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Theoretical performance analysis of ethanol-fuelled solid oxide fuel cells with different electrolytes

W. Jamsak [a], S. Assabumrungrat [a,*], P.L. Douglas [b], N. Laosiripojana [c], S. Charojrochkul [d]

[a] Center of Excellence in Catalysis and Catalytic Reaction Engineering, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand
[b] Department of Chemical Engineering, University of Waterloo, Ontario, Canada
[c] The Joint Graduate School of Energy and Environment, King Mongkut's University of Technology Thonburi, Bangkok 10140, Thailand
[d] National Metal and Materials Technology Center (MTEC), Thailand

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Abstract

The theoretical performance of ethanol-fuelled solid oxide fuel cells (SOFCs) with oxygen ion conducting and proton conducting electrolytes are presented in this paper. It was reported in a previous work that an SOFC with a proton conducting electrolyte (SOFC-H^+) offers higher efficiency than an SOFC with an oxygen ion conducting electrolyte (SOFC-O^{2-}). However, the study was based on the same steam-to-hydrocarbon feed ratio. Our previous work demonstrated the potential benefit of the SOFC-O^{2-} over the SOFC-H^+ in terms of a lower requirement for steam in the feed. Therefore, in this article, this benefit is taken into account in the performance comparison. Influences of mode of operation (i.e. plug flow (PF) and well-mixed (WM)) on the performance of SOFCs were also investigated. In the PF mode, two feeding patterns (i.e. co-current (Co) and counter-current (CC)) were considered.

The results show that theoretical SOFC efficiencies depend on the type of electrolyte, mode of operation, inlet H_2O:EtOH ratio and fuel utilization. Although it was found that the feeding pattern has an influence on EMF distribution along the cell, the average EMF is not affected. At the best conditions for each type of SOFC, it was observed that SOFC-O^{2-} yields a maximum efficiency at the minimum inlet H_2O:EtOH ratio which is the limit for carbon formation for each value of fuel utilization. On the other hand, in SOFC-H^+, optimum inlet H_2O:EtOH ratios are higher than the limit of carbon formation. At the optimum conditions, the rank of the various SOFCs is as follows: SOFC-H^+(PF) > SOFC-O^{2-}(PF) > SOFC-H^+(WM) > SOFC-O^{2-}(WM) over the temperature range (1000–1200 K). No difference in SOFC efficiency between both feeding patterns was observed. It is clear from our theoretical studies that the SOFC-H^+(PF) is the most promising SOFC system.

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1. Introduction

Fuel cells are currently regarded as the most promising technology for conversion of chemical to electrical energy. Solid oxide fuel cells (SOFC) have attracted considerable interest as they offer the widest range of potential applications, possibility in operation with an internal reformer, and possessing a high system efficiency. Many fuels have been suggested for use in SOFCs; however, among these, ethanol is considered to be an attractive green fuel because of its renewability from various biomass sources including energy plants, waste materials from agro-industries, forestry residue materials, and even organic fractions from municipal solid wastes. They also offer advantages related to natural availability and safety in storage and handling.

There are a number of studies published dealing with the use of ethanol for fuel cells. Ethanol was found to provide higher electrical and overall efficiency than methane in a direct internal reforming molten carbonate fuel cell (DIR-MCFC) [1]. Thermodynamic analysis of an indirect internal reforming molten carbonate fuel cell (IIR-MCFC) revealed that among different fuels (i.e. methane, methanol, and ethanol), ethanol presented the highest power density and the highest cell voltage. At a constant power density, ethanol allows the system to operate close to its thermal equilibrium better than does methanol but not as well as methane [2]. Tsiakaras and Demin [3] investigated performances

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* Corresponding author. Tel.: +662 218 6868; fax: +662 218 6877.
E-mail address: Suttichai.A@chula.ac.th (S. Assabumrungrat).

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Nomenclature

a	inlet moles of ethanol (mol)
b	inlet moles of steam (mol)
c	extent of the electrochemical reaction of hydrogen (mol)
E	electromotive force of a cell (V)
F	Faraday constant (C mol^{-1})
ΔH^0	lower heating value of ethanol (J mol^{-1})
K	equilibrium constant of the hydrogen oxidation reaction (kPa$^{-0.5}$)
n_i	number of moles of component i (mol)
p_i	partial pressure of component i (kPa)
$p_{r,i}$	relative partial pressure of component i
q	electrical charge (A)
R	gas constant (J mol^{-1} K^{-1})
T	temperature (K)
U_{f}	operating fuel utilization (%)
$U_{\mathrm{f},i,}$	partial fuel utilization (%)
W	electrical work (W)
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 letters	
η	electrical efficiency (%)
φ	potential (V)
Subscripts	
a	anode
c	cathode

of SOFCs *fuelled* by products from different ethanol processing; i.e. steam reforming, dry reforming, and partial oxidation with air. The product from ethanol steam reforming showed the highest maximum efficiency. Performances of external reforming SOFCs (ER-SOFC) fed by different fuels, e.g. methane, methanol, ethanol, and gasoline, were compared within a temperature range of 800–1200 K [4]. It was observed that at low temperatures, methane required a lower inlet steam:fuel ratio to prevent unfavorable coke formation than did methanol and ethanol. Nevertheless, at high temperatures the steam:fuel ratio at the limit of coke formation for ethanol was the same as for methane.

