AN ENHANCED MODEL FOR NUMERICAL INVESTIGATION OF MASS TRANSPORT IN AN OPERATIONAL PEM FUEL CELL

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ABSTRACT: A mathematical model for the proton exchange membrane fuel cell (PEMFC) is developed in this study. The model features assessing the thermodiffusion effect on the PEM fuel cell performance, which has been conventionally neglected in existing fuel cell modeling studies. Also, instead of treating catalyst layers simply as interfaces, the model assigns a finite thickness for catalyst layers, allowing for a more realistic description of electrochemical reaction kinetics arising in the operational PEM fuel cell. The complete model consisting of the equations of continuity, momentum, energy, species concentrations, and electric potentials in different regions of a PEM fuel cell are numerically solved using the finite element method. Various flow and transport phenomena in an operational PEM fuel cell are simulated using the newly developed model. Through comparison of numerical simulation results using the model developed in this study and the conventional thermodiffusion-free model, no significant impact of thermodiffusion is demonstrated on the performance of a PEM fuel cell during its steady operation.

KEYWORDS: Proton exchange membrane (PEM) fuel cell, thermodiffusion, numerical simulation

NOMENCLATURE

\( a \) catalyst surface area per unit volume \((m^2/m^3)\)

\( A_{MEA} \) Full active MEA area \((m^2)\)

\( c \) concentration (mole fraction, or mass fraction) (-)

\( C \) electric charge \((C)\)

\( C \) Concentration \((mol/m^3)\)

\( C_p \) specific heat capacity at constant pressure \((J/kg/K)\)

\( D \) diffusion coefficient \((m^2/s)\)

\( D^T \) thermal diffusion coefficient \((m^3/s/K)\)

\( e \) membrane constant \((mol/m^3)\)

\( E \) potential \((V)\)

\( EW_m \) equivalent molecular weight of the membrane \((kg/mol)\)

\( f \) swelling coefficient of membrane (-)

\( F \) Faraday’s constant, \((96487 \: C/mol)\)

\( i \) current density \((A/m^2)\)

\( I \) current \((A)\)

\( j_0 \) exchange current density \((A/m^5)\)

\( k \) thermal conductivity \((W/m/K)\)

\( k_p \) electro-kinetic permeability \((m^2)\)

\( k_h \) hydraulic permeability \((m^2)\)

\( k_p \) permeability of electrode/membrane \((m^2)\)

\( M \) molecular weight of mixture \((kg/mol)\)

\( M_i \) molecular weight of component \(i\) \((kg/mol)\)

\( n \) molar number of electrons transferred (-)

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1. INTRODUCTION

Fuel cells are devices that convert chemical energy of the reactants directly into DC electricity and heat with high efficiency. This research focused on the PEMFC which is the most common type of “regenerative fuel cell”. The high power density and rapid adjustment to power demands make proton exchange membrane fuel cells (PEMFCs) one of the best candidates for a clean alternative energy source in the twenty-first century, especially for transportation applications.

The polymer electrolyte membrane fuel cells (PEMFCs), sometimes also referred to as proton exchange membrane fuel cells, consists of a negatively charged electrode (anode), a positively charged electrode (cathode), and an electrolyte membrane. An electrochemical oxidation reaction at the anode produces electrons that flow through the bipolar plate/cell interconnect to the external circuit, while the ions pass through the electrolyte to the positive electrode (cathode). The electrons return from the external circuit, while the ions pass through the electrolyte to the positive electrode. The electrons return from the external circuit to participate in the electrochemical reduction reaction at the cathode. The reactions at the electrodes are:

Anode: \( \text{H}_2(g) \rightarrow 2 \text{H}^+_\text{(aq)} + 2e^- \)  

(1)
ENHANCED MODEL FOR NUMERICAL INVESTIGATION OF MASS TRANSPORT IN AN OPERATIONAL PEM FUEL CELL

Cathode: \[
\frac{1}{2} \text{O}_2(g) + 2 \text{H}_2\text{O}(aq) + 2e^- \rightarrow \text{H}_2\text{O}(l)
\] (2)

Overall: \[
\text{H}_2(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{H}_2\text{O}(l)
\] (3)

where "\(\text{g}\)" refers to the gaseous state, "\(\text{aq}\)" stands for a substance in the aqueous phase that is dissolved in water [1], and "\(\text{l}\)" denotes the liquid state.

