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Effect of CO in the reformatted fuel on the performance of Polymer Electrolyte Membrane (PEM) fuel cell

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Abstract

There are several obstacles to the commercialization of PEM fuel cells. One of the reasons is that the presence of carbon monoxide (CO) in the reformatted fuel, even at a very small scale, decreases the fuel cell performance. The aim of this paper is to investigate the effect of CO in reformatted fuel on PEM fuel cell performance. For this purpose, a steady state, one-dimensional and non-isothermal model is utilized to evaluate the PEM fuel cell performance with and without CO in the fuel stream. The governing equations which includes the conservation of mass, energy and species equations are solved in MATLAB software and validated by the available data in the literatures. The results indicate that when pure hydrogen is used as anode fuel the activation loss of the cathode is very large relative to the anode value; also, the maximum temperature occurs in the cathode catalyst layer. When reformatted fuel is applied as anode gas stream, activation loss and anode temperature increase by increasing the CO concentration in the reformatted fuel. As example, when CO concentration is over 50 ppm in the fuel stream, the activation loss and anode will be higher than the relevant amounts in cathode catalyst layer. Also it is observed that by increasing the fuel cell temperature and anode pressure, the CO effects on fuel cell performance are reduced.

1. Introduction

Fuel cells are direct energy conversation devices that convert the chemical energy of fuel and oxidant into electrical energy without the Carnot limitation. The advantages of PEM fuel cells include the ability to provide high power densities at relatively low operating temperature and quick start-up as well as

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being a leading candidate for a zero or low emission for transportation applications [1]. Even though PEM fuel cells have a lot of advantages, they have several obstacles to commercialization. One of these is CO poisoning which occurs when reformatted fuel present in the anode gas stream inhibits the hydrogen oxidation reaction; and consequently, results in a decrease in the energy conversion efficiency and the output voltage of the fuel cell [2]. In addition to carbon monoxide there are other contaminants that can be harmful to fuel cell components. Table 1 provides a list of contaminants presented in the operation of PEM fuel cells. This list may not be complete; however, it represents the majority of the contaminants identified in fuel cell operations [3].

The most suitable fuel for all kinds of fuel cells is pure hydrogen, due to the simple kinematic of reaction, but pure hydrogen is not found in the natural environment and must be generated in some way. There are various methods to produce hydrogen from renewable and non-renewable energy sources. But at the current stage of technology, hydrogen production from non-renewable energy sources is more popular. With this method, hydrogen is generated by reforming a liquid hydrocarbon such as methanol or a light hydrocarbon such as methane at a temperature near 600°C. But, in the process of fuel reforming other species, which can be harmful to fuel cell components, can also be produced. For example, the result of methanol reforming is a fuel mixture consisting of approximately 74% hydrogen, 25% carbon dioxide and 1% carbon monoxide [4]. Since the platinum catalysts of PEM fuel cell are very sensitive to CO even at this value, CO concentration must be reduced to approximately less than 100 ppm otherwise these levels of CO concentration can effect PEM fuel cell performance resulting in CO poisoning. The anode catalyst layer of a PEM fuel cell is very sensitive to CO because the CO present in the anode catalyst is adsorbed into the anode platinum catalyst surface and creates a strong molecular bond with it [2]. Of course, there exist three methods to mitigate the effect of CO poisoning such as: the use of platinum alloy, higher cell operating temperature and introduction a small value of oxygen into reformatted fuel gas flow [2]. Among of these methods, the third method is the most practical but the second method is not possible for PEM fuel cell.

Improving the capital cost and setting reliability of a PEM fuel cell requires a better understanding of the design and operating condition of a PEM fuel cell. Accordingly, the modeling of a detailed structure of a PEM fuel cell including its catalysts, membrane and electrode in addition to knowing the effects of temperature, pressure and concentration of gas stream on the PEM fuel cell performance are very important. Several models are available in the published literature. With regard to the anode gas stream, we can identify two fuel cell models. In the first the anode gas stream includes pure hydrogen, and in the second the anode gas stream includes hydrogen with a small concentration of CO. In each of these two models the cathode gas stream is free of any contaminants.

Some articles that were formulated using the first model are explained in the following. Bernardi and

Table 1. Major contaminants in PEM fuel cells [3]

Impurity source	Typical contaminant
Air	N_2, NO_x (NO, NO_2), SO_x (SO_2, SO_3) NH_3, O_3
Reformate hydrogen	CO, CO_2, H_2S, NH_3, CH_4
Bipolar metal plates (end plates)	Fe^{3+} , Ni^{2+}, Cu^{2+}, Cr^{3+}
Membranes (Nafion®)	Na^+, Ca^{2+}
Sealing gasket	Si
Coolants, DI water	Si, Al, S, K, Fe, Cu, Cl, V, Cr
Battlefield pollutants	SO_2, NO_2, CO, propane, benzene
Compressors	Oils

Verbrugge [5] used the first model by focusing on the cathode side of the fuel cell including the cathode gas diffusion layer, membrane, and cathode catalyst layer. Their model was isothermal, one-dimensional steady state and assumed perfect membrane hydration similar to [1]. A one-dimensional, isothermal, steady-state model of a PEM Fuel cell was made by Springer et al. [6] to understand the processes occurring in a PEM fuel cell including variable membrane hydration.

While most models use a macro homogenous formulation for the catalyst layer, Gloaguen and Durand [7] used an agglomerate model. Baschuk and Li [8] formulated the mass diffusion in the electrode and catalyst layer such that the diffusion coefficient represented diffusion through gas, liquid water and polymer electrolyte; thus, the PEM fuel cell could be modeled with a variable degree of water flooding. A model by Wohr and Bolwin [9] describes the temperature profile across a number of PEM fuel cells using a model developed by Rowe and Li [10] who studied the water and thermal management of PEM fuel cells using a steady-state and one-dimensional approach to determine the water vapor mole flux at the interfaces of catalyst layers and electrodes.

