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Article Type: Full Length Article

Keywords: HT-PEMFC, boiling phase change, warm-up, heating strategy, analytical model

Abstract: This paper investigates the thermal and water balance as well as the electro-kinetics during the warm-up process of a Hydrogen/Oxygen high-temperature proton exchange membrane fuel cell (HT-PEMFC) from room temperature up to the desired temperature of 180 °C. The heating strategy involves the extraction of constant current from the fuel cell, while an external heating source with a constant heat input rate is applied at the end plates of the cell simultaneously. A simple analytical unsteady model is derived addressing the boiling phase changing phenomenon in the cathode catalyst layer (CCL) and cathode gas diffusion layer (CGDL) of the cathode that occurs when the temperature of the fuel cell reaches the boiling temperature of water. Parameters such as the heat input rate, extracted current, cathode pressure and cathode stoichiometric flow ratio are varied and their effects on the temperature, liquid water fraction and most importantly, the voltage profiles with respect to time, are explored. A comparison between other existing heating strategies using the model suggests that there is insignificant improvement in warm-up time when current is extracted from room temperature considering a single cell. However, considering the solution for a typical 1-kW stack suggests that reductions in warm-up time and energy consumption can be expected. In addition, the results show that boiling phase change is found to be a key factor that affects the level of water saturation in the porous media such as the CCL and CGDL during the warm-up process, when current is extracted from the start of the process i.e. room temperature. However, the energy consumption due to boiling phase change is found to be negligible as compared to external heating input rate. The parametric studies show that the variation of heat input rate, extracted current and cathode pressure have significant effect on the cell voltage that is strongly dominated by the liquid water fraction in the porous media. On the other hand, the variation of cathode stoichiometric flow ratio is found to have minimal effect on the output cell voltage. The parametric studies also indicate that boiling phase change is present for a significant period of time under typical operating conditions.
An Analysis of Boiling Phase Change Phenomenon in High-Temperature Proton Exchange Membrane Fuel Cells during Warm-Up Process

1. A brief background regarding the research involved or how the data was collected.

This paper investigates the warm-up process of a Hydrogen/Oxygen high-temperature proton exchange membrane fuel cell. This is done by the consideration of thermal and water balance, electrochemistry as well as boiling phase change in an analytically solved unsteady model. The key novelty of the study relates to the inclusion of boiling phase change phenomena in the model. The data as shown in all the figures were plotted with the use of Microsoft Excel, Origin and MATLAB. The analytical model itself was derived by hand.

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4. Details of any previous or concurrent submissions.

This manuscript has not been submitted concurrently or previously.

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Analytical modelling of boiling phase change phenomenon in high-temperature proton exchange membrane fuel cells during warm-up process

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Abstract

This paper investigates the thermal and water balance as well as the electro-kinetics during the warm-up process of a Hydrogen/Oxygen high-temperature proton exchange membrane fuel cell (HT-PEMFC) from room temperature up to the desired temperature of 180 °C. The heating strategy involves the extraction of constant current from the fuel cell, while an external heating source with a constant heat input rate is applied at the end plates of the cell simultaneously. A simple analytical unsteady model is derived addressing the boiling phase changing phenomenon in the cathode catalyst layer (CCL) and cathode gas diffusion layer (CGDL) of the cathode that occurs when the temperature of the fuel cell reaches the boiling temperature of water. Parameters such as the heat input rate, extracted current, cathode pressure and cathode stoichiometric flow ratio are varied and their effects on the temperature, liquid water fraction and most importantly, the voltage profiles with respect to time, are explored. A comparison between other existing heating strategies using the model suggests that there is insignificant improvement in warm-up time when current is extracted from room temperature considering a single cell. However, considering the solution for a typical 1-kW stack suggests that reductions in warm-up time and energy consumption can be expected. In addition, the results show that boiling phase change is found to be a key factor that affects the level of water saturation in the porous media such as the CCL and CGDL during the warm-up process, when current is extracted from the start of the process i.e. room temperature. However, the energy consumption due to boiling phase change is found to be negligible as compared to external heating input rate. The parametric studies show that the variation of heat input rate, extracted current and cathode pressure have significant effect on the cell voltage that is strongly dominated by the liquid water fraction in the porous media. On the other hand, the variation of cathode stoichiometric flow ratio is found to have minimal effect on the output cell voltage. The parametric studies also indicate that boiling phase change is present for a significant period of time under typical operating conditions.

Keywords: HT-PEMFC, boiling phase change, warm-up, heating strategy, analytical model

1. Introduction

Fuel cells are generally perceived to be one of the next promising alternative energy sources considering its potential uses in a variety of applications [1]. One of the major reasons for this direction strongly relates to the bloom of Hydrogen production methods and storage capabilities [2]. As far as fuel cells are concerned, HT-PEMFCs are considered as the next generation of power producing devices due to their superior performance compared to the low-temperature proton exchange membrane fuel cells (LT-PEMFCs) [3, 4]. Nevertheless, several obstacles dominate the field of HT-PEMFC, causing a delay of its commercialization.
The whole dynamics and directions of these new challenges pertaining to high-temperature operation are different as compared to the ones experienced in LT-PEMFC. Over the past decade, research activities were mainly focused on the development of fuel cell components that have high temperature degradation resistance. Producing high-temperature membranes with sufficient proton conductivity are one of the key focuses and numerous efforts have been reported in the literature [5, 6].

Another key area has become popular recently is related to the analysis and optimization of warm-up strategy during the start-up period of a HT-PEMFC [7]. Conceptually, there are number of ways of starting up the HT-PEMFC and generally, two main parameters define a heating strategy. Firstly, the mode of operation of the fuel cell during the cold start-up process, which can be set by controlling the extracted current or voltage (holding either one of them at a constant value or setting at any desired profile) [8-10]. Secondly, the set temperature during the warm-up period, above which the fuel cell is put on operation, is another key factor. As far as this is concerned, there are three different methods for start-up, i.e., (a) the fuel cell to be heated up to a temperature above the boiling point of water, after which the fuel cell is operated, (b) similar to (a) but the fuel cell is operated below the boiling point of water, (c) the fuel cell is operated when the heating temperature arrives at the desired operating temperature of HT-PEMFC, i.e., 180 °C in this case. A literature survey revealed that only a few efforts have been reported to be exclusively dedicated to the modelling of transient heating in HT-PEMFC.

Andreason and Kær [11] proposed a dynamic lumped model to predict the energy required to heat up HT-PEMFC stack to above 120 °C from room temperature by comparing the different heating methods. Singdeo et al. [12] compared different warm-up methods through numerical modelling and the results were validated with experimental data from a HT-PEMFC stack concluding that coolant heating gives the better uniformity in temperature distribution enabling the shortest warm-up time. Andreason and Kær [13] also proposed a model for predicting the dynamic temperature of a HT-PEMFC stack as a way to test different thermal control strategies. All of these models consider the heating strategy by assuming a lumped thermal mass that is transiently heated, but totally disregarding the operating mode of the fuel cell during cold start-up period. However, these models are beneficial to the optimization of heating strategies especially for larger stacks.

Intuitively, investigating the heating strategy that involves the consideration of operating mode of the fuel cell during start-up period might give a better understanding of the overall issue. Wang et al. [14] recently proposed a numerical model considering the effect of reaction heating when the temperature of the HT-PEMFC reaches 120 °C by external heating. Obviously, the product water in this case was treated as a gas. Apart from this study, there is no other literature to date that considers the heating strategy of the HT-PEMFC operating from room temperature, which would cross the boiling temperature of water before arriving at the desired operating temperature of the fuel cell.

The objective of this study is to develop an analytical model that describes a heating strategy where current is drawn from the fuel cell from room temperature, with simultaneous application of heat at a constant rate through an external heating source. This includes the investigation of the effect of liquid water accumulation and boiling on the thermal and water balance as well as the electro kinetics of the fuel cell. This simple fundamental model would help establish the relationship between boiling phase change and the operating parameters. Furthermore, the model will be used to compare between different heating strategies for warm-up time and energy consumption. Even though it is widely perceived by material scientists that a heating strategy which involves current extraction from room temperature
might not be suitable for HT-PEMFCs due to membrane degradation caused by liquid water interaction, there is a lack of knowledge on the potential benefits that may exist, especially from an “energy efficiency” point of view [15]. Thus, this model will serve as an initiation for a better understanding of the heating strategy with such operational mode and setup from a perspective of energy analysis.

