**MODELLING AND EXPERIMENTAL INVESTIGATION OF HIGH
TEMPERATURE PROTON EXCHANGE MEMBRANE FUEL CELLS**

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Abstract

Although high-temperature proton exchange membrane fuel cells (HT-PEMFC) have many attractive features, they are not yet at the same level of development or performance as compared to the low-temperature proton exchange membrane fuel cells (LT-PEMFCs). There are several technical challenges that contribute to the delay for commercialization of HT-PEMFCs. One of these challenges includes suitable warm-up strategy during start-up of the device and obviously, reducing time and energy consumption is critical. Thus, the research is aimed towards the investigation of novel dynamics of start-up with key interests in time and energy management. Firstly, an analytical model was developed to explore novel concept and extend the existing boundaries that defined start-up. Start-up with current extraction from room temperature was conceptualized and investigated with a transient analytical model that inherently included the boiling phase change. Secondly, an existing start-up process by current extraction at an intermediate temperature (e.g. 120 °C) was further investigated. This effort accounts for a substantial portion of the thesis, where carbon monoxide (CO) poisoning is investigated under transient temperature conditions during start-up. A numerical three dimensional model was developed and validated experimentally. The model was further used for sensitivity analysis to assess the critical importance of start-up parameters. The key novelty of this effort relates to the generation of transient adsorption kinetics behavior and the resulting anode overpotential, with a key emphasis on assessing whether a start-up process, in the presence of CO, can be performed successfully. Next, an experimental investigation of the open circuit voltage (OCV) was also done in the presence of an external heating input, which mimics the typical scenario experienced during the start-up of a HT-PEMFC. A comparison between the OCV under a temperature increase rate with respect to time, and the existing Nernst equation was done.

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Nomenclature

Alphabets

Symbol	Description	Units
a	ratio of reaction surface to catalyst layer volume	m^{-1}
A	Area	m^2
b	Tafel slope	V decade^{-1}
b	Backward forward ratio	mol m^{-3}
c	Concentration	mol m^{-3}
C_p	Specific heat	$\text{J kg}^{-1} \text{K}^{-1}$
D	Diffusion coefficient	$\text{m}^2 \text{s}^{-1}$
E_a	Activation energy	J mol^{-1}
$\dot{E}_{gen}$	Heat generation rate in catalyst layer	W or J s^{-1}
F	Faraday's constant	96487 C mol^{-1}
g	temperature increase rate	K s^{-1}
G	Gibbs free energy	J mol^{-1}
h_{lg}	Enthalpy change between liquid water and water vapor	J mol^{-1}
h_s	Interfacial thermal conductance between domains	$\text{W K}^{-1} \text{m}^{-2}$
H	Enthalpy	J mol^{-1}
i	Current density	A m^{-2}
i_o	Reference exchange current density	A m^{-2}
j	Volumetric current density	A m^{-3}

k	Rate constant	$\text{s}^{-1}, \text{mol m}^{-3} \text{s}^{-1}$
L_{lg}	Latent heat of vaporization	J kg^{-1}
M	Molar mass	g mol^{-1}
n	Number of electrons	-
OCV	Open circuit voltage	V
p	Pressure	Pa or atm
$\dot{Q}_{in}$	Heat input rate	W or J s^{-1}
R	Universal gas constant	$8.314 \text{ J mol}^{-1} \text{ K}^{-1}$
R_{Ω}	Cell ohmic resistance	$\Omega \text{ m}^2$
S_e	Energy source term	W m^{-3}
S_i	Species source term	$\text{mol m}^{-3} \text{s}^{-1}$
S_m	Momentum source term	N m^{-3}
S	Entropy	$\text{J mol}^{-1} \text{ K}^{-1}$
t	Time	s
T	Temperature	K or $^{\circ}\text{C}$
u	Velocity	m s^{-1}
V	Potential	V
V	Diffusion volume of species	$\text{m}^3 \text{mol}^{-1}$
w	Mass fraction	-
x	Mole fraction	-

Greek letters

Symbol	Description	Units
α	Transfer coefficient	-
ε	Porosity	%

η	Over-potential	V
ρ	Density	kg m ⁻³
σ	Conductivity	S m ⁻¹
φ	Potential	V
ζ	Stoichiometric flow ratio	-
κ	Hydraulic permeability	m ²
μ	Kinematic viscosity	Pa s
θ	Fractional surface coverage	-
v_{liq}	Specific volume of liquid water	18.015×10 ⁻⁶ m ³ mol ⁻¹

Subscripts and superscripts

Symbol	Description
0	Reference condition or initial value
a	Anode
ads	Adsorption
c	Cathode
ch	Channel
CCL	Cathode catalyst layer
eff	Effective
eox	Electro-oxidation
eq	Equivalent
fc	Fuel cell
CGDL	Cathode gas diffusion layer
gen	Generation
H ₂	Hydrogen

H^+	Hydrogen ion or proton
H_2O	Water
i	Species
in	Inlet
j	Species
l	Electrolyte
mem	Membrane
N_2	Nitrogen
O_2	Oxygen
out	Outlet
ref	Reference
rev	Reversible
T	Transpose of 2 nd order tensor

Other notations

Symbol	Description
e^-	Electron
Δ	Change
∂	Single dimension partial derivative operator
Σ	Summation
∇	Partial derivative operator
$\rightarrow$	Vector
$\bar{\bar{D}}$	Symmetric diffusivity
I	Identity matrix
$\vec{n}$	Normal vector

List of Abbreviations

Abbreviation	Description
LT-PEMFC	Low-temperature proton exchange membrane fuel cell
CO	Carbon monoxide
CCL	Cathode catalyst layer
CGDL	Cathode gas diffusion layer
HOR	Hydrogen oxidation reaction
HT-PEMFC	High-temperature proton exchange membrane fuel cell
MEA	Membrane electrode assembly
OCV	Open circuit voltage
ORR	Oxygen reduction reaction
PEMFC	Proton exchange membrane fuel cell
PBI	polybenzimidazole
ppm	Parts per million
SEM	Scanning electron microscope
TEM	Transmission electron microscope

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1.1 Background

1.1.1 Fundamentals of fuel cell technology

A hydrogen/air proton exchange membrane fuel cell (PEMFC) is a device that electrochemically converts the hydrogen and oxygen from the air into electricity.