Some articles formulated mathematical models of carbon monoxide poisoning of the anode catalyst layer using the second PEM fuel cell model. Springer et al. [11, 13] used fundamental, electrochemical, reaction kinetics to model CO poisoning. Additionally, Woher et al. [12] used a one-dimensional, non-isothermal and transient model of a PEM fuel cell. Baschuk and Li [2] reviewed the current knowledge of CO poisoning and investigated the electrochemistry of CO and hydrogen, and then studied the mathematical model of a PEM fuel cell anode catalyst layer by simulating both CO poisoning and O_2 bleeding to compare the anode activation lost together [4]. Subsequently, they made a complete model of a PEM fuel cell that incorporated CO poisoning and O_2 bleeding, and considered the reaction kinetics in the catalyst layers for a steady, isothermal and fully hydrated PEM fuel cell [14]. Mishra et al. [15] combined the transport model from Rowe and Li [10] and the CO poisoning kinetics from Springer et al. [13], to study the maximum allowable temperature difference, the maximum allowable cell voltage and the minimum desirable membrane hydration.

The effect of contaminants on fuel cells is one of the most important issues in fuel cell operation and applications. It has been identified that the fuel cell component most affected by a contamination process is the membrane electrode assembly (MEA). In this paper, we intend to examine the kinetic effect of CO on the performance of the PEM fuel cell. To do this, a one-dimensional non-isothermal steady state model is used to evaluate the PEM fuel cell performance by studying the reaction kinetics in the catalyst layers, mass transport of reactants in the electrode and catalyst layers, and proton migration in the electrolyte membrane.

2.Mathematical model

The PEM fuel cell, which is made up of four major components: the bipolar plate, electrode layer, catalyst layer and polymer electrolyte membrane, needs a physical model to introduce the transport and electrochemical phenomena. In this study all components of the PEM fuel cell, except the bipolar plate, are modeled as shown schematically in Fig.1. Both the transport model from Rowe and Li [10] and the electrochemical kinetics model from Springer et al. [13] are combined to illustrate the effect of a gas stream including CO on the PEM fuel cell performance.

The reversible cell voltage, E_{rev}, obtained at thermodynamic equilibrium can be calculated from the Nernst equation. Due to a low carbon monoxide concentration along with hydrogen fuel, its effects on the reversible voltage are ignored. The cell output voltage can be represented by [8]:

$$\text{Output voltage}: V = E_{rev} - \eta_{act} - \eta_{ohm} \quad (1)$$

The loss potential of a PEM fuel cell consists of two terms. First, the activation loss, η_{act}, due to

electrochemical kinetics in the anode and cathode catalyst layer; and second, the ohmic loss, η_{ohm}, due to electron transfer in the gas diffusion layers, catalyst layers and bipolar plates and proton migration in the polymer electrolyte membrane [14]. It is necessary to emphasize that, if in the calculation of the reversible voltage and the activation loss if the concentration values in the catalyst layer are used, the loss due to concentration will be zero.

The PEM fuel cell is assumed to operate at steady state, non-isothermal and all parameters change through the cell thickness which is the x-direction. This one-dimensional approach is reasonable because the other dimensions of the cell are typically orders of magnitude larger than the cell thickness. Similarly, the structure of the catalyst is uniformly distributed in both the cathode and anode layer, and the dissolution of reactant gases in liquid water follows Henry's law. Additionally, both the hydration of the electrolyte and the pressure difference between the anode and cathode in the membrane are assumed to be a linear variation. Therefore, with these assumptions the PEM fuel cell is formulated, and the governing equations for the electrode, catalyst and membrane are the species and energy equations for ideal gas. The viscous force and the gradient of the gas pressure are assumed to be negligible in the electrode layer. Fourier's law is considered for heat conduction. To consider the sum of the individual species equations the Stefan-Maxwell equation is applied for multi-component gas diffusion.

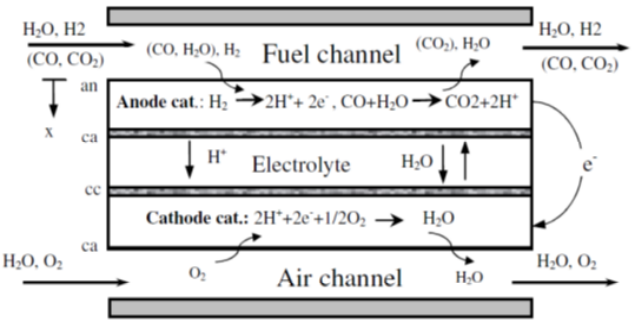

Fig. 1. A schematic of a PEM fuel cell .

To avoid rewriting the equations, Rowe and Li's equations [10] are used in the present study to calculate parameters of the electrode layers and membrane. But due to the presence of CO in the fuel stream, the governing equations in the anode catalyst layer have been slightly changed. The equations of the anode catalyst layer are presented in the following.

2.1. Catalyst layer

All electrochemical reactants of a PEM fuel cell happen in the catalyst layers, and even though the catalyst layers are very small they can be considered the heart of the fuel cell. In this study, the catalyst layers are considered to be pseudo-homogenous. That is, they are a mixture of membrane and solid along with void space. When pure hydrogen is used in the anode channel, the overall half-cell electrochemical reaction in the anode and cathode catalyst layer are taken as [10]:

$$\text{Anode}: H_2 \rightarrow 2H^+ + 2e^- \tag{2}$$

$$\text{Cathode}: 2H^+ + 2e^- + \frac{1}{2}O_2 \rightarrow H_2\text{O} \tag{3}$$

When a reformatted fuel is used at the anode channel, the electrochemical reactions of the cathode catalyst layer do not change but the anode catalyst layer has a new electrochemical reaction where the adsorption and oxidation processes of CO and H_2 are represented by the four processes expressed in the following [13].

$$H_2 + 2Pt \leftrightarrow 2\left(Pt - H\right) \tag{4}$$

$$CO + Pt \leftrightarrow CO - Pt \tag{5}$$

$$CO + Pt \leftrightarrow CO - Pt \tag{6}$$

$$H_2O + \left(CO - Pt\right) \rightarrow Pt + CO_2 + 2H^+ + 2e^- \tag{7}$$

Both equations 4 and 5 are bidirectional, whatever hydrogen and CO present in the anode catalyst layer is absorbed by a vacant catalyst site or may be desorbed from the catalyst surface. The two processes in equations 6 and 7 generate the current corresponding to the electrochemical oxidation of the

adsorbed hydrogen and CO, respectively. Obviously a high concentration of CO in the anode gas stream can prevent the adsorption of the hydrogen, which is called the CO poisoning effect [13].