2. Model description

The unsteady analytical model is formulated based on thermal and water balance, chemical species diffusion and electrochemistry for a Hydrogen/Oxygen HT-PEMFC during the warm-up process. The heating strategy considers the extraction of constant current from the fuel cell, while an external heating source with a constant heat input rate is applied at the end plates of the fuel cell simultaneously. The model serves to describe mathematically the effects of boiling phase change on the transport phenomena and the response of output voltage. The focuses are on the CCL and CGDL within which the produced water boils when it reaches the saturation temperature. The effect of the heating process is expected to cause a general transient behaviour that is divided into the three following phases, typically dominated by the temperature of the fuel cell.

Phase (i) - This refers to the period between the point (in time) when the fuel cell operation starts and the point when liquid water in the cathode starts to boil. Concurrently, when the fuel cell is started, the external heating is also applied. During this period, the fuel cell produces liquid water in the CCL when current is drawn from the fuel cell. Liquid water builds up to the point when the temperature reaches boiling point of water, which marks the end of Phase (i).

Phase (ii) - This refers to the period between the point when the boiling temperature has reached and the point when all the liquid water is converted to saturated vapour.

Phase (iii) - This is the period which starts from the point when all the liquid water is converted to saturated vapour to the point when the catalyst layer temperature reaches 180 °C, which is the operating temperature of the HT-PEMFC.

Generally, the model neglects the contribution of Joule heating (contributed by the electronic and protonic resistances) and anode source due to their relatively low magnitude [16]. In addition, the HT-PEMFC is assumed to be well insulated. Furthermore, spatial irregularities that can affect the respective multi-physical properties within each domain are neglected as well. All porous media are considered to have uniform pore size distribution.

All the governing equations were solved analytically through Laplace transform.

2.1 Heat and water balance

The following sections describe mathematical equations for heat and water balance in the three phases.

2.1.1 Phase (i)

In phase (i), the heat from the external heat source and the exothermic reaction of the fuel cell results in the formation of coupled heat transfer equations between the CCL (Domain 1) and the effective layer that comprises of cathode end plate, cathode bipolar plate and CGDL (Domain 2). The heat transfer equations are shown in Eq. (1) and (2). The two domains are formed based on thermal symmetry.

\[
\left( V \rho C_p \right)_1 \frac{\partial T}{\partial t} = \dot{Q}_{in} - h_x^{eff} (T_1 - T_2)
\]  
(1)
\[
\left(V \rho C_p\right)_2 \frac{\partial T_2}{\partial t} = \dot{E}_{gen} + h_s^{eff} (T_i - T_2)
\]  
(2)

where
\[
\dot{E}_{gen} = I A_{MEA} (E_0 - V_{cell})
\]  
(3)

and
\[
h_s^{eff} = h_s A_{MEA}
\]  
(4)

Eq. (3) stands for the heat generation in the CCL while Eq. (4) relates to the effective interfacial thermal resistance between the Domain 1 and 2. The effect of evaporation is assumed to be negligible during this period. In addition, the heat generation in the catalyst layer is assumed to be independent of temperature for simplicity. This can be justified because the external heat input has greater dominance in terms of the magnitude. Thus, fluctuation of the heat generation within the CCL due to the changing temperature is assumed to be negligible as compared to the magnitude of the heat input rate. In addition, the voltage difference, \((E_0 - V_{cell})\) as expressed in Eq. (3) which contributes to the heat generation, is assumed to be a constant value, which otherwise results in multiple coupling of equations. The variation of the voltage difference is expected to have a relatively low effect on the exothermic reaction heat in comparison to the heat input rate.

The subscript “1” refers to the effective thermal mass of the cathode end plate, cathode bipolar plate and CGDL and is shown in Eq. (5), while “2” refers to the effective thermal mass of the CCL and is given in Eq. (6). For simplicity, the effect of water fraction variation on the thermal mass of CCL is assumed to be negligible.

\[
\left(V \rho C_p\right)_1 = \sum \left(V \rho C_p\right)_{EP+GDL+BP}
\]  
(5)

\[
\left(V \rho C_p\right)_2 = V_{CCL} \left( \varepsilon_{CCL} s_{liq}^{H_2O} \left( \rho C_p \right)_{liq} + (1 - \varepsilon_{CCL}) \left( \rho C_p \right)_{CCL} \right)
\]  
(6)

The water fraction is defined as the ratio of the volume of liquid H\(_2\)O to the total volume of the pores in the CCL.

The liquid water produced in the CCL can be expressed by Eq. (7). The effect of water uptake and electro-osmotic drag in the membrane are assumed to achieve a net zero water transfer for simplicity.

\[
\dot{n}_{H_2O}^{prod} = \frac{I A_{MEA}}{2F}
\]  
(7)

Eq. (8) shows the liquid water removal rate from the CGDL as follows:

\[
\dot{n}_{H_2O}^{CGDL} = \dot{n}_{outflow} = \xi_c \frac{IA_{MEA} P_{sat}}{4F \varphi_2} \frac{P}{p_c}
\]  
(8)

Thus, the total water accumulation rate in the CCL can be expressed as:

\[
\dot{n}_{acc}^{H_2O} = \dot{n}_{H_2O}^{prod} - \dot{n}_{H_2O}^{CGDL} = I \left( \frac{A_{MEA}}{2F} + \frac{\xi_c A_{MEA} P_{sat}}{4F \varphi_2} \right)
\]  
(9)

The relationship between the liquid water fraction in the CCL and the water accumulation rate can be expressed by integrating Eq. (10). When \(t=0\), the liquid water fraction in the CCL is set as zero.
In the CGDL, the liquid water is assumed to start building up once the CCL is fully saturated with liquid water and the dynamic of accumulation is similar to that in the CCL.

2.1.2 Phase (ii)

In phase (ii), the heat transfer for Domains 1 and 2 are expressed by Eq. (11) and (12), respectively. The heat equation for the CCL (Domain 2) is balanced by boiling phase change that contributes to the consumption of heat provided by the external heating source. Eq. (13) represents the rate of liquid water fraction reduction due to the boiling phase change in the CCL and CGDL.

\[
\left( V \rho C_p \right)_1 \frac{\partial T_1}{\partial t} = \dot{Q}_{in} - h_s^{H_2O} (T_1 - T_2)
\]

\[
\left( V \rho C_p \right)_2 \frac{\partial T_2}{\partial t} = \dot{E}_{gen} + h_s^{H_2O} (T_1 - T_2) - \varepsilon_{CCL} V_{CCL} L_{tg} \rho_w \frac{\partial h_{liq}}{\partial t}
\]

\[
\frac{\partial h_{liq}}{\partial t} = \frac{V_{liq} h_{acc}^{H_2O}}{\varepsilon_{CCL} \delta_{CCL} A_{CCL}} - \frac{V_{liq}}{\varepsilon_{CCL} \delta_{CCL} A_{CCL} h_{tg}} (\dot{E}_{gen} + h_s^{H_2O} (T_1 - T_2))
\]

Once the temperature reaches the boiling temperature, the liquid water production rate in the porous layers becomes zero because further H$_2$O produced is assumed to be in vapour state.

2.1.3 Phase (iii)

In phase (iii), all the liquid water in the CCL and CGDL exists in vapour form, thus the liquid water fraction remains zero throughout this phase. Further production of H$_2$O is assumed to be in vapour phase. The heat balance equations are shown in Eq. (14) and (15).

\[
\left( V \rho C_p \right)_1 \frac{\partial T_1}{\partial t} = \dot{Q}_{in} - h_s^{H_2O} (T_1 - T_2)
\]

\[
\left( V \rho C_p \right)_2 \frac{\partial T_2}{\partial t} = \dot{E}_{gen} + h_s^{H_2O} (T_1 - T_2)
\]

2.2 Chemical species diffusion

The diffusion of Oxygen within the porous layers of the cathode is governed by the general equation shown in Eq. (16).

\[
\varepsilon_{CCL/CGL} \frac{\partial C}{\partial t} = \frac{\partial C}{\partial x} \left( D_{O_2} \frac{\partial C}{\partial x} \right) + S_{O_2}
\]

The approximation as shown in Eq. (17) is important for the estimation of the transient period of Hydrogen or Oxygen diffusion across the porous layers. A look at the approximation implies that the transient time constant is in the range of $10^{-4}$ to $10^{-5}$ seconds depending on the thickness of the diffusion layer.

\[
\tau_{diffusion} = \frac{\delta_{CCL/CGL}^2}{D_{eff}}
\]

This implies that the time taken during transience is very short and thus, Eq. (16) can be reduced to Eq. (18).
\[
\frac{\partial C}{\partial x} \left( D_{O_2} \frac{\partial C}{\partial x} \right) + S_{O_2} = 0
\]  
(18)

where the source term for the consumption of Oxygen is shown in Eq. (19).

\[
S_{O_2} = -\frac{j}{4F} = -\frac{I}{4F\delta_{CCL}}
\]  
(19)

The distinction of the effective diffusion coefficients between Phases (i), (ii) and (iii) is the main consideration for Oxygen transport where two mechanisms have significant domination. The first mechanism relates to the increase in temperature, which corresponds to a higher diffusion coefficient. The second mechanism relates to the effect of the liquid saturation of the CCL or CGDL that hinders the diffusion of Oxygen. Specifically, the diffusion coefficient of Oxygen in liquid water is by magnitude, lower by a factor of $10^{-4}$, than the diffusion coefficient of Oxygen in any gas [17].

