Thermodynamic Analysis of Methane-fueled Solid Oxide Fuel Cells Considering CO Electrochemical Oxidation*

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Abstract Thermodynamic analyses in the literature have shown that solid oxide fuel cells (SOFC) with proton conducting electrolyte (H-SOFC) exhibited higher performance than SOFC with oxygen ion conducting electrolyte (O-SOFC). However, these studies only consider H₂ electrochemical oxidation and totally neglect the contribution of CO electrochemical oxidation in O-SOFC. In this short communication, a thermodynamic model is developed to compare the theoretically maximum efficiencies of H-SOFC and O-SOFC, considering electrochemical oxidation of CO in O-SOFC anode. It is found that O-SOFC exhibits higher maximum efficiency than H-SOFC due to the contribution from CO electrochemical oxidation, which is contrary to the common understanding of electrolyte effect on SOFC performance. The effects of operating temperature and fuel utilization factor on the theoretical efficiency of SOFC are also analyzed and discussed.

Keywords solid oxide fuel cell, thermodynamics, proton conductor, oxygen ion conductor, hydrocarbon fuels

1 INTRODUCTION

Solid oxide fuel cells (SOFC) have been identified as efficient and environmental-friendly electrochemical devices for power generation. Compared with low temperature fuel cells (such as proton exchange membrane fuel cells), one attraction of SOFC is their fuel flexibility. At typical working temperatures (i.e. 1073 K), hydrogen fuel or hydrocarbon fuels, such as methane and ethanol, can be utilized in SOFC for power generation as internal reforming of hydrocarbon fuels can occur in the

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porous anode of SOFC [1-4]. Electrolyte is a key component of SOFC and can be built
with oxygen ion conducting ceramics (i.e. yttria-stabilized zirconia, YSZ) or proton
conducting materials, such as BaCeO$_3$ doped with Gd or Nd. The use of different
electrolytes not only yields different ohmic losses, but also influences the mass transfer
in porous electrodes, as steam is produced in the cathode of H-SOFC, which in turn
impedes the diffusion of oxygen [5,6].

In order to clarify the differences between H-SOFC and O-SOFC and to identify
suitable electrolyte materials for SOFC operation, several thermodynamic analyses have
been performed for both H$_2$ and hydrocarbon fueled SOFCs. Demin and Tsiakaras were
the first who thermodynamically compared the maximum efficiencies of H-SOFC and
O-SOFC fed with hydrogen fuel [7]. It was found that the hydrogen fed H-SOFC had an
essential advantage as compared to O-SOFC, due to higher hydrogen concentration in
the anode of H-SOFC [7]. In a subsequent study, the model was extended to investigate
the methane fed H-SOFC and O-SOFC [8]. It was found that the maximum efficiency
of methane fed H-SOFC was evidently higher than that of O-SOFC [8,9]. In other
thermodynamic analyses of SOFCs fed with ethanol or ammonia fuels, it was also
observed that H-SOFC performed better than O-SOFC in terms of maximum efficiency
due to higher hydrogen concentration in the anode of H-SOFC [10-12].

However, in the above mentioned thermodynamic analyses on methane or
ethanol fed SOFCs, only H$_2$ electrochemical oxidation was considered while the
contribution of CO electrochemical oxidation to O-SOFC power generation was totally
neglected. From experiments, it has been confirmed that CO electrochemical oxidation
could occur in the anode of O-SOFC, although its reaction kinetics was slower than that
of H$_2$ electrochemical oxidation [13]. Since CO electrochemical oxidation in H-SOFC
would not occur, it is still unclear whether the methane fed H-SOFC is superior to O-
SOFC in terms of maximum efficiency if H$_2$ and CO electrochemical oxidation
reactions are considered for O-SOFC. In this short communication, a simple
thermodynamic model is developed to compare the maximum efficiencies of methane
fed H-SOFC and O-SOFC, considering CO electrochemical oxidation in the anode of
O-SOFC. Due to lack of experimental data, comparison of the present simulation results
with literature data is not provided. However, comparison can be easily made once the
relevant data are available.