Subscripts 1=O_2, 2=H^+ and 3= H_2O(l) are normally used for the cathode catalyst layer, when the anode gas stream includes pure hydrogen the subscripts 1=H_2, 2=H^+ and 3= H_2O(l) are used, and when the anode gas stream includes hydrogen with CO the subscripts 1=H_2, 2=H^+,3= H_2O(l), 4=CO and 5=CO_2 are used. A set of governing equations can be derived by an application of the conservation laws for the species and energy, the electrochemical reactions are obtained from the Butler-Volmer equation, and the flux of aqueous species in the membrane are calculated from the Nernst-Planck equation. Also, Fourier's law and Ohm's law are considered for heat conduction and electron transfer, respectively. The government equations of the catalyst layer are defined for the two kinds of modeled fuel cell.

2.1.1. Modeling anode gas stream including pure hydrogen

The government equations for the anode and cathode catalyst are similar, the difference is to define the species that react. The formulations of the catalyst layer are shown in the following [10]:

$$\text{Energy}: -k^{eff}\frac{d^2T}{dx^2}+\sum_{i=1,3}\left(N_iM_iC_{pi}\right)\frac{dT}{dx} + \left|\frac{j(x)}{nF}\right|\left(T\Delta\bar{S}\right)=\frac{i_m^{\,2}}{\kappa^{eff}}+j(x)\left(\phi_{s-}\phi_m\right) \tag{8}$$

$$\text{Flux1: } H_2 \text{ (or } O_2) \quad \frac{dN_1}{dx}=\frac{-\upsilon_1 j(x)}{nF} \tag{9}$$

$$\text{Flux2: } H^+ \quad \frac{dN_2}{dx}=\frac{di_m/dx}{F}=\frac{j(x)}{F} \tag{10}$$

$$\text{Flux3: } H_2O \quad \frac{dN_3}{dx}=\frac{-\upsilon_3 j(x)}{nF} \tag{11}$$

$$\text{Butler-Volmer} \quad j(x)=ai_0^{ref}\left(\frac{c_1}{c_1^{ref}}\right)^{\gamma_1}\times \left[\exp\left(\frac{\alpha_aF}{RT}(\phi_s-\phi_m\right)-exp\left(-\frac{\alpha_cF}{RT}(\phi_s-\phi_m\right)\right] \tag{12}$$

1: H_2 (or O_2)

concentration

$$D_1^{eff}\frac{d^2c_1}{dx^2}-\frac{N_3}{c_3}\frac{dc_1}{dx}-\frac{c_1}{c_3}\frac{dN_3}{dx}+\frac{dN_1}{dx}=0 \tag{13}$$

$$\text{Protonpotential}: \frac{d\phi_m}{dx}=-\frac{i_m}{\kappa^{eff}}+\frac{F}{\kappa^{eff}}c_2\frac{N_3}{c_3} \tag{14}$$

$$\text{Electron potential}: \frac{d\phi_s}{dx}=-\frac{i_s}{\sigma^{eff}} \tag{15}$$

Where the stoichiometric coefficient for species i in the anode and cathode are illustrated by υ_i , as given in equations 2 and 3, φ is the electrical potential,$\Delta\bar{s}$ is the entropy change for electrochemical reaction, c is the concentration of species, i_m and i_s are the current density in the proton-conducting membrane and the electron-conducting solid, respectively, α_a and α_c are the transfer coefficient, and a is the catalyst reactive surface area per unit volume. The reference concentration c_1^{ref} determines the amount of the reference exchange current density i_0^{ref}. Also, k^{eff} is the effective heat transfer coefficient, κ^{eff} is the effective proton conductivity of the membrane, σ^{eff} is the effective electrical conductivity and D_i^{eff} is the effective diffusion coefficient of H_2 (or O_2) which are expressed as follows:

$$k^{eff}=\varepsilon k_g+(1-\varepsilon)k_s \qquad \kappa^{eff}=\kappa\times\varepsilon^{0.5}$$
$$\sigma^{eff}=\sigma\times\varepsilon^{0.5} \qquad D_i^{eff}=D_i\times\varepsilon^{0.5} \tag{16}$$

In these relations ε is the porosity coefficient of catalyst layers, and k_g and k_s are gas and solid thermal conductivity coefficients, respectively.

The diffusion coefficient for oxygen and hydrogen are determined by two equations that are a function of temperature in kelvin units [1]:

$$\text{Oxygen}: \quad D_{O_2}=3.1\times10^{-3}\exp\left(-\frac{2768}{T}\right) \tag{17}$$

$$\text{Hydrogen}: \quad D_{H_2}=4.1\times10^{-3}\exp\left(-\frac{2602}{T}\right) \tag{18}$$

Generally when pure hydrogen is used for the anode gas stream, solving equations for the catalyst layers can be determined using 7 unknown parameters, N_1,

N_3,i_m,T, c_1,φ_m and φ_s to calculate activation loss.