In phase (i), the liquid water is assumed to build up at the cathode in a linear manner till the water fraction in the CCL reaches unity followed by a build up in the CGDL. Thus, the Oxygen diffusion through the CCL is affected by the liquid water. As shown in Eq.(20), the diffusion coefficient of Oxygen is assumed to behave accordingly [18].

\[
D_{O_2,\text{eff},CCL/CGDL} = \varepsilon_{CCL/CGDL}^{1.5} \left( \frac{1}{\rho_{\text{eff}}} D_{O_2} \rho_{O_2} \left( 1 - s_{\text{liq}}^{H_2O} \right) + \rho_{\text{liq}} D_{O_2,\text{eq}} s_{\text{liq}}^{H_2O} \right), \text{phase (i) and phase (ii)}
\]

\[
D_{O_2,\text{vapor}}, \text{phase (iii)}
\]

(20)

In phase (ii), the liquid water boils till the liquid water fraction in the catalyst layer reaches zero. An important assumption undertaken here relates to the omission of bubbling that is induced during liquid water boiling in the porous media, although bubbling is expected to affect the diffusion of Oxygen. Thus, the Oxygen diffusion is assumed to be solely affected by the reduction of liquid water during boiling phase change and is reflected in Eq. (20) as well. Finally, in phase (iii), the liquid water fraction in the CCL remains zero and the diffusion of Oxygen occurs in the presence of water vapour.

For all diffusion coefficient correlations, the Bruggeman correlation is assumed to account for the effects of porosity in the CGDL and CCL [19, 20].

### 2.3 Electrochemistry

The cell voltage can be expressed by Eq. (21). The transient behaviour of the voltage response is neglected since the extracted current density is constant. In addition, the anode over potential due to Hydrogen oxidation reaction is neglected due to its relatively lower effect on the cell voltage [21].

\[
V_{\text{cell}} = U_a - |\eta_a| - R_\Omega I
\]  
(21)

The total ohmic resistance is contributed by the protonic resistance of the electrolyte in both the membrane and the CCL, the contact resistance, and the electronic resistances of CCL, CGDL, and bipolar plates. Since the electronic resistances are relatively small, they are neglected in this model [22], hence the total ohmic resistance can be expressed as Eq. (22).

\[
R_\Omega = \frac{\delta_{\text{mem}}}{\kappa_{\text{mem}}} + \frac{\delta_{a,ACL}}{2\kappa_{a,ACL} \varepsilon_{ACL}^{1.5}} + \frac{\delta_{c,CCL}}{2\kappa_{c,CCL} \varepsilon_{CCL}^{1.5}}
\]  
(22)
The open-circuit voltage shown in Eq. (23) is assumed to behave according to the piecewise function where instantaneous transition occurs as the water generated changes from a liquid to a vapour upon reaching the boiling temperature [23].

\[
U_0 = \begin{cases} 
1.482 - 8.45 \times 10^{-4}T + 4.31 \times 10^{-5}T \ln \left( \frac{P_{H_2} P_{O_2}^{0.5}}{P_{H_2O}} \right), & T < T_{\text{Boiling}} \\
1.18 - 18.449 - 0.01283T (T - 298.15) + \frac{RT}{nF} \ln \left( \frac{P_{H_2}}{P_{H_2O}} \right), & T_{\text{Boiling}} \leq T \leq T_{\text{Desired}}
\end{cases}
\] (23)

The cathode over potential can be obtained by relating the Oxygen concentration across the cathode to the Butler-Volmer relation shown in Eq. (24). It is assumed that Oxygen reduction reaction occurs uniformly in the CCL [24, 25].

\[
j_c = \frac{I}{\delta_c} = a_{i_{0_c}}^\text{ref} \left( 1 - s_{\text{H}_2O}^\text{ref} \right) \left( \frac{C_{O_2}}{C_{O_2}^\text{ref}} \right) \exp \left( -\frac{\alpha F \eta_c}{RT} \right)
\] (24)

All other physical, thermal, geometrical, diffusive and electrochemical properties are shown in Table 1.

3. Design of study

The first study includes the comparison of three different existing heating strategies for the warm-up time of a single cell which is further explained in Section 4.1. The next study involves parametric studies pertaining to the warm-up process of the single cell, where constant current is extracted from room temperature, while an external heating source with a constant heat input rate is applied at the end plates of the cell simultaneously. These are studied to analyze the effects of the system parameters on temperature profile and water fraction in the porous media and overall voltage profile of HT-PEMFC. The parameters considered are as follows.

- Effect of extracted current density (1000, 2000 and 3000 A m\(^{-2}\))
- Effect of heat input rate (100, 150 and 200 W)
- Effect of cathode pressure (1 atm, 2 and 3 bars)
- Effect of cathode stoichiometric flow ratio (1, 1.5 and 2)

The baseline values of the extracted current density, heat input rate, cathode pressure and cathode stoichiometric flow ratio are set at 1000 A m\(^{-2}\), 100 W, 1 atm and 1, respectively. The active area of the MEA for the two studies is set at 0.0045 m\(^2\) while the area of the end plates where the external heating source is applied is set at 0.007 m\(^2\).

4. Results and discussion

4.1 General description, observations and simplifications of the solutions

The solutions of the decoupled temperature profiles of the catalyst layer are found to be in the following form.

\[
T_{\text{CCL}} = A + Bt + Ce^{-Dt}
\] (25)

Where \(A\), \(B\), \(C\) and \(D\) are obtained constants based on the geometric and thermal properties. However, the coefficient, \(C\) that corresponds to the exponential term is observed to have insignificant effect on the temperature profile of the catalyst layer. Thus, neglecting the exponential term, defines the temperature to increase in a linear manner and coefficient \(B\), serves as the temperature gradient. Specifically, this means that the temperature profile is dominated by the heat input rate from the external source and the heat generation rate from
the exothermic reaction according to the obtained solution. The temperature gradients for phases (i), (ii) and (iii) are given in the Eq. (26) and (27). This simplification also suggests that the temperature difference at any point of time between the catalyst layer and Domain 1 is negligible which is also observed from the original solution.

\[
B_{\text{phase}(i,iii)} = \frac{\dot{Q}_{\text{gen}} + \dot{E}_{\text{gen}}}{(V \rho C_p)_1 + (V \rho C_p)_2}
\]  

(26)

\[
B_{\text{phase}(ii)} = \frac{(1+ M) \left(\dot{Q}_{\text{gen}} + \dot{E}_{\text{gen}}\right) - N}{(1+ M)(V \rho C_p)_1 + (V \rho C_p)_2}
\]

(27)

where

\[
M = \frac{\varepsilon_{\text{CCL}} L_p \rho_n V_{\text{CCL},\text{liq}}}{h_{\text{lg}} \varepsilon_{\text{CCL}} \delta_{\text{CCL}} A_{\text{CCL}}} = \frac{\rho_n v_{\text{liq}}}{M_{\text{H}_2,\text{O}}} = 1
\]

(28)

and

\[
N = \frac{\varepsilon_{\text{CCL}} L_p \rho_n V_{\text{CCL},\text{liq}}}{\varepsilon_{\text{CCL}} \delta_{\text{CCL}} A_{\text{CCL}}} \hat{n}_{\text{acc}} = h_{\text{lg}} \hat{n}_{\text{acc}}
\]

(29)

In addition, as shown in Eq. (29), the effect of the liquid water phase change on the temperature profile during the period of boiling is observed to be negligible. This might be attributed to the small amount of water accumulation rate that was observed during phase change in contrast with the high magnitude of heat input rate.

