

Short communication

Effects of electrolyte type and flow pattern on performance of methanol-fuelled solid oxide fuel cells

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Abstract

A comparison is made of the performances of methanol-fuelled solid oxide fuel cells (SOFCs) with different types of electrolyte (i.e., oxygen ion- and proton-conducting electrolytes) and flow patterns (i.e., plug flow (PF) and mixed flow (MF)). Although it was demonstrated earlier that, under the same inlet steam:methane ratio, an SOFC with a proton-conducting electrolyte (SOFC-H⁺) thermodynamically offers higher efficiency than one with an oxygen ion-conducting electrolyte (SOFC-O²⁻), the benefit of a lower steam requirement for the SOFC-O²⁻ was not taken into account. Therefore, this study attempts to consider the benefit of differences in the steam requirement on the performance of SOFCs operated with different electrolytes and flow patterns. The efficiencies under the best conditions are compared in the temperature range of 900–1300 K. It is found that the maximum efficiencies decrease with increasing temperature and follow the sequence: SOFC-H⁺ (PF) > SOFC-O²⁻ (PF) > SOFC-H⁺ (MF) > SOFC-O²⁻ (MF). The corresponding inlet H₂O:MeOH ratios are at the carbon formation boundary for the SOFC-O²⁻ electrolyte, but are about 1.3–1.5 times the stoichiometric ratio for the SOFC-H⁺. It is clearly demonstrated that the PF mode is superior to the MF mode and that, although the benefit from the lower steam requirement is realized for the SOFC-O²⁻, the use of the proton-conducting electrolyte in the SOFCs is more promising.

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1. Introduction

The solid oxide fuel cell (SOFC) is a promising technology for electrochemical power generation. Due to its high operating temperature, the SOFC offers the prospect of a wide range of applications, flexibility of fuel choices and the possibility of operation with an internal reformer. Among the various possible fuels, i.e., methane, methanol, ethanol and gasoline, both ethanol and methanol have been reported [1] to offer high electromotive force output and efficiency.

Methanol is preferable given its availability, high energy density and ready storage and distribution [2,3], as well as the claim [4] that methanol can be injected directly onto anodes without serious carbon blockage [4]. In operation, the SOFC can use either an oxygen ion-conducting electrolyte or a proton-conducting electrolyte. Most current research efforts have been focusing on the SOFC with the oxygen ion-conducting electrolyte (SOFC-O²⁻) rather than with the proton-conducting electrolyte (SOFC-H⁺). A number of recent studies on advanced SOFC operations, such as development of intermediate temperature-SOFCs [5] and the integration of SOFCs with intercool gas turbines [6], are still based mainly on the use of the oxygen ion-conducting electrolyte.

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Nomenclature

E	electromotive force of a cell (V)
F	Faraday constant (C mol^{-1})
ΔH^0	lower heating value of methanol (J s^{-1})
K	equilibrium constant of the hydrogen oxidation reaction ($\text{kPa}^{-0.5}$)
p_i	partial pressure of component i (kPa)
q	electrical charge (A)
R	gas constant ($\text{J mol}^{-1} \text{K}^{-1}$)
T	temperature (K)
U_f	fuel utilization (%)
W	electrical work (W)

Greek letters

φ	potential (V)
η	system efficiency (%)

Subscripts

a	anode
c	cathode

Some research efforts have been carried out to compare the performances of SOFCs with different electrolytes. Thermodynamic analysis reveals that the SOFC- H^+ shows higher efficiency for the conversion of chemical energy to electrical power than the SOFC- O^{2-} for systems fed by hydrogen [7]. The same conclusion has also been reached for methane-fuelled SOFCs [8]. The comparisons were, however, performed under the same inlet steam:methane ratio [8]. Our previous work employed thermodynamic analysis to determine the carbon formation boundary for a direct internal-reforming (DIR) SOFC fed by methanol [9] and found that the SOFC- O^{2-} is more attractive than the SOFC- H^+ in terms of a lower steam requirement at the feed to the anode due to the simultaneous formation of steam by the electrochemical reaction of H_2 and O^{2-} .

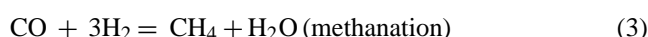
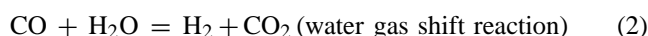
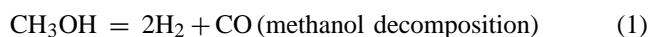
The difference in the steam requirement among both types of SOFC is particularly pronounced at high values of the extent of the electrochemical reaction. The effect of the SOFC operation modes (i.e., external reforming (ER), indirect internal-reforming (IIR) and direct internal-reforming (DIR)) on the steam requirement at the carbon formation boundary has been investigated for SOFCs fed by methane [10]. It was found that when using the SOFC- O^{2-} , the ER-SOFC and the IIR-SOFC show the same values of the steam:methane ratio at the carbon formation boundary, independent of the extent of electrochemical reaction. By contrast, due to the presence of extra steam from the electrochemical reaction at the anode chamber, the DIR-SOFC can be operated at lower values of the steam:methane ratio compared with the other modes. For the SOFC- H^+ , the required steam:methane ratios are higher than those for the SOFC- O^{2-} , but they are independent of the SOFC operation modes.

In the performance comparisons among the SOFCs with different types of electrolyte, the differences in the steam requirement should be taken into account as it is generally known that extra steam can act as a diluent and lower the SOFC efficiency. Therefore, it remains unclear whether the SOFC- H^+ is superior to the SOFC- O^{2-} .

It is the objective of this study to compare the performances of DIR-SOFCs with different electrolytes (i.e., oxygen ion- and proton-conducting electrolytes) and flow patterns (i.e., plug flow (PF) and mixed flow (MF)) by taking into account the benefit from the differences in their steam requirement. The flow pattern should be considered because it affects both the steam requirement of the system, particularly for the SOFC- O^{2-} , and the cell performance. The information obtained from this work is important for determining whether research into fuel cell development should be directed towards the system using the proton-conducting electrolyte.

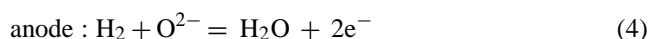
2. Theory

The reactions involved in the production of hydrogen from methanol steam-reforming can be represented by Eqs. (1)–(3) [11,12], i.e.,

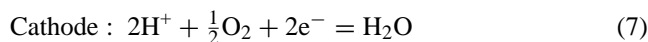


The reactions taking place at the anode and the cathode for the two types of electrolyte can be summarized as follows:

SOFC- O^{2-} :



SOFC- H^+ :



As seen from the above equations, it should be noted that water is produced in the anode chamber for the SOFC- O^{2-} , but in the cathode chamber for the SOFC- H^+ .

The electromotive force (E) of a cell is the difference in the potential of the two electrodes. Thus, the electromotive force can be represented as follows:

$$E = |\varphi_c - \varphi_a| \quad (8)$$

where φ_c and φ_a are the potentials of the cathode and the anode, respectively. The electrode potential can be calculated from Nernst equation. Because the electrochemical reactions at the electrodes are different, depending on the electrolyte

type, the potential can be expressed as follows:

$$\text{SOFC-O}^{2-} : \quad \varphi = \left(\frac{RT}{4F} \right) \ln p_{\text{O}_2} \quad (9)$$

$$\text{SOFC-H}^+ : \quad \varphi = \left(\frac{RT}{2F} \right) \ln p_{\text{H}_2} \quad (10)$$

where p_i is the partial pressure of component i , R the universal gas constant, T the absolute temperature and F is the Faraday constant.

For SOFC-O²⁻, the partial pressure of oxygen in the cathode chamber is calculated from its mole fraction, while the following equation is used to determine the partial pressure of oxygen in the anode chamber.

$$p_{\text{O}_2} = \left(\frac{p_{\text{H}_2\text{O}}}{K p_{\text{H}_2}} \right)^2 \quad (11)$$

For the SOFC-H⁺, the partial pressure of hydrogen in the anode chamber is calculated from its mole fraction, while the partial pressure of hydrogen in the cathode is given by:

$$p_{\text{H}_2} = \frac{p_{\text{H}_2\text{O}}}{K p_{\text{O}_2}^{1/2}} \quad (12)$$

In Eqs. (11) and (12), K is the equilibrium constant of the hydrogen oxidation reaction.

Regarding the possible SOFC configurations, gas flow within the flow channels of the SOFC stack can be classified broadly into two ideal flow patterns, i.e., plug flow and mixed flow. The former is characterized by the fact that the gas mixture moves orderly through the channel with no element of the gas mixing with any other element ahead or behind, whereas with mixed flow the contents are well-mixed and uniform throughout. Although most typical SOFCs are operated under a condition close to the PF mode, the MF mode can be realized by using a high recycle rate.

In the PF mode, the electromotive force (E) changes along the SOFC stack due to the distribution of gas compositions along the flow channels in both the anode and the cathode sections. The average electromotive force (\bar{E}) can be obtained from numerical integration of the gas distribution along the stack. To simplify the calculation, the gas compositions at the anode are assumed to reach their equilibrium compositions along the stack. The calculation procedures of the equilibrium compositions in SOFCs have been described in our previous work [9].

When current is drawn from the SOFC cell, the maximum electrical work (W) produced by the SOFC and the system efficiency (η) defined as the ratio of the maximum conversion of the chemical energy of the fuel fed in the SOFC system to electrical work, are calculated from Eqs. (13) and (14), respectively.

$$W = q\bar{E} \quad (13)$$

$$\eta = \frac{q\bar{E}}{-\Delta H^0} \times 100\% \quad (14)$$

where q is the electrical charge passing through the electrolyte and ΔH^0 is the lower heating value (LHV) of methanol at the standard condition.

It should be noted that the assumption of the equilibrium state of gas compositions along the flow channel may be reasonable because the rates of methanol steam-reforming and the water gas shift reaction are fast, particularly at high temperature [13–16]. Several researchers reported that the conversion of methanol from the methanol steam-reforming always close to 100% when the operating temperature above 573 K is applied [13–15]. Moreover, at 1173 K, methanol steam-reforming has been reported [16] to occur homogeneously and reach equilibrium. Deviation from this equilibrium condition would result in lower values of the electromotive force and the efficiency of SOFCs as less hydrogen would be generated in the anode chamber to compensate for the hydrogen consumed by the electrochemical reaction. Therefore, the results shown in this work represent the best performances for all SOFC cases.

3. Results and discussion

The efficiency and electromotive force at different fuel utilizations for methanol-fuelled SOFCs with different electrolyte types and flow patterns are shown in Fig. 1. The inlet steam:methanol (H₂O:MeOH) ratio is at the stoichiometric value of 1 for all SOFCs. The fuel utilization, U_f , is defined as the moles of hydrogen consumed by the electrochemical reaction divided by the maximum moles of hydrogen produced from the methanol steam-reforming (3 mol of hydrogen per 1 mol of methanol). As can be seen from Fig. 1(a), efficiencies increase with increasing fuel utilization for all SOFCs because more hydrogen is utilized for electrical power production. At high fuel utilization, however, the efficiencies of the SOFCs with the MF mode decrease, which corresponds to a sharp drop in the electromotive force observed in the MF mode (Fig. 1(b)). Although it is typical that the electromotive force decreases with increasing fuel utilization as the hydrogen partial pressure becomes smaller at higher fuel utilization, the flow characteristics of the PF mode allow the electromotive force to decrease gradually along the flow channel. Consequently, the PF mode provides a higher average electromotive force than the MF mode in which the electromotive force is at its minimum value over the entire cell area. It should be noted that although both ideal flow modes are not achieved in real operations, experimental SOFCs using tubular and planar cells show behaviour close to the PF and MF modes, respectively.

At present, most experimental studies related to the investigation of SOFC performance are based on systems that use an oxygen ion-conducting electrolyte, and experimental comparison of SOFC performance for the two flow patterns at the same operating condition is not available in the literature. According to Yeyo and Forbes [17], an efficiency of 66–70% was achieved at 85% fuel utilization when pure hy-

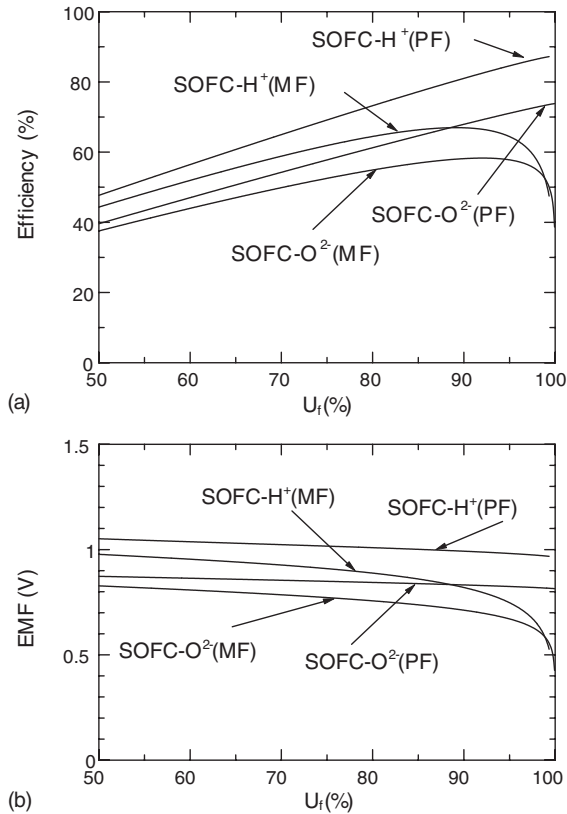


Fig. 1. Performance of SOFC-O²⁻ and SOFC-H⁺ operated under plug flow (PF) and mixed flow (MF): (a) efficiency; (b) electromotive force (inlet H₂O:MeOH = 1, $T = 1300$ K, $P = 101.3$ kPa).

drogen was used as a fuel in a tubular SOFC. At the same level of utilization, the data in Fig. 1(a) show that the efficiency is reduced to 65% if methanol is fed to the system and a SOFC-O²⁻ (PF) combination is used. The information obtained has strengthened the fact that operation with pure hydrogen fuel yields higher efficiency than using any fuel of an equivalent amount. In addition, when methane was fed to a planar SOFC, at a methane utilization of 86% an efficiency of 53.6% was obtained [18], which is close to the value of 55% if methanol is applied in place of methane in our study (SOFC-O²⁻ (MF)).

The results in Fig. 1 also show that the SOFC-H⁺ offers higher efficiency than the SOFC-O²⁻ for both flow pattern modes. This is in good agreement with previous results obtained for SOFCs fuelled by hydrogen [7] and methane [8]. The electrolyte type plays an important role on the value of the hydrogen partial pressure in the anode side and, therefore, on the electromotive force and efficiency of the SOFC. The partial pressure of hydrogen for the SOFC-H⁺ is relatively higher than that for the SOFC-O²⁻ because the water generated from the electrochemical reaction is present and acts as an inert gas at the anode side for the SOFC-O²⁻, whereas it appears at the cathode side for the SOFC-H⁺. It is noted that when pure hydrogen is fed to the anode, the mole fraction of hydrogen in the anode chamber is always unity along the cell length for the SOFC-H⁺.

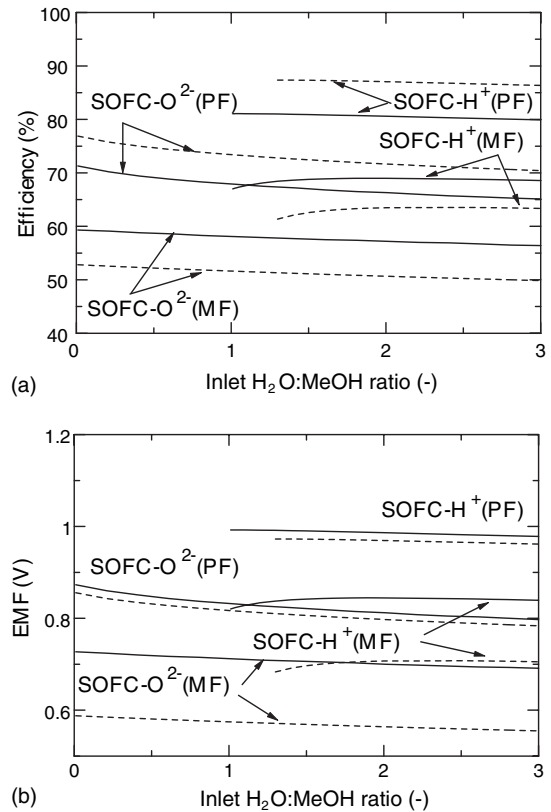


Fig. 2. Influence of inlet H₂O:MeOH ratio on SOFC performance at fuel utilization of 90% (solid line) and 99% (dashed line): (a) efficiency; (b) electromotive force ($T = 1300$ K, $P = 101.3$ kPa).

According to the above analysis for SOFCs with different electrolyte types and flow patterns under the same inlet H₂O:MeOH ratio, it is demonstrated that the SOFC with the proton-conducting electrolyte operated under the PF mode (SOFC-H⁺ (PF)) is the most favourable choice. Our previous work [9] has shown, however, that the steam requirement to operate the SOFC without carbon formation for the SOFC-O²⁻ is lower than that of the SOFC-H⁺. Thus, it is important to take into account this benefit in efficiency comparisons between different SOFCs. The effect of the inlet H₂O:MeOH ratio on the efficiency and electromotive force of the SOFC at the fuel utilizations of 90% (solid lines) and 99% (dashed lines) is presented in Fig. 2. The minimum inlet H₂O:MeOH ratios represent values at the carbon formation boundary. Details of the calculations for the carbon formation boundary in each operating mode have been described in our earlier work [9]. It was found that the SOFC-O²⁻ can be operated at the carbon-free condition without a requirement for extra steam in the methanol feed, and both the efficiency and electromotive force decrease with an increase in the inlet H₂O:MeOH ratio. Therefore, an addition of steam in the feed lowers the performance of the SOFC-O²⁻. For the SOFC-H⁺, the inlet H₂O:MeOH ratios at the carbon formation boundary are higher than those for the SOFC-O²⁻, particularly at high fuel utilization, and the effect of the inlet H₂O:MeOH ratio on the SOFC performance is less pronounced. As the water from

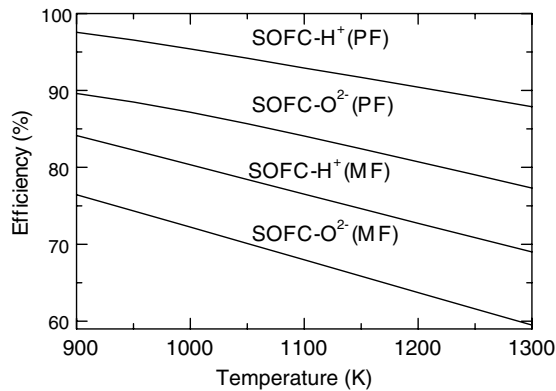


Fig. 3. Maximum efficiency of different SOFCs at different operating temperatures ($P = 101.3$ kPa).

the electrochemical reaction is generated at the cathode side, additional steam is required in the methanol feed at the anode side to promote hydrogen production. On the other hand, excessive steam will reduce the hydrogen concentration of the gas mixture at the anode side.

As it has been found that the SOFC performance is dependent on fuel utilization and inlet $H_2O:MeOH$ ratio, it is possible to determine the maximum efficiency and the corresponding conditions for all SOFC cases at a specified temperature by performing calculations at various values of the inlet $H_2O:MeOH$ ratio and the fuel utilization. The results for a temperature range of 900–1300 K are shown in Figs. 3 and 4. The maximum efficiencies follow the sequence: $SOFC-H^+ (PF) > SOFC-O^{2-} (PF) > SOFC-H^+ (MF) > SOFC-O^{2-} (MF)$. The corresponding inlet $H_2O:MeOH$ ratios are at the carbon formation boundary for both the $SOFC-O^{2-} (PF)$ and $SOFC-O^{2-} (MF)$, but are about 1.3 and 1.5 times the stoichiometric ratio for the $SOFC-H^+ (MF)$ and the $SOFC-H^+ (PF)$, respectively. The values of fuel utilization at the maximum efficiency are mainly governed by the flow pattern. For SOFCs operated under the PF mode, the utilization is constant at approximately 99%, but decreases slightly from 96.1 to 92.3% and from 95.5 to 92.0% for the $SOFC-H^+ (MF)$ and

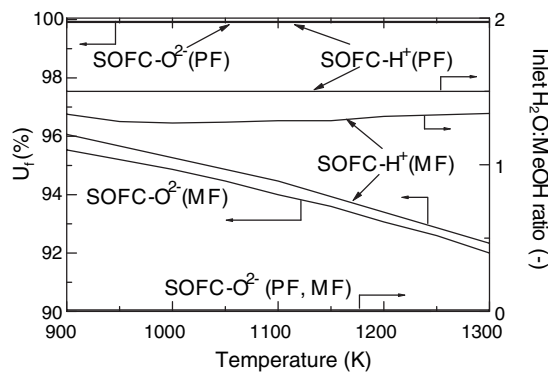


Fig. 4. Operating conditions corresponding to those in Fig. 3, at maximum efficiency ($P = 101.3$ kPa).

the $SOFC-O^{2-} (MF)$, respectively, when the temperature is increased from 900 to 1300 K. From these results, it is obvious that the proton-conducting electrolyte is more preferable for use in SOFCs. In addition, the PF mode is better than the MF mode. The $SOFC-H^+$ provides approximately 7.7–10.6% higher efficiency than the $SOFC-O^{2-}$ with the same flow pattern mode in the range of temperature studied. The maximum efficiency for all cases decreases with increasing temperature. This is in good agreement with the decrease in electromotive force due to the thermodynamic Gibb's free energy.

From the above studies, it is found that although the benefit of lower steam requirement is taken into account in the calculations for the $SOFC-O^{2-}$, the $SOFC-H^+$ still shows higher efficiency than the $SOFC-O^{2-}$ for both the PF and the MF modes. This implies that the development of SOFCs should be directed towards the use of the proton-conducting electrolyte. It should also be noted, however, that this study has not taken into account all the losses presented in real SOFC operation and, therefore, it will be the aim of our next investigation to consider these losses when undertaking efficiency comparisons. The $SOFC-H^+$ allows the cell to reach easily a high hydrogen utilization without an additional effort to separate steam from the anode gas and circulate it back to the cell as required for the $SOFC-O^{2-}$.

4. Conclusions

The performance of methanol-fuelled SOFCs using proton- and oxygen ion-conducting electrolytes and operating under plug flow and mixed flow modes is investigated. The electromotive force and efficiency are dependent on fuel utilization, inlet $H_2O:MeOH$ ratio, operating temperature, operation mode and electrolyte type. The benefit of less steam requirement for the $SOFC-O^{2-}$ is taken into account in comparisons of SOFC performance. It is demonstrated that the plug flow is superior to the mixed flow and that the use of the proton-conducting electrolyte is more preferable. These findings indicate that SOFC development should be directed towards a system that was the proton-conducting electrolyte.

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