Fig. 1-1 Diagram of a hydrogen/air PEMFC and its components

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As long as there is continuous supply of hydrogen and oxidant, the PEMFC is able to generate electricity based on the chemical reactions as follows:

Hydrogen is oxidized in the anode side by the following chemical reaction

The hydrogen ions travel from the anode to the cathode through the proton exchange membrane. The electrons produced however, flows across the external circuit and ends up at the cathode.

At the cathode, the oxygen from the air is reduced to water with the hydrogen ions and the electrons through the following chemical reaction:

Hence, the overall reaction in the PEMFC is as follows:

Generally, there are seven basic components in a PEMFC comprising of the membrane, anode and cathode catalyst layers, anode and cathode gas diffusion layers and the anode and cathode bipolar plates as shown in Fig. 1-1. Each of these components plays a critical role in the operation of the PEMFC. A brief discussion of the various components is as follows.

The membrane is the key component in the PEMFC and its primary role is to facilitate the transport of the hydrogen ions from the anode to the cathode. Other key requirements include high electronic resistivity, high thermal and chemical stability, ability to prevent oxygen and hydrogen gas crossover, ease of fabrication and low cost. In PEMFCs, the membrane is in the

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form of a polymer. Nafion, a proton conducting membrane, and its derivatives are commonly used as the electrolyte materials for the membrane.

The catalyst layer is responsible for the hydrogen oxidation reaction (HOR) for hydrogen ion production and oxygen reduction reaction (ORR) for water production on the anode and cathode side, respectively. Generally, nano-sized platinum particles that are supported on carbon particles are used as electro-catalyst and are coated onto the surface of the polymer membrane. The key requirements for the catalyst layer include high exchange current density, high durability under chemical and thermal conditions and most importantly, low cost. The catalyst layer is usually the highest contributor to the cost of the fuel cell because precious metals such as platinum are used. This is considered as a key challenge in fuel cell technology.

The gas diffusion layer (GDL) is situated between the catalyst layer and the bipolar plates. This component helps to evenly distribute the fuel and oxidant to the anode and cathode catalyst layers, respectively, and at the same time, help remove the product water from the cathode. In addition, it also aids in strengthening the membrane electrode assembly (MEA) against the stresses built up during operation. Its key requirements include good electrical conductivity, controlled pore size distribution, good mechanical strength, high thermal and chemical resistance. Good understanding of the design of this component is important to control the water content in the membrane and the fuel cell, which might otherwise cause dehydration or flooding. Another key feature of the GDL is the micro-porous layer on one side of the surface of the GDL. This micro-porous layer creates better electrical and thermal contact between the catalyst layer and the GDL by providing a more continuous interface, enabling improved water management [1]. Common materials used for the fabrication of the GDL are carbon paper and its derivatives.

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Finally, the bipolar plates are usually made of graphite, stainless steel, aluminum or composites and function to ensure proper fuel and oxidant supply to the GDL via the flow channels that are machined into the plates. The requirements for the bipolar plates include good electrical and thermal conductivity, corrosion resistance, ease of production and low cost. The design of the flow channels on the plates can come in many forms and this has been the area of research for years.

1.1.2 A brief introduction to LT-PEMFCs and its critical challenges

Hydrogen/oxygen or air fed PEMFCs possess many attractive features, including high power density, rapid start-up, high efficiency, etc., which makes them a promising clean energy technology. Great advances have been made in PEM fuel cell development. Catalyst loading has been significantly reduced, power density has been increased, and prototype PEM fuel cell vehicles have been successfully tested on many continents.

The use of hydrogen is perceived to be one of the key fuels for energy production [2]. Hydrogen production is being extensively researched with an objective of finding cheaper and “greener” methods [3]. Currently, there are many hydrogen production methods that are popular signifying the abundant availability of hydrogen. Another significant factor as with any other fuel is the storage capability for practical use. In fact, it is even more complex for hydrogen gas to be stored because of its extremely low density. Nevertheless, current technology enables its bulky storage in the form compressed hydrogen in cylinders. These trends directly fulfil the fundamental requirements for the use of PEMFCs from a practical and commercial sense, where the technological advancement of PEMFC together with its supporting infrastructure such as hydrogen production and storage are in place.

In spite of these successes, there is a strong need to further enhance the performance of current PEM fuel cells. Several technical obstacles hinder their widespread

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commercialization for transportation and stationary applications. These include improper water and heat management, the intolerance to impurities such as CO, sluggish electrochemical cathode kinetics, and high cost. Because of these problems, a new approach that serves as a solution to PEMFCs is required and high temperature operation (160 to 180°C) of the PEMFC is regarded as one.

The following section gives an overview of the various advantages of high temperature operation and the current challenges that dominate the field of HT-PEMFCs.

1.1.3 High temperature operation of PEMFC as solutions - Advantages and challenges

1.1.3.1 Improved cathode kinetics

The term kinetics can refer to the anode or cathode kinetics. For a hydrogen/oxygen fuel cell, oxygen reduction reaction (ORR) takes place in the cathode, while hydrogen oxidation reaction in the anode. However, cathode kinetics is considered the limiting factor for fuel cell performance since the rate of ORR is relatively slower than HOR [4]. Therefore, improving sluggish cathode kinetics is one of the key areas for researchers. It is a well-established fact that increasing the temperature does improve both the anode and cathode reaction kinetics as expected from the following equations.

The Tafel equation shown in Eqs. (1:4) and (1:5), is a simplistic way to describe the electrochemical polarization/performance of a PEMFC, when the reverse reaction rate is negligible compared to the forward reaction rate. It is also critical to be noted that the Tafel equation does not account for the mass-transfer limitations. Nevertheless, it is still a convenient way to assess the performance of the fuel cell.

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$$E = E_{rev} + b \log i_0 - b \log i \quad (1:4)$$

$$b = -2.3 \frac{RT}{\alpha nF} \quad (1:5)$$

where E , E_{rev} , b , i , i_0 , n , T and α are the electrode potential, reversible potential, Tafel slope, current density, exchange current density, the number of electrons transferred in the rate determining step, temperature and the transfer coefficient, respectively.