The average concentration drop of Oxygen across the CGDL and CCL are obtained as shown in Eqs. (30) and (31) respectively. Comparing between the membrane/catalyst interface and the inlet, the average Oxygen concentration in the CCL can be obtained as shown in Eq. (32).

\[
\Delta C_{\text{O}_2}^{\text{CGDL}} = C_{\text{O}_2}^{\text{CGDL},\text{in}} - C_{\text{O}_2}^{\text{CGDL},\text{out}} = \frac{I \delta_{\text{CCL}}}{4FD_{\text{O}_2,\text{eff,CCL}}}
\]

(30)

\[
\Delta C_{\text{O}_2}^{\text{CCL}} = \frac{2}{3} \frac{I \delta_{\text{CCL}}}{8FD_{\text{O}_2,\text{eff,CCL}}}
\]

(31)

\[
C_{\text{O}_2}^{\text{CCL}} = C_{\text{O}_2}^{\text{CCL},\text{in}} - \frac{I \delta_{\text{CCL}}}{4FD_{\text{O}_2,\text{eff,CCL}}} - \frac{2}{3} \frac{I \delta_{\text{CCL}}}{8FD_{\text{O}_2,\text{eff,CCL}}}
\]

(32)

The Damköhler number is a dimensionless measure of the catalyst layer and is given by the ratio of the reaction rate over the mass transport rate, as shown in Eq. (33).

\[
Da = \frac{I \delta_{\text{CCL}}}{8FD_{\text{O}_2,\text{eff,CCL}} C_{\text{O}_2}^{\text{ref,CCL}}}
\]

(33)

Finally, the cathode over potential is obtained as the following relationship [24].

\[
\eta_c = -\frac{RT}{\alpha_e F} \ln \left( \frac{1}{\alpha_{e_{\text{CCL}}} \delta_e (1-s) C_{\text{CCL}}} \right)
\]

(34)

4.2 Comparison between different heating strategies
Based on analytical solutions obtained from the physical model, three heating strategies pertaining to the single cell are studied and compared for the respective warm-up time as shown in Fig. 1 (bottom). The description of the three various heating strategies are as follows; (a) the fuel cell is heated by external source to 393 K (120 °C), after which current is extracted while external heating remains, (b) the fuel cell is heated by external source from room temperature and at the same time, current is extracted, and (c) the fuel cell is solely heated by the external source to a temperature of 453 K (180 °C). All three cases are considered to be heated externally with a constant heat input rate of 100 W, where Hydrogen and Oxygen are fed under ambient pressure and a stoichiometric flow ratio of 1.

The results show that the temperature profiles are almost similar comparing between the various heating strategies for the single cell. Specifically, the magnitude of heat generation rate from the exothermic reaction is found to be insignificant in comparison to the magnitude of the external heat input rate. Thus, this is reflected in the temperature profiles showing no major difference in the warm-up time.

Next, the solution, although simple in nature can be used to estimate the warm-up period of a 1-kW HT-PEMFC stack containing 65 cells [11]. Considering a desired warm-up of the stack from room temperature to a desired temperature of 180 °C, the warm-up time and energy consumption, involving the heating strategies as described in (a), (b) and (c) are plotted for different heat input rate, as shown in Fig. 1 (top). The results suggest that there are considerable differences in warm-up time and energy consumption, especially at lower heat input rate values between the various heating strategies. This is in contrast with the single cell results that show minimal improvement in warm-up time because as the number of cells increase, the rate of exothermic heat generation increases and contributes more to the heat required to increase the temperature to 180 °C. Thus, the energy consumption due to the external source also reduces when current is extracted from the stack at a temperature of 120 °C, and is even lower when current is extracted from room temperature.

4.3 Parametric study

4.3.1 Effect of heat input rate

4.3.1.1 Effect of heat input rate on the temperature and water fraction profiles of the CCL and CGDL

Fig. 2 shows the effect of heat input rate variation on the temperature profile and the water fraction profiles of the CCL and the CGDL. As the heat input rate is increased, the temperature gradient is observed to increase as well albeit to different extents. This is in agreement with existing literature where the increase in heat input rate results in a linear increase in the temperature gradient as shown in Eq. (35) [11].

$$Q = mC_p \frac{\partial T}{\partial t}$$

The liquid water fraction in the CCL reaches unity before boiling phase change occurs for all magnitudes of input heat rate and the liquid water accumulation occurs at a uniform rate. However, the period where the water fraction remains at unity reduces as the input heat increases. This is obviously due to the faster rate of temperature increase for a higher input heat which reaches the boiling temperature of water at an earlier time. The liquid water fraction in the CGDL that is assumed to start accumulating once the CCL is fully saturated, shows to reach different levels of saturation as the input heat rate increases. Specifically, the level of saturation in the CGDL shows maximum approximated values of 0.09, 0.05 and 0.02 for the 100 W, 150 W and 200 W, respectively. This is due to the reduction of time available for the saturation of the CGDL because the boiling temperature is reached faster for greater...
magnitude of heat input rate. Once boiling phase change begins the liquid water fraction in the
CCL and CGDL reduces linearly. The rate of liquid water fraction reduction is similar for
the different magnitudes of heat input rate because of its negligible dependence on the
vaporization mechanism. The input heat rate is not directly related to the domain of the
catalyst layer and is formulated to be transferred through the combined domain (Domain 1)
consisting of the end plate, bipolar plates and the CGDL. The obtained solution pertaining to
the rate of liquid water reduction suggests that the heat transfer between the two domains is
dominated by their temperature difference at particular points in time. Since, the temperature
difference between the two domains at any point in time is found to be negligible, the input
heat has minimal effect on the liquid water reduction rate as well.

4.3.1.2 Effect of heat input rate on the diffusion coefficient, mole fraction and Damköhler number

The main parameter that affects the performance of the fuel cell below the boiling point is the
diffusion coefficient that is governed by the liquid water fraction in the porous layers as
shown in Fig. 3. There are two observations that correspond to the increase in the heat input
rate. The first observation relates to the increase in diffusion coefficient with respect to time
which is due to the temperature dependence of diffusion coefficient since temperature
increases with time in this case. Comparing between the three heat input rate magnitudes, the
rate of increase of the diffusion coefficient is highest for 200 W, which is due to the higher
temperature gradient achieved during heating. The second observation relates to the effect of
water fraction in the CGDL. For all magnitudes of the heat input rate, the time when the
diffusion coefficient of Oxygen starts to reduce drastically is the same, which is a result from
the similar liquid water accumulation rate in the CGDL. Upon reaching the minimal value
which is lowest for the case of 100 W, it remains for a period of time until boiling phase
change occurs to reduce the level of saturation. This results in an exponential increase in the
diffusion coefficient. As the input heat rate increases, the onset of boiling occurs at an earlier
time and thus, the sudden exponential increase in the diffusion coefficient follows as well.

The mole fraction of Oxygen is observed to reduce and then increase, both in a linear manner
as the diffusion coefficient of Oxygen decreases drastically and recovers exponentially,
respectively. The increase in heat input rate shows a decrease in the lowest Oxygen mole
fraction reached. This is based on the lowest value of diffusion coefficient of Oxygen attained
for the particular heat input rate. Since the lowest value of diffusion coefficient occurs for the
case of 100 W, the reduction of mole fraction is greatest as compared to 150 and 200 W. The
linear rate of increase in mole fraction from the lowest point is similar for all cases because of
similar rate of liquid water fraction reduction due to boiling.

The Damköhler number pertaining to the catalyst layer is related to the liquid water fraction
in the CCL. As the liquid water fraction in the catalyst layer increases, the diffusion of
Oxygen across the catalyst layer reduces. The increase of the heat input rate from 100 to 200
W is observed to increase the Damköhler number at similar rates reaching peaks that is
highest for 100 W and lowest for 200 W. This behaviour is expected considering that the rate
of temperature increase is highest for 200 W which slightly increases the baseline value of
the Oxygen diffusion coefficient in the CCL due to its temperature dependence. From the
peak, the Damköhler number reduces in a linear manner for all cases, due to the linear
increase in temperature till the time when boiling phase change starts. Variation in the
reduction gradient is noticed although insignificant. The drastic exponential reduction in the
Damköhler number occurs during boiling phase change at extended times as the heat input
rate is increased. This behaviour exactly follows the liquid water fraction profiles in the CCL
pertaining to the respective heat input rates as well.
4.3.1.3 Effect of heat input rate on the cathode over potential and cell voltage

The magnitude of the cathode over potential is found to decrease with time because the cathode exchange density increases with temperature as shown in Fig. 4 [26]. This mechanism overshadows the direct dominance of temperature on cathode over potential, which tends to increase the magnitude according to the Butler-Volmer relation. It can be seen that the cathode over potential increases from the same baseline value, at an almost linear rate with time corresponding to the increase in input heat rate. A very slight increase, followed by a drop of the cathode over potential is observed for the case of 100 W at around 400 to 500 seconds, respectively. This is due to the rising level of liquid water to the maximum value and its reduction due to the boiling phase change observed in this time period. This behaviour is non-existent for the other heat input rate magnitudes due to the lower maximum liquid water fraction in the CGDL.