Although two types of electrolytes are possible for the SOFC operation, an oxygen ion conducting electrolyte is more commonly used than a proton conducting electrolyte. Until now, there are very few studies related to the use of the proton conducting electrolytes in SOFCs in the open literature [5–8]. In addition, all the studies of the ethanol-fed SOFCs employed only the oxygen ion conducting electrolyte. Demin et al. [7] reported an interesting result that an SOFC with a proton conducting electrolyte (SOFC-H$^+$) provides higher efficiency than an SOFC with an oxygen ion conducting electrolyte (SOFC-O^{2-}) for the system fed with methane. The comparison study was based on the same steam:methane feed ratio for both SOFC-O^{2-} and SOFC-H$^+$. It was demonstrated in our previous work that the steam requirement of SOFC-O^{2-} *is* lower than that of the SOFC-H$^+$ because water produced from the electrochemical reaction of hydrogen appears in the anode chamber [9]. Therefore, when the benefit from the lower steam requirement in SOFC-O^{2-} is taken into account, it is unclear whether the SOFC-H$^+$ still shows better performance than the SOFC-O^{2-}.

In this study, the theoretical performance of ethanol-fuelled SOFCs with two electrolytes in different modes of operation (i.e. plug flow (PF) and well-mixed (WM)) were investigated. Two feeding patterns of the PF mode (i.e. co-current (Co) and counter-current (CC)) were also considered. The efficiencies of SOFC-O^{2-} and SOFC-H$^+$ were compared, taking into account the benefit from the lower steam requirement for SOFC-O^{2-}. This is important in determining whether future SOFCs should be based on the use of the proton conducting electrolyte.

2. Theory

The reaction system involving the production of hydrogen via ethanol steam reforming can be represented by the following reactions [1]:

$$C_2H_5OH + H_2O = 4H_2 + 2CO \tag{1}$$

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

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

Previous results confirmed that a gas mixture at thermodynamic equilibrium contains only five components with noticeable concentration, e.g. carbon monoxide, carbon dioxide, hydrogen, steam, and methane [10,11].

Two types of solid electrolytes can be employed in the SOFC, i.e. 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:

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

$$\text{cathode}: \tfrac{1}{2}O_2 + 2e^- = O^{2-} \tag{5}$$

Proton conducting electrolyte:

$$\text{anode}: H_2 = 2H^+ + 2e^- \tag{6}$$

$$\text{cathode}: 2H^+ + \tfrac{1}{2}O_2 + 2e^- = H_2O \tag{7}$$

The difference between both electrolyte types is the location of the water produced. With the oxygen ion conducting electrolyte, water is produced in the reaction mixture in the anode chamber. In the case of the proton conducting electrolyte, water appears on the cathode side. The theoretical number of moles of each component at equilibrium is given by the following expressions:

$$n_{\mathrm{EtOH}} = a - x \tag{8}$$

$$n_{CH_4} = z \tag{9}$$

$$n_{CO} = 2x - y - z \tag{10}$$

$$n_{CO_2} = y \tag{11}$$

$$n_{H_2} = 4x + y - 3z - c \tag{12}$$

$$\begin{aligned} n_{H_2O} &= b + c - y + z \text{ (for oxygen ion conducting electrolyte)} \\ n_{H_2O} &= b - y + z \text{ (for proton conducting electrolyte)} \end{aligned} \tag{13}$$

$$n_{tot} = \sum_{i=1}^{6} n_i \tag{14}$$

The following three reactions are the most probable reactions which lead to carbon formation in the reaction system.

$$2CO = CO_2 + C \tag{15}$$

$$CH_4 = 2H_2 + C \tag{16}$$

$$CO + H_2 = H_2O + C \tag{17}$$

The reactions take place under a carbon-free condition when the carbon activities are less than one [10].

2.1. Electromotive force (EMF) calculations

The EMF of a cell is the maximum possible voltage, which drives charges around an electrical circuit in an SOFC. In practice, the actual voltage is less than this theoretical value due to activation, ohmic, and concentration losses. In this article, only the maximum possible voltage or EMF of the cell was considered, neglecting all losses. The EMF can be calculated from a difference in potentials between both electrodes in the cell as shown in Eq. (18).

$$E = |\varphi_c - \varphi_a| \tag{18}$$

where φ_c and φ_a are the potentials at the cathode and the anode, respectively. The electrode potential can be calculated using the Nernst equation. Since the electrochemical reactions at the electrodes are different, depending on the type of electrolyte, the potential can be expressed as:

$$\begin{aligned} \text{SOFC} - O^{2-} : E &= \frac{RT}{4F} \ln p_{r,O_2} \\ &= -\frac{\Delta G}{2F} - \frac{RT}{2F} \ln \frac{P_{H_2O,a}}{P_{H_2,a} P_{O_2,c}^{0.5}} \end{aligned} \tag{19}$$

$$\begin{aligned} \text{SOFC} - H^{+} : E &= \frac{RT}{2F} \ln p_{r,H_2} \\ &= -\frac{\Delta G}{2F} - \frac{RT}{2F} \ln \frac{P_{H_2O,c}}{P_{H_2,a} P_{O_2,c}^{0.5}} \end{aligned} \tag{20}$$

where p_{r,O_2} and p_{r,H_2} are relative oxygen partial pressure and relative hydrogen partial pressure, respectively, R the universal gas constant, T the absolute temperature, F the Faraday's constant, ΔG the Gibb's free energy and P_i the partial pressure of component i. The second terms of the right-hand side expression of Eqs. (19) and (20) are the Nerstian term comprising the partial pressure of hydrogen, oxygen, and steam. It should be noted that the partial pressures of steam for the SOFC-H^+ and the SOFC-O^{2-} represent the values at the anode and the cathode, respectively.