The discussion of the effect of temperature on the various components of the Tafel equation is elaborated in the following sections.

1.1.3.1.1 Effect of temperature on E_{rev} and Open Circuit Voltage (OCV)

The derived relationships shown in Eqs. (1:6) to (1:8) are between OCV , E_{rev} , temperature and the partial pressures of oxygen, hydrogen and product water for a hydrogen/oxygen fed PEMFC [5].

$$\left(\frac{\partial E_{rev}}{\partial T} \right)_p = \frac{E_{rev} - E_{rev}^0}{T - 298} \quad (1:6)$$

$$\left(\frac{\partial E_{rev}}{\partial T} \right)_p = \left(\frac{\Delta S}{nF} \right)_p \quad (1:7)$$

$$E_{rev} = E_{rev}^0 + \left(\frac{\partial E_{rev}}{\partial T} \right)_p (T - 298) = E_{rev}^0 + \left(\frac{\Delta S}{nF} \right)_p (T - 298) \quad (1:8)$$

where E , E_{rev}^0 , F , n , T , p and S are the electrode potential, reference reversible potential, Faraday's constant, the number of electrons transferred, temperature, pressure and entropy, respectively.

A comparison of the entropy for the H_2/O_2 reaction below and above 100°C shows that the change of entropy is approximately four times lesser. The change of entropy below 100°C and above 100°C are -163.5 J/Kmol , and -44.5 J/Kmol , respectively. This is a comparison

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between the states of product water, being a liquid below 100°C and being a gas above 100°C [6]. Therefore, the value of dE_{rev}/dT is lesser when the water exists as a gas which means that the rate of E_{rev} reduction with temperature is lower. Moreover, Eq. (1:7) shows that the temperature also causes the E_{rev} to decrease due to a linear relationship and the change in entropy being negative. Therefore the overall E_{rev} reduces as the temperature increases as shown in Eq. (1:8).

The effect of partial pressures of the hydrogen, oxygen and the product water on the OCV can also be extended from Eq. (1:8) and is shown in Eq. (1:9). The OCV decreases as the partial pressure of product water increases at a higher temperature [7]. Therefore, the overall OCV decreases due to higher temperature operation of the PEMFC.

$$OCV = E_{rev}^0 + \left(\frac{\Delta S}{nF} \right)_p (T - 298) + \frac{RT}{2F} \ln \frac{P_{H_2} P_{O_2}^{1/2}}{P_{H_2O}} \quad (1:9)$$

where R , T , p_{O_2} , p_{H_2} and p_{H_2O} are the universal gas constant, temperature and partial pressures of oxygen, hydrogen and water, respectively.

Xu *et al.* investigated the effect of temperature on the OCV by increasing the temperature from 60 to 120 °C and maintaining the relative humidity [8]. It was concluded that the theoretical OCV reduced from 1.22 to 1.14 V due to the increase of the water partial pressure which is in agreement with theoretical OCV in comparison, as shown in Eq. (1:10).

$$OCV = 1.23 - 0.9 \times 10^{-3} (T - 298) + 2.3 \frac{RT}{4F} \log \frac{P_{H_2}^2 P_{O_2}}{P_{H_2O}^2} \quad (1:10)$$

1.1.3.1.2 Effect of temperature on the Tafel slope, b

The effect of temperature on b , the Tafel slope for both the HOR and ORR, can be obtained by differentiating Eq. (1:5). The linear relationship can be obtained between b and

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temperature assuming that the reaction mechanism and α , are independent of temperature, shown in Eq. (1:11) [5].

$$\frac{\partial b}{\partial T} = -\frac{2.3R}{\alpha nF} \quad (1:11)$$

where R , F , b , n , T and α are the universal gas constant, Faradays constant, Tafel slope, the number of electrons transferred, temperature and the transfer coefficient, respectively.

However, several experimental studies reported a major difference on the change in the Tafel slope between low and high current density operation [9, 10]. At low current density operation, the Tafel slope increases directly with the increase in temperature. However, at high current density operation, the Tafel slope increases but is indirectly related to the change in the reaction mechanism from the temperature increase. Specifically, the reaction mechanism of ORR has been reported to show changes at high current density operation, which contribute to the corresponding increase of the Tafel slope and the exchange current density. Nevertheless, the increase in the Tafel slope at high and low current densities caused by the higher temperature operation generally ensures better performance.

1.1.3.1.3 Effect of temperature on exchange current density, i_o

The exchange current density, i_o , is a fundamental characteristic that can be defined as the rate of oxidation or reduction of the electrode at equilibrium, expressed in terms of current. The higher the value, the better the electrochemical performance of the PEMFC will be. The exchange current density is an intrinsic material property and varies with different materials, and with pressure and temperature [11, 12]. Song *et al.* studied the effect of temperature on the ORR and HOR exchange current densities [13]. It was reported that the exchange current densities increase with temperature which is another benefit of high temperature operation.

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1.1.3.2 Improved tolerance of the catalyst to CO

Even though, the terms pure hydrogen/pure oxygen-fed PEMFCs are commonly used, hydrogen is often supplied with traces of CO which is inherent from the various reforming processes. Carbon monoxide poisoning is one of the main problems that can cause detrimental effects on the performance of the PEMFC [14]. Carbon monoxide can get adsorbed onto the surface of the platinum catalyst, which poses as hindrance for HOR at the anode [15]. Studies on CO tolerance revealed that CO concentration of as low as 10 parts per million (ppm) can result in a drastic loss of performance at 80 °C [16-19]. In addition, CO from the anode can crossover to the cathode via the membrane and affect the ORR [20].

The effective remedy to this issue is to increase the operating temperature. Several studies performed decades ago have concluded that CO adsorption is highly unfavoured at higher temperatures due to its association with highly negative entropy [21, 22]. Li *et al.* studied the effect of temperature on CO poisoning of platinum catalyst supported on carbon and loaded on a phosphoric acid doped polybenzimidazole (PBI) membrane. The study that ranged from 80 to 200 °C indicated that CO tolerance is significantly improved at elevated temperatures [22].

With this remedy, the need for complex and thus expensive reformers to produce hydrogen is eliminated.