Since the early nineties, many papers on single PEM fuel cell models have been published to investigate different aspects of the heat and mass transport processes in the fuel cell. Springer et al. [2] and Bernardi et al. [3] were the first to publish complete fuel cell models, which are isothermal, one-dimensional, and steady state, but one-dimensional models are unable to simulate the species and phase distribution along the channel within the gas diffusion layer (GDL). In late nineties, the models were more advanced; involving multi-dimensionality (2D or 3D), multiphase flow, and entire fuel cell structure. There exist an enormous number of fuel cell analytical/numerical studies; however, no research has been done to investigate the effect of thermodiffusion on fuel cell performance other than the work by Jaralla et al. [4]. In recent years, thermodiffusion has become a subject of extensive scientific research both theoretically and experimentally. If the temperature of a liquid mass varies with spatial position, there will be a transport of energy from the hotter regions to the colder ones, [5]. A temperature gradient applied to a liquid mixture not only causes a heat flux but also gives rise to a diffusion current of constituent components. The resulting separation of the components causes a concentration gradient parallel or antiparallel with respect to the temperature gradient. This cross-effect between temperature and concentration is known as thermodiffusion or Ludwig-Soret-effect, since this effect was discovered by Ludwig [6] and systematically investigated by Soret [7] for liquid mixtures. Thermodiffusion plays a crucial role in many important processes. Research on thermal-solutal convection in porous media has gained more attention; such attention has been focused on areas including underground diffusion of nuclear waste, oil reservoir analysis, tar sand extraction. The significant role played by thermodiffusion in many applications motivated the present work.

A two-dimensional, steady-state, and general-purpose PEMFC model was developed by Jaralla et al [4], with emphasis placed on effects of thermodiffusion that have been neglected in previous fuel cell modeling studies. A noticeable impact of thermodiffusion is demonstrated on the constituent species of an operating PEM fuel cell. The oxygen consumption in the presence of thermodiffusion is found to be 3.4% less than in the case of nil thermodiffusion; that warns PEMFC researchers against the overestimation of oxidant supply using conventional computer models that ignore the thermodiffusion effect. Further investigation of thermodiffusion effects is done in this work, as an extension to Jaralla et al. [4].

The investigation of the thermodiffusion effect in the current model is based on the determination of \(D^T\) (thermal diffusion coefficient). For multicomponent gas mixtures, the thermal diffusion coefficient \(D^T\) is more commonly used as a measure of thermodiffusion, and at moderate pressures, the Maxwell-Stefan equations in the form developed by Curtiss and Bird [8] will be used to model the transport of reactants in the electrodes. By considering \(D^T\) in the Maxwell-Stefan equations, the thermodiffusion effects on the molar fraction of each species can be investigated [4]. In this work, \(D^T\) is determined for each species: hydrogen, water vapor and carbon dioxide at the anode side and, oxygen, water vapor and nitrogen at cathode side. Important electrochemical and physical phenomena during operation of PEM fuel cell were successfully simulated in this study.
2. MATHEMATICAL MODEL OF A PEM FUEL CELL

2.1 Computational domain

As illustrated in Fig. 1, a two-dimensional cell model established in the $y$-$z$ plane is studied. There are five primary transport phenomena during fuel cell operation, namely, the heat transfer in the solids and in the gases, the flow of reactant gases, the convection and diffusion of different species, as well as the transport processes for the proton and the liquid water.

For computation convenience, these five flow and transport phenomena are modeled using seven computational sub-domains (from the top to the bottom as schematically shown in Figure 1: on the anode side, the collector plate, gas diffusion layer (GDL) and catalyst layer (CL); the ionomeric membrane; the catalyst layer, gas diffusion layer, and collector plate on the cathode side. In the $y$-$z$ plane, components involved in the two-dimensional model include the two current plates, two GDLs, and two CLs at the anode and cathode sides, along with a membrane in the middle. However, the anodic and cathodic gas channels may be extracted from the computational domain since the cross flow within the channels is insignificant.

![Fig. 1: Schematic diagram of computation model of a 2-D PEM fuel cell for (y-z) plane.](image)

2.2 Assumptions

The following assumptions will be invoked to make the model more tractable and the computation faster:

1. The transport processes are steady-state.
2. The thermodiffusion is taken into account.
3. The flow in the gas-distribution channels is laminar and all of the gaseous mixtures are assumed to be ideal gases and incompressible. Though heat generation due to the electrochemical reaction is considered, the fluid properties are assumed to be independent of temperature.
4. The gas diffusers, the catalyst layers, and the membrane are all considered as isotropic and homogeneous porous media.
5. No water phase change is taken into account within each component except that all water vapor at each interface between the catalyst layer and the membrane is entirely transformed to liquid water.
2.3 Governing equations

2.3.1 Mass equation

The continuity equation describing the conservation of mass is used for the entire fuel cell

\[ \nabla \cdot \rho \vec{V} = 0 \]  \hspace{1cm} (4)

with \( \rho \) denoting the density, \( \vec{V} \) is the velocity of the fluid mixture and \( \varepsilon \) is the porosity \( \varepsilon = \varepsilon_{ct} \) at CL, \( \varepsilon = \varepsilon_{g} \) at GDL, \( \varepsilon = \varepsilon_{m} \) at membrane).