The cell voltage with respect to time is found to increase before reaching the boiling temperature due to the effect of temperature increase that tends to decrease the OCV and reduce the cathode over potential. Thus, it can be deduced that the rate of cathode over potential decrease over shadows that of the OCV reduction rate. Once the boiling temperature is reached, the generated water switches from being produced in liquid phase to gaseous phase. This reduces the change in entropy that affects the rate of reduction of the theoretical voltage and is assumed to occur instantaneously. Above the boiling temperature, the cell voltage is observed to increase with time owing to the same mechanism which was explained for the period before boiling starts. However, the rate of increase of the cell voltage is greater due to the lower reduction rate of the OCV with temperature increase.

For all magnitudes of heat input rate, the voltage starts from the same value. The increase in heat input rate causes a “scaling effect” on the voltage profile to fit a shorter time period. The cell voltage at the desired fuel cell temperature of 453 K is almost similar for all magnitudes of heat input rate as well. This is probably due to the similar dynamics in which the only difference is the rate of temperature increase which corresponds to similar electrochemical properties that govern the output performance.

4.3.2 Effect of current density

4.3.2.1 Effect of current density on the temperature and water fraction profiles of the CCL and CGDL

Fig. 5 shows the effect of current density on the CCL temperature profile as well as the water fraction profiles of the CCL and the CGDL. The temperature gradients are observed to increase slightly for the increase in the current density between 1000, 2000 and 3000 A m\(^{-2}\). This might be due to the greater dominance of the heat input rate on the temperature gradient where in magnitude, calculates to be a lot higher than the heat generation rate by the exothermic reaction at the cathode side. If the base case heat input rate input is lowered, the heat generation rate at the cathode can play a greater role in the variation of the temperature gradient.

The water accumulation rate in the CCL and CGDL is found to increase as the current density increases. This is obviously due the linear proportionality of current density with respect to the liquid water generated. Once the CCL reaches total saturation, liquid water in the CGDL accumulates and the maximum level of saturation reached increases with the increase in current density, again due to the higher liquid water accumulation rate as explained. Once the boiling temperature is reached, which is observed to occur almost at the same time for different current densities, the water fraction in the CCL and CGDL decreases. The rate of liquid water reduction consists of two mechanisms; firstly, the rate of accumulation that is
zero because further produced H₂O is assumed to be in vapour phase and secondly, the vaporization process. As the current density increases, the rate of reduction reduces because there is no further generation of liquid water and also, the increase in heat generation from the exothermic reactions is found to contribute to the vaporization process. This is brought upon by the direct dependence of exothermic heat generation on the rate of liquid water reduction according to the obtained solution.

4.3.2.2 Effect of current density on the diffusion coefficient, mole fraction and Damköhler number

Since the temperature gradients for the different current densities are almost similar, the increase of the Oxygen diffusion coefficient increases in a similar fashion as well, as shown in Fig. 6, considering its temperature dependence. However, the sudden decrease of the diffusion coefficient occurs at earlier times when the current density is increased. This is obviously due to the higher liquid water accumulation rate that fully saturates the CCL and starts saturating the CGDL faster as compared to the operation with a lower current density. The minimum value attained is almost similar for all cases. The diffusion coefficient remains at the minimal value till boiling phase change starts. A comparison between current densities shows that the recovery or the exponential increase in the diffusion coefficient occurs at a slightly later time for the higher current density of 2000 A m⁻². This is due to the greater level of saturation attained in the CGDL before boiling starts.

The mole fraction on the other hand reduces drastically once the diffusion coefficient of Oxygen starts reducing as well. There are two mechanisms that contribute to the reduction of the mole fraction in this study. The first mechanism relates to the reduction of the Oxygen diffusion coefficient in the CGDL resulting from the liquid saturation. The second mechanism involves the proportionality of current density on the mole fraction reduction according to the obtained solution. Thus, the combined effect of having higher level of liquid saturation in the CGDL and high Oxygen consumption rate at the cathode gives rise to the starvation effect that is clearly depicted in the obtained solution. Specifically, the current density of 2000 A m⁻², results in a minimum mole fraction reaching as low as 0.2. As for the case of 3000 A m⁻², the mole fraction reaches zero and is deemed to have stopped operation due to very high cathode over potential overshadowing the positive OCV of the fuel cell. This behaviour is clearly shown in the Section 4.3.2.3.

The trend of Damköhler number variation in this parametric study is noticeable for two reasons. Firstly, the peak value attained is highest for the largest current density which is attributed to its direct proportionality to the current density, leading to greater Oxygen transport limitation as the rate of liquid water fraction accumulation rate increases. In comparison with other magnitudes of current densities, the peak values reduce with the decrease in current density owing to the same mechanism. From the peak value, the rate of decrease of the Damköhler number is almost similar for all magnitudes of current density. The next phase occurs at the onset of boiling phase change which for the case of 3000 A m⁻², is assumed to have stopped operation due to high cathode over potential. A comparison between 1000 and 2000 A m⁻² suggests that the drastic reduction of the Damköhler number occurs at a slightly later time for 2000 A m⁻². This is clearly due to the slightly higher temperature gradient observed in Section 4.3.2.3, which attributes to faster onset of boiling phase change.

4.3.2.3 Effect of current density on the cathode over potential and cell voltage

As shown in Fig. 7, the cathode over potential is found start from a lower magnitude as the current density is increased. This is due to logarithmic relationship between the over potential and the current density which is in accordance to existing literature [24]. The expected linear
decrease in the cathode over potential can be attributed to the slightly higher temperature gradient observed as the current density is increased. However, another mechanism that is dominant in this study relates to the liquid water fraction in the CGDL. For the current density of 2000 A m$^{-2}$, it can be seen that there is significant increase in the over potential and reaches a “notch” at around 420 seconds, after which the over potential reduces. This behaviour is due to the relatively high liquid water fraction in the CGDL reaching a maximum and reducing due to boiling phase change. However, in the case of applied current density of 3000 A m$^{-2}$, the maximum liquid water fraction in the CGDL reaches a higher value that causes serious mass transport limitation of Oxygen. This shoots up the magnitude of cathode over potential value along a vertical asymptote just after 200 seconds.

As far as the profile is concerned, the cell voltage is observed to be strongly influenced by the cathode over potential, easily overshadowing the effects of variation of OCV and the ohmic losses for the different current density magnitudes. This behaviour is clearly visible right from the initial cell voltage at the time when the fuel cell starts. For a current density of 2000 A m$^{-2}$, the important transition of OCV probably coincides with that of the cathode over potential, thus showing a larger voltage difference between the lowest point and the recovered baseline voltage. For the case of 3000 A m$^{-2}$, the cell voltage approaches a limit in the negative direction, similar to the cathode over potential.

4.3.3 Effect of cathode pressure

4.3.3.1 Effect of cathode pressure on the temperature and water fraction profiles of the CCL and CGDL

Fig. 8 shows the effect of cathode pressure on the temperature and water fraction profiles. There is no change in the temperature gradient between the three different pressures. The fundamental effect of pressure is the increase of the boiling point as depicted by the Antoine equation. Specifically, the boiling temperature increases from 373 K to 393.23 K and 416.5 K as the pressure was increased from 1 atm to 2 and 3 bars, respectively. This increases the time before the onset of boiling phase change occurs at the CCL and CGDL.

The liquid water accumulation rate increases with the cathode pressure. This is in agreement with existing literature which suggests that a higher pressure at the flow channel reduces the liquid water removal capability of the fuel cell [16]. Even then, the difference in the accumulation rates for the three cathode pressures is found to be slight. A major difference is the time period where the saturation level of the CCL remains at unity and increases with the cathode pressure. Furthermore, the highest saturation level of the CGDL increases as well, mainly due to the greater time available for liquid water accumulation and partly due to the higher accumulation rate brought upon by the pressure increase.

During the boiling phase change, there is no visible variation in the liquid water reduction rate given the fact that the latent heat of vaporization slightly reduces according to the Clausius-Clapeyron relation.