1.1.3.3 Improved water management and gas transport

1.1.3.3.1 Water management

The issue with liquid water is one of the major problems that have dominated research efforts in LT-PEMFCs. Numerous experimental and modelling works have been done to understand the key mechanisms of water transport suggesting improvements for better water management [23]. Two of the main effects of poor water management are flooding and

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dehydration [24]. Flooding occurs when excess water accumulates both at the porous regions of anode and cathode or even the flow channels and is most significant at the cathode [25]. In all cases, a distinct drop in the current density is observed since the reactants are temporarily blocked from reaching the reaction sites. The pressure then builds up due to the blockage and pushes the excess liquid water out of the anode, cathode or the channels. This occurs in a periodic manner causing inconsistent, unreliable and unfit performance for practical application [26]. Even though the effects are the same, there are several mechanisms differentiating between anode and cathode flooding. Cathode flooding occurs for two main reasons. Firstly, it is where water is catalytically generated with oxygen, hydrogen ions and electrons. Secondly, the electro-osmotic drag of water molecules due to transport of protons under an electric potential, from the anode to the cathode [27].

On the other hand, anode flooding occurs less frequently due to several reasons. One main reason is the back diffusion of water from the cathode to the anode, especially when low hydration level of the hydrogen gas stream creates a force that is stronger than the electro-osmotic drag [27]. Secondly, anode flooding has also been observed to occur when the PEMFC is operated at low current densities, temperatures and reactant flow rates [28]. Finally, the gas channels can get flooded if the design is not proper for water removal. Poor design of the gas channel can induce behaviours like uneven temperature, pressure and current density distributions that lead to undesirable condensation of water, thus resulting in flooding of the gas channels [29].

In opposite contrast to flooding, dehydration is also a problem in LT-PEMFC operation. This is strongly related to the proton conductivity of the membrane. Water in the proton exchange membranes such as Nafion acts as a dominant proton transport mechanism where protons travel in the hydrated parts of the ionomer via dissociation of sulphonic acid bonds [30]. In

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dehydrated conditions, the role of this mechanism is affected and as a result, the performance degrades significantly. Furthermore, prolonged operation of the PEMFC under dehydrated conditions for as long as 100 seconds is enough to cause permanent damages such as delamination and pinholes developed in the MEA [31].

Achieving the thin line between flooding and membrane dehydration has always been the objective of proper heat and water management and aim for researchers pertaining to LT-PEMFCs. There are a lot of factors that have to be controlled in order to achieve a balance between flooding and dehydration. In the aim of achieving this, a lot of energy can be wasted as more problems arise from controlling these factors. Clearly, a fundamental change is required. High temperature operation might offer a solution to flooding in PEMFCs as only gas phase exists. However, the problem of dehydration and its detrimental effect on the proton conductivity of the membrane cannot be catered with this solution. That is why the fabrication of a new class of membranes that can maintain sufficient and consistent proton conductivity in low relative humidity conditions or better, in fully anhydrous conditions have been the core research objective for HT-PEMFCs over the years.

1.1.3.3.2 Effect of temperature on oxygen transport

The diffusion coefficient of oxygen is an important property that determines the performance of the fuel cell. The supplied oxygen from the cathode flow channels must reach the catalyst layer through the gas diffusion layer. Therefore, a higher value of the diffusion coefficient can ensure faster transport of oxygen. At the same time, the product liquid water is also removed through the cathode catalyst layers via the flow channels.

Flooding is one of the effects where liquid water which is of high density, clogs up the porous CL and GDL, and results in oxygen starvation and eventual performance degradation of the

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PEMFC. This is expected because the transport of oxygen in liquid is lower by 10^{-4} in magnitude, as compared to the oxygen transport in a gaseous medium.

This effect can be significantly reduced if the product water is in vapour form which is a unique characteristic in elevated temperature operation, in particular above the saturated temperature of vapour pressure. This is because oxygen diffusion coefficient through water vapour is several orders of magnitude higher than that through liquid water. Therefore, high temperature operation facilitates better oxygen transport through the gas diffusion layers and the cathode catalyst layers which leads to an increase in fuel cell performance in the mass transport controlled regime.

1.1.3.3 Simpler flow field design without the presence of two phase flow in the channel

The flow field in the PEMFC serves two functions. Firstly, it serves as an effective way to distribute the reactants over the entire area of the electrode. Secondly, it also serves to effectively remove the excess water from the anode and cathode in order to reduce the possibility of flooding. These two features must be integrated into the flow field design. In addition, the design has to be done considering two phase flow and its interactions. These result in great complexity of the flow fields in which time and money are wasted because intricate machining is required. High temperature operation of PEMFC can eliminate the need for designing the flow field to cater for liquid water removal, since water is in the vapour phase. Therefore, flow channels can be simplified without having to consider two phase flow.

1.1.3.4 Improved thermal management

A large fraction of the energy generated by a typical PEMFC is removed as heat. This comes in the form of entropic, joule and reaction heating. The product heat must be well managed in

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order to maintain membrane hydration and at the same time prevent flooding ,i.e., to maintain at the desired working temperature which requires a complex cooling system to reject all the heat [32]. In case of high temperature operation, the higher temperature difference enables easier and less complex heat rejection systems. This directly relates to heat exchangers that have lesser frontal area and thus cheaper and takes less space. The LT-PEMFC operates at a temperature of 60 to 80 °C and this corresponds to an electrical efficiency of 40 to 60 %. It was estimated that, in order to increase the efficiency to 56%, the stack temperature would have to be maintained at 145 °C. Therefore, having a higher temperature difference between the stack and ambient conditions is important for improving the efficiency of the PEMFC [32]. Furthermore, the larger waste heat energy from the HT-PEMFC has greater practical value as compared to the waste heat from the LT-PEMFC. For example, if the HT-PEMFC can be operated at 200 °C, it is potentially possible to obtain the steam at 15 atm. This can be used to heat other components of the system. Therefore, the system efficiency also improves.

1.1.4 Challenges of operating PEMFCs at high temperature

Even though high temperature operation offers as a solution to problems experienced in LT-PEMFCs, it gives rise to new challenges. This section gives an overview of the various obstacles that have to be overcome before high temperature operation can be perceived as an ultimate option to PEMFC technology.