2.3.2 Momentum equation

To describe the momentum conservation in porous media, the gas mixture flow in the porous electrodes is governed by Darcy’s law in its revised version:

\[ \vec{V} = -\frac{k_p}{r^{(p)}\mu} \nabla p \] \hspace{1cm} (in GDLs) \hspace{1cm} (5)

\[ \vec{V} = -\frac{k_n}{r^{(n)}\mu} \nabla p \] \hspace{1cm} (in CLs and membrane) \hspace{1cm} (6)

where \( p \) is the pressure, \( k_p \) and \( k_n \) are the permeability of the porous electrode and the hydraulic permeability, respectively; \( \mu \) is the viscosity of the fluid; and \( r^{(2)} \) is a coefficient describing the effect of the porosity of the medium to the viscous force. The coefficient \( r^{(2)} \) can be determined using [9]:

\[ r^{(2)} = 2.25 \left(1 - \varepsilon_g^2 \right)^2 \] \hspace{1cm} (in GDLs) \hspace{1cm} (7)

\[ r^{(2)} = 2.25 \left(1 - \varepsilon_{ct}^2 \right)^2 \] \hspace{1cm} (in CLs and membrane) \hspace{1cm} (8)

where \( \varepsilon_g \) is the porosity of the gas diffusers, \( \varepsilon_{ct} \) is the effective porosity of the catalyst layer which can be calculated by:

\[ \varepsilon_{ct} = \varepsilon_m \cdot \theta_{mc} \] \hspace{1cm} (9)

with \( \varepsilon_m \) and \( \theta_{mc} \) denoting the porosity of the membrane and the volume fraction of the membrane in the catalyst layer, respectively. It is obvious that Eqs. (5) and (6) reduce to Darcy’s law when \( r^{(2)} = 1 \).

Since gas diffusion layers (GDLs), catalyst layers (CLs) and the membrane domains are porous structure, Darcy’s law can be apply within these entire domains. The pressure boundary values are prescribed at the operating pressures for the interfaces between the gas channels and GDLs for both anode and cathode sides. That is:

For Boundaries #1, #9: \hspace{1cm} \( p = p_a \) \hspace{1cm} (10)

For Boundaries #1’, #9’: \hspace{1cm} \( p = p_c \) \hspace{1cm} (11)

where \( p_a \) and \( p_c \) are the operating pressures at the anode and cathode sides, respectively.
2.3.3 Mass transfer equation

Based on the Maxwell-Stefan equations in the form developed by [9], the transport model for the multigases passing through the GDLs and CLs accounts for both diffusion and convection:

\[
\nabla \cdot \left[ -\rho \omega_j \sum_{j=1} D_{ij}^{\text{eff}} \left\{ \chi_j + (x_j - \omega_j) \frac{\nabla P}{P} \right\} - D_l \frac{\nabla \chi}{T} \right] = -\rho \frac{\nabla \cdot \nabla \omega_j}{T} + \left\{ S_{\text{sink}} \right\}
\]

where \( \chi_j \) and \( \omega_j \) represent the mole and mass fraction of the species \( j \) in the mixture. In Eq. (12), the effective binary diffusivities \( D_{ij}^{\text{eff}} \) for the flow in porous media are obtained using the original binary diffusivities via Bruggemann correction formula [10]:

\[
D_{ij}^{\text{eff}} = D_{ij} E^{1.5}
\]

and

\[
D_{ij} = D_{ij}^0 (T_0, p_0) \left( \frac{T}{T_0} \right)^{1.5}
\]

where \( D_{ij}^0, T_0, p_0 \) are the reference binary diffusivities, temperature and pressure, respectively.

In addition, Eq. (12) takes into account the thermodiffusion effect due to the presence of temperature gradient. The multicomponent thermodiffusion coefficient, \( D^T \), is calculated by [11]:

\[
D^T = -2.59 \cdot 10^{-7} \cdot T_f^{0.659} \left( \frac{M_i^{0.511} \cdot w_i}{\sum_i M_i^{0.511} \cdot w_i} - x_i \right) \left( \frac{\sum_i M_i^{0.489} \cdot w_i}{\sum_i M_i^{0.489} \cdot w_i} \right)
\]

where \( M_i \) indicates the mole mass of the species \( i \) in the mixture, and \( T_f \) is the fluid temperature, \( x_i \) the molar fraction of the species \( i \), and \( w_i \) is the term of mass fraction of species \( i \).

As indicated in Eq. (12), the right-hand side corresponding to the GDLs vanishes because there is no reaction on the sites; but a sink term at the anodic CL must be prescribed:

\[
S_{\text{H}_2} = -\frac{j_{\text{H}_2}}{2F} M_{\text{H}_2}
\]

\[
S_{\text{H}_2, \text{O}} = 0
\]

due to the oxidization of hydrogen; meanwhile a sink term for oxygen and a source term for water should be considered at the cathodic CL representing the oxygen reduction reaction:

\[
S_{\text{O}_2} = \frac{j_{\text{O}_2}}{4F} M_{\text{O}_2}
\]

\[
S_{\text{H}_2, \text{O}} = -\frac{j_{\text{H}_2}}{2F} M_{\text{H}_2, \text{O}}
\]
In the above source/sink terms, \( M \) is the molecular weight of the species, \( j_a \) and \( j_c \) are the anodic and cathodic exchange current densities, respectively, which can be modeled by the Butler-Volmer equations [12]:

\[
j_a = \left( a_{j_0}^{\text{ref}} \right)_a \left( \frac{c_{H_2}}{c_{H_2,\text{ref}}} \right)^{1/2} \left[ \exp \left( \frac{\alpha_a^e F}{RT} \eta_a \right) - \exp \left( -\frac{\alpha_a^c F}{RT} \eta_a \right) \right]
\]