Typically, conventional SOFC operations are close to plug flow mode in which the gas compositions vary along the length of the cell. However, SOFCs can be operated under a well-mixed mode by using a high recycle rate. In the PF mode, the feeding pattern of fuel and air to the SOFC stack affects the composition distribution and, consequently the, EMF distribution along the SOFC cell. Two feeding patterns (i.e. co-current and counter-current) were considered in this study. An average EMF ($\overline{E}$) in the PF mode can be determined by the numerical integration of EMF along the stack. It should be noted that the EMF also depends significantly on the inlet H_2O:EtOH ratio, operating temperature, and the fuel and air utilizations. To simplify the calculations, it was assumed that the gas compositions in the anode are at their equilibrium compositions along the stack. Deviation from this equilibrium condition would result in lower SOFC EMF values as less hydrogen was 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. Details of the calculations of the equilibrium composition were presented in our previous work [9]. It should be noted that our calculations were compared with the results of Hernandez-Pacheco et al. [12] and found to be in good agreement. Using the same operating conditions ($U_f = 80\%$, $T = 1200$ K and 100% hydrogen feed) our calculations gave an EMF of approximately 0.92 V whereas Hernandez obtained 0.9 V.

2.2. SOFC efficiency

When a current is drawn from the SOFC, the maximum work produced by the SOFC can be calculated using the following equation:

$$W = q\overline{E} \tag{21}$$

where W is the electrical work from the SOFC and q is an electrical charge passing through the electrolyte. The electrical efficiency is defined as the ratio of electrical work produced by the SOFC to the chemical energy of fuel fed to the SOFC. Therefore, the maximum SOFC efficiency is obtained from in the following equation:

$$\eta = \frac{q\overline{E}}{-\Delta H^0} \times 100\% \tag{22}$$

where $-\Delta H^0$ is lower heating value of ethanol at standard conditions.

3. Results and discussion

The influences of the mode of operation (plug flow and well-mixed), feeding pattern (co-current and counter-current) and

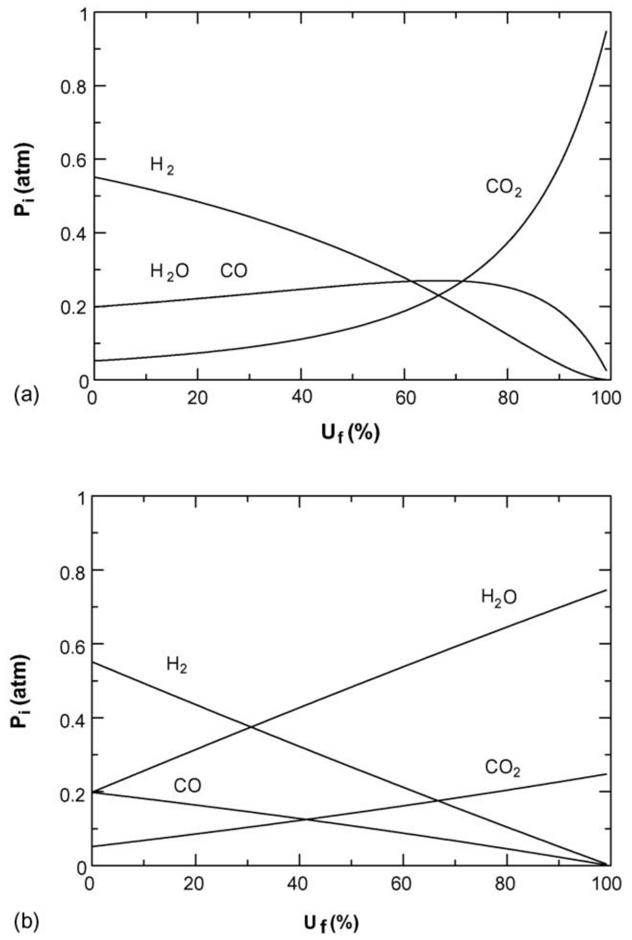

Fig. 1. Anode components' partial pressure at different fuel utilization for SOFCs with different types of electrolytes: (a) H^+ electrolyte and (b) O^{2-} electrolyte (inlet H_2O:EtOH = 3, T = 1200 K, P = 101.3 kPa, 400% excess air).

type of electrolyte on the partial pressure of each component along the cell are studied. Fig. 1 shows the anode components' partial pressure at different fuel utilizations (U_f) defined as the moles of hydrogen consumed by the electrochemical reaction divided by the maximum number of moles of hydrogen produced from ethanol (6 mol of hydrogen:1 mol of ethanol). The inlet H_2O:EtOH ratio is at the stoichiometic value of 3 and the temperature is 1200 K. For the WM mode, the partial pressure along the cell is equal to the value at the exit U_f due to the well-mixed condition. In contrast, in the PF mode, the composition change along the cell is represented by the partial pressure profiles from U_f of 0 to the exit U_f. The type of electrolyte has a significant effect on the anode partial pressure as shown in Fig. 1(a) and (b). The partial pressure of steam for the SOFC-H^+ and SOFC-O^{2-} are considerably different due to the different location of steam generation. In the SOFC-H^+ case, the partial pressure of steam increases slightly with increasing U_f because the total moles in the anode chamber decreases as hydrogen is consumed. However, at high fuel utilizations, the partial pressure of steam drops significantly because the hydrogen consumption shifts the water–gas shift reaction and results in higher carbon dioxide production as shown in Fig. 1(a). In contrast, for the SOFC-O^{2-} case, the partial pressure of steam increases dramatically over the entire anode chamber due to the major effect of electrochemical steam production at the anode side. The partial pressure of hydrogen in the SOFC-H^+ case is higher than that in the SOFC-O^{2-} case because there is no dilution effect of the electrochemical steam at the anode side in the SOFC-H^+ case. It should be noted that there is a negligible amount of ethanol and methane observed from the calculations due to the complete reforming reaction and insignificant methanation at this operating temperature.

As mentioned in the previous section, two feeding patterns (i.e. SOFC-(PF-Co) and SOFC-(PF-CC)) were considered for the PF mode. No difference in the profile of anode components' partial pressure for different feeding patterns was observed because it was assumed in our calculations that all anode components are in equilibrium which relates to the fuel utilization (U_f) along the anode chamber. Therefore, at the same operating fuel utilization the profiles of anode components in both feeding patterns are similar. In other words, the feeding patterns have no effect on the profile of anode components' partial pressure for both electrolytes.