2.1.2.Modeling anode gas stream including hydrogen with CO

In this case, in addition to the presence of hydrogen and water vapor, carbon monoxide and carbon dioxide are also present in the fuel stream. When CO is present in the anode gas stream, the governing equations of cathode catalyst layer are similar to the previous equations, but the governing equations of the anode catalyst layer will be changed as is shown below [15]:

$$\text{Energy}: -k^{eff}\frac{d^2T}{dx^2}+\sum_{i=1,3-5}\left(N_iM_iC_{pi}\right)\frac{dT}{dx}+\left|\frac{j_1(x)+j_4(x)}{nF}\right|\left(T\Delta\bar{S}\right)=\frac{i_m^{\ 2}}{\kappa^{eff}}+\left(j_1(x)+j_4(x)\right)\left(\phi_{s-}\phi_m\right) \tag{19}$$

Where the first and second terms in right hand of equation 19 are the heat generation due to Joule heating and irreversible heat generation due to activation loss in the cathode catalyst layer respectively. At constant current density, with more CO concentration, activation loss may increase considerably.

$$\text{Flux } 1: \mathrm{H_2} \qquad \frac{dN_1}{dx}=\frac{-\upsilon_1 j_1(x)}{nF} \tag{20}$$

$$\text{Flux } 2: \mathrm{H^+} \qquad \frac{dN_2}{dx}=\frac{di_m/dx}{F}=\frac{(j_1(x)+j_4(x))}{F} \tag{21}$$

$$\text{Flux } 3: \mathrm{H_2O} \qquad \frac{dN_3}{dx}=\frac{-\upsilon_3 j_4(x)}{nF} \tag{22}$$

$$\text{Flux } 4: \mathrm{CO} \qquad \frac{dN_4}{dx}=\frac{-\upsilon_4 j_4(x)}{nF} \tag{23}$$

$$\text{Flux } 5: \mathrm{CO_2} \qquad \frac{dN_5}{dx}=\frac{-\upsilon_5 j_4(x)}{nF} \tag{24}$$

Butler – Volmer

$$H_2$$

$$j_1(x)=ai_0^{ref}\theta_1\left(\frac{c_1}{c_1^{ref}}\right)^{\gamma_1}\times\left[\exp\left(\frac{\alpha_aF}{RT}(\phi_s-\phi_m)\right)-exp\left(-\frac{\alpha_cF}{RT}(\phi_s-\phi_m)\right)\right] \tag{25}$$

Butler – Volme

$$CO$$

$$j_4(x)=ai_0^{ref}\theta_4\left(\frac{c_4}{c_4^{ref}}\right)^{\gamma_4}\times\left[\exp\left(\frac{\alpha_aF}{RT}(\phi_s-\phi_m)\right)-exp\left(-\frac{\alpha_cF}{RT}(\phi_s-\phi_m)\right)\right] \tag{26}$$

As shown in equations 25 and 26 the current densities and are proportional to the surface coverage of θ_1 and θ_4.

$1:\mathrm{H_2}$ concentration

$$D_1^{eff}\frac{d^2c_1}{dx^2}-\frac{N_3}{c_3}\frac{dc_1}{dx}-\frac{c_1}{c_3}\frac{dN_3}{dx}+\frac{dN_1}{dx}=0 \tag{27}$$

$4:$ CO concentration

$$D_4^{eff}\frac{d^2c_4}{dx^2}-\frac{N_3}{c_3}\frac{dc_4}{dx}-\frac{c_4}{c_3}\frac{dN_3}{dx}+\frac{dN_4}{dx}=0 \tag{28}$$

Pr oton potential

$$\frac{d\phi_m}{dx}=-\frac{i_m}{\kappa^{eff}}+\frac{F}{\kappa^{eff}}c_2\frac{N_3}{c_3} \tag{29}$$

Electron potential

$$\frac{d\phi_s}{dx}=-\frac{i_s}{\sigma^{eff}} \tag{30}$$

The definition of all parameters is similar to the first modeling. The important point is that two equations of electrochemical reactions are written in the anode catalyst layer. Obviously, the current density in the proton-conducting membrane and the two electrochemical reactions are connected to equation 21, which affects the output voltage.

The reaction rate $j_1(x)$ is a function of the coverage of hydrogen molecules θ_1, which is defined as the fraction of the catalyst reactive surface area covered by the adsorbed hydrogen. Similarly, the reaction rate of CO species $j_4(x)$ is a function of the CO coverage θ_4. Also, the coverage of hydrogen and CO at steady state condition are obtained from a kinetic analysis for mass balance as shown in the following [2, 15].

$$\text{Coverage1}: (\mathrm{H_2}) \qquad k_{fh}x_1p_a\left(1-\theta_4-\theta_1\right)^2-b_{fh}k_{fh}\theta_1^{\ 2}-j_1=0 \tag{31}$$

$$\text{Coverage 4 : (CO)}$$
$$k_{fc} x_4 p_a \left(1-\theta_4-\theta_1\right) - b_{fc} k_{fc} \theta_4 - j_4 = 0 \quad (32)$$

Where the two equations depend on kinetic parameters to express b_{fh} the hydrogen adsorption rate, k_{fh} the hydrogen desorption rate, b_{fc} the CO adsorption rate, and k_{fc} the CO desorption. The CO adsorption rate is a function of the free energy variation, $\delta(\Delta G_{CO})$ as shown in the following [13]:

$$\text{CO adsorption rate: } b_{fc} = b_{fc0} e^{\theta \frac{\delta(\Delta G_{CO})}{RT}} \quad (33)$$

Table 2. Kinetic parameters for the electrochemical reactions of CO and H_2 [12]

b_{fc0}(atm)	1.5×10^{-5}
b_{fh}(atm)	0.5
k_{fc}($Acm^{-2}atm^{-1}$)	10
k_{fh}($Acm^{-2}atm^{-1}$)	4000
$\Delta G_{CO}/RT$	6.8

Generally, when the anode gas stream includes hydrogen and CO, the equations of the anode catalyst layer are determined by 10 unknowns, N_1, N_3, N_4, N_5, i_m, T, c_1, c_4, φ_m and φ_s, to calculate anode activation loss. To solve the equations of a PEM fuel cell we need to determine the boundary condition at the interface of electrodes, channels, catalyst layers and membrane. A summary of the boundary conditions is given in Table 3. It must be pointed out that the water vapor flux can be calculated by considering the condensation/vaporization processes in the porous electrode layer. However because of the difficulty in solving two-phase flow in the porous electrodes, N_3, at the electrode/catalyst interface, is set to be 10% of the corresponding flux of the reactant mixture as suggested by Row and Li [10]. The amount of known parameters and kinetics data used for modeling of fuel cell in this study are given in Table 4.

