



Comparative study of hydrogen production from solid oxide electrolysis cell with different electrolyte types

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Abstract

Solid oxide electrolysis cell (SOEC) is one of technologies for producing hydrogen through the water splitting by electricity. In general, two types of electrolyte (i.e., oxygen-ion and proton conducting electrolytes) can be used in the SOEC. The different between both types of electrolyte is the location of steam fed and hydrogen produced. As a consequence, it is expected that the quality and quantity of hydrogen produced are difference. In order to clarify in this issue, this work aims to investigate the hydrogen production performance of oxygen-ion conducting SOEC (O-SOEC) and proton conducting SOEC (H-SOEC). The hydrogen production process from SOEC is designed and simulated by using Aspen Plus simulator. The electrochemical model which takes into account all overpotentials (i.e., ohmic, concentration and activation overpotentials) is implemented in the calculator block to calculate the cell potential used for hydrogen production. The impact of key operating conditions on cell potential is further examined. The results showed that the H-SOEC is suitable for operation at below 1050 K whereas the high temperature operation is recommended for O-SOEC.

Keywords: Hydrogen production, Solid oxide electrolysis cell, Proton conducting electrolyte, Oxygen-ion conducting electrolyte, Process Simulation

Introduction

Most of electricity generated nowadays mainly comes from fossil fuel resources, even though it is responsible for emitting a great amount of carbon dioxide which is one of the greenhouse gases that affect negatively to the environment. The effect can vary from air pollution to the increasing of average global temperature and sea-water level; overall the problems can be as big as a climate change. However, electricity can be generated from several kinds of resources other than fossil fuel, for example, renewable sources. Renewables energy consists of solar, wind, geothermal, wave, biomass and nuclear have been studying and developing, but there are many obstacles for using it directly [1]. Thus, hydrogen is used as an energy carrier. In this method, electricity is generated from reaction between hydrogen and oxygen, creating electricity and water as by-product, resulting in the reduction of air pollution in the environment. Although, generating electricity from hydrogen seem to be environmental friendly, 96 % of the production use energy from fossil fuel such as steam reforming, gasification and oil refineries which still emit carbon dioxide to the environment [2], leaving only 4 % or 8 GW of the production that comes from truly environmental friendly alternative methods (emit no carbon dioxide) [3]. Among all in the 4 %, there is water electrolysis. The water electrolysis uses the electricity to separate water and then, hydrogen and oxygen is generated. If the electricity produces from renewable energy such as solar, wind, wave and nuclear energy that are clean technology, hydrogen production through the water electrolysis becomes the cleanest method.

Among many kinds of electrolysis, the solid oxide electrolysis cell (SOEC) has received much interest since it requires low energy consumption and provides high efficiency of conversion. In general, there are two types of electrolyte used in the SOEC, i.e. oxygen ion-conducting and proton-conducting electrolytes. Many research in the area of oxygen ion-conducting solid oxide electrolysis cell (O-SOEC) reported that its high temperature operation, at

around 973 – 1273 K is useful for eliminating expensive catalyst and increasing conversion efficiency [4]. On the other hand, a proton-conducting solid oxide electrolysis cell (H-SOEC) operated at lower operating temperature (573 – 973 K) is more compatible to be used with wider range of materials [5].

Since both types of SOEC have distinct advantages and disadvantage, the aim of this work is to investigate the hydrogen production through different types of SOEC. The favorable operating condition of each SOEC is determined. The performance of H-SOEC and O-SOEC is analyzed by using Aspen Plus simulator based on thermodynamic calculation. Electrochemical model which shows the relation between current density and all overpotentials (i.e., ohmic, concentration and activation overpotentials) is implemented in the calculator block to compute the cell potential used for hydrogen production. After that, the optimizations of H-SOEC and O-SOEC are performed to identify the optimal operating condition that uses minimum cell potential.