(20)

\[
j_c = \left( a_{j_0}^\text{ref} \right)_c \left( \frac{c_{O_2}}{c_{O_2,\text{ref}}} \right) \left[ \exp \left( \frac{\alpha_c^e F}{RT} \eta_c \right) - \exp \left( -\frac{\alpha_c^c F}{RT} \eta_c \right) \right]
\]

(21)

The surface over-potential for an electrochemical reaction, \( \eta \) is considered the driving force for an electrochemical reaction, and can be described as:

\[
\begin{align*}
\eta_a &= \phi_s - \phi_p \quad \text{at anode} \\
\eta_c &= \phi_s - \phi_p - E_0 \quad \text{at cathode}
\end{align*}
\]

(22)

where \( \phi_s \) is the solid-phase potential, \( \phi_p \) is membrane-phase potential, and \( E_0 \) is the thermodynamic open circuit potential for overall reaction, which is expressed by the Nernst equation [13] as a function of the reactant and product concentrations at the interface:

\[
E_0 = 1.23 - 0.9 \times 10^{-3} (T - 298) + 2.3 \frac{RT}{4F} \log \left( \frac{p_{H_2}^s}{p_{O_2}^s} \right)
\]

(23)

The boundary conditions at the anodic and cathodic interfaces between the gas channels and GDLs, i.e., boundaries #1, #1', #9, and #9' (as shown in Fig. 1), for each of the mass fractions of \( H_2 \), \( O_2 \) is prescribed using a constant inlet value. The mass fractions of water vapor at the anode and cathode sides can be determined as follow respectively:

\[
\omega_{H_2,O,a} = RH \frac{p_{\text{sat}}^w M_{H_2}}{p_a M}
\]

(24)

\[
\omega_{H_2,O,c} = RH \frac{p_{\text{sat}}^w M_{H_2}}{p_c M}
\]

(25)

where \( RH \) is the relative humidity, \( p_a \) and \( p_c \) are the operating pressures at the anode and cathode sides; \( p_{\text{sat}}^w \) is the saturated water partial pressure calculated using the following empirical equation [2]:

\[
\log_{10} p_{\text{sat}}^w = -2.1794 + 0.02953T - 9.1837 \times 10^{-5} T^2 + 1.4454 \times 10^{-7} T^3
\]

(26)

### 2.3.4 Potential equations

To describe the fuel cell potential distribution, two kinds of potentials are modeled. One is the membrane-
phase potential, which is obtained by solving the equation of proton transport in the catalyst layer and membrane:

\[
\vec{\nabla} \cdot (-\sigma^P \vec{\nabla} \phi_p) = \begin{cases} 
j_s & \text{in anode catalyst layer} \\
\text{Function}(T, p, c_w, ...) & \text{in membrane} \\
j_c & \text{in cathode catalyst layer} 
\end{cases}
\]  

(27)

where \( \phi_p \) is the ionic potential, and \( \sigma^P \) is the ionic conductivity.

The proton current density at the interface between the catalyst layers and the GDL is set to zero. Dirichlet boundary conditions are used to solve the protonic potential equations at the interface between the membrane and catalyst layers at anode and cathode sides. Elsewhere homogeneous Neumann boundary conditions are applied.

The second kind of potential in the model is the solid-phase potential which results from the solution to the equation of electron transport in the catalyst layers, gas diffusers and collector plates:

\[
\vec{\nabla} \cdot (-\sigma^\varepsilon \vec{\nabla} \phi_e) = \begin{cases} 
-j_s & \text{in anode catalyst layer} \\
0 & \text{in GDLs and collector plates} \\
-j_c & \text{in cathode catalyst layer} 
\end{cases}
\]  

(28)

where \( \phi_e \) is the electric potential, and \( \sigma^\varepsilon \) is electrical conductivity.

The solid-phase potential \( \phi_e \) is the cell voltage; the value of solid-phase potential along the cathode collector plate edge, i.e., Boundary #5', is prescribed while the value of the cell voltage along the anode current plate edge, i.e., Boundary #5, is assumed to be zero.