Table 3. A summary of boundary conditions for fuel cell modeling

Cathode (channel–GDL) interface:	T_{an} , p_{an} , x_{H2}, x_{CO}, φ_s, N''_{water} = known
Anode (channel–GDL) interface:	T_{ca} , p_{ca}, x_{O2}, x_{N2} = known
Cathode (catalyst–membrane) interface:	Anode (catalyst –membrane) interface
$N''_{H2}=0$	$N''_{O2}=0$

Table 4. Parameters used for basic case condition [1, 10, 13]

Anode pressure , p_a(atm)	3
Cathode pressure , p_c(atm)	5
Cell temperature, T_c(K)	353
Anode relative humidity, (%)	100
Cathode relative humidity, (%)	100
Electrode thickness, t_e(μm)	180
Catalyst layer thickness, t_{cl}(μm)	10
Membrane thickness, t_m(μm)	180
Volume fraction of membrane in catalyst layer, ε_m^{cl}	0.45
Volume fraction of solid in catalyst layer, ε_s^{cl}	0.5
Cathode dry gas mole fraction, N_2/O_2	3.76
Reversible potential, E_{rev}(V)	1.19
Anode: ai_0^{ref}(Acm^{-3})	30000
cathode: ai_0^{ref}(Acm^{-3})	0.0095
sh×f_e/L(cm^{-2})	20000
O_2 reference concentration, $C_{O_2}^{cl}$(mol/cm^3)	3.39×10^{-6}
H_2 reference concentration, $C_{H_2}^{cl}$(mol/cm^3)	5.64×10^{-5}
Thermal conductivity electrodes k^{eff}(W/cmK)	0.016
Thermal conductivity catalyst layers k^{eff}(W/cmK)	0.016
Thermal conductivity membrane k^{eff}(W/cmK)	0.0034

3.Validation

The governing equation is solved by using MATLAB software, which has several programs for solving differential equations. The algorithm was written with the help of the BVP4C solver in the MATLAB library. The present models predictions were compared to numerical and experimental results in the literatures [10, 13]. The results of the literature are well documented, and therefore, selected for comparison. The first modeling of the PEM fuel cell with only pure hydrogen as the anode gas stream is validated by results of Rowe and Li [10], and the second modeling of the PEM fuel cell when the anode gas stream includes hydrogen and CO is validated by the results of Springer [13]. The results of the two models, shown in the Fig. 2, seem to be in good agreement with references [10, 13] for the range of current density considered.

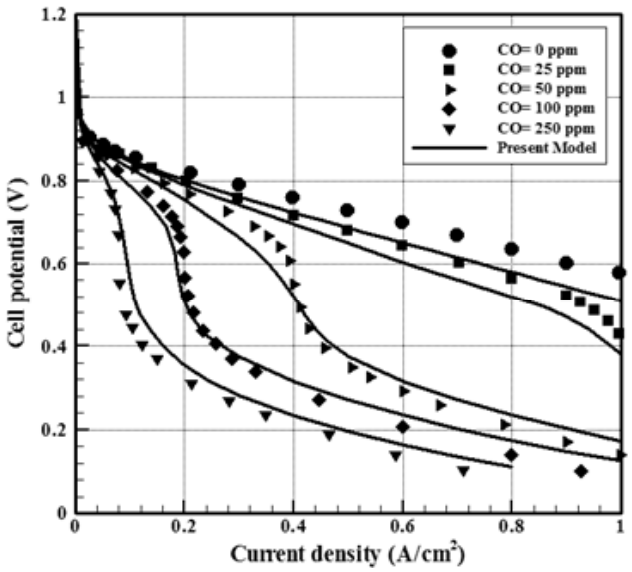

Fig. 2. Validation of the present model with references of [10, 13] at different CO concentration.

4.Results1: Pure hydrogen

As mentioned, each of components of a PEM fuel cell has loss potential that affects the fuel cell output voltage. All loss potentials that occur in the each components of the fuel cell can be divided as shown in Fig. 3. According to the Fig. 3, the cathode activation loss

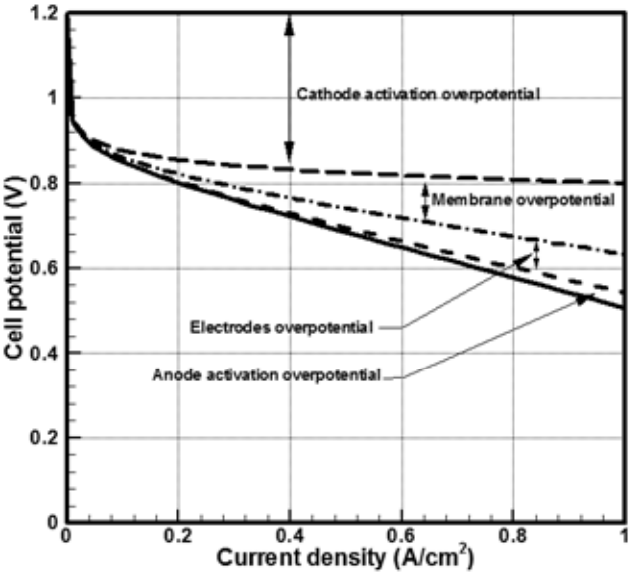

Fig. 3. The contribution of fuel cell potential losses as function of current density in the base case condition.

is the most loss potential in the PEM fuel cell when the anode gas stream includes only pure hydrogen. Next, the ohmic loss that occurs in the membrane and electrodes become more significant. Unlike the cathode activation loss, the ohmic loss becomes higher as the current density increases. Finally, the amount of the anode activation loss has the least effect on the output voltage of fuel cell because the reaction in the catalyst anode is very fast [1].