Materials and methods

Modeling of SOEC

The SOEC has three components, consisting of anode, electrolyte and cathode. Each type of SOEC is made from materials. For the H-SOEC considered in this work, platinum (Pt) and BaCe_{0.9}Y_{0.1}O_{3δ} are used as the electrodes and electrolyte, respectively. Figure 1(a) demonstrates the basic component and operation of H-SOEC. Water is fed into the anode side where it is decomposed into oxygen, proton (H⁺) and electron. Due to the protonic conduction of H-SOEC, proton can move from the anode side to the cathode side via electrolyte. At the cathode side, the combination of proton and electron can generate hydrogen. Eqs. (1) – (3) present the chemical reactions occurred at the anode and cathode side and the overall reaction of H-SOEC, respectively.



In case of the O-SOEC, the cathode, electrolyte and anode are made from Ni-YSZ, YSZ and LSM-YSZ, respectively. As seen in Figure 1(b), for the O-SOEC, water is fed at the cathode side and reacts with electron is to further generate hydrogen and oxygen-ion. Then, oxygen-ion travels through electrolyte and is oxidized to combine oxygen. The overall reaction of O-SOEC is same with the H-SOEC. The chemical reactions at cathode (Eq. (4)) and anode sides (Eq. (5)) of O-SOEC are shown below:

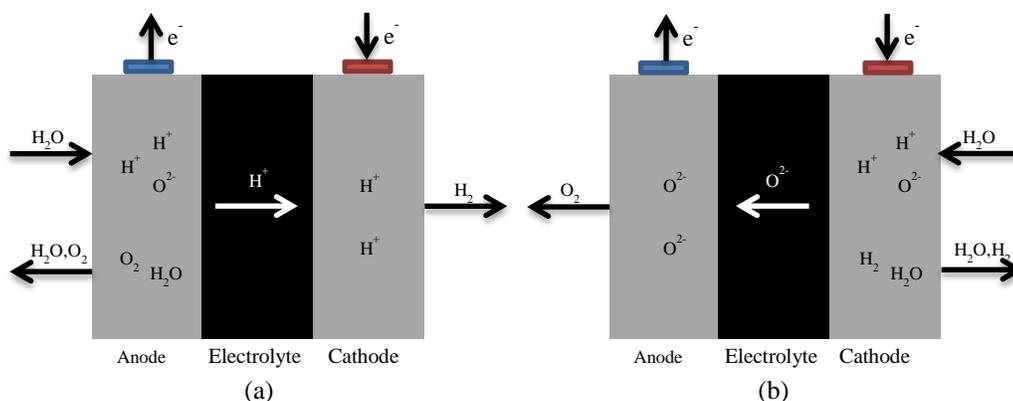


Figure 1 The basic component and operation of the (a) H-SOEC and (b) O-SOEC

Electrochemical model

Electrochemical model can predict the performance of H-SOEC and O-SOEC which presents the relationship between current density (j) and cell potential (V). Not only the operating conditions (e.g., temperature, pressure and feed component) but also structural parameters (e.g., thickness of each component) have a significant effect on the SOEC performance. The real cell potential is the summation of reversible potential (E) and overpotentials which can be expressed as:

$$V = E_r + \eta_{conc,anode} + \eta_{conc,cathode} + \eta_{act,anode} + \eta_{act,cathode} + \eta_{ohm} \quad (6)$$

The reversible potential (E_r) is minimum potential of electrolysis cell consumed which can be calculated from the Nernst equation as follows:

$$E_r = E^0 + \frac{RT}{n_{te}F} \ln \left(\frac{P_{H_2} P_{O_2}^{0.5}}{P_{H_2O}} \right) \quad (7)$$

where E^0 is standard potential; R is the gas constant; T is the operating temperature; n_{te} is number of transferred electrons; F is Faraday's constant; P_i is the partial pressure of each species. The standard potential can be given as the below equation [6].