2 THE MODEL
The present thermodynamic analyses are based on the assumption of chemical and electrochemical reactions. The working principles of the methane fed H-SOFC and O-SOFC are shown in Figs. 1(a) and 1(b), respectively. In operation, H₂O-CH₄ mixture at a molar ratio of 2:1 is supplied to the anode channel of SOFC while air is supplied to the cathode. In both H-SOFC and O-SOFC, direct internal reforming (DIR) and water gas shift reaction (WGSR) take place in the porous anode, as shown by Reactions (1) and (2) respectively:

\[
\begin{align*}
\text{CH}_4 + \text{H}_2\text{O} &\leftrightarrow \text{CO} + 3\text{H}_2 \\
\text{CO} + \text{H}_2\text{O} &\leftrightarrow \text{CO}_2 + \text{H}_2
\end{align*}
\] (1) (2)

\[
\begin{align*}
\text{Anode: } \text{H}_2 &\rightarrow 2\text{H}^+ + 2e^- \\
\text{Cathode: } 0.5\text{O}_2 + 2e^- + 2\text{H}^+ &\rightarrow \text{H}_2\text{O}
\end{align*}
\] (a)
Figure 1 Working principle of CH₄-fueled SOFC: (a) H-SOFC and (b) O-SOFC

2.1 H-SOFC

In the H-SOFC (Fig. 1a), H₂ molecules produced from DIR and WGSR diffuse through the porous anode to the anode-electrolyte interface, where they are oxidized to proton and electrons (Reaction 3). Subsequently, protons are transported to the cathode through the dense electrolyte while the electrons flow through the external circuit to the cathode side, where they react with oxygen molecules and protons to form steam (Reaction 4).

\[ \text{H}_2 \rightarrow 2\text{H}^+ + 2e^- \]  \hspace{1cm} (3)
\[ 0.5\text{O}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{H}_2\text{O} \]  \hspace{1cm} (4)

To evaluate the theoretically maximum efficiency of CH₄ fed SOFCs, the equilibrium potential is calculated. According to thermodynamics of fuel cells, the equilibrium potential of SOFC can be expressed as

\[ E_{\text{H}_2} = E_{\text{H}_2}^0 + \frac{RT}{2F} \ln \left[ \frac{P_{\text{H}_2}(P_{\text{O}_2})^{0.5}}{P_{\text{H}_2\text{O}}} \right] \]  \hspace{1cm} (5)
where $E^0$ is the voltage at standard pressures and can be calculated from the Gibbs free energy change. $P_{H_2}$, $P_{H_2O}$, and $P_{O_2}$ are the partial pressure (0.1 MPa) of hydrogen (anode), steam (cathode), and oxygen (cathode), respectively, $R$ is the ideal gas constant (8.3145 J·mol$^{-1}$·K$^{-1}$), $T$ is temperature (K), and $F$ is the Faraday constant (96485 C·mol$^{-1}$).

In order to calculate the equilibrium potential, the partial pressures of gas species must be obtained. The calculation procedures developed by Demin et al. [8] and Assabumrungrat et al. [11] are employed in this study. Both DIR and WGSR are assumed to be in equilibrium. Thus, the number of moles of gases reacted in DIR and WGSR can be determined by using the equilibrium constants [8,11]. Considering DIR, WGSR and electrochemical reaction, the number of moles ($n$) of each component at the SOFC outlet can be calculated as follows.

In the anode,

$$n_{CH_4} = a - x$$

$$n_{CO_2} = y$$

$$n_{H_2} = 3x + y - c$$

$$n_{CO} = x - y$$

$$n_{H_2O} = b - x - y$$

In the cathode,

$$n_{H_2O} = c$$

$$n_{O_2} = d - 0.5c$$

where $a=1/3$, $b=2/3$, and $d=0.21$ are the mole numbers of CH$_4$, H$_2$O, and O$_2$ at two inlets of SOFC, respectively. $c$ is the moles of H$_2$ electrochemically consumed (related to current generated and thus the fuel utilization). $x$ and $y$ are the number of moles of CH$_4$ and CO reacted in the DIR and WGSR reactions. The equilibrium constant of Reactions (1) and (2) are respectively:

$$K_{CH_4} = \frac{(P_{H_2})^3 \cdot P_{CO}}{P_{CH_4} \cdot P_{H_2O}}$$

$$K_{CO} = \frac{P_{CO_2} \cdot P_{H_2}}{P_{CO} \cdot P_{H_2O}}$$
where the partial pressures can be calculated very easily from Eq. (6) to Eq. (12). The equilibrium constant can also be calculated by

$$K = \exp(-\frac{\Delta G_i}{RT})$$  \hspace{1cm} (15)

where $\Delta G_i$ is the change of Gibbs free energy between products and reactants of chemical reaction at a standard state.

Based on the mass balance and the equilibrium constants, the partial pressures of gaseous species can be determined. Detailed information can be found in [8,11,12]. Then the equilibrium potential can be calculated, which is used in turn for subsequent calculation of the theoretical work output ($W$) as

$$W = qE$$  \hspace{1cm} (16)

where $q$ is the electrical charge generated from SOFC.