Cell potential distribution over the entire fuel cell is shown in Fig. 4, which is along the thickness of the

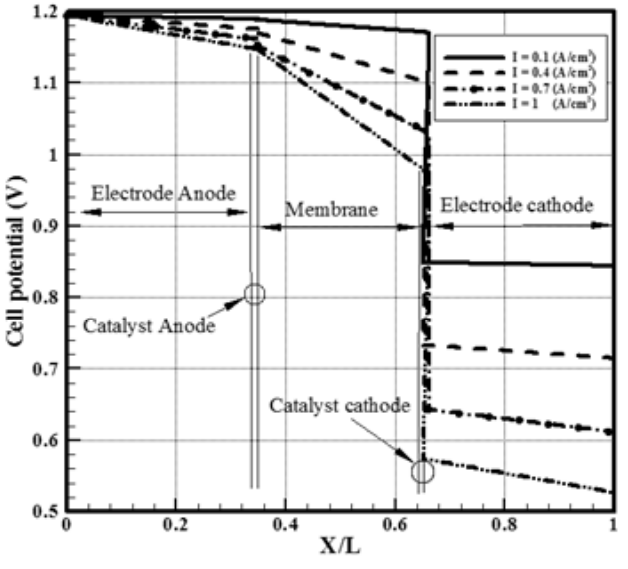

Fig. 4. Cell potential distribution over the entire fuel cell in the base case condition.

PEM fuel cell. The horizontal axis is thickness of fuel cell, which is normalization. As it is seen, when pure hydrogen is used in the fuel cell the activation loss in the cathode catalyst is significant compared to the anode catalyst and increases as the current density increases. Also, as the current density increases the resistant of the membrane and electrode become higher. This is reasonable because the proton and electron production rate increase so the membrane and electrode cannot transfer very well which affects the proton and electron migration. Therefore, the largest effect of variation of current density on the output voltage of the fuel cell is to the activation loss of the cathode catalyst, the next largest effect is on the ohmic loss of membrane, and finally it has the least effect on the ohmic loss of electrodes.

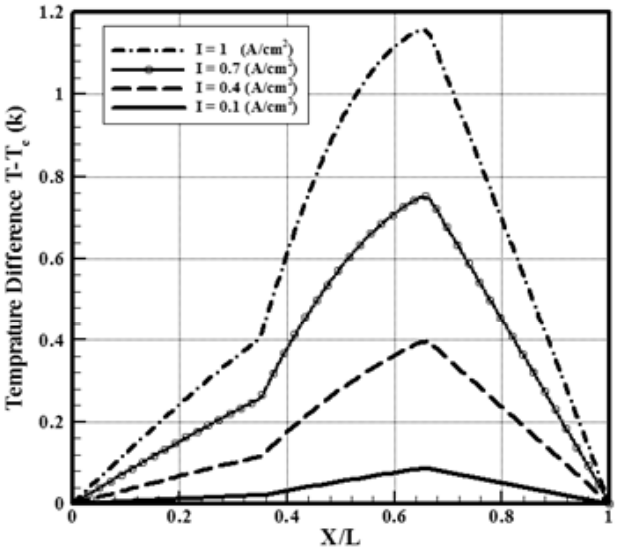

Fig. 5. Temperature distribution over the entire fuel cell in the base case condition.

The temperature distribution across the entire cell is shown in Fig. 5. The heat generation occur in the PEM fuel cell due to the activation loss in the catalyst layers and ohmic losses in the fuel cell component. Heat generation due to current across the fuel cell defines Joule heating. As seen in Fig.5, at constant current density the temperature of the cathode catalyst layer is the highest because the electrochemical reaction of the cathode is exothermic. In other words, according to Fig. 4, the most loss potential belongs to the cathode activation loss which results in more heat generation. Similarly, by increasing the current density the cell temperature will increase because an increase in the sources of heat generation. In Fig. 5, linear and nonlinear variation is seen in the electrodes and membrane, respectively, because the amount of Joule heating due to the proton current in the membrane is greater than the electron current in the electrodes [10]. Since several cells are stacked together to use as a vehicle, increasing the temperature within a single cell causes dehydration of the membrane so the proton migration will be greatly reduced. Therefore, thermal management is a critical issue for PEM fuel cell performance.

5. Results 2: Reformatted fuel

Obtaining pure hydrogen for the anode feed stream is difficult because hydrogen does not occur naturally. The hydrogen is typically derived from hydrocarbon fuels through external and internal reformers. The process of reforming fuels produces CO; therefore, the effect of CO concentration on the fuel cell performance will be illustrated in this section.

As shown in Fig. 2, if pure hydrogen is used in the anode gas stream output voltage of fuel cell decreases monotonically, but a sharp drop of the cell potential is shown when the CO concentration increases more than 50 ppm. The kinetic parameters of electrochemical reaction of CO were used in the calculations given in Tables 2 and 3. Recall that the CO species is adsorbed on the catalyst surface, blocking the electrochemical reaction of the hydrogen.

As seen in Fig. 2, if a small concentration of CO is present in the anode gas stream, the output voltage of the fuel cell decreases noticeably because CO chemisorbs on the catalyst sites to the exclusion of hydrogen. This is possible because CO is more strongly bonded to the catalyst site than hydrogen. Also, the oxidation of CO require greater potential than the oxidation of hydrogen, and the sticking probability of CO on the catalyst site is 15 times higher than that of hydrogen. Also, if the Gibbs free energy of adsorption of hydrogen and CO are

considered, the Gibbs free energy of adsorption for CO becomes more negative [2]. It can be seen that CO will preferentially adsorb to the catalyst site. The results show that even a relatively small concentration of CO can completely cover the catalyst surface to the exclusion of hydrogen adsorption. Therefore, the coverage of CO on the catalyst surface becomes a significant parameter. Also, increasing the amount of CO concentration results in higher coverage of CO on the anode catalyst surface resulting in decreasing fuel cell performance.