$$E^0 = 1.253 - 0.00024516T \quad (8)$$

In matter of facts, the electrical conductivity of electrode at cathode and anode is higher than the electrolyte ($\rho_{electrode} \gg \rho_{electrolyte}$). Thus, the electrode value can be neglected. The ohmic overpotential is calculated Ohm's law as Eq. (9) - (10):

$$\eta_{ohm} = j \times R_{ohm} \quad (9)$$

$$R_{ohm} = \frac{\tau_{electrode}}{\rho_{electrode}} + \frac{\tau_{electrolyte}}{\rho_{electrolyte}} \approx \frac{\tau_{electrolyte}}{\rho_{electrolyte}} \quad (10)$$

where j is the current density, $\tau_{electrode}$ and $\tau_{electrolyte}$ are the cell thickness of electrode and electrolyte, respectively; $\rho_{electrode}$ and $\rho_{electrolyte}$ are the conductivity of electrode and electrolyte, respectively.

The concentration overpotentials are the resistance to mass transport of gas species at the electrode-electrolyte interface (Triple Phase Boundary, TPB). The concentration overpotential at the anode and cathode of H-SOEC can be computed by Eqs. (12) and (13) while O-SOEC can be computed by Eqs. (14) and (15), respectively.

$$\eta_{conc,an} = \frac{RT}{n_{te}F} \ln \left[\left(\frac{P_{H_2O}}{P_{H_2O}^{TPB}} \right) \left(\frac{P_{O_2}^{TPB}}{P_{O_2}} \right)^{0.5} \right] \quad \text{for H-SOEC} \quad (12)$$

$$\eta_{conc,ca} = \frac{RT}{n_{te}F} \ln \left(\frac{P_{H_2}^{TPB}}{P_{H_2}} \right) \quad (13)$$

$$\eta_{conc,an} = \frac{RT}{n_{te}F} \ln \left(\frac{P_{O_2}^{TPB}}{P_{O_2}} \right)^{0.5} \quad \text{for O-SOEC} \quad (14)$$

$$\eta_{conc,ca} = \frac{RT}{n_{te}F} \ln \left[\left(\frac{P_{H_2O}}{P_{H_2O}^{TPB}} \right) \left(\frac{P_{H_2}^{TPB}}{P_{H_2}} \right) \right] \quad (15)$$

The partial pressures of H₂O, O₂ and H₂ at TPB of SOEC derived from Fick's law are shown in the following equations which the H-SOEC, it is calculated from Darcy's law [7], and O-SOEC cannot use the same equation because feed and outlet position are difference, so it is used by L. Namwong [11] and Y. Patcharavorachot [12]. The effective diffusion coefficient can be explained in the Bosanquet equation as Eq. (16);

$$\frac{1}{D_i^{eff}} = \frac{\phi}{\xi} \left(\frac{1}{D_{i,j}} + \frac{1}{D_{i,k}} \right) \quad (16)$$

Table 1 The used parameters in SOEC validation and modeling results.

Parameters	Value
Operating pressure, P	1 bar
Area contact of cell, A	0.04 m ²
Number of cell, N_{cell}	500 cells
For H-SOEC	
Inlet steam, $\dot{n}_{H_2O,Feed}$	1 kmol/h
Steam composition	95 mol% H ₂ O/5 mol% H ₂
Electrolyte conductivity, $\rho_{electrolyte}$ [9]	$7.66 \times 10^6 / T \times \exp(-8.74 \times 10^3 / T) \Omega^{-1} m^{-1}$
Cathode thickness, $\tau_{cathode}$	100×10^{-6} m
Electrolyte thickness, $\tau_{electrolyte}$	100×10^{-6} m
Anode thickness, τ_{anode}	200×10^{-6} m
Activation energy [11]	
$E_{a,an}$	53.123 kJ/mol
$E_{a,ca}$	56.739 kJ/mol
Pre-exponential factor [11]	
k_{an}	$2.802 \times 10^5 \Omega^{-1} m^{-2}$
k_{ca}	$8.569 \times 10^5 \Omega^{-1} m^{-2}$
For O-SOEC	
Inlet steam, $\dot{n}_{H_2O,Feed}$	5 kmol/h
Steam composition	60 mol% H ₂ O/5 mol% H ₂
Electrolyte conductivity, $\rho_{electrolyte}$ [12]	$33.4 \times 10^3 \times \exp(-10.3 \times 10^3 / T) \Omega^{-1} m^{-1}$
Cathode thickness, $\tau_{cathode}$	500×10^{-6} m
Electrolyte thickness, $\tau_{electrolyte}$	10×10^{-6} m
Anode thickness, τ_{anode}	50×10^{-6} m
Activation energy [12]	
$E_{a,an}$	137 kJ/mol
$E_{a,ca}$	140 kJ/mol
Pre-exponential factor [12]	
k_{an}	$235 \times 10^9 \Omega^{-1} m^{-2}$
k_{ca}	$654 \times 10^9 \Omega^{-1} m^{-2}$

