2O/CH_4 ratio at the carbon formation boundary, independent of the extent of electrochemical reaction of hydrogen. In contrast, due to the presence of extra H_2O from the electrochemical reaction at the anode chamber, DIR-SOFC can be operated at lower values of the H_2O/CH_4 ratio compared to the other modes. The difference becomes more pronounced at higher values of the extent of electrochemical reaction.

For comparison purpose, SOFCs with the hydrogen-conducting electrolyte were also investigated. According to the study, they were observed to be impractical for use, regarding to the tendency of carbon formation. Higher values of the H_2O/CH_4 ratio are required for the hydrogen-conducting electrolyte, which is mainly due to the difference in location of water formed by the electrochemical reaction at the electrodes. In addition, with this type of electrolyte, the required H_2O/CH_4 ratio is independent on the SOFC operation modes. From the study, DIR-SOFC with the oxygen-conducting electrolyte seems to be the promising choice for operation.
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1. Introduction

Solid oxide fuel cell (SOFC) is an energy conversion unit that produces electrical energy and heat with greater energy efficiency and lower pollutant emission than the conventional heat engines, steam and gas turbines, and combined cycles. Due to its high operating temperature, SOFC offers the widest potential range of applications, flexibility of fuel choices and

possibility for operation with an internal reformer. Recent developments on SOFCs seem to move towards to two main issues: intermediate temperature operation and use of other fuels instead of hydrogen. The uses of various alternative fuels, i.e. methane, methanol, ethanol, gasoline and other oil derivatives, in SOFCs have been widely investigated [1–3]. To date, methane is a promising fuel as it is an abundant component in natural gas and the methane steam reforming technology is relatively well established. As SOFC is operated at such a high temperature, methane can be reformed effectively by either catalytic steam reforming or partial oxi-

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Nomenclature

a	inlet moles of methane (mol)
b	inlet moles of steam (mol)
c	extent of the electrochemical reaction of hydrogen (mol)
K_1	equilibrium constant of reaction (25) (kPa^{-1})
K_2	equilibrium constant of reaction (26) (kPa)
K_3	equilibrium constant of reaction (27) (kPa^{-1})
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)

Subscripts

R	reforming chamber
F	fuel cell chamber

Greek letter

α_c	carbon activity

dation to produce a H_2/CO rich gas, which is eventually used to generate the electrical energy and heat. However, several major problems remain to be solved before such SOFCs can be routinely operated on the direct feed of alternative fuels other than hydrogen. One of them is the problem of carbon deposition on the anode, causing loss of active site and cell performance as well as poor durability. The growth of carbon filaments attached to anode crystallites can generate massive forces within the electrode structure leading to its 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 in order to lower the rate of carbon formation. For example, the addition of molybdenum and ceria-based materials to Ni-based anode was reported to reduce carbon deposition, and in some cases, to increase the fuel conversion [5,6]. Addition of alkali, 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].

For the steam reforming, addition of extra steam to the feed is a conventional approach to avoid carbon deposition. Selection of a suitable steam/hydrocarbon ratio becomes an important issue. Carbon formation can occur when the SOFC is operated at low steam/hydrocarbon ratio. However, use of high steam/hydrocarbon ratio is unattractive as it lowers the electrical efficiency of the SOFC by steam dilution of fuel and the system efficiency [6]. Consequently, it is necessary to optimize the suitable steam/hydrocarbon ratio at the carbon

formation boundary whose value represents the minimum steam/hydrocarbon ratio required to operate the SOFC at carbon-free condition. Our previous works employed thermodynamic calculations to predict the required steam/alcohol ratio for direct internal reforming SOFCs fed by ethanol [8] and methanol [9]. It was found that the SOFCs with an oxygen-conducting electrolyte require less steam/alcohol ratio than that with a hydrogen-conducting electrolyte because extra steam generated from the electrochemical reaction is available for use in the anode chamber.