1.1.4.1 Degradation of engineering materials and mechanical failure

Fuel cell components come into contact with a number of corrosive agents during operation. For example, the bipolar plates come in direct contact with fuel and oxidant that therefore are exposed to oxidizing and reducing conditions in the respective sides. Current collector plates are also subjected to similar conditions. In addition, elevated temperature above 140 °C can increase the material degradation rate [33].

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1.1.4.2 Degradation of the gas diffusion electrode

At higher temperatures, the durability of the high surface area carbon supports onto which catalysts are loaded poses as an issue. Firstly, these carbon supports can react to form gases such as CO when oxidized in the presence of Pt catalysts, especially at the cathode. This behaviour is amplified at higher temperatures [34]. The effect of this behaviour is the reduced catalyst utilization when the carbon supports disappear, thus resulting in the degradation of performance over time, leading to cell damage.

Secondly, agglomeration of catalyst particles can also be caused and amplified by elevated temperature operation as reported by Wilson *et al.* [35]. As particles agglomerate together, the surface area to volume ratio decreases, affecting the ORR activity rate. It was reported that the optimal size of platinum particles for maximum ORR activity lies in the range of 3 to 5 nm and further growth of these particles can reduce the catalyst utilization. In addition, platinum is also susceptible to electrochemical dissolution and re-deposition over time which is sped up at elevated temperatures [36].

1.1.4.3 Membrane conductivity and degradation

In low temperature operation, Perfluorosulfonic acid based polymers were widely used as proton exchange membranes. These exhibit high proton conductivity at temperature below the boiling point. However, at elevated temperatures and anhydrous conditions, the water activity decreases drastically, which in turn reduces the membrane proton conductivity [37]. Thus, improving this property is one of the key challenges of HT-PEMFC operation. Another key issue is the thermal degradation that can occur at elevated temperatures. Most polymers start to undergo morphological relaxation as the glass transition is exceeded in operation [38]. Nafion has a glass transition temperature in the range of 80 to 160 °C inclusive of hydrated or dehydrated condition [39]. The proton conductivity of the most HT-PEMs that have been

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reported is usually a value around 0.15 S/cm, at a temperature range of 160 to 180 °C [40]. Efforts to fabricate novel membranes with improved proton conductivity have been popular over the years. Nafion-based [41], PBI-based [42] and even hetero-polyacid-based [43] membranes have been proposed for HT-PEMFCs. Recently, pyridine-based proton exchange membranes have also been reported [44].

1.1.4.4 Heating strategies

Conceptually, operating the fuel cell at higher temperatures may have many benefits. However, creating a high temperature environment is not an easy task. In LT-PEMFC, self startup of PEM is possible at 5 °C below the freezing point [45], and the steady state self sustaining temperature reaches around 50 to 70°C due to the heat generated from ohmic heating, reaction heating and entropic heating [46].

One of the key differences between HT-PEMFC and LT-PEMFC operation is the requirement of an external heating source in order to warm-up the fuel cell. Studies have been done to investigate strategies in order to reduce the warm-up time during start-up of HT-PEMFCs, which pose as one of the challenges for the HT-PEMFCs. Another key challenge is to maintain the operating temperature above 160°C. As far as this is concerned, there are two ways this could be achieved at the current stage. One method deals with creating a high temperature environment such as with the use of an external heating oven. The other method requires maintaining the environment at ambient temperature while heating the fuel cell components only. In comparison, the latter strategy provides better thermal efficiency due to a greater temperature difference. However, a greater challenge will be to provide a solution that can eliminate the use of external sources for maintaining the temperature above 160 °C.

*Chapter 1. Introduction***1.2 Objective and Significance**

Currently, PEMFC technology is moving towards operation at high temperatures and as with any change, there exists technical challenges that must be overcome. One of these, which is related to HT-PEMFCs, is the heating strategy to achieve the desired temperatures of around 160 to 180 °C during start-up as explained in section 1.1.4.4.

Thus, considering the limited number of references that have been dedicated to HT-PEMFC heating strategies, this thesis is aimed at comprehending the fundamentals of heating strategies through analytical and numerical modelling techniques and experimentation. These efforts are designed to extend the existing knowledge of the domain and at the same time, explore ways to improve the heating strategies, from a scientific perspective.

1.3 Scope

The scope of the research is divided into the following sections. Section (I), (II), (III) and (IV) focus on the studies that relate to warm-up. These are explained in the following section.

(I). Analytical modelling of boiling phase change phenomena in HT-PEMFCs during warm-up process - (Chapter 3)

The warm-up process of a hydrogen/oxygen HT-PEMFC that is electrochemically operated from room temperature while external heating is simultaneously applied, is investigated. 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) 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

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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. In addition, a comparison between existing and the considered heating strategies is done.

(II). An analysis of transient CO poisoning kinetics during warm-up process of a HT-PEMFC- (Chapter 4)

Part 1 - Physical model and parametric study

The first of a two-part study, investigates the anode electro-kinetics during the start-up or warm-up process of a HT-PEMFC from a temperature above 100 °C, to the desired temperature of 180 °C, where CO contaminated hydrogen is used as a fuel. The heating strategy considered involves an initial heating of the HT-PEMFC by external means to a temperature above 100 °C, after which current is extracted, where electrochemical reaction heating is expected to contribute to certain extent of the heating process. Thus, a numerical transient three dimensional model is derived addressing the anode electro-kinetics, under a temperature gradient that is expected during the warm-up process. Operational parameters such as temperature gradient, initial start-up temperature, CO mole fraction and extracted current density are varied and their effects on the CO and hydrogen coverage fractions, the anode overpotential and the cell potential with respect to time, are explored.