The influence of mode of operation, feeding pattern, and type of electrolyte on the cathode components' partial pressure at various fuel utilizations are shown in Fig. 2. The partial pressure of oxygen in the SOFC-H^+ case is always lower than that in the SOFC-O^{2-} case due to the presence of the electrochemical steam at the cathode for the SOFC-H^+. However, the differences are not significant due to high value of excess air (400%) used in the calculations. It should be noted that 300–600% excess air is commonly used in SOFC operations for good heat management in SOFC cell stacks [13]. The mode of operation and feeding pattern show a slight impact on the partial pressure of oxygen in the cathode. For the SOFC (PF-Co) cases, air is fed co-currently with the fuel. The partial pressure of oxygen decreases whereas the partial pressure of steam increases (for the SOFC-H^+ case) with increasing fuel utilization. The partial pressure profiles within the cell of the SOFC (PF-Co) cases are represented by the partial pressures between the fuel utilization at 0 and the exit U_f; however, those of the SOFC (WM) correspond to the value at the exit fuel utilization. In contrast, for the SOFC (PF-CC), air is introduced to the cathode entrance located at the exit of the anode stream and, therefore, the partial pressure profile is different among different fuel utilizations. The partial pressure of oxygen in the cathode is 0.21 atm at the entrance to the cathode side and decreases along the cathode chamber until the cathode exit located at the entrance of the anode feed.

From the obtained partial pressure profiles, the EMF at different fuel utilization for all SOFCs can be calculated using Eqs. (18) and (19). From Fig. 3, it is shown that the EMF distributions in all SOFC-H^+ cases are higher than those in all SOFC-O^{2-} cases. This can be explained by considering the partial pressure of components involved in the Nerstian term of Eqs. (19) and (20). Because the partial pressure of hydrogen in the anode for the SOFC-H^+ case is higher than that for the SOFC-O^{2-} case due to no dilution effect of the electrochemical steam at the anode side in the SOFC-H^+ case and the partial pressure of steam in the cathode side for the SOFC-H^+ case is much lower than that in the anode side for the SOFC-O^{2-} case

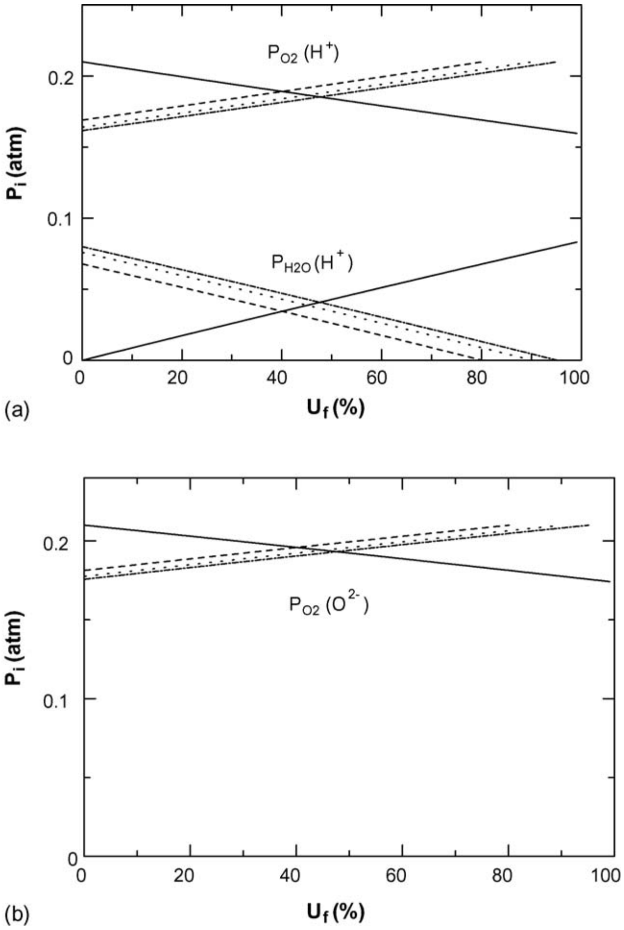

Fig. 2. Cathode components' partial pressure at different fuel utilization for SOFCs with different types of electrolytes for co-current (solid line) and counter-current at 80% U_f (dashed line), 90% U_f (dotted line), 95% U_f (dashed dotted line): (a) H^+ electrolyte and (b) O^{2-} electrolyte (inlet H_2O:EtOH = 3, T = 1200 K, P = 101.3 kPa, 400% excess air).

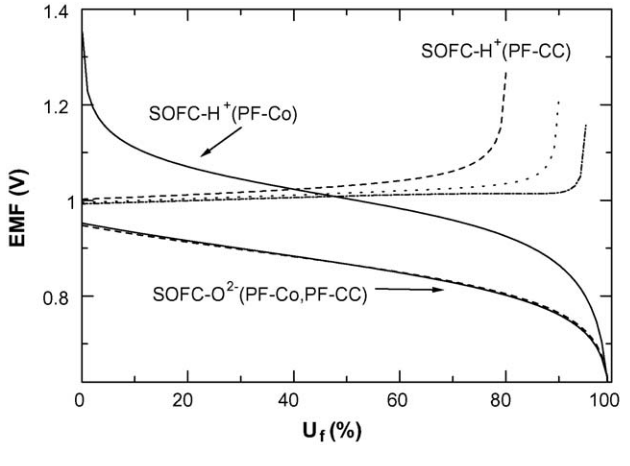

Fig. 3. EMF distribution along the SOFC-O^{2-} and SOFC-H^+ operated under PF and WM modes for co-current (solid line) and counter-current at 80% U_f (dashed line), 90% U_f (dotted line), 95% U_f (dashed dotted line): (a) H^+ electrolyte and (b) O^{2-} electrolyte (inlet H_2O:EtOH = 3, T = 1200 K, P = 101.3 kPa, 400% excess air).