where ϕ is the electrode tortuosity; ξ is the electrode porosity; and $D_{i,j}$ and $D_{i,K}$ are the binary and Knudsen diffusion coefficients, respectively. The activation overpotentials are loss due to the kinetic reactions at the electrodes. The Butler-Volmer equation is used to calculate these losses as Eqs. (17);

$$\eta_{act,i} = \frac{RT}{F} \sinh^{-1} \left(\frac{j}{n_{te} j_{0,i}} \right), \quad i = an, ca \quad (17)$$

where $j_{0,ca}$ and $j_{0,an}$ are the exchange current densities at the cathode and anode. In general, the exchange current density is defined in several forms. It can be constant value or depends on operating conditions. Since the operating conditions are affected to the performance of H-SOEC, the constant exchange current density may result in the different performance between the calculation and real operation. Thus, this thesis aims to develop the exchange current density in the format of Arrhenius equation as follows:

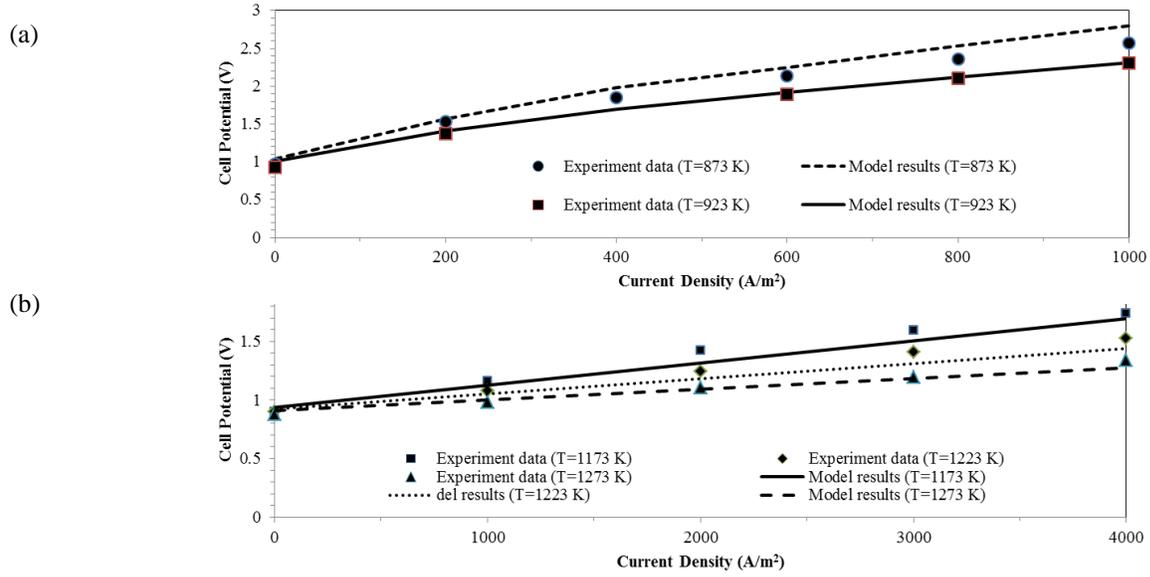


Figure 2 The comparison results of the simulation results and the experiment results of (a) H-SOEC and (b) O-SOEC at 1kmol/h, 1 bar 0.04 m² of area contact of cell and 500 cells of number of cell used

$$j_{0,i} = \frac{RT}{n_{ie} F} k_i \exp\left(-\frac{E_{a,i}}{RT}\right), \quad i = an, ca \quad (18)$$

where $E_{a,an}$ and $E_{a,ca}$ are the activation energy levels at the anode and cathode, respectively. The conversion of reaction which represents the steam utilization can be expressed by Y. Fu et al [8].