In this paper, a detailed thermodynamic analysis is carried out to predict the carbon formation boundary for SOFCs fueled by methane. Three operating modes of SOFCs, i.e. external reforming (ER), indirect internal reforming (IIR) and direct internal reforming (DIR), with two electrolyte types, i.e. oxygen- and hydrogen-conducting electrolytes, are investigated to compare the required steam/methane (H_2O/CH_4) ratios between different SOFC operating modes.

2. Theory

The main reactions involved in the production of hydrogen from methane and water are the methane steam reforming and water gas shift reactions as shown in Eqs. (1) and (2), respectively.

$$CH_4 + H_2O = 3H_2 + CO \tag{1}$$

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

The former is strongly endothermic while the latter is mildly exothermic. Methane steam reforming is commercially operated at 1000–1100 K and 2.17–2.86 MPa over nickel based catalysts [10]. The feed contains steam in excess of the stoichiometric amount with H_2O/CH_4 molar ratios of 3–5 to prevent soot formation [11].

When SOFCs are operated with a fuel, such as hydrocarbon and alcohol, three modes of operation, i.e. external reforming SOFC (ER-SOFC), indirect internal reforming SOFC (IIR-SOFC) and direct internal reforming SOFC (DIR-SOFC) as shown in Fig. 1, are possible. For ER-SOFC operation, the endothermic steam reforming and the electrochemical reactions are operated separately in different units, and there is no direct heat transfer between both units. High energy supply to the outside reformer is required due to the high endothermic over this part. In contrast, for both IIR-SOFC and DIR-SOFC, the endothermic reaction from the steam reforming reaction and the exothermic reaction from the oxidation reaction are operated together in a single unit. Therefore, the requirement of a separate fuel reformer and energy supply to this unit can be eliminated. This configuration is expected to simplify the overall system design, making SOFC more attractive and efficient means of producing electrical power.

For IIR-SOFC, the reforming reaction occurs in the vicinity of the cell stack. This enables heat transfer from the fuel
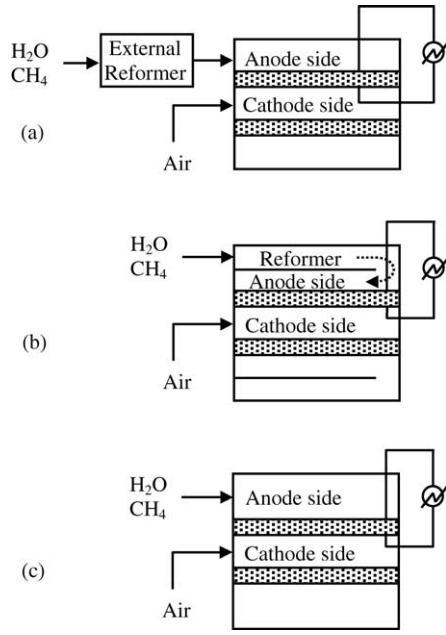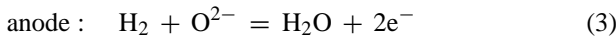
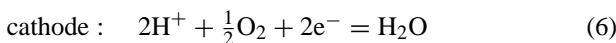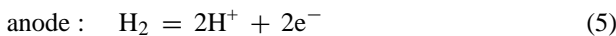Fig. 1. Configurations of various SOFC modes. (a) ER-SOFC, (b) IIR-SOFC and (c) DIR-SOFC.

cell chamber to the reformer, which leads to energetic economy. However, part of heat may not be efficiently utilized due to its limited heat transfer rate. For DIR operation, the reforming reaction takes place at the anode of the fuel cell. Heat and steam released from the electrochemical reaction upon power generation is effectively used for the endothermic reforming reaction since both processes take place simultaneously at the anode. Therefore, in term of energy aspect, DIR-SOFC is more attractive than the others. It should be noted that state-of-the-art SOFC nickel cermet anodes can provide sufficient activity for the steam reforming and shift reactions without the need for additional catalysts [4,12].