(see Figs. 1 and 2), the Nerstian term of the SOFC-O^{2-} case shows a more negative value than that in the SOFC-H^+ case, and consequently, the SOFC-H^+ cell gives a higher EMF than does the SOFC-O^{2-} cell. It should be noted that the partial pressures of oxygen in the cathode for both SOFCs are not taken into account in the Nerstian term comparison due to the use of excess air in the operation. The result confirms that the SOFC-H^+ cell has a higher performance than the SOFC-O^{2-} cell when the steam:fuel feed ratio is the same as reported earlier in other system [7]. From Fig. 3, it is noticed that the feeding pattern has a significant impact on the EMF distribution in the SOFC-H^+ cell whereas only a slight effect is observed in the SOFC-O^{2-} cell. For the SOFC-H^+ case, the value of EMF is strongly dependent on both the partial pressures of oxygen and steam in the cathode. The components' partial pressures in the anode are not considered as they are similar for both feeding patterns as mentioned earlier. The feeding pattern significantly impacts the partial pressure profile of steam in the cathode as shown in Fig. 2(a) and, therefore, the EMF distribution is different with different feeding patterns. For the SOFC-O^{2-} case, the value of the EMF depends on the partial pressure of oxygen in the cathode, but it is not significantly dependent on the feeding pattern due to the high excess air. Consequently, with the same partial pressure profile in the anode, partial pressure profile of oxygen in the cathode for both feeding patterns and nearly identical, the observed values of the EMF are almost the same. The average value of the EMF for the SOFC (PF) can be obtained by the numerical calculation of the EMF distribution, while the EMF of SOFC (WM) can be achieved directly from the value at the corresponding fuel utilization. At 80% operating fuel utilization, the SOFC-H^+(WM) and the SOFC-O^{2-}(WM) yield EMF of 0.92 and 0.80 V, respectively, whereas the average values of the EMF are 1.03 and 0.89 V for the SOFC-H^+(PF) and the SOFC-O^{2-}(PF), respectively. It was found that the feeding pattern has no significant effect on the average EMF for both electrolytes although the EMF distributions are different. The average EMF of SOFCs at a inlet H_2O:EtOH ratio of 3 and 80% fuel utilization can be ordered as follows SOFC-H^+(PF-Co) ≈ SOFC-H^+(PF-CC) > SOFC-H^+(WM) > SOFC-O^{2-}(PF-Co) ≈ SOFC-O^{2-}(PF-Co) > SOFC-O^{2-}(WM).

Fig. 4(a) and (b) show the comparative results of average EMF and efficiency of SOFCs for various fuel utilizations, respectively. From Fig. 4(a), it is clear that the SOFC-H^+ provides greater EMF than the SOFC-O^{2-} for both PF and WM modes. Furthermore, it can be noticed that the WM mode results in a lower EMF than the PF mode for both electrolytes because the partial pressure of hydrogen in the WM mode is kept at its lowest value along the cell. In addition, there is no effect of feeding patterns on the average EMF in SOFCs although EMF distribution in both feeding patterns is different.

The electrochemical efficiency, η, is one indicator to identify the performance of fuel cells. The efficiency calculated from Eq. (22) is shown in Fig. 4(b). The efficiency increases in sequence SOFC-H^+(PF) > SOFC-H^+(WM) > SOFC-O^{2-}(PF) > SOFC-O^{2-}(WM); however, at high fuel utilization, the SOFC-O^{2-}(PF) case shows a higher efficiency than the SOFC-H^+(WM) case. It is obvious that under

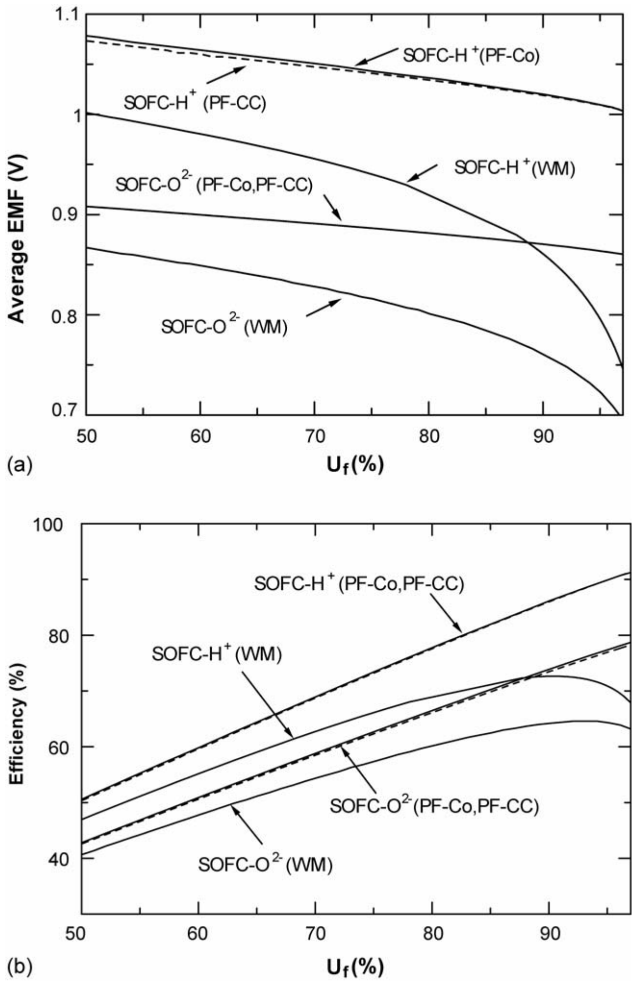

Fig. 4. Performances of SOFC-O^{2-} and SOFC-H^+ operated under PF and WM modes: (a) average EMF and (b) efficiency (inlet H_2O:EtOH = 3, T = 1200 K, P = 101.3 kPa, 400% excess air).