Model validation

The model validation is performed to confirm that simulation results can predict the performance of SOEC. In this work, the experiment of P.A. Stuart [9] and A. Momma [10] are used for model validation of H-SOEC and O-SOEC, respectively. Figure 2 shows the comparison results of cell potential obtained from the simulation results and the experiment data. The error of simulation result compared with the experiment is around 8%; this value is acceptable. Therefore, it can be concluded that the proposed model can be used for studying the hydrogen production through H-SOEC and O-SOEC. The pre-exponential factor and activation energy for H-SOEC and O-SOEC are used by L. Namwong [11] and Y. Patcharavorachot [12], respectively.

Results and Discussion

Effect of temperature

In this section, the operating temperature of SOEC, varying in a range of 773 to 1373 K is investigated whereas other parameters are set as a constant value. Figure 3a presents the effect of operating temperature on cell potential of both SOECs. The simulation result indicates that the cell potential of both SOECs will decrease as an exponential function with increasing temperature. Considering the individual voltage loss (Figure 4), it can be seen that the higher temperature operation causes a significant decrease in ohmic overpotential. This is because the conductivity of electrolyte increases with an increase in operating temperature and thus, the ohmic overpotential is lower. Moreover, increasing operating temperature leads to a slight reduction of activation overpotential. Interestingly, under the operating temperature below 1050 K, the H-SOEC will use cell potential less than O-SOEC. In contrast, the H-SOEC requires more cell potential than O-SOEC when the SOEC is operated at high temperature. This is because the conductivity of proton conducting solid oxides is higher at lower temperature. As a result, it can be concluded that

the H-SOEC is suitable for lower temperature operation whereas the higher temperature operation is recommended for O-SOEC.

Effect of pressure

Figure 3b demonstrates the cell potential of both SOECs as a function of operating pressure which is adjusted between 1 and 20 bar. The temperature are kept constant as 1073 K. From Figure 3b, it can be seen that the pressure has a little effect on the cell potential in which it will increase when pressure increase. In general, the variation of pressure affects to reversible potential and concentration overpotential. Higher pressure operation can increase the reversible potential. In contrast, the concentration overpotential is lower since the gas easily diffuses to the reaction site under high operating pressure. However, the simulation results, as seen in Figure 5, reveal that the increase of reversible potential and the decrease of concentration overpotentials has a slight effect on cell potential. From Figure 3b, it is found that the variations of the H-SOEC and O-SOEC at different pressure are the same tendency. Nevertheless, the H-SOEC has more cell potential than the O-SOEC.