Fig. 6 shows the cell potential distribution over the entire fuel cell in a constant current density of i=0.7A/cm^2. The difference between this figure and Fig. 4 is the amount of activation loss in the anode catalyst layer, which is due to the presence of CO. For a small value of CO the anode activation loss is very small, but by increasing the value of CO concentration the value of anode activation loss also increases little by little, so that for a CO concentration more than 50 ppm the anode activation loss is greater than the cathode activation loss.

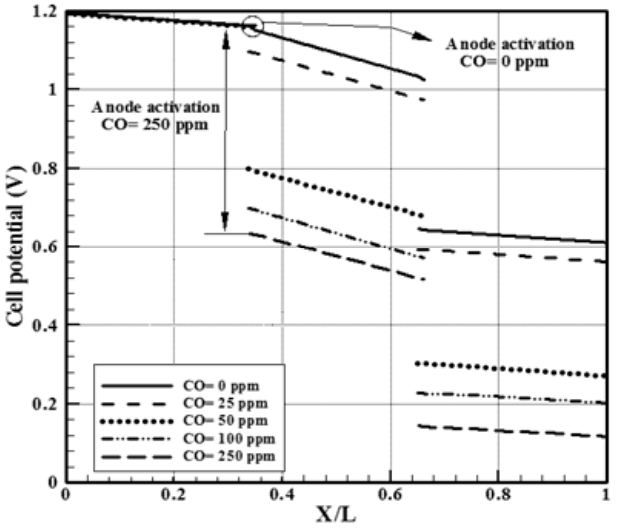

Fig. 6.Cell potential distribution over the entire fuel cell in the base case condition at i=0.7A/cm^2.

Fig. 7 shows the variation of the anode activation loss with current density at different values of CO concentration. When the CO concentration becomes more than 50 ppm, a sudden change of curve slopes can be seen in Fig. 7, after that the curve slopes become normally. This is reasonable because the oxidation of CO requires greater potential than the oxidation of hydrogen; and since the anode activation loss increases, according to equation 7, the oxidation of CO starts to produce a proton, in addition space is provided for absorbing hydrogen. Therefore, before the start of CO oxidation the slopes of the anode activation loss has a sudden change. If the value of CO concentration increases, a sudden change of activation loss occurs at the lower current density.

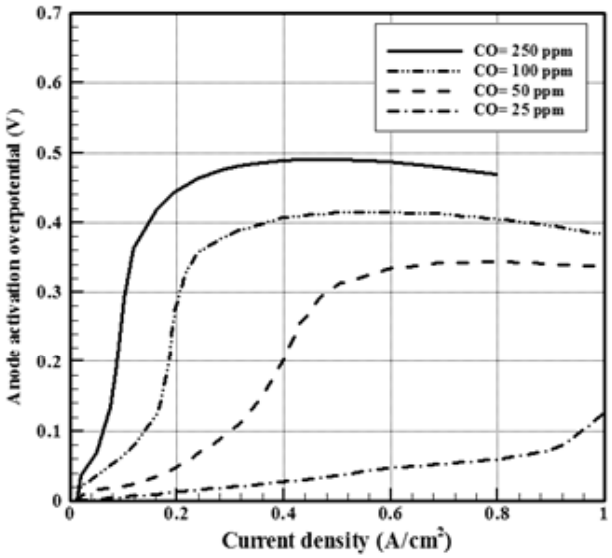

Fig. 7. The anode activation loss with different concentrations of CO in the base case condition.

Temperature distribution over the entire fuel cell with CO present is shown in Fig. 8 and was set for the base case condition at i=0.7A/cm^2.

As mentioned, CO present in the anode catalyst layer leads to an increase in the anode activation loss and as a result the temperature of the catalyst anode rises. According to the this figure, when CO concentration becomes more than 50 ppm, the highest temperature belongs to the anode catalyst layer due to anode activation loss, which affects the entire temperature of the fuel cell components.

Fig. 9 shows the variation of output voltage of the fuel cell with current density at different cell temperature, while the CO concentration of the anode gas stream is 50 ppm. If the cell temperature increases the fuel cell performance improves. Because increasing cell temperature leads to a better rate of electrochemical reaction, the activation loss in the catalyst layers

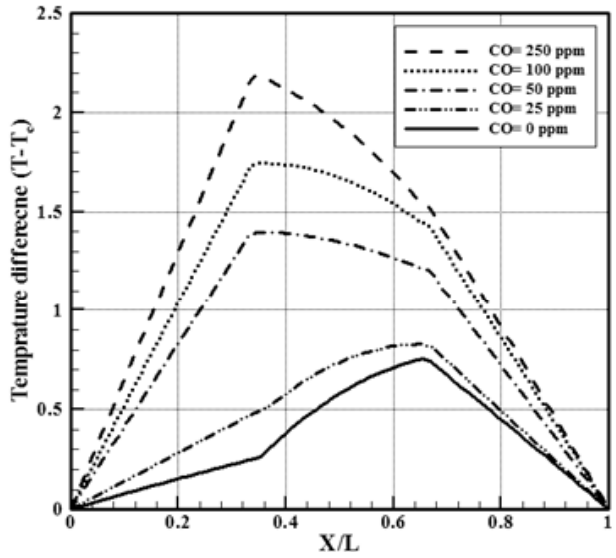

Fig. 8. Temperature distribution over the entire fuel cell with different concentrations of CO in the base case condition at i=0.7A/cm^2.