The maximum efficiency ($\eta$) of CH$_4$ fed SOFC can thus be calculated as

$$\eta(\%) = \frac{W}{-\Delta H^0} \times 100\%$$  \hspace{1cm} (17)

where $\Delta H^0$ is the formation enthalpy of CH$_4$ at standard condition. For H-SOFC, the efficiency is noted as $\eta_{HSOFC}$. The fuel utilization is defined as the ratio of consumed fuel (CH$_4$) to the feeding fuel, $x/a$, and the oxygen utilization similarly as $0.5c/d$.

### 2.2 O-SOFC

In the O-SOFC, O$_2$ molecules diffuse through the porous cathode to the cathode-electrolyte interface and react with electrons to produce oxygen ions (Reaction 18), which are transported through dense electrolyte to the anode side. At the anode, H$_2$ and CO molecules diffuse through the porous anode layer to the anode-electrolyte interface where they react with oxygen ions to produce electrons, H$_2$O and CO$_2$ (Reactions 19 and 20).

$$2e^- + 0.5O_2 \rightarrow O^{2-}$$  \hspace{1cm} (18)

$$H_2 + O^{2-} \rightarrow H_2O + 2e^-$$  \hspace{1cm} (19)

$$CO + O^{2-} \rightarrow CO_2 + 2e^-$$  \hspace{1cm} (20)

In the O-SOFC, both H$_2$ and CO are involved in the electrochemical reactions for power generation. The Nernst potential for H$_2$ electrochemical oxidation can be
determined by Eq. (5), except that the partial pressure of H$_2$O in the anode should be used. The Nernst potential for CO electrochemical oxidation can be determined by
\[
E_{\text{CO}} = E_{\text{CO}}^0 + \frac{RT}{2F} \ln \left( \frac{P_{\text{CO}} \left(P_{\text{O}_2}^0\right)^{0.5}}{P_{\text{CO}_2}} \right)
\]  
(21)
where $E_{\text{CO}}^0$ is the equilibrium potential at a standard pressure.

The electric power output from the O-SOFC can be calculated as
\[
W = q_{\text{CO}} E_{\text{CO}} + q_{\text{H}_2} E_{\text{H}_2}
\]  
(22)
where $q_{\text{CO}}$ is the electric current generated from CO electrochemical oxidation in O-SOFC. The maximum efficiency of O-SOFC ($\eta_{\text{O-SOFC}}$) can be determined with Eq. (17) but $W$ should be calculated from Eq. (22).

The rate of CO electrochemical oxidation in O-SOFC can be evaluated as $rc$, where $r$ is the ratio of CO oxidation rate to H$_2$ oxidation rate ($c$). According to experimental measurements by Matsuzaki and Yasuda [13], the rate of H$_2$ electrochemical oxidation is about 2-3 times that of CO electrochemical oxidation. Thus, the value of $r$ is set to be 0 to 1/3 in the present study. When $r$ is 0, the contribution from CO is neglected and the present study is reduced to the previous studies [11].

To determine the partial pressures of gaseous species in the O-SOFC, the similar approach for H-SOFC is adopted. The effects of electrochemical reaction, DIR and WGSR (Reactions (1) and (2)) on the molar fractions are all considered by using the parameters of $x$ and $y$, as can be seen from Eqs. (6) – (10) and Eqs. (23) – (27). Since steam is produced in the anode, the number of moles of gas species should be modified as follows.

In the anode,
\[
n_{\text{CH}_4} = a - x \quad (23)
\]
\[
n_{\text{CO}_2} = y + rc \quad (24)
\]
\[
n_{\text{H}_2} = 3x + y - c \quad (25)
\]
\[
n_{\text{CO}} = x - y - rc \quad (26)
\]
\[
n_{\text{H}_2O} = b - x - y + c \quad (27)
\]
In the cathode,
\[
n_{\text{O}_2} = d - 0.5c - 0.5rc \quad (28)
\]
2.3 Solution of models

The model is based on previous thermodynamic analyses [8,11,12]. The detailed methodology description can be found in refs. [11,12]. The number of moles of H₂O (b), CH₄ (a), and O₂ (d) are specified at the inlet. The unknowns x and y are dependent on the extent of steam reforming and water gas shift reactions, which are calculated based on reaction equilibrium. In the simulation, an oxygen utilization factor ((0.5c+0.5rc)/d for O-SOFC and 0.5c/d for H-SOFC) of 20% is used while the fuel utilization factor x/a is varied to calculate the theoretically maximum efficiency [8,11,12].

3 RESULTS AND DISCUSSION

In this section, parametric simulations are performed to compare the maximum efficiencies of H-SOFC and O-SOFC running on methane fuel. In this study, the operating temperature (T) and the value of r are varied to examine their effects on the theoretically maximum efficiency of SOFC running on CH₄.