(III). An analysis of transient CO poisoning kinetics during warm-up process of a HT-PEMFC - (Chapter 4)

Part 2 - Sensitivity analysis

The second of the two-part study, investigates the anode electro kinetics during the start-up or warm-up process of a HT-PEMFC from room temperature to the desired temperature of 180 °C, where CO contaminated hydrogen is used as a fuel. The heating strategy considers an

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initial heating of the HT-PEMFC by external means to a temperature above 100 °C, after which current is extracted, where electrochemical reaction heating contributes to the heating process. In Part 1 (Physical model and parametric study), a numerical transient three-dimensional model was derived addressing the anode electro-kinetics, under a temperature gradient that is expected during the warm-up process. The effects of operational parameters such as temperature gradient, initial start-up temperature, CO mole fraction and extracted current density were explored. In this study, the model is further investigated to determine the relative importance of the above mentioned operational parameters on the anode overpotential, during the start-up process.

(IV). An analysis of OCV during warm-up process of high temperature proton exchange membrane fuel cell - (Chapter 5)

An experimental effort that aims to highlight the limitations of the Nernst equation is conducted. A key focus on the responsiveness of the OCV with respect to temperature gradients experienced during the start-up process of a HT-PEMFC.

Chapter 2. Literature review

2.1 Outline of the literature review

This literature review is aimed to critically evaluate the analytical and numerical modelling efforts that has been dedicated to HT-PEMFCs. The basic outline of the literature review is divided into areas which are of interest in context to HT-PEMFCs and are as follows:

- History of PEMFC modelling
- HT-PEMFC models
 - HT-PEMFC performance validation models
 - Hydrogen crossover
 - CO poisoning
 - Dynamic performance models
 - Transient heating strategy
 - Electrical models
 - System level analysis

The review starts with the a brief history of early modelling works and also discusses the various approaches researchers took to describe the complex systems such as the membrane and catalyst layers and how they have evolved over the decades.

2.2 The history of PEMFC modelling

The earliest works on PEM fuel cell modelling started in the 1990s by pioneers such as Springer *et al.* [35, 47] and Bernardi and Verbrugge [48, 49], with one-dimensional models. Springer *et al.* [35, 47] proposed mechanisms that explained the water transport through the membrane and proposed the relationship between the membrane conductivity and the water content in the membrane. Bernardi and Verbrugge [48, 49] similarly predicted fuel cell

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performance based on a fully hydrated membrane. The work from these pioneers served as the basic platform, especially for more complicated numerical studies that were published much later.

2.2.1 Membrane models

Two distinct approaches have been reported for the modelling of proton exchange membranes. One way deals with statistical mechanics and molecular dynamics to capture the micro-scale or nano-scale transport in membranes [50, 51]. Although these were useful on one hand, they were highly unpopular because it was often difficult to compare against experimental data from a typical PEMFC. In addition, these models were highly complex to be developed and computationally expensive.

The second approach is related to macroscopic models that combine experimental results with fully or semi empirical relations that touch on fundamental theories. In contrast to microscopic models, these are much useful and easier to implement in simulations as they efficiently simplified the modelling problem to cater for practical use. Many models have been proposed over the decades which were strongly attributed to a few popular and fundamental ones, that served the foundations to future modelling of the membrane [27, 47, 52, 53]. Springer *et al.* [47], Fuller and Newman [52] and Nguyen and White [27] proposed correlations of the membrane conductivity in terms of the water content per sulphonic acid group, λ , in a typical Nafion membrane. The main difference between their correlations is the way the dimensionless diffusion coefficient of water in the membrane was expressed. Several models have been published [54-56] based on further refinement from the works of Springer *et al.* [47]. De Francesco *et al.* [54] proposed a kinetic model for the prediction of dynamic behaviour of the membrane. Fimrite *et al.* [55] developed a binary friction membrane model

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and binary friction conductivity model that explained the Schroeder's paradox in detail. Thampan *et al.* [56] developed the Dusty Fluid Model to further include two phase effects.

Recent works on HT-PEMFCs based on phosphoric acid doped PBI membranes have also been recently published by Cheddie and Munroe [53]. This was an attempt to model and express the membrane conductivity in terms of amorphous phosphoric acid doping level and temperature, and understand the underlying mechanisms of transport phenomena that is much different from the Nafion membranes.

2.2.2 Catalyst layer models

Researchers also attempted to look closer into the catalyst layer as ways to describe it with different characteristic models. The catalyst layer is a complex porous structure that can be described with the most physical interfaces as compared to the other components of the PEMFC. Similar to the membrane, both pore scale and macro modelling approaches have been published for the catalyst layer.

Pore scale modelling of the catalyst layer attempt to reconstruct the catalyst layer based on scanning electron microscope (SEM) and transmission electron microscope (TEM) images mainly aimed for fundamental understanding of the coupled mechanism of transport phenomena and electrochemistry [57-59]. However, these were not as popular as the macro models.

Fundamental macro-modelling of the catalyst layer can be referenced to the interfacial model [60], pseudo-homogenous model [61] and the agglomerate model [62]. The interfacial model is the easiest way to describe the catalyst layer as an interface with constant chemical and physical properties [60]. It is assumed as an interface because of its lower thickness as compared to the gas diffusion layers and the membrane. This model is computationally

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cheaper than the other two. The pseudo-homogenous model assumes the layer to have constant physical and chemical properties like the interfacial model [61]. However, this is designed as a separate computational domain with thickness. The agglomerate model is the most complicated of the three and assumes the catalyst layer to be an agglomerate of carbon supported Pt, ionomer, and void space for the transfer of gasses [62]. This model can calculate the over-potential for the anode reaction, and the potential distribution in the membrane. These catalyst layer models served as the foundation work and are widely in use as compared to the pore scale models.

2.3 HT-PEMFC models

Modelling of HT-PEMFCs in this temperature range is a lot lesser as compared to the LT-PEMFCs. There are two major reasons for this trend. Firstly, HT-PEMFCs have been introduced less than a decade ago. In LT-PEMFCs, the major challenge was inclined towards heat and water management which are clearly design issues. Therefore, a great deal of modelling effort was channeled in that direction to address them. However, in HT-PEMFCs, the challenge is inclined towards the material aspects, one of which being the fabrication of membranes that are suitable for high temperature operation. A lot of work has been done to improve the membrane conductivity in low humidity or even anhydrous conditions [40] and is still in progress. Therefore, finding solutions for the critical material problem is of higher priority than mathematical modelling to be done for HT-PEMFCs. Secondly, in LT-PEMFC modelling, efforts were aimed to address problems such as flooding and dehydration. High temperature operation of the PEMFC is targeted to eliminate these problems and thus the need for advanced modelling of HT-PEMFCs is greatly reduced. In addition, modelling of HT-PEMFCs is perceived to be less complicated. There are several important assumptions that are generally taken, that have greatly simplified the modelling of HT-PEMFCs. They are as follows:

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Water production at the cathode is realistically assumed to be in the vapor phase only. The water transport through the membrane is also neglected due to the dry environment in HT-PEMFCs and negligible electro-osmotic drag effect for phosphoric acid medium-based membranes. Due to these reasons, heat and mass transfer modelling of HT-PEMFCs is not as popular as LT-PEMFCs.