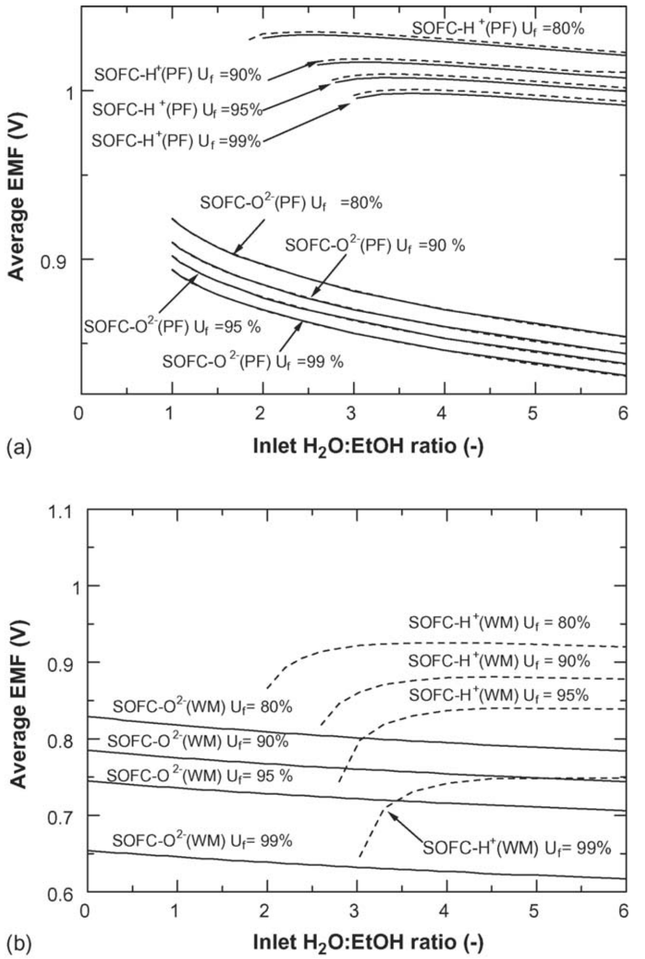

Fig. 5. Influence of inlet H_2O:EtOH ratio on SOFCs average EMF at different values of fuel utilization: (a) PF mode and (b) WM mode (T = 1200 K, P = 101.3 kPa, 400% excess air).

the same operation mode, the SOFC-H^+ cell is superior to the SOFC-O^{2-} cell. This is in good agreement with the previous work [7] which reported that the SOFC-H^+ case gives a maximum efficiency 15% higher than that of the SOFC-O^{2-} case in the range of inlet H_2O:CH_4 ratio of 2.0–3.0. Furthermore, it can be noticed that the feeding pattern has no influence on the calculated efficiency of SOFCs for both types of electrolyte.

It was reported in our previous study [9] that the SOFC-O^{2-} cell can be operated at much lower inlet H_2O:EtOH ratios than the SOFC-H^+ cell due to the difference in location of water production. Therefore, in order to compare the performance of SOFCs with different electrolyte types, it is necessary to take this SOFC-O^{2-} benefit into account in the calculations. The influence of the inlet H_2O:EtOH ratio on EMF and efficiency of SOFCs is investigated.

Figs. 5 and 6 show the influence of the inlet H_2O:EtOH ratio on the EMF and efficiency of SOFCs at different fuel utilizations. The inlet H_2O:EtOH ratio is considered only in the range where carbon formation is thermodynamically infeasible. The minimum ratio for the SOFC-O^{2-}(WM) and SOFC-O^{2-}(PF) cells is almost 0 and 1, respectively. However, the minimum ratio is higher for the SOFC-H^+ cell particularly at high fuel utilization for both modes of operation. The SOFC-O^{2-}(WM) cell can be operated without steam input because steam is produced from the electrochemical reaction of hydrogen. It should be noted that some steam is still needed in the feed during the start-up period before the cell can be self-sustaining. For both SOFC-O^{2-}(PF) and SOFC-O^{2-}(WM) cases, the EMF and efficiency decrease with increasing inlet H_2O:EtOH ratio. Therefore, their highest values are at the limit of carbon formation for each value of the fuel utilization. This indicates that the introduction of steam into the cell decreases the EMF and efficiency due to hydrogen dilution. In the SOFC-H^+(WM) and SOFC-H^+(PF) cases, the minimum inlet H_2O:EtOH ratios are 1.9 and 3.2 at 80 and 90% fuel utilization, respectively. The greater fuel utilization requires greater steam input. This is consistent with our previous work [9]. From Figs. 5 and 6, it is found that there is an optimum steam input in the SOFC-H^+ for both modes of operation at each fuel utilization. The introduction of steam initially increases the EMF and efficiency but has the negative effect at higher values. An appropriate inlet H_2O:EtOH ratio should be selected because steam is essential for the hydrogen production from the ethanol steam reforming but, on the other hand, it also acts as a diluent in the system. All optimum points found for