Two types of solid electrolytes can be employed in the SOFC, i.e. oxygen- and hydrogen-conducting electrolytes. The reactions taking place in the anode and the cathode can be summarized as follows:

- Oxygen-conduction electrolyte:

$$\text{anode}: \quad H_2 + O^{2-} = H_2O + 2e^- \tag{3}$$

$$\text{cathode}: \quad O_2 + 4e^- = 2O^{2-} \tag{4}$$

- Hydrogen-conducting electrolyte:

$$\text{anode}: \quad H_2 = 2H^+ + 2e^- \tag{5}$$

$$\text{cathode}: \quad 2H^+ + \tfrac{1}{2}O_2 + 2e^- = H_2O \tag{6}$$

The difference between both electrolyte types is the location of the water produced. With the oxygen-conducting electrolyte, water is produced in the reaction mixture in the anode chamber. In the case of the hydrogen-conducting electrolyte, water appears on the cathode side. The number of

moles of each component involved in different SOFC modes is discussed in the following sections.

2.1. ER-SOFC and IIR-SOFC

For ER-SOFC and IIR-SOFC, the methane steam reforming and water gas shift reaction take place initially at the reforming chamber. Then the exit gas from the reformer is fed to the fuel cell chamber where all the methane steam reforming, water gas shift reaction and electrochemical reactions occur. If required, additional water feed can be added to the reformer exit gas before being fed to the fuel cell chamber. The number of moles of each component is given by the following expressions:

- Reforming chamber

$$n_{CH_4} = a - x_R \tag{7}$$

$$n_{CO} = x_R - y_R \tag{8}$$

$$n_{CO_2} = y_R \tag{9}$$

$$n_{H_2} = 3x_R + y_R \tag{10}$$

$$n_{H_2O} = b_R - x_R - y_R \tag{11}$$

$$n_{total} = \sum_{i-1}^{5} n_i \tag{12}$$

where a and b_R represent the inlet moles of methane and water, respectively, and x_R and y_R are the converted moles in the reforming chamber associated to the reactions (1) and (2), respectively.

- Fuel cell chamber

$$n_{CH_4} = a - x_R - x_F \tag{13}$$

$$n_{CO} = x_R - y_R + x_F - y_F \tag{14}$$

$$n_{CO_2} = y_R + y_F \tag{15}$$

$$n_{H_2} = 3x_R + y_R + 3x_F + y_F - c \tag{16}$$

$$\begin{aligned} n_{H_2O} &= b_R - x_R - y_R + b_F - x_F - y_F \\ &\quad \text{(for hydrogen-conducting electrolyte)} \\ n_{H_2O} &= b_R - x_R - y_R + b_F - x_F - y_F + c \\ &\quad \text{(for oxygen-conducting electrolyte)} \end{aligned} \tag{17}$$

$$n_{total} = \sum_{i-1}^{5} n_i \tag{18}$$

where b_F is the additional mole of water fed to the fuel cell chamber, x_F and y_F the converted moles in the fuel cell chamber associated to the reactions (1) and (2), respectively and c is the extent of the electrochemical reaction of hydrogen. It should be noted that only hydrogen is assumed to react electrochemically with oxygen supplied from the cathode side. Then, the overall inlet H_2O/CH_4 ratio for these modes is equal to $(b_R + b_F)/a$.

2.2. DIR-SOFC

For DIR-SOFC, as described, there is no requirement of the separated reforming chamber in the system. All the reactions mentioned earlier take place simultaneously in the fuel cell chamber. The number of moles of each component is given by the following expressions:

$$n_{CH_4} = a - x_F \tag{19}$$

$$n_{CO} = x_F - y_F \tag{20}$$

$$n_{CO_2} = y_F \tag{21}$$

$$n_{H_2} = 3x_F + y_F - c \tag{22}$$

$$
\begin{aligned}
&n_{H_2O} = b_F - x_F - y_F + c\\
&\quad\text{(for oxygen-conducting electrolyte)}\\
&n_{H_2O} = b_F - x_F - y_F\\
&\quad\text{(for hydrogen-conducting electrolyte)}
\end{aligned} \tag{23}
$$

$$n_{total} = \sum_{i-1}^{5} n_i \tag{24}$$

Calculations of the thermodynamic equilibrium composition are accomplished by solving a system of non-linear equations relating 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 in the reaction system [13]:

$$2CO = CO_2 + C \tag{25}$$

$$CH_4 = 2H_2 + C \tag{26}$$

$$CO + H_2 = H_2O + C \tag{27}$$

The Boudard reaction (Eq. (25)) and the decomposition of methane (Eq. (26)) are the major pathways for carbon formation at high operating temperature [14]. It should be noted that due to the exothermic nature of the water gas shift reaction (Eq. (2)), the amount of CO becomes significant at high temperature [15]. All reactions are employed to examine the thermodynamic possibility of carbon formation. The carbon activities, defined in Eqs. (28)–(30), are used to determine the possibility of carbon formation.

$$\alpha_{c,CO} = K_1 \frac{p_{CO}^2}{p_{CO_2}} \tag{28}$$

$$\alpha_{c,CH_4} = K_2 \frac{p_{CH_4}}{p_{H_2}^2} \tag{29}$$

$$\alpha_{c,CO-H_2} = K_3 \frac{p_{CO} p_{H_2}}{p_{H_2O}} \tag{30}$$

where K_1, K_2 and K_3 represent the equilibrium constants of the reactions (25), (26) and (27), 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 $\alpha_c = 1$. 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.

In order to identify the range of SOFC operation, which does not suffer from the formation of carbon, the operating temperature and the extent of the electrochemical reaction of hydrogen are specified. Then the initial value of the H_2O/CH_4 ratio is varied and the corresponding values of α_c are calculated. The carbon formation boundary is defined as the value of H_2O/CH_4 whose value of $(1 - \alpha_c)$ is approaching zero. This value represents the minimum inlet H_2O/CH_4 mole ratio at which carbon formation in the equilibrium mixture is thermodynamically impossible. For ER-SOFC and IIR-SOFC, the calculations for both reformer and fuel cell chambers are required. It should be noted that although recent investigators estimated the carbon concentration in the steam reforming reactions by the method of Gibbs energy minimization, the principle of equilibrated gas to predict the carbon formation in this study is still meaningful because the calculations are carried in order to determine the carbon formation boundary where the carbon starts forming on the surface. In addition, other possible 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 calculation based on equilibrium bulk compositions. Moreover, other forms of carbonaceous compounds such as C_nH_m may be formed and result in comparable damages.

3. Results and discussion

The influence of inlet steam/methane (H_2O/CH_4) ratio on equilibrium composition of species at the reformer section was firstly carried out as illustrated in Fig. 2. The molar fractions of CO_2, H_2O and H_2 increased with increasing the inlet steam/methane ratio, whereas the decrease in CO production
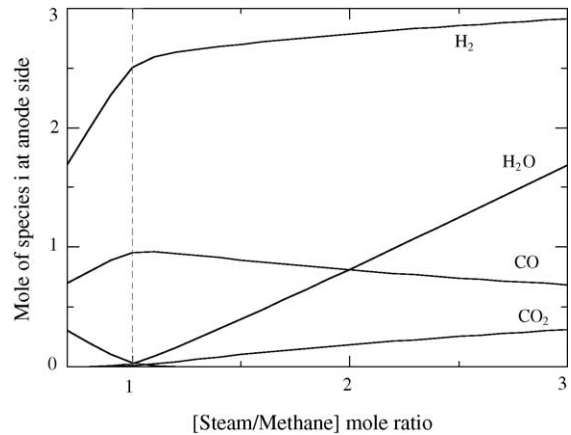

Fig. 2. Effect of inlet H_2O/CH_4 ratio on each component mole in the reformer ($a = 1$ mol, $P = 101.3$ kPa and $T = 1173$ K).