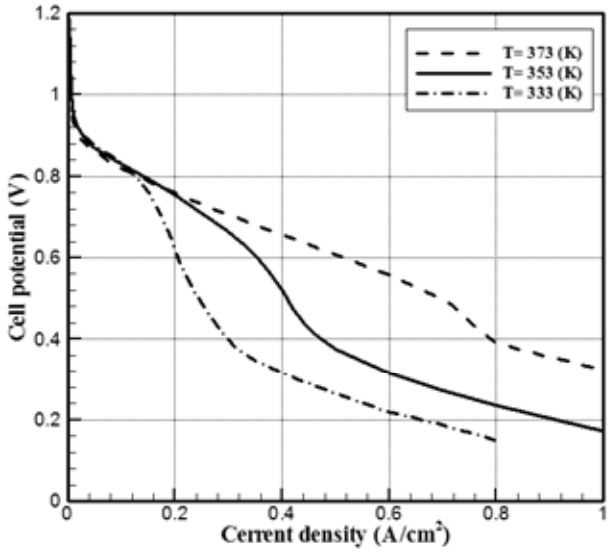

Fig. 9. Fuel cell polarization curves with different cell temperature in basic case condition at CO=50ppm.

decreases. Also, because of the presence of CO a sudden decrease in the loss of the anode occurs at higher current density, but high temperature is limited because it can lead to dehydration of membrane and increasing ohmic loss. Therefore, a fuel cell must operate at its optimum temperature.

The variation of power density versus current density for different values of CO concentration is shown in fig. 10 and observed with increasing the value of CO concentration the output power is decreased so that when CO concentration is more than 50ppm, output power density decreases to small values. In fact, with increasing the CO concentration, the major part of the fuel cell output voltage is consumed for activating the CO oxidation reaction and also the output voltage are reduced largely.

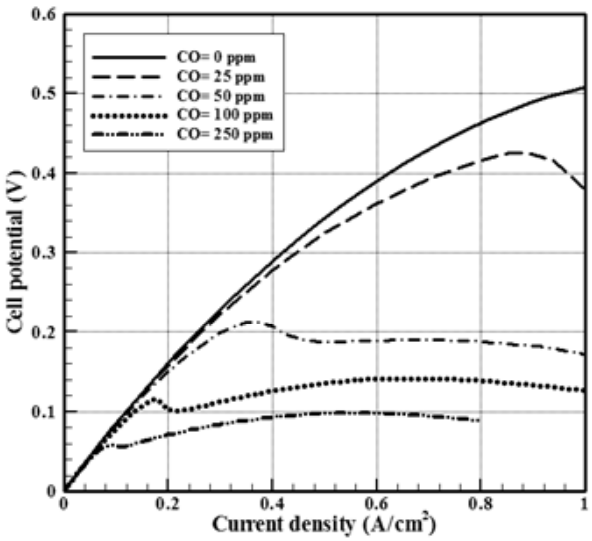

Fig. 10. The power density distribution for different values of CO concentration at P_c=5atm, P_a=3atm.

Effect of anode gas stream pressure variations on the output voltage of the fuel cell is shown in Fig. 11 when the CO concentration of anode gas stream is 50 ppm. Increasing the anode gas stream pressure leads to a rise in the concentration of hydrogen in the catalyst layer

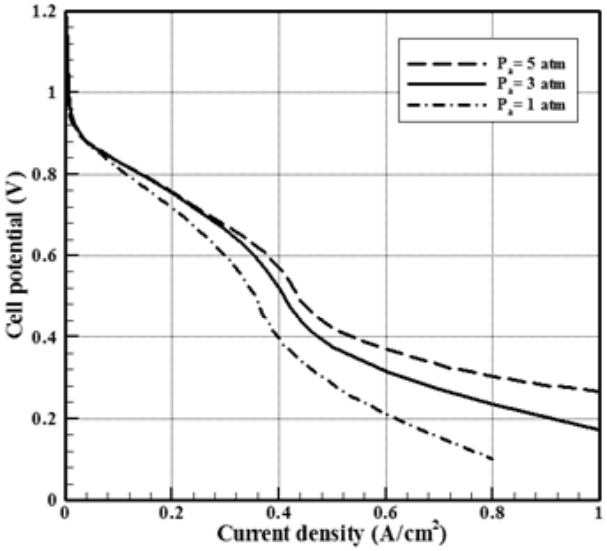

Fig. 11. Fuel cell polarization curves with different anode gas stream pressures in basic case condition at CO=50ppm.

thereby increasing the rate of oxidation of hydrogen and improving output voltage, but increasing the pressure of the anode gas stream leads to an increase in the CO chemisorbs and the possibility of coverage of CO on the catalyst surface becomes higher. In addition, higher pressure can make the process of constructing fuel cells more difficult. Therefore, a fuel cell must operate at the optimum pressure of anode gas stream.

6. Conclusions

In this study, two mathematical models of a PEM fuel cell that compare two conditions of the anode gas stream are provided. Firstly, pure hydrogen is used as the anode gas stream. The second assumption presents CO with hydrogren in the anode gas stream. The models considered that the PEM fuel cell operates in a one-dimensional, steady-state and non-isothermal condition. Since the anode feed stream includes CO, the adsorption and desorption of CO and hydrogen were investigated. The first model illustrated that the cathode activation loss has the most loss potential and also occurs in the lower current density. The second model illustrated that when CO is present in the anode catalyst the anode activation loss has the most loss potential, and increasing the value of CO leads to the occurrence of a sudden change of output cell potential at lower current density. Also, the results show that increasing cell temperature and pressure improve fuel cell performance because of an increasing rate of electrochemical reactant and increasing concentration of species, respectively; but increasing cell temperature and pressure have limitations because of dehydration of the membrane and increasing CO adsorption, respectively. The second model shows that the effect of increasing the cell temperature is better than the effect of increasing the anode gas stream pressure. This is because even though increasing the pressure of the anode gas stream increases the concentration of hydrogen, the strength of CO adsorption increases in the catalyst surface. Generally, the parameters operation must be optimized, and when CO is present in the anode gas stream the output voltage extremely decreases so the fuel cell power extremely decreases.

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