4.3.3.2 Effect of cathode pressure on the diffusion coefficient, mole fraction and Damköhler number

Since the temperature gradients for different cathode pressures are similar, the rate of increase of Oxygen diffusion coefficient resulting from the constant increase of temperature is similar as well, as shown in Fig. 9. However, the diffusion coefficient of Oxygen is found to reduce by the ratio of the ambient pressure over the applied pressure due to its dependence on pressure which is clearly shown by the downward shift of the baseline value. Once the CCL is completely saturated with liquid water, the CGDL starts to saturate from then onwards which drastically reduces the diffusion coefficient of Oxygen.
In addition, as the cathode pressure is increased, the drastic reduction of the Oxygen diffusion coefficient is observed to start at a slightly faster time which is an effect of higher liquid water accumulation rate. For the different pressures, the minimal value of the diffusion coefficient reached is almost the same. The recovery of the diffusion coefficient occurs when the boiling phase change occurs. As the pressure is increased, the recovery of diffusion coefficient occurs at a later time as compared to the base case pressure of 1 atm. This is because the level of saturation of the CGDL attained for a greater pressure is higher. In addition, given the fact that the rate of liquid water reduction due to boiling phase change is slightly lower at a higher pressure, it take a longer time for the diffusion coefficient in the CGDL to recover exponentially to a relatively higher value. A clear distinction in the recovery time is shown based on the comparison between cathode pressures of 1 atm and 3 bars.

The mole fraction being a function of the Oxygen diffusion coefficient reduces in an almost linear manner as saturation of liquid water occurs. As compared to the case with atmospheric pressure, the rate of mole fraction reduction is greater for higher pressures. This is clearly due to the reduction of the baseline of Oxygen diffusion coefficient that is brought upon by its pressure dependence. Another observation involves the minimum mole fraction that is reached before the onset of boiling phase change. The reason for this behaviour is the extended time before boiling phase change occurs that follows the increase in cathode pressure. Due to this, the maximum level of saturation in the CGDL is higher which results in a lower mole fraction as the cathode pressure is increased. During boiling phase change, a longer period is required for the reduction of all liquid water in the CGDL. This behaviour therefore results in the slower recovery of the Oxygen diffusion coefficient which translates to the slower recovery of mole fraction to unity.

4.3.3.3 Effect of cathode pressure on the cathode over potential and cell voltage

As shown in Fig. 10, the cathode over potential is observed to have a lower initial value as the cathode pressure is increased. This is due to the pressure dependence of the cathode exchange current density which improves the electro kinetics [27]. Even though, the CGDL liquid water fraction is found to be higher and the diffusion coefficient of Oxygen is reduced at higher cathode pressure, which are key mechanisms that can increase the cathode over potential, the exchange current density proves to be a dominating factor which evidently reduces it. The rate of decrease of the cathode over potential occurs in an almost linear manner and equally for the different cathode pressures and this is due to the temperature dependence of the exchange current density which follows the linear temperature increase. For the pressures of 2 and 3 bars, the cathode over potential is observed to reduce to almost zero.

The cell voltage is observed to start with the highest value for the highest pressure which is due to the manner the cathode over potential starts as well and also due to the cathode pressure dependence of the OCV. For all pressures, the cell voltage gradually increases till the time when boiling occurs corresponding to the different pressures. The voltage then suddenly shoots up at the liquid vapour transition. From then onwards, the voltage gradually increases for the cathode pressure of 1 atm and 2 bars. However, as further pressure is applied to 3 bars, voltage is observed to drop. This might be due to the behaviour of the cathode over potential showing zero rate of change. Since the OCV drops with temperature, thus having a negative gradient, the overall summation of the gradients proves to result in the decrease of the cell voltage.

4.3.4 Effect of cathode stoichiometric flow ratio
4.3.4.1 Effect of cathode stoichiometric flow ratio on the temperature and water fraction profiles of the CCL and CGDL

Fig. 11 shows the effect of cathode stoichiometric flow ratio on the temperature profile and the liquid water fraction profiles of the CCL and CGDL. There is no effect on the temperature gradient. This might be due to the assumption neglecting the role of heat loss from the flow channels of the fuel cell. Outflow is one of the means where heat can be transferred to the environment and the rate of heat transfer increases as the flow rate is increased. This analytical model however, assumes the insignificance of this mechanism for simplicity.

The rate of liquid water accumulation in the CCL and CGDL reduces as the stoichiometric flow ratio increases. This is obviously due to the higher capability of the CGDL to remove the liquid water resulting from the increase in flow rate [16]. The maximum liquid water fraction attained in the CGDL reduces as the stoichiometric flow ratio increases due to the same mechanism. The time that is available for liquid water to build up in the CGDL is the same due to similar temperature profiles for all three cases. Thus, since the rate of liquid water accumulation decreases as the stoichiometric flow ratio increases, the maximum liquid water fraction reduces as well. During boiling phase change, the rate of liquid water reduction remains uniform for the three cases since the relationship between heat transfer and flow rate is assumed to be negligible as explained.

4.3.4.2 Effect of cathode flow stoichiometric ratio on the diffusion coefficient, mole fraction and Damköhler number

As shown in Fig. 12, the diffusion coefficient of Oxygen increases at a uniform rate for all magnitudes of stoichiometric flow ratios due to its temperature dependence but is also observed to reduce drastically once the CGDL starts saturating with liquid water. The time it starts when the diffusion coefficient of Oxygen reduces drastically, extends to a later time as the stoichiometric ratio is increased. This is clearly due to the reduced liquid water accumulation rate for a higher stoichiometric flow ratio that saturates the CGDL at a later period. Once the diffusion coefficient reaches the minimum value which is evident for all values of stoichiometric flow ratio, the exponential increase follows as boiling phase change occurs. In addition, the time it takes for the recovery of the diffusion coefficient shortens with the increase of the stoichiometric flow ratio. This is because of the maximum level of saturation of the CGDL is lower for the case of the higher stoichiometric ratio and thus, it takes a shorter time for the total elimination of the liquid water in the CGDL through boiling.

The mole fraction starts with the value of one and starts to reduce almost in linear fashion as the diffusion coefficient drastically reduces to the minimal value. As the stoichiometric flow rate is increased, the reduction of mole fraction occurs at a later time. This is obviously due to the higher liquid water removal capability for a higher stoichiometric flow ratio. The rate of mole fraction reduction is observed to decrease as the stoichiometric flow ratio is increased with all of them reaching their respective minimum values at the same time. The reason for this is as follows. For the case of the stoichiometric flow ratio being 2, the time when the drastic reduction of diffusion is later as compared to the base setting of stoichiometric flow ratio of 1. This results in the increase of the baseline diffusion coefficient due to its temperature dependence considering the temperature gradient. Thus, the path of diffusion coefficient in time, for the case of stoichiometric flow ratio being 2 is slightly higher as compared to the base setting. This results in the lower rate of mole fraction reduction. Upon reaching their minimum values before boiling phase change starts, the recovery of mole fraction occurs in a linear manner and at constant rate for all the cases finally reaching unity.
Again, the time for the mole fraction to reach the value of one, is proportional to the maximum level of saturation in the CGDL.

The Damköhler number is found to increase at a later time as the stoichiometric flow ratio increases. This is due to the higher liquid water accumulation rate as the stoichiometric flow ratio reduces. The peak value is lower for a higher flow rate because the temperatures corresponding to the particular times when the CCL is fully saturated increase with increasing flow rate. Since total saturation of the CCL occurs at a later time for the highest Oxygen flow rate, the temperature at that point is relatively higher, thus showing a slightly increased diffusion coefficient in comparison. The reduction of the Damköhler number occurs linearly with time till boiling phase change occurs for all three cases, with the paths being exact due to similar temperature profiles.

4.3.4.3 Effect of cathode stoichiometric ratio on the cathode over potential and cell voltage

As shown in Fig. 13, the cathode over potential is observed to increase with time in an almost similar manner for all values of stoichiometric flow ratios. This might be due to the exact temperature profiles and almost similar liquid water accumulation rates. The maximum liquid water fraction attained in the CGDL is observed to reduce as the stoichiometric flow ratio increases. This slight variation in the maximum liquid water fraction results in very slight changes in the cathode over potential in the time period from 300 to 550 seconds considering that the temperature profiles are similar as well.