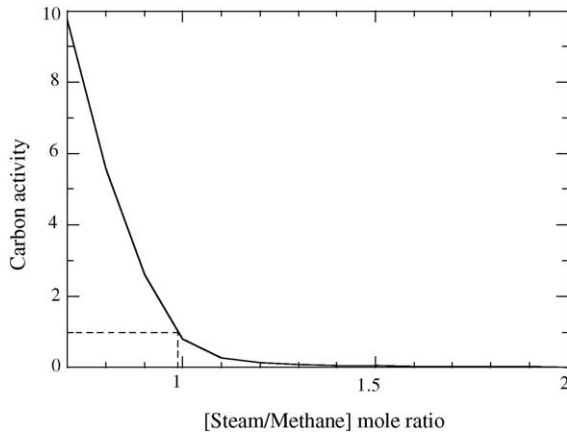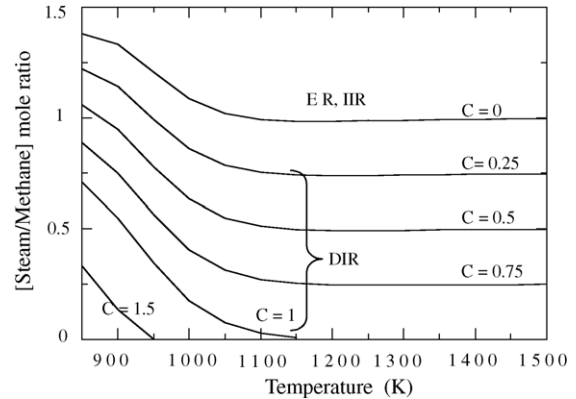Fig. 3. Effect of inlet H_2O/CH_4 ratio on carbon activity in the reformer ($a = 1$ mol, $P = 101.3$ kPa and $T = 1173$ K).

Fig. 4. Influence of the operation mode on the requirement of inlet H_2O/CH_4 ratio at different operating temperatures (oxygen-conducting electrolyte, $a = 1$ mol and $P = 101.3$ kPa).

is observed. Apparently, the increasing of inlet H_2O/CH_4 ratio moves both methane steam reforming (Eq. (1)) and water gas shift reaction (Eq. (2)) into the forward direction. The number of mole for methane is very small since it is the reactant of the endothermic reaction, which proceeds in great extent at high temperature. It should be noted that according to Eqs. (25)–(27), the presence of high molar fractions of CO_2, H_2 and H_2O is effective for preventing the carbon formation in the system.

Fig. 3 shows the influence of inlet H_2O/CH_4 ratio on the corresponding values of the carbon activity calculated from the equilibrium compositions. The initial high slope at the low H_2O/CH_4 ratio implies that the opportunity of the carbon formation is rapidly decreased with an addition of steam into the system. The carbon formation becomes thermodynamically unfavored, as the carbon activity is less than one, when the H_2O/CH_4 ratio is approximately greater than one. It is therefore indicated that the carbon formation is less likely as the H_2O/CH_4 ratio is increased. It should also be noted that the values of carbon activities calculated from Eqs. (28)–(30) are equal because the calculations are based on the gas phase compositions at equilibrium. This is also observed by other investigator [16].

Fig. 4 shows the H_2O/CH_4 ratio at the carbon formation boundary for typical SOFCs with the oxygen-conducting electrolyte for different operating modes and various extents of electrochemical reaction of hydrogen. It can be seen from the figure that the required inlet H_2O/CH_4 ratio for avoiding carbon formation decreases with increasing operating temperature and becomes constant at high temperature. This similar behavior was reported in our previous works with other types of fuel including ethanol [8] and methanol [9]. Therefore, raising the SOFC operating temperature is one possibility to prevent carbon formation at the anode, however, the cost of high temperature materials as well as the problem of cell sealing must also be considered. Comparison between different operating modes indicates that the required H_2O/CH_4 ratios for ER-SOFC and IIR-SOFC are the same, independent of the extent of electrochemical reaction

of hydrogen. In contrast, for DIR-SOFC, hydrogen from the electrochemical reaction is converted to steam at the anode side, where the reforming reaction simultaneously takes place and, consequently reduces the requirement of H_2O/CH_4 ratio in the feed. It is particularly pronounced when DIR-SOFC is operated at high current density. Nevertheless, due to the fact that DIR-SOFC requires anode material with sufficient catalytic activity for both reforming and electrochemical reactions whereas ER-SOFC and IIR-SOFC can employ two separated materials readily available for each reaction, ER-SOFC and IIR-SOFC may be preferred at the moment. In case that either ER-SOFC or IIR-SOFC with the oxygen-conducting electrolyte is employed, it should be noted that the damage from carbon deposition in the fuel cell chamber would be less likely, comparing to that in the reformer. Water produced from the electrochemical reaction in the fuel cell chamber in addition to the amount of water in the inlet stream, which is already adjusted to avoid the formation of carbon in the reformer, further decreases the possibility of carbon deposition in the fuel cell chamber.