3.1 Effect of CO electrochemical oxidation rate

The value of r is varied from 0 to 1/3 to examine the effect of CO electrochemical oxidation rate on O-SOFC efficiency. Simulations are performed at an operating temperature of 873 K and an oxygen utilization factor of 20%. As can be seen from Fig. 2, the maximum efficiency of O-SOFC is lower than that of H-SOFC at r = 0, when the electrochemical oxidation of CO is excluded. The result is consistent with the previous thermodynamic analysis by Demin et al. [8]. The higher efficiency of H-SOFC than O-SOFC is due to the fact that the fuel-diluting steam is produced in the cathode of H-SOFC, thus the hydrogen molar fraction in the anode of H-SOFC is higher than that of O-SOFC. This results in higher Nernst potential of H-SOFC, leading to higher maximum efficiency of H-SOFC than O-SOFC. However, when CO electrochemical oxidation is included in O-SOFC, more electrochemical power can be produced from O-SOFC, as can be seen from Eq. (22). Thus, the maximum efficiency of O-SOFC is considerably higher than that of H-SOFC, even at a low r of only 1/6. In addition, this difference increases with increasing r, as more CO is involved in electrochemical reaction for power generation from O-SOFC. This finding is different from our common understanding that H-SOFC is always better than O-SOFC in terms of maximum efficiency [7-12]. At a higher fuel utilization, the difference between different scenarios becomes more obvious, which is consistent with the previous
thermodynamic analyses [8,12]. The larger advantage of O-SOFC over H-SOFC at a high fuel utilization is caused by the fact that more CO is involved in electrochemical reaction in O-SOFC.

Figure 2 Efficiencies of H-SOFC and O-SOFC with different reaction rate of CO

3.2 Effect of operating temperature

The effect of operating temperature on SOFC maximum efficiency is simulated and the results are shown in Fig. 3. The maximum efficiencies of both O-SOFC and H-SOFC decrease considerably as temperature is increased from 873 K to 1273 K, especially at high fuel utilization factors. This is mainly caused by a decrease in equilibrium potential at standard pressure ($E_{H_2}^0$ and $E_{CO}^0$) with increasing temperature, which in turn tends to decrease the power generation and efficiency at a given fuel utilization factor.
To further elucidate the difference between O-SOFC and H-SOFC, the efficiency differences between H-SOFC and O-SOFC are shown in Fig. 4. As can be seen from Fig. 4(a), the value of \( \eta_{\text{H-SOFC}} - \eta_{\text{O-SOFC}} \) at \( r = 0 \) increases with increasing fuel utilization and operating temperature. At a fuel utilization of 70\%, the maximum efficiency difference is about 13\%, which is consistent with Demin’s data in Refs. [7] and [14]. However, the value of \( \eta_{\text{O-SOFC}} - \eta_{\text{H-SOFC}} \) at \( r = 1/3 \) increases with increasing fuel utilization but decreases with increasing temperature [Fig. 4(b)]. This behavior may be caused by the fact that the H-SOFC produces higher current density from \( \text{H}_2 \) electrochemical oxidation than O-SOFC at a higher temperature [see Fig. 4(a)], which tends to narrow down the difference between O-SOFC and H-SOFC [Fig. 4(b)].
Figure 4. Efficiency difference between H-SOFC and O-SOFC: (a) $\eta_{\text{H-SOFC}} - \eta_{\text{O-SOFC}}$ at $r = 0$; (b) $\eta_{\text{O-SOFC}} - \eta_{\text{H-SOFC}}$ at $r = 1/3$
4 CONCLUSIONS

A simple thermodynamic model is developed to compare the maximum efficiencies of methane fed H-SOFC and O-SOFC with consideration of CO electrochemical oxidation in O-SOFC anode. It is found that H-SOFC shows higher maximum efficiency than O-SOFC when CO electrochemical oxidation is excluded, which is consistent with the results in the literature. When CO electrochemical oxidation in O-SOFC is considered, the maximum efficiency of O-SOFC is obviously higher than that of H-SOFC, and this efficiency difference increases significantly with increasing rate of CO electrochemical oxidation and fuel utilization. The maximum efficiencies of both H-SOFC and O-SOFC decrease with increasing temperature. It is also found that with an increase in temperature, the value of \( \eta_{\text{H-SOFC}} - \eta_{\text{O-SOFC}} \) at \( r = 0 \) increases while the value of \( \eta_{\text{O-SOFC}} - \eta_{\text{H-SOFC}} \) at \( r = 1/3 \) decreases.

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