2.3.1 HT-PEMFC performance validation models

Nevertheless, there have been several publications on modelling that have attempted to capture the essence of HT-PEMFC operation through validation with data from PBI-based HT-PEMFCs. This section discusses all of these models. Cheddier and Munroe published the first and several others pertaining to the modelling of HT-PEMFCs. Cheddier and Munroe [63] started off with a one-dimensional, steady-state and non-isothermal mathematical model of a HT-PEMFC and validated against previously presented experimental data. This was an attempt to study the effect of geometric factors of the MEA on high temperature performance. Since then, they had made several refinements. Analytically solved correlations were presented for comparison of performance prediction between their previous work [64]. They have also concluded through another one-dimensional, steady state mathematical model that improvements to the membrane conductivity at the catalyst interface can greatly enhance the performance [65]. In order capture greater details with modelling, a three-dimensional steady state model was also proposed to predict the oxygen depletion phenomena that occurs in the catalyst area under the ribs [66]. Furthermore, to include the effects that arise from gas solubility in the PBI membrane and aqueous phase reactions, a two-phase model was also proposed [53]. A final refinement to reduce computational time was also proposed by implementing a semi-analytical three-dimensional model [67]. This reduced the computational time by a factor of four and the memory space required by a factor of three but

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at the same time, managed to capture the polarization performance and the species distribution.

Several others have also contributed as modifications to the works proposed by Cheddle and Munroe. Hu *et al.* [68] proposed a two-dimensional model based on electrochemical techniques that was validated against data from a PBI based HT-PEMFC. This was claimed to be a novel way to predict the performance as compared to the model proposed by Cheddle and Munroe [65]. Korsgaard *et al.* [69] improved the work proposed by Cheddle and Munroe [65] to include factors such as temperature and cathode stoichiometric ratio variations on the performance. Peng and Lee [70] proposed a three-dimensional, single phase, non- isothermal model with added computational fluid dynamics based features to improve the details of the model proposed by Cheddle and Munroe [71].

Recently, there have been more progress in the fundamental model development as well. Ubeda *et al.* developed an estimation model that can be applied to HT-PEMFCs, designed to be straightforwardly applicable as well as effective. Experimental results from the sensitivity analysis of the HT-PEMFC was used as validation to the model [72]. Chippar and Ju developed a three-dimensional non-isothermal model for a (HT-PEMFC) with phosphoric acid-doped PBI membrane to numerically investigate the effect of the thermal gradient along the coolant flow path [73]. Sharmadina *et al* developed a model for HT-PEMFC with the detailed description of transport processes in the cathode catalyst layer which was experimentally validated [74]. Ionescu developed HT-PEMFC models focussing on the hydrogen, oxygen and water vapour concentrations in the channels [75, 76]. Azami *et al.* developed a two dimensional model to capture the transport and polarization phenomena [77]. Yin *et al.* proposed a a 3D model of HT-PEMFC based on sulfonated PBI membranes

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with experimental validation [78]. Girimurugan *et al.* developed a model to analyze the effects of different operating voltage and temperatures on the cell performance [79].

Authayunan *et al.* developed a HT-PEMFC multi-stack HT-PEMFC model to minimize the CO poisoning effect and to maximize its efficiency [80]. Krastav *et al.* proposed a detailed 3D model to simulate the HT-PEMFC under different anode fuel compositions [81]. Salomov *et al.* proposed a three dimensional model to optimize the catalyst layer and the performance of the HT-PEMFC [82]. Sun *et al.* developed a numerical model based on a poly(2,5-benzimidazole) (ab-PBI) membrane which was experimentally validated [83].

Furthermore, the fundamental models have also been improved to cater for the analysis of thermal management. Reddy and Jayanti proposed a numerical thermal model to simulate the flow and heat transfer within HT-PEMFC stack coupled with a hydrogen storage system [84]. Reddy *et al.* proposed a CFD model to investigate the thermal management of a HT-PEMFC incorporated with an external coolant system [85]. Reddy *et al.* developed a stack model of a HT-PEMFC over a power range of 1 to 10 kWe, to assess the thermal management [86].

2.3.2 CO poisoning models

These early models that were highlighted in the previous sections were aimed towards capturing the basic dynamics of transport phenomena. As these models strengthened the fundamental understanding of HT-PEMFC operation, they opened up the room for greater complexities suited to cater for the different issues that were inspired from the LT-PEMFC models. These were models to describe phenomena such as CO poisoning.

As far as the modelling of CO poisoning is concerned, the existence of tracer amount of CO in hydrogen-rich fuels generated from any fuel reforming methods, requires the consideration of CO electrokinetics in the electrodes, since the presence of CO in the hydrogen stream has