2.3.5 Water transport equation

The water transport in the membrane is driven by the electro osmotic drag, diffusion, and hydraulic permeation, which is induced respectively by the moving protons, the water concentration difference, and the pressure difference between the two sides of the membrane. A good water management procedure aims at balancing the three water fluxes such that neither flooding of the electrodes nor drying out of the membrane occurs. The following equation describes the distribution of water concentration, \( c_w \), within the membrane:

\[
-D_w \nabla^2 c_w - e_w \frac{k_w}{\mu_l} \left( \vec{\nabla} c_w \cdot \vec{\nabla} p_l \right) + \frac{5}{44} \frac{e}{F(e - fc_w)} \left( \vec{\nabla} c_w \cdot \vec{I} \right) = 0
\]  

(29)

It is obtained through combination of the diffusion represented by the diffusion coefficient, \( D_w \), the pressure drop, \( \vec{\nabla} p_l \), and the electro osmotic drag that is related to the current density, \( \vec{I} \). More details about Eq. (29) and its derivation can be found in Cao et al. [14]. In this model equilibrium is assumed between the gas phase and the membrane phase of water in Nafion membrane. Since the water can be transported through the catalyst layers to the membrane, Dirichlet boundary conditions should be applied at the interface between the membrane and the catalyst layers at the anode and cathode sides. And the water content at these interfaces can be calculated using [2]:

\[
\lambda = 0.043 + 17.8a - 39.85a^2 + 36a^3 \quad \text{for} \quad 0 < a \leq 1 \quad \text{in catalyst layers}
\]  

(30)
where \( a \) is the activity of water vapor defined as:

\[
a = \frac{x_{H_2O} P}{P^*_{H_2O}}
\]  

(31)

As the water mole fraction exceeds saturation, a linear relation is assumed between the water content and water activity [2]:

\[
\lambda = 14 + 1.4(a - 1) \quad \text{for} \quad 1 < a \leq 3 \quad \text{in the membrane}
\]  

(32)

the Neumann boundary condition is applied at the left and right sides of the membrane:

\[
\vec{n} \cdot \nabla c_w = 0
\]  

(33)

where \( \vec{n} \) denotes the unit vector normal to the boundaries.

### 2.3.6 Energy equation

In an operational PEM fuel cell, the overall mechanism of water transport is further complicated by the globally exothermic electrochemical reaction. The heat generated increases water evaporation rates at the cathode and, in situations where the membrane is allowed to dehydrate, can combine with ohmic heating in the membrane leading to a deterioration of the membrane-electrode bond. The temperature distribution can be obtained by solving the following energy equation in the GDLs, CLs and membrane of a PEM fuel cell:

\[
\rho c_p \left( \vec{V} \cdot \nabla T \right) = k_{eff} \Delta T + \begin{cases} 
\frac{i_e^2}{\sigma_{GDL}} & \text{in GDLs} \\
\frac{i_p^2}{\sigma_m} & \text{in membrane} \\
\frac{i_e^2}{\sigma_{ct}} + \frac{i_p^2}{\sigma_m} + \eta_a \cdot \vec{j}_a & \text{in anode catalyst layer} \\
\frac{i_e^2}{\sigma_{ct}} + \frac{i_p^2}{\sigma_m} + \eta_e \cdot \vec{j}_e & \text{in cathode catalyst layer}
\end{cases}
\]  

(34)

At GDLs, the last term, \( \frac{i_e^2}{\sigma_{GDL}} \), represents the heat source term produced as a result of the ohmic heating of electron current, \( i_e \), as there is an electronic resistances through the gas diffusers. In the membrane an additional Joule heating source, \( \frac{i_p^2}{\sigma_m} \), arising from protonic resistances through the membrane has been added to the energy equation, \( \sigma_m \) appears in the Joule heating source term representing the ionic conductivity in the membrane. At the catalyst layers, on the right hand side of the above equation, the second and third terms describe the ohmic heating of both proton current \( i_p \) and electron current \( i_e \) within catalyst layers; and the last term represents the heat generation or absorption because of electrochemical reaction at the catalyst.
3. NUMERICAL PROCEDURES

The PEM fuel cell modeling equations describing fluid flow, multi-species transport, heat transfer, and electric potentials are strongly nonlinear and coupled with each other. To numerically solve this large set of nonlinear equations, a finite element computational fluid dynamics package, COMSOL 3.4 is selected. In finite element analyses, it is often necessary to resolve the geometry in more details for more accuracy, thus, numerical tests were performed for the base case geometry to ensure that the solutions were independent of further refinement for the mesh. In the current simulation, the total number of elements is 13,264, and a stationary non-linear solver is used together with Direct (UMFPACK) linear system solver in this simulation.

The relative tolerance for the error criteria was $1.0 \times 10^{-6}$.

4. RESULTS AND DISCUSSION

4.1 Model Validation

To validate the fuel cell model presented in this paper, a comparison using fuel cell performance curves is made between the simulation results and the available experimental data [15] corresponding to the same operating conditions grouped in Table 1. Table 2 lists the base case operational parameters and electrode properties for the current model.

The polarization curve is the most important characteristic of a fuel cell. It may be used for diagnostic purposes. As shown in Fig. 2, the sample points used to plot polarization curves are picked in such a way that the cell voltage can range from 0.3V to 0.9V with 0.1V as increment. The polarization curve looks steeper and exhibits slight nonlinearity in the activation region.