The cell voltage is observed to show slight variation, although insignificant, in the time period from 300 to 550 seconds as the stoichiometric flow ratio is increased and this behaviour is similar to the cathode over potential. Since the temperature and CGDL saturation profiles are almost similar for cases involving the three stoichiometric flow ratios as explained previously, the variation of voltage with time is expected in the manner as shown also. This is because the OCV and the cathode over potential are affected solely by the temperature and the CGDL water fraction. Thus, if negligible variation in these parameters are observed between the different stoichiometric flow ratios, then the output voltage, as expected should be similar as well.

5. Conclusion

An analytical transient model was derived considering the effects of boiling phase change in the CCL and CGDLs of the cathode. The thermal and water balance as well as the electro-kinetics during the warm-up period of a high-temperature proton exchange membrane fuel cell were better understood through a parametric study.

Comparing the different heating strategies, the model suggests that there is insignificant improvement in warm-up time when current is extracted from the fuel cell during warm-up process of a single cell. However, considering the solution for a typical 1-kW stack suggests that considerable reduction in warm-up time and energy consumption can be expected which is due to the greater contribution of exothermic reaction heat, neglecting heat losses.

In addition, through this model, the behaviour trend of the boiling phase change has been highlighted and observed to be present for a significant period of time during the warm-up of the fuel cell, which causes a drastic decrease of the accumulated liquid water in the CCL and CGDL. This, in turn, creates a “recovery” phase of Oxygen transport through the porous layers and thus affecting the electrochemical performance as well.

The parametric studies indicate that varying the heat input rate, extracted current and cathode pressure show significant impacts on the voltage profiles. However, the effect of cathode
stoichiometric flow ratio variation is found to have minimal little effect on the cell voltage. These results indicate that a significant period of boiling phase change will be present under the typical operating conditions. It was observed that increasing the heat input rate and stoichiometric flow ratio, and minimizing the cathode pressure and extracted current can reduce the boiling period. In addition, it was also observed that the extracted current is an important parameter that must be controlled, which will otherwise result in flooding and Oxygen starvation before boiling starts.

Thus, this model has been useful in understanding the fundamentals and dynamics of a warm-up process with simultaneous current extraction from room temperature. Even though there are no fuel cell membranes to date that can operate satisfactorily in both liquid and gas states of water, the potential benefits exists, which has been highlighted through this model. The advantages of this heating strategy for a typical stack are the significant reductions in warm-up time and energy consumption, as compared to the other two heating strategies. However, it is unknown how boiling phase change phenomenon which was found to be present for a significant amount of time during the warm-up process, can affect the fuel cell, considering the random bubbling that is expected. Thus, this heating strategy is concluded to be potentially useful based on the energy analysis. Future research should be focused towards realizing these benefits through membrane research and the comprehension of the physical effects of boiling on the fuel cell components.

References


An Analysis of Boiling Phase Change Phenomenon in High-Temperature Proton Exchange Membrane Fuel Cells during Warm-Up Process

Highlights:

1. Model suggests reductions in warm-up time and energy consumption for HT-PEMFC stack.
2. Energy consumption due to boiling phase change is found to be negligible.
3. Boiling phase change affects liquid saturation in porous media for significant period.
4. Variations in operating parameters affects cell voltage dominated by boiling.
Ms. Ref. No.: HE-D-13-03048

Title: An Analysis of Boiling Phase Change Phenomenon in High-Temperature Proton Exchange Membrane Fuel Cells during Warm-Up Process

International Journal of Hydrogen Energy

Dear Mr. Raj Kamal s/o Abdul Rasheed

Dear Editor

Thank you for your valuable comments and suggestions on the language and structure of our manuscript. We have modified the manuscript accordingly, and detailed corrections are listed below:

Reviewer #1:

Thank you for the valuable suggestions.

General comments:
The manuscript under review introduced an analytical model to describe a heating strategy where the fuel cell is operated from room temperature, with simultaneous application of heat at a constant rate through an external heating source. The effect of liquid water accumulation and boiling on the thermal, water balance and electro kinetics of the fuel cell was investigated. And the relationship between boiling phase change and the operating parameters was established by this model. This study is systematically and comprehensive; however, some minor errors should be fixed.

Comment 1. When "GDL" was firstly used in section 2, paragraph 1, the authors should give the full description.
Reply: The full description has been added in the manuscript at its first point of use as advised.

Comment 2. In Equation 4, the "hs" is not described in the symbol table.
Reply: The above notation has been described in the symbol table as advised.

Comment 3. For the symbol "I", current density, the unit is not right. It should be A m^2, not A cm^2.
Reply: The symbol for current density has been changed as advised throughout the manuscript, figures and tables as advised.

Reviewer #2:

Thank you for the constructive comments which were beneficial for deeper comprehension of the model.

Comments:
Comment 1. The water diffusion from cathode to anode as well as the water removal by hydrogen flow should be considered or discussed.
Reply: These were assumptions that was considered in the model in order to reduce the non-linearity of the coupled thermal and water balance equations which would otherwise make it difficult to be solved analytically. Indeed these mechanisms of water transport are critical, especially for the temperature range from room temperature to 100 °C. However, since one of the major emphasis of the model is to describe the boiling phenomenon, the only difference these assumptions would make is the level of saturation prior to the onset of boiling. The trend of boiling phenomenon would theoretically not be affected by the level of saturation because boiling becomes the dominant liquid water removal mechanism then, with other liquid water removal methods being relatively smaller.

Comment 2. The authors used the room temperature of 22oC as the initial temperature in the studies. Please specify the suitable temperature for start-up and current extraction for the proposed model. Because the "room temperature" difference can be more than 20oC at different places and in different seasons - this could significantly affect the heat balance.

Reply: The spatial variation of room temperature and the concept of localised ambient temperature is indeed a key consideration. However, this model assumes that the ambient temperature remain constant at 295 K. In case a higher or lower ambient temperature is considered, the mechanisms of heat transfer are expected to be the same, with slight variations (reductions and increase, respectively) in the warm-up time and energy consumption.

Reviewer #3:

I would like to thank you for the comments and improvements proposed for this manuscript.

Comment 1. This paper is related with the development of a model for the study of thermal and water balance and the electrokinetic during the warm-up process for a HTPEMFC fed with H2 and O2. (from room Temp to 180 ºC). Although the study is interesting this manuscript is uncompleted. As the authors say, the membrane is a key part of the PEMFCs and it has not been considered. The authors say that is under development.

Reply: This proposed model investigates a scenario that may be observed when current is extracted from a HT-PEMFC from room temperature onwards. When it is said that the membrane is under development, it meant that there are no high temperature proton exchange membrane to date that can operate when the product water is in liquid phase at the cathode, with might practically cause acid leaching from the membrane based on literature survey. Keeping that in mind, this theoretical model suggests the benefits of operating the HT-PEMFC from room temperature which relates to the reduced energy consumption predicted during start-up. Thus, this model serves as new direction for future material scientists to look into, so as to produce high temperature membranes that can perform below 100˚C without degradation. In conclusion, the membrane is an important aspect practically, however, it has negligible effect on the energy balance as far as this theoretical model is concerned, and is thus not considered for the model.

Comment 2. This study is more useful for a stack than for single cells. Every researcher has his/her own protocol to warm up or break-in the PEMFC test.

Reply: This statement was inspired by the model where the difference in thermal masses were considered and calculated for energy consumption. The protocol of heating method that is
considered in the manuscript is in its simplest form, from a control volume point of view. This considers thermal balance of the fuel cell with source terms being the external heat input rate, exothermic heat production and boiling phase change. Having said that the benefits of reduced energy consumption and reduced start-up time is greater for a stack because of the bigger role played by the exothermic reaction heat, from the number of cells. For a single cell, the magnitude of exothermic heat is found to be negligible as compared to the that of the heat input rate. These explanations lead to the conclusion that the extracting current from room temperature is more beneficial for a stack rather than a single cell.

Comment 3. It should be said which GDL and CL has been considered. To know the data in Table 1 comes from.
Reply: Changes have been made throughout the manuscript, figures and nomenclature and tables to include the terms "cathode" when the GDL and CL are described. Thus, they are changed to CGDL and CCL respectively.

Comment 4. Captions for figures are missing!!! For example in Figure 8. The legend appears in the central figure but is it for the three figures? The same thing can be said for the rest of figures. They must be improved and checked.
Reply: Firstly, all the 13 figure captions have been submitted in a separate file named "Figure and Table captions" as instructed by the journal. Secondly, the legend is designed for the three graphs where these three graphs are compiled as one figure. The colour and line types have been designed to be similar for each graph. The rationale for this design relates to the fact that they share the same "x" axis variable being "time", so as to present the data in a neat fashion and not repeat the legend for every graph.