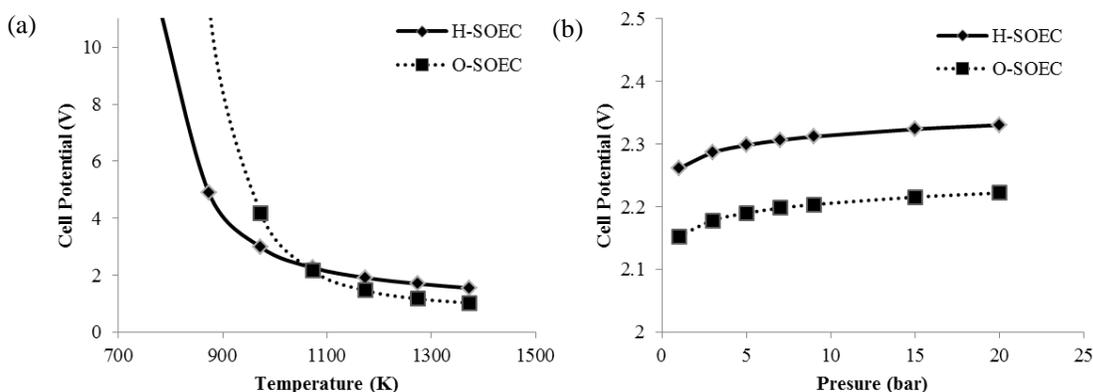


Figure 3 Effect of (a) temperature and (b) pressure on the cell potential for H-SOEC and O-SOEC

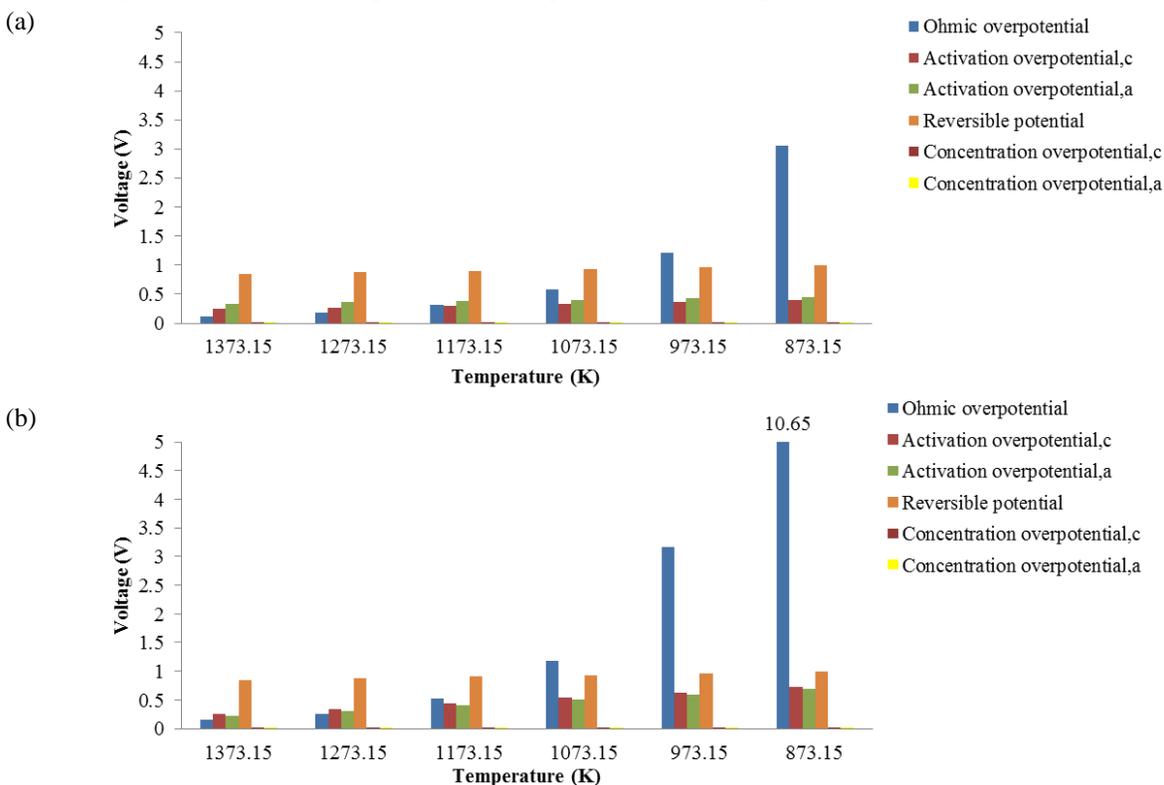


Figure 4 Effect of overpotential on the cell potential for difference operating temperature of (a) H-SOEC and (b) O-SOEC