Table 1: Physical dimension of the PEM fuel cell, and operating parameters under a base case computation, [15]

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas diffuser width (z-direction)</td>
<td>$3 \times 10^{-3}$</td>
<td>m</td>
</tr>
<tr>
<td>Gas diffuser height (y-direction)</td>
<td>$2.54 \times 10^{-4}$</td>
<td>m</td>
</tr>
<tr>
<td>Collector width</td>
<td>$1.3 \times 10^{-3}$</td>
<td>m</td>
</tr>
<tr>
<td>Catalyst layer thickness</td>
<td>$2.87 \times 10^{-3}$</td>
<td>m</td>
</tr>
<tr>
<td>Membrane thickness (y-direction)</td>
<td>$2.3 \times 10^{-4}$</td>
<td>m</td>
</tr>
<tr>
<td>$T$ : fuel cell (ambient) temperature</td>
<td>333</td>
<td>K</td>
</tr>
<tr>
<td>$\zeta_a$ : stoichiometric ratio at anode</td>
<td>1.3</td>
<td>-</td>
</tr>
<tr>
<td>$\zeta_c$ : stoichiometric ratio at cathode</td>
<td>3</td>
<td>-</td>
</tr>
<tr>
<td>$p_a$ : fuel inlet pressure at anode</td>
<td>1</td>
<td>atm</td>
</tr>
<tr>
<td>$p_c$ : air inlet pressure at cathode</td>
<td>3</td>
<td>atm</td>
</tr>
<tr>
<td>$RH$ : relative humidity of inlet gas mixture</td>
<td>100</td>
<td>%</td>
</tr>
</tbody>
</table>
Then, the two sets of results reach good agreement at intermediate current densities $0.246 \text{ A/cm}^2 \leq i \leq 0.632 \text{ A/cm}^2$, showing the cell voltage drops clearly in a linear trend as the current density increases within this ohmic loss region. However, a remarkable discrepancy is found for high current densities ($i \geq 0.632 \text{ A/cm}^2$). This is due to the lack of a successful mathematical model to accurately quantify the effect of mass transport losses. As of today, all existing fuel cell models underestimate the mass-transport limitation. As shown in Fig. 2, the limiting current density captured from the simulation results is close to 0.8 $\text{A/cm}^2$, which appears generally in good agreement with the findings through experiments.

**Table 2:** Electrode and electrochemical properties of PEM fuel cell

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
<th>Unit</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon_g$: gas diffuser porosity</td>
<td>0.4</td>
<td>-</td>
<td>[16]</td>
</tr>
<tr>
<td>$\varepsilon_m$: membrane porosity</td>
<td>0.28</td>
<td>-</td>
<td>[16]</td>
</tr>
<tr>
<td>$\theta_m$: volume fraction membrane in catalyst layer</td>
<td>0.5</td>
<td>-</td>
<td>[16]</td>
</tr>
<tr>
<td>$k_p$: permeability to air in the gas diffuser</td>
<td>1.76x10¹¹</td>
<td>m²</td>
<td>[16]</td>
</tr>
<tr>
<td>$k_a$: hydraulic permeability of the membrane</td>
<td>1.58x10¹⁸</td>
<td>m²</td>
<td>[16]</td>
</tr>
<tr>
<td>$k_{ab}$: electrokinetic permeability of membrane</td>
<td>1.13x10¹⁰</td>
<td>m²</td>
<td>[16]</td>
</tr>
<tr>
<td>$k_{aw}$: air thermal conductivity</td>
<td>30x10⁻²</td>
<td>W / m / K</td>
<td>[17]</td>
</tr>
<tr>
<td>$k_{ap}$: thermal conduc. of matrix of gas diffuser</td>
<td>150.6</td>
<td>W / m / K</td>
<td>[16]</td>
</tr>
<tr>
<td>$k_{m,dry}$: thermal conductivity of dry membrane</td>
<td>100</td>
<td>W / m / K</td>
<td>[16]</td>
</tr>
<tr>
<td>$c_{p,air}$: air specific heat at constant pressure</td>
<td>1008</td>
<td>J / kg / K</td>
<td>[15]</td>
</tr>
<tr>
<td>$c_f$: fixed charged site concentration in memb.</td>
<td>1.2x10¹⁰</td>
<td>mol / m³</td>
<td>[15]</td>
</tr>
<tr>
<td>$z_f$: charge of sulfonate site in memb.</td>
<td>-1</td>
<td>-</td>
<td>[16]</td>
</tr>
<tr>
<td>$\rho_m^{dry}$: membrane solid dry mass density</td>
<td>1980</td>
<td>kg / m³</td>
<td>[16]</td>
</tr>
<tr>
<td>$EW_m$: equivalent membrane weight</td>
<td>1.1</td>
<td>kg / mol</td>
<td></td>
</tr>
<tr>
<td>$f$: membrane swelling coefficient</td>
<td>0.0126</td>
<td>-</td>
<td>[13]</td>
</tr>
<tr>
<td>$a_{0,ref}^{\text{H}_2}$: reference exchange current density times specific area at the anode</td>
<td>1.0x10⁶</td>
<td>A / m²</td>
<td>[15]</td>
</tr>
<tr>
<td>$a_{0,ref}^{\text{O}_2}$: reference exchange current density times specific area at the anode</td>
<td>2.5x10⁰</td>
<td>A / m²</td>
<td>[15]</td>
</tr>
<tr>
<td>$c_{H_2,ref}$: reference molar concentration</td>
<td>40.88</td>
<td>mol / m³</td>
<td>[15]</td>
</tr>
<tr>
<td>$c_{O_2,ref}$: reference molar concentration</td>
<td>40.88</td>
<td>mol / m³</td>
<td>[15]</td>
</tr>
<tr>
<td>$\alpha^{\text{an}}$: anodic transfer coefficient at cathode</td>
<td>0</td>
<td>-</td>
<td>[16]</td>
</tr>
<tr>
<td>$\alpha^{\text{cat}}$: cathodic transfer coefficient at cathode</td>
<td>1.2</td>
<td>-</td>
<td>[16]</td>
</tr>
<tr>
<td>$\alpha^{\text{an}}$: cathodic transfer coefficient at anode</td>
<td>1/2</td>
<td>-</td>
<td>[16]</td>
</tr>
<tr>
<td>$\alpha^{\text{cat}}$: anodic transfer coefficient at anode</td>
<td>1/2</td>
<td>-</td>
<td>[16]</td>
</tr>
</tbody>
</table>
Fig. 2: Comparison of modeling results with experimental data by Ju and Wang [15].