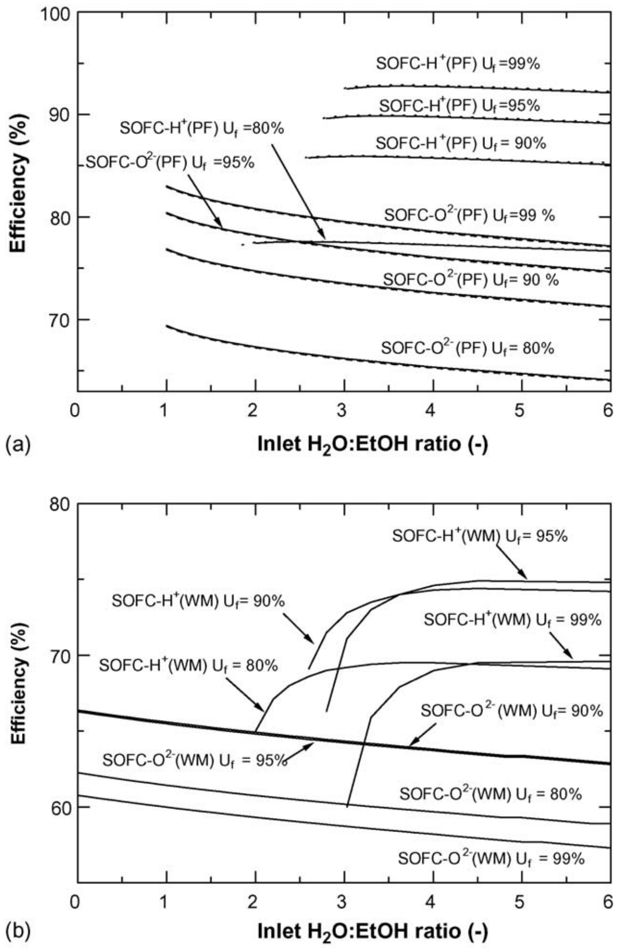

Fig. 6. Influence of inlet H_2O:EtOH ratios on SOFCs efficiency at different values of fuel utilization: (a) PF mode and (b) WM mode ($T = 1200$ K, $P = 101.3$ kPa).

each value of fuel utilization are beyond the limit of carbon formation. Furthermore, it is confirmed that there is no influence of feeding patterns on the EMF and efficiency for all ranges of the inlet H_2O:EtOH ratio.

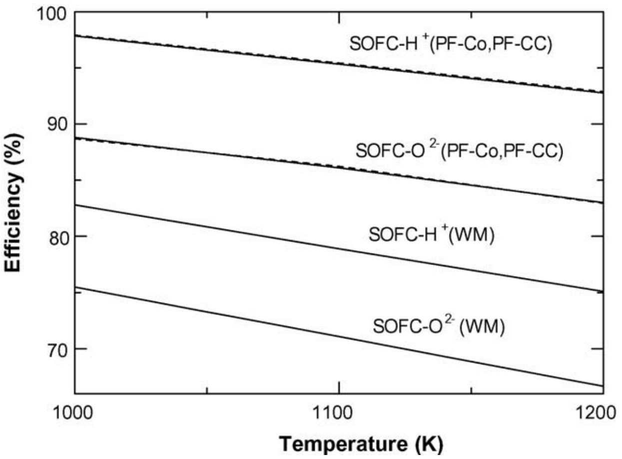

Fig. 7. Maximum efficiency of SOFC-O^{2-} and SOFC-H^+ at different operating temperatures ($P = 101.3$ kPa, 400% excess air).

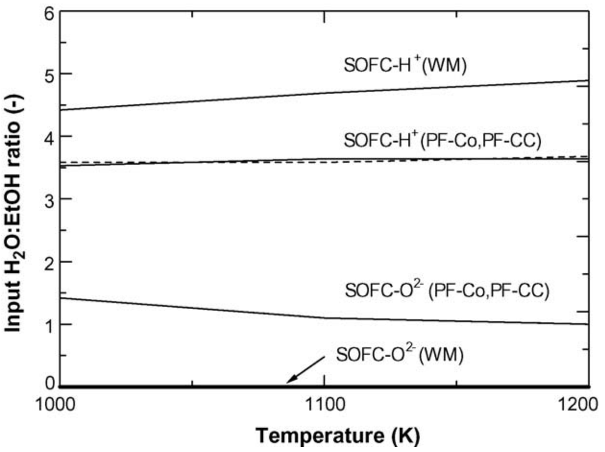

Fig. 8. Inlet H_2O:EtOH ratio at maximum efficiency ($P = 101.3$ kPa, 400% excess air).

By performing the calculations at various values of inlet H_2O:EtOH ratio and fuel utilization, it is possible to determine the maximum efficiency and the corresponding conditions for both SOFC-O^{2-} and SOFC-H^+ cells at each temperature level as shown in Figs. 7–9. It is obvious that the maximum SOFC efficiency follows the sequence of SOFC-H^+(PF) > SOFC-O^{2-}(PF) > SOFC-H^+(WM) > SOFC-O^{2-}(WM) for all temperatures (1000–1200 K). The maximum efficiency for all cases decreases with increasing temperature. This is consistent with the decrease in the EMF due to Gibb's free energy. The corresponding inlet H_2O:EtOH ratio is always approximately 0 for the SOFC-O^{2-}(WM). For the SOFC-O^{2-}(PF), the corresponding ratio is about 1.4 and 1 at 1000 and 1200 K, respectively. In the case of the proton conducting electrolyte, the SOFC-H^+(PF) requires a lower inlet H_2O:EtOH ratio than the SOFC-H^+(WM). For the SOFC-H^+(PF), the corresponding inlet H_2O:EtOH ratio is about 3.5 at 1000 K and increases with increasing temperature. While that for the SOFC-H^+(WM), is about 4.4 at 1000 K and also increases when operating temperature increases. This is probably because the water–gas shift reaction is exothermic and therefore more steam is required to move the reaction to the right to produce hydrogen. The corresponding fuel utilization at the maximum efficiency of the SOFC (PF) for both electrolytes is almost constant at approximately 99% but it slightly decreases