For comparison, the requirement of H_2O/CH_4 ratios to prevent the carbon formation for ER-SOFC, IIR-SOFC, and DIR-SOFC with the hydrogen-conducting electrolyte are also carried out as shown in Fig. 5. Independent of the operating modes, more inlet steam is required when the cell is operated at high extents of electrochemical reaction of hydrogen. It should be noted that the benefit of steam generation at the cathode by the electrochemical reaction is not recognized for this system. The disappearance of hydrogen from the anode side by electrochemical reaction favors the carbon formation and, consequently required higher steam in order to prevent the formation of carbon species.

From the above results, DIR-SOFC with the oxygen-conducting electrolyte seems to be a promising operation mode due to the good heat utilization within the system and the reduction of inlet H_2O/CH_4 ratio requirement. This summary is in contrast to one previous work, which reported that the SOFC with the hydrogen-conducting electrolyte provides higher electrical efficiency than that with the oxygen-
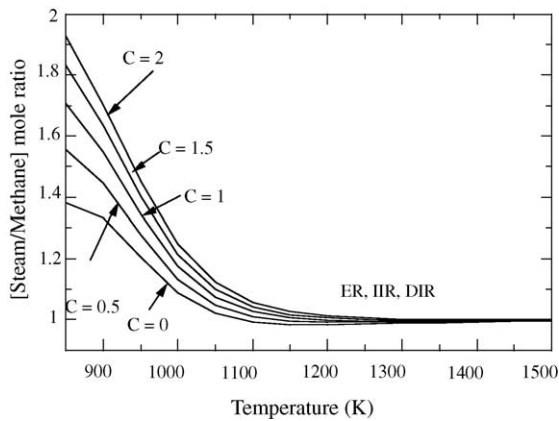
Fig. 5. Influence of operation mode on the requirement of inlet H_2O/CH_4 ratio at different operating temperatures (hydrogen-conducting electrolyte, $a = 1$ mol and $P = 101.3$ kPa).

conducting electrolyte because high partial of hydrogen is maintained at the anode side [17]. However, since the comparison in that work was based on the calculations using the same value of inlet H_2O/CH_4 ratio, the benefit from the reduced steam requirement was not taken into account. This subject will be discussed in more details in our next paper dealing with the efficiency of the overall SOFC system.

4. Conclusion

Theoretical thermodynamic analysis was performed to predict the carbon formation boundary for the SOFCs with different operating modes. It was observed that the required H_2O/CH_4 ratio to prevent the carbon formation mainly depended on the operating temperature, SOFC operation mode, and electrolyte type. In general, operation at high temperature reduces the required inlet H_2O/CH_4 ratio in all cases. The oxygen-conducting electrolyte is more attractive than the hydrogen-conducting electrolyte as the former system requires less steam. This is directly related to water generated from the electrochemical reaction of hydrogen at electrodes. The difference in steam requirement is particularly pronounced at high extent of the electrochemical reaction of hydrogen. The required H_2O/CH_4 ratio is independent of the SOFC operating modes for those with the hydrogen-conducting electrolyte. On the other hand, for the SOFC with the oxygen-conducting electrolyte, DIR-SOFC requires less steam than both ER-SOFC and IIR-SOFC. In summary, the DIR-SOFC with the oxygen-conducting electrolyte seems to be a favorable choice for SOFC operation in the point of view of the amount of steam required.

It should be noted that although the thermodynamic calculations can be used to predict the minimum inlet H_2O/CH_4 ratio for which carbon formation is not favored, the deactivation of anode is not solely the result from 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 crude guideline for operating condition of SOFC.

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