Fig. 3: Comparison of modeling results with and without thermodiffusion on the PEM fuel cell performance.
4.2 Effect of thermodiffusion on polarization curve

A set of systematic comparisons are made between the results with the thermodiffusion effects turned off against the thermodiffusion term switched on. By using the two types of simulation results, Figure 3 shows the comparison of modeling results with and without thermodiffusion and their effects on the PEM fuel cell performance. All comparisons show that the overall performance of a fuel cell during its steady-state operation does not significantly change no matter whether the thermodiffusion term is switched on or off; because of the relatively small magnitude of the thermodiffusion coefficients of the species at anode and cathode sides, as shown in Figs. 4 and 5.

4.3 Results of the base case

Transport phenomena play an important role in many engineering applications and scientific research. In this numerical simulation, detailed information of transport phenomena in the fuel cell that are usually hard to examine by in situ measurements can be provide by the comprehensive current model. In the following sections, distributions of different physical variables, including the velocity, distributions of mole fractions of reactant gases, cell temperature, local current density, membrane water content, potential loss, and the activation over-potential distribution at the cathode side will be examined for better understanding the fuel cell working mechanism; taking the thermodiffusion into account. The numerical simulation employs fuel cell operational conditions as described in Table 1.

4.3.1 Distributions of reactants and products

Figures 6-9 illustrate the important effects of the transport of reactant and product gases on the performance of PEM fuel cell. Figure 6 depicts the hydrogen mole fraction distribution inside the anode-side porous electrode for three different nominal current densities: on the top a higher one (0.9179 A/cm²), on the middle (0.6959 A/cm²), and the lower one (0.2862 A/cm²) on the bottom.

In all cases, the hydrogen mole fraction decreases gradually from the inlet toward the anode catalyst layer due to the consumption of the hydrogen through the hydrogen oxidation reaction (HOR) that takes place at the anode side catalyst. Also the hydrogen mole fractions decrease in higher rate in GDLs from the side toward the center where the current collector is positioned due to lack of convection and higher diffusivity on the sites; as, the hydrogen has high diffusivities in both carbon-oxide (CO2) and in water vapor. Thus, no significant reduction of hydrogen mole fraction is found, as shown on Fig. 6, even at the high current density of \( i = 0.179 \text{ A/cm}^2 \).
Fig. 4: The Thermal diffusion coefficients of species (H2, H2O, CO2) at anode side
Fig. 5: The Thermal diffusion coefficients of species (O2, H2O, N2) at cathode side
Fig. 6: Hydrogen mole fraction at anode-side catalyst layer and gas diffusion layer for three loading conditions: 0.9179 A/cm² (top), 0.6959 A/cm² (middle), and 0.2862 A/cm² (bottom).

Figure 7 shows the oxygen mole fraction distribution inside the cathode-side porous electrode for three different current densities. In general, the oxygen concentrations decrease gradually from inlet at cathode side toward the cathode catalyst layer due to the consumption of oxygen through the oxidation-reduction reaction (ORR) in the cathode catalyst layer. In addition, the oxygen depletion is more noticeable than the hydrogen because of the relatively low diffusivity of the oxygen compared to that of hydrogen and the low concentration of oxygen in ambient air that leads to slower oxygen diffusion in the cathode, causing dramatic oxygen mass fraction gradients. From Figs. 6-8 one can observe that as the loading
current density increases, more hydrogen and oxygen are depleted and higher water vapor concentration is produced, as a result, the mass transport limitation for the oxygen within GDL and catalyst layer becomes significant.