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the ability to poison the Pt catalysts in the anode [20, 87-90]. Modelling of CO poisoning has been popular in the area of LT-PEMFCs [16, 17, 91-93]. Recently, the modelling of CO poisoning in HT-PEMFCs has been the one of the focuses and a handful of publication can be found in the literature. Chu *et al.* [94] developed a transient one-dimensional mathematical model that was validated with a PBI based HT-PEMFC, to predict current density degradation due to CO poisoning. Bergmann *et al.* proposed a dynamic time dependant two-dimensional, non-isothermal model of a PBI based HT-PEMFC that accounts for the CO poisoning and concluded that a recovery time of 20 minutes was observed after feeding with pure hydrogen [95]. Jiao *et al.* presented a three-dimensional non-isothermal model that was experimentally validated with a PBI based HT-PEMFC and concluded the feasibility of using hydrogen gas produced by reforming hydrocarbon fuels [96]. Doubek *et al.* presented a couple of three-dimensional models that described the catalyst layer using a pseudo-homogenous model and an agglomerate model [97]. Mamlouk *et al.* proposed a one dimensional model to investigate the effect of CO and methane in reformat gas, on the electrochemical performance [98]. The comparison with a PBI based HT-PEMFC suggested that the pseudo-homogenous model matched better against the experimental data. Jiao *et al.* extended their numerical model to simulate the effects of varying flow channel dimensions on the CO poisoning effect [99]. Furthermore, Oh *et al.* refined the CO model of Springer *et al.* in order to predict the behaviour of a phosphoric acid based HT-PEMFC [100]. Oh and Ju developed a numerical model to investigate the characteristics of CO and hydrogen adsorption/desorption and the subsequent electro-oxidation on the anode catalyst and identify the tolerance level of CO over a typical range of operating temperatures [101]. The models were clearly aimed describing the catalyst layer of the HT-PEMFC and the effects of CO, accurately and uniquely.

2.3.3 Dynamic performance models

Several HT-PEMFC dynamic behaviour models were also proposed. Zenith *et al.* developed a control oriented model successfully explaining the shape of the transient current-voltage paths, including the different time constants observed when reversing a transient [102]. The research efforts pertaining to this area are as follows. Peng *et al.* proposed a transient three-dimensional, single-phase and non-isothermal numerical model and concluded that the peak of overshoot (undershoot) is related to cathodic air stoichiometric mass flow rate instead of anodic hydrogen stoichiometric mass flow rate [103]. This was a novel method to simulate the transient response that included the charge double layer and thermal effects on the performance. Mamouk *et al.* proposed a two-dimensional isothermal model for a PBI based HT-PEMFC to include the effects of the anode catalyst layer poisoning relating to the usage of reformed gas as fuel [104]. In addition, several models have been developed to simulate the transient performance of HT-PEMFCs under a dynamic load. Sousa *et al.* developed a dynamic two-dimensional non-isothermal model to simulate the transient response of an intermediate-temperature fuel cell using phosphoric acid doped PBI membrane [105]. Park and Min developed a quasi three-dimensional non-isothermal dynamic model and concluded the dependence of performance on the fuel cell temperature [106]. Recently, park and Min also proposed a detail dynamic model to predict the characteristics of the overall system and individual component under dynamic conditions [107]. These models were beneficial in predicting the transient response during the load stepping, enabling greater controllability of power.

2.3.4 Start-up process optimization models

Several dynamic heating models were also proposed to investigate warm-up strategies which is one of the major direct issues in HTPem operation. Andreason and Kær proposed a

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dynamic lumped model to predict the energy required to heat up HT-PEMFC stack to above e.g. 120 °C, from room temperature by comparing the different heating methods [108]. Singdeo *et al.* 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 [109]. Andreason and Kær also proposed a model for predicting the dynamic temperature of a HT-PEMFC stack as a way to test different thermal control strategies [110]. 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.* recently proposed a numerical model considering the effect of reaction heating when the temperature of the HT-PEMFC reaches 120 °C by external heating where the product water in this case was treated as a gas [111]. In addition, Wang *et al.* developed a physical model comparing the start-up duration of the different start-up concepts [112]. Apart from these studies, there is no other literature to date that investigates the heating strategy of the HT-PEMFC operating from room temperature, .

2.3.5 Electrical models

In addition, there were numerous modelling efforts that included electrical and control related theories and ways to improve the existing computational fuel cell dynamics. The research efforts pertaining to this area are as follows. Hu *et al.* proposed a steady two-dimensional mathematical model validated with a PBI based HT-PEMFCs that modified using an

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alternative current impedance technique [113]. This was a new attempt to combine the electrical and fuel cell dynamics theories to predict the performance, oxygen and water distribution. Andreason *et al.* proposed an equivalent circuit model that was experimentally validated against a one-kilowatt PBI based HT-PEMFC stack [114]. It was concluded that the model was accurate in predicting the stack impedance at different temperature profiles. Scott and Mamlouk developed a zero-dimensional isothermal model for a HT-PEMFC to relate the cell potential and the current density with validation against experimental data [115]. The purpose of the study was to provide a simple semi-empirical equation for the easy prediction of voltage and power during operation. Boaventura *et al.* developed a dynamic one-dimensional isothermal phenomenological model validated against a PBI based HT-PEMFC and included the effects of electric double layer to predict the Nyquist plots [116]. Vang *et al.* developed a two-dimensional transient model to predict the performance and impedance spectra. Experimental data with a HT-PEMFC did not match well with the model results [117]. However, it was concluded the mismatch is expected because the model did not incorporate the effects of unrealistic fitting parameters. Sharmadina *et al.* developed a pseudo two-dimensional, isothermal transient model to simulate and analyze electrochemical impedance spectra of the cell in both potentiostatic and galvanostatic modes, current interrupt results and step changes in the cell current or potential [118].

2.3.6 System-level analysis

Another area where there have been a lot of publications over the decade, is system modelling. The research efforts pertaining to this are as follows. Pfeifer *et al.* proposed a system model of a HT-PEMFC coupled with a hydride tank to assess its feasibility in practical applications [119]. Arsalis *et al.* developed a detailed thermodynamic, kinetic and geometric model of a micro-Combined-Heat-and-Power residential system based HT-PEMFC which was validated [120]. Arsalis *et al.* proposed a micro-CHP (combined-heat-

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and-power) residential system based HT-PEMFC model and operational technique of a on HT-PEMFC to investigate its commercialization prospects [121]. Reamer *et al.* proposed a three-dimensional, steady state model based on a HT-PEMFC stack consisting of five cells, in order to predict the local current density inside the stack [122]. Arsalis also developed a model to simulate a 100 kW_e liquid-cooled HT-PEMFC subsystem integrated with an absorption chiller subsystem to investigate feasibility of the design. [123]. Arsalis *et al.* developed a HT-PEMFC-based micro-combined-heat-and-power system model for a residential system, and optimized to obtain an optimum configuration using a genetic algorithm optimization strategy [124]. Rabui *et al.* proposed a heat recovery system for a HTPEM fuel cell-