Comment 5. Please include the word "model" in the title.
Reply: The title has been changed to include the word model as advised. Thus, the final title of the manuscript is as follows:
"Analytical modelling of boiling phase change phenomenon in high-temperature proton exchange membrane fuel cells during warm-up process"

Comment 6. In the introduction section, at the end of the second page of introduction, please, add a reference to address the statement. "Even though it is widely perceived by material.. Point of view"
Reply: A relevant reference has been added as advised at the end of that sentence.

Comment 7. It is a weak manuscript from my point of view. How these results influence on the steady state of the cell once the work Temp has been reached?
Reply: The steady state performance based on the proposed heating strategy is indeed a crucial aspect which can be better understood by detailed modelling coupled with experimental analysis. However, the main emphasis of this model is to investigate this heating strategy in two aspects, the first being the energy consumption and start-up time analysis and second being the parametric study that highlights the relationship between boiling phase change and controllable operational parameters. Thus, this model is a preliminary step towards the next direction where further investigation on the effects of boiling phenomenon on the steady state of the cell should be conducted as advised. Due to the anticipated complexities and time constraints of that direction which leans towards the degradation mechanisms induced by boiling coupled with the electro kinetics, it is not considered in this model.
Comment 8. The variable time is 800-1000 seconds, which means 15 min approx and in most of the cases 24 h or even more it must be waited to start to test the performance. I do not see that this paper contribute to a significant progress of the knowledge in the field.

Reply: The break-in period is indeed a crucial aspect that is performed prior to performance testing. However, the model considers a typical fuel cell which is suitable for commercial use i.e. one which does not require further break-in of 24 hours or more. The same consideration has been adopted as seen in recent publications (as referenced in the introduction section of the manuscript) that relates to transient thermal modelling of high temperature proton exchange membrane fuel cells. Thus, this manuscript is aimed at highlighting the dynamics of a start-up strategy that is catered towards commercial HT-PEMFCs.

Editor's additional comments

Comment 1. The third referee was very critical of your manuscript. Please be sure to address carefully the concerns raised by Reviewers.

Reply: All the comments raised by the three reviewers have been addressed carefully with an emphasis on the third reviewer.

Comment 2. Titles of article; the first letter of only the initial word should be capital (all the others lower case).

Reply: The title has been changed as advised.

Comment 3. Highlights are too long (maximum 85 characters each, including spaces). Please shorten. Each research highlight provided in bullet points should not exceed a maximum of 85 characters (including spaces) per bullet point.

Reply: The highlights have been shortened as advised.

Comment 4. Please provide fax number(s) of the corresponding author in correspondence.

Reply: The fax number of the corresponding author has been added in the cover letter as advised. Please note that the telephone number and the fax number are the same.

Comment 5. Avoid ":;" after heading of "Abstract"

Reply: ":;" has been removed from the Abstract as advised.

Comment 6. Abbreviations should be defined at first mention and used consistently thereafter. I.e. HT-PEMFC is used in keywords before definition (It was defined in next section, introduction). Please make the similar corrections throughout the text.

Reply: The above mentioned corrections has been done throughout the manuscript as advised.

Comment 7. Only mathematical variables should be in italics, i.e. "reaction rate" and "mass transport rate" are not variables. The operators should also not be in italic.

Reply: The above mentioned corrections has been done for the equation as advised. The operators have also been changed correctly.

Comment 8. Please put a single space between numbers and units, i.e. "373 K" not "373K"

Reply: The above mentioned correction and all other similar corrections has been done throughout the manuscript, tables and figures as advised.
Comment 9.

- Note shortened form for last page number. e.g., 264-78, not 264-278, and that for more than 6 authors the first 6 should be listed followed by 'et al.'

- Titles of articles; the first letter of only the initial word should be capital (all the others lower case). The titles should not be in italic.

- Issue numbers are not required for this journal.

- Abbreviated journal names must be provided.

- Check the format for the names of authors, titles, journal, year, volume, page range etc.

Reply: All the formats of the references as advised in the above section have been corrected as advised. The referencing style suitable for the International Journal of Hydrogen Energy has been adopted in the referencing system.

Thank you
Table 1 List of multi-physical properties and parameters

<table>
<thead>
<tr>
<th>Property/Parameter</th>
<th>Correlation/ Value</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Thermal</strong></td>
<td></td>
</tr>
<tr>
<td>Initial Temperature</td>
<td>$T_1(0) - 295$ K</td>
</tr>
<tr>
<td></td>
<td>$T_2(0) - 295$ K</td>
</tr>
<tr>
<td>Heat capacity, $\rho C_p$</td>
<td>CL - $1.69 \times 10^8$ J K$^{-1}$ m$^{-3}$</td>
</tr>
<tr>
<td></td>
<td>GDL - $5.68 \times 10^5$ J K$^{-1}$ m$^{-3}$</td>
</tr>
<tr>
<td></td>
<td>EP - $3.82 \times 10^6$ J K$^{-1}$ m$^{-3}$</td>
</tr>
<tr>
<td>Molar volume of liquid water</td>
<td>$18.015 \times 10^{-6}$ m$^3$ mol$^{-1}$</td>
</tr>
<tr>
<td>Molar mass of H$_2$O</td>
<td>$18.015 \times 10^{-3}$ kg mol$^{-1}$</td>
</tr>
<tr>
<td>Interfacial thermal resistance, $h_i$</td>
<td>1 W K$^{-1}$ m$^{-2}$</td>
</tr>
</tbody>
</table>

*Effective thermal mass of Domain 1*

\[
(V \rho C_p) \_1 = \sum (V \rho C_p) \_{EP+GDL+BP}
\]

*Volume of Domain 1, $V_1$*

$7 \times 10^{-3}$ m$^3$

*Density of species, $\rho$*

\[
\rho_i = \rho_{i,0} \left(1 + \beta_i (T - T_0)\right)^{-1} \text{ kg m}^{-3}
\]

<table>
<thead>
<tr>
<th><strong>Geometric</strong></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness, $\delta$</td>
<td>CL - $50 \times 10^{-6}$ m</td>
</tr>
<tr>
<td></td>
<td>GDL - $260 \times 10^{-6}$ m</td>
</tr>
<tr>
<td></td>
<td>Membrane - $120 \times 10^{-6}$ m</td>
</tr>
<tr>
<td>Active area of MEA, $A_{MEA}$</td>
<td>0.0045 m$^2$</td>
</tr>
<tr>
<td>Porosity, $\varepsilon$</td>
<td>CL - 0.2</td>
</tr>
<tr>
<td></td>
<td>GDL - 0.6</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Diffusive</strong></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Diffusion coefficient of oxygen</td>
<td>$D_{O_2} = 3.2 \times 10^{-5} \left(\frac{T}{295}\right)^{\frac{3}{2}} \left(\frac{101325}{p}\right)$ m$^2$ s$^{-1}$</td>
</tr>
<tr>
<td>Diffusion coefficient of oxygen in liquid H$_2$O</td>
<td>$D_{O_2,liq} = 2.2 \times 10^{-5} \left(\frac{T}{298}\right)^{\frac{3}{2}} \left(\frac{101325}{p}\right)$ m$^2$ s$^{-1}$</td>
</tr>
<tr>
<td>Diffusion coefficient of oxygen in water vapour</td>
<td>$D_{O_2,vapor} = 2.82 \times 10^{-5} \left(\frac{T}{308.1}\right)^{\frac{3}{2}} \left(\frac{101325}{p}\right)$ m$^2$ s$^{-1}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Electrochemical kinetics</strong></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Conductivity, $\kappa$</td>
<td>Membrane - 9 S m$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>Catalyst layer - 300 S m$^{-1}$</td>
</tr>
<tr>
<td>Transfer coefficient, $\alpha$</td>
<td>Anode - 1</td>
</tr>
<tr>
<td></td>
<td>Cathode - 1</td>
</tr>
</tbody>
</table>
| Effective catalyst area per unit volume $\times$ Cathode exchange current density | $a_{i,c,0}^{ref} (T) = a_{i,c,353.15}^{ref} \exp \left[ - \frac{E_{\alpha,cathode}}{R} \left( \frac{1}{T} - \frac{1}{353.15} \right) \right]_{p = 1 \text{ atm}}$
|                                             | $a_{i,c}^{ref} (p) = 1724.5 \exp \left[ 2.06 \frac{p_e}{101325} \right]$ |
|                                             | $a_{i,c,353.15}^{ref} = 1 \times 10^4$ A m$^{-3}$ |
1. Suggested reviewers

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