Fig. 7: Oxygen mole fraction at anode-side catalyst layer and gas diffusion layer for three loading conditions: 0.9179 A/cm\(^2\) (top), 0.6959 A/cm\(^2\) (middle), and 0.2862A/cm\(^2\) (bottom)

4.3.2 Temperature distribution

Maintaining the desired temperature in PEM fuel cell is required to remove the heat generated by the electrochemical reaction in order to prevent drying of the membrane. Figure 9 illustrates the temperature distribution in the y-z plane for PEM fuel cells for high, intermediate and low load conditions. The presence of current plates as a medium of cooling in y-z plane causes significant temperature gradient along the z-direction. The peaks of temperature are observed within the cathode gas diffusion layer at the corner of current plate for the high and intermediate current density. While, for the low current density the peak of the temperature can be observed at the corner of the cathode gas channels; where, the concentration of the oxygen is higher at the inlet of the cathode. It can be obviously seen that the temperature distribution is symmetric about its vertical central line due to the symmetry of flow field. Also, the temperature at the cathode side is slightly higher than at the anode side; as, air at the cathode
side is closer to the major heat source. It is also noticed from Fig. 9 that the nominal current density has an influence on the increasing of temperature during fuel cell operation, as when the current density increases, the temperature maximum gets increased as a result of more heat generated from the chemical reaction.

Fig. 9: Temperature distribution across fuel cell in z-y plane for the three different current densities: 0.9179 (top), 0.6959 (middle) and 0.2862 (bottom)
4.3.3 Water content in the membrane

The water transport in the membrane is mainly caused by the electro-osmotic drag related to the protonic current in the electrolyte that leads to the transport of water from anode to cathode; and transport through diffusion related to the water-content gradients in the membrane.

These transport mechanisms usually effect the distribution of the water in the fuel cell. Figure 10 shows the profiles for water content in the membrane for the base case conditions at three different average current densities. The influence of the electro-osmotic drag and back diffusion are obvious from these results on Fig. 10. Across the membrane, the water content at the anode side is lower than that at the cathode side, as water is dragged toward the cathode via electro-osmotic transport and due to insufficient back-diffusion to the anode side from the cathode side, where water is produced.

Fig. 10: Water content distribution in membrane z-y plane for the three different current densities: 0.9179 (top), 0.6959 (middle) and 0.2862 (bottom)
Figure 10 demonstrates that the water content at the anode side decreases from 14.01 to 14.002 as the current density increases from 0.2862 to 0.9179, while at the cathode side rises from 14.273 to 14.427. As when current density increases, a higher electro-osmotic drag drives more water from the anode side to the cathode side that leading to lower water content at the anode side while a higher water content at the cathode side; also, more water is produced at the cathodic catalyst layer in response to a higher current density.

Fig. 11: Membrane-phase potential distribution in MEA z-y plane for the three different current densities: 0.9179 (top), 0.6959 (middle) and 0.2862 (bottom)
4.3.5 Membrane-phase potential loss

The Protons generated within the anodic catalyst layer and pass through the membrane to consume inside the cathodic catalyst layer cause what is called membrane-phase potential loss as a result to the resistance to proton transport across the membrane electrode assembly (MEA), which is a combination of a membrane sandwiched between two catalyzed porous electrodes. Figure 11 shows the membrane-phase potential loss distribution for three different loading conditions. For all the three current densities, the electric potential on the upper boundary of the membrane is assumed to be a constant value-zero at the anode side for convenience of computational simulation.

The membrane-phase potential loss at the lower current density is small owing to the small amount of protons flowing through the membrane. The membrane-phase potential loss becomes significant as the current density increases. The maximum potential loss can be observed at the inlet of the anode side, due to the highest rate of electrochemical reaction that results from the fastest consumed of the protons.

5. CONCLUSION

A two-dimensional, steady-state, and general-purpose PEMFC model was developed in this work with emphasis placed on effects of thermodiffusion that have been neglected in previous fuel cell modeling studies. The simulation based on this new model can predict the overall performance of PEMFC, which reach good agreement with available experimentally-obtained data. Simulation results also provided valuable information about the detailed distribution of the reactant gases inside the PEM fuel cell. Due to the relatively small magnitude of the thermodiffusion coefficient in the fuel cell application, the overall performance of a steady-state PEMFC exhibits no significant change after the thermodiffusion term is incorporated into the model.

The comprehensive fuel cell model developed in this study can be used to examine details of mass and heat transport encountered in an operational PEMFC, which are usually unobservable by in-situ measurements due to the tiny dimension of the cell. The simulation results also provide insights that may assist practitioners in optimizing PEMFC design and reducing the manufacturing cost.

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REFERENCES