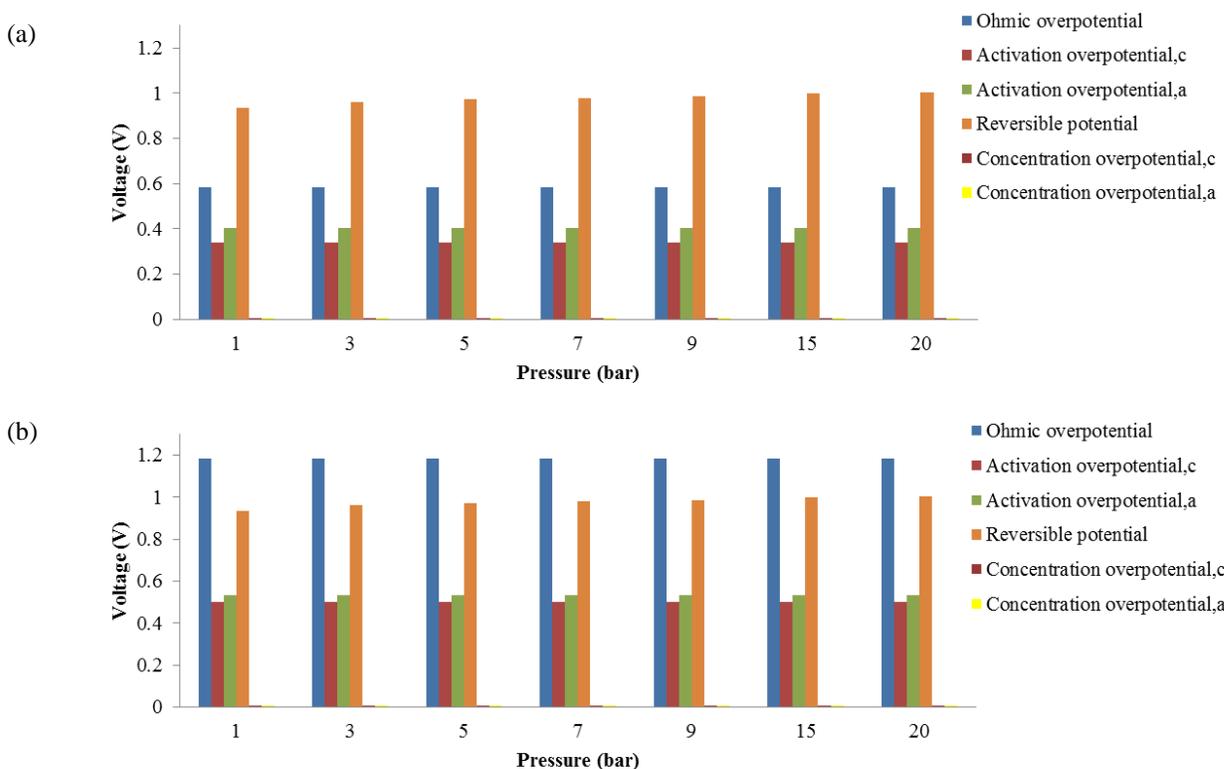


Figure 5 Effect of overpotential on the cell potential for difference operating pressure of (a) H-SOEC and (b) O-SOEC

Conclusion

In this work, a performance of SOEC for hydrogen production was studied by using the Aspen plus simulator. In addition, the simulation result of the H-SOEC and the O-SOEC obtained from proposed model was validated with the experiment data extracted from the literature. It was found that the difference between the simulation result and experiment data is less than 9%. Then, the effect of important parameters, i.e., temperature and pressure on cell potential was examined. The simulation results indicated that the higher operating temperature is suitable for O-SOEC whereas the H-SOEC is better when the operating temperature is lower than 1050 K. The main effect on cell potential is ohmic overpotential since the conductivity of electrolyte will increase when temperature increases. Therefore, the selection of material used for SOEC is an important point. On the other hand, the obtained results confirm that the concentration overpotential has a slight effect on cell potential and thus, it can be neglected to decrease the computation time. Moreover, the results indicate that the operating pressure has an insignificant on cell potential.

Acknowledgements

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