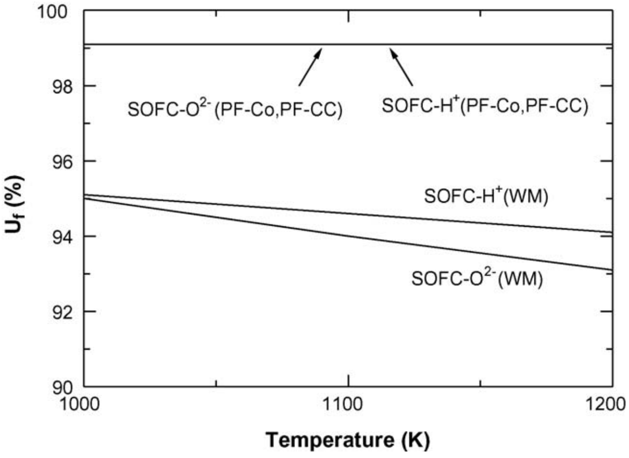

Fig. 9. Fuel utilization at maximum efficiency ($P = 101.3$ kPa, 400% excess air).

for the SOFC (WM) in both electrolytes when the temperature increases from 1000 to 1200 K.

From the above studies, it was found that although the benefit of lower steam requirement in the SOFC-O^2 is taken into account in the calculations, the SOFC-H$^+$ cell still shows higher efficiency than the SOFC-O^{2-} cell. This implies that the development of SOFCs should be directed to the use of a proton conducting electrolyte.

4. Conclusions

Thermodynamic analysis of ethanol-fuelled SOFCs using proton and oxygen ion conducting electrolytes in different modes of operation (plug flow and well-mixed) and feeding patterns (co-current and counter-current) has been presented in this article. At stoichiometric inlet H_2O:EtOH ratios, the SOFC-H$^+$(PF) provides the highest EMF and efficiency among various electrolytes and modes of operation. In order to compare the theoretical performances of SOFCs with different electrolytes, the benefit of reduced inlet steam requirement for the oxygen ion conducting electrolyte is taken into account.

It was demonstrated from the theoretical calculations assuming no polarization losses that the use of proton conducting electrolytes is more attractive than the use of oxygen ion conducting electrolytes. The SOFC-H$^+$(PF) gives the highest efficiency. Moreover, it was found that there is no influence of the feeding patterns on the average EMF and efficiency even though the EMF distribution along the cell is different.

Although the proton conducting electrolyte seems to be the most appropriate one for use in a solid oxide fuel cell from the theoretical calculations, it has a higher resistance than that of oxygen ion conducting electrolyte. If the ohmic loss of the electrolyte and other losses are considered, proton conducting electrolyte might perform worse than oxygen ion conducting electrolyte. If the overall resistance of proton conducting electrolyte could be reduced to be comparable with the oxygen ion conducting electrolyte, the proton conducting electrolyte is recommended as the most interesting electrolyte in the future. More details of the electrolyte selection including all resistances (i.e. ohmic loss and activation loss) must be calculated and justified.

Acknowledgements

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References

[1] S. Freni, G. Maggio, S. Cavallaro, Ethanol steam reforming in a molten carbonate fuel cell: a thermodynamic approach, J. Power Sources 62 (1996) 67–73.

[2] G. Maggio, S. Freni, S. Cavallaro, Light alcohols/methane fuelled molten carbonate fuel cells: a comparative study, J. Power Sources 74 (1998) 17–23.

[3] T. Tsiakaras, A. Demin, Thermodynamic analysis of solid oxide fuel cell system fueled by ethanol, Chem. Eng. Sci. 102 (2001) 210–217.

[4] S.L. Douvartzides, F.A. Coutelieris, A.K. Demin, P.E. Tsiakaras, Fuel options for solid oxide fuel cell: a thermodynamic analysis, AIChE J. 49 (2003) 248–257.

[5] A. Demin, P. Tsiakaras, Thermodynamic analysis of a hydrogen fed solid oxide fuel cell based on a proton conductor, Int. J. Hydrogen Energy 26 (2001) 1103–1108.

[6] R. Salar, H. Taherparvar, I.S. Metcalfe, M. Sahibzada, SOFCs Based on SrCe$_{0.95}$Yb$_{0.05}$O$_3$ Proton Conductor, in 2001 Joint International Meeting—the 200th Meeting of The Electrochemical Society Inc. and the 52nd Annual Meeting of the International Society of Electrochemistry, San Francisco, California, 2001.

[7] A.K. Demin, P.E. Tsiakaras, V.A. Sobyanin, S.Yu. Hramova, Thermodynamic analysis of a methane fed SOFC system based on a protonic conductor, Solid State Ionics 152–153 (2002) 555–560.

[8] T. Shimada, C. Wen, N. Taniguchi, J. Otomo, H. Takahashi, The high temperature proton conductor BaZr$_{0.4}$Ce$_{0.4}$In$_{0.2}$O$_{3-\alpha}$, J. Power Sources 131 (2004) 289–292.

[9] S. Assabumrungrat, V. Pavarajarn, S. Charojrochkul, N. Laosiripojana, Thermodynamic analysis for solid oxide fuel cell with direct internal reforming fueled by ethanol, Chem. Eng. Sci. 59 (2004) 6015–6020.

[10] E.Y. Garcia, M.A. Laborde, Hydrogen production by the steam reforming of ethanol: thermodynamic analysis, Int. J. Hydrogen Energy 16 (1991) 307–312.

[11] K. Vasudeva, N. Mitra, P. Umasankar, S.C. Dhinggra, Steam reforming of ethanol for hydrogen production: thermodynamic analysis, Int. J. Hydrogen Energy 21 (1996) 13–18.

[12] E. Hernandez-Pacheco, D. Singh, P.N. Hutton, N. Patel, M.D. Mann, J. Power Sources 138 (2004) 174.

[13] K.W. Bedringas, I.S. Ertesvag, S. Byggstoyle, B.F. Magnussen, Energy analysis of solid-oxide fuel cell (SOFC) systems, Energy 22 (1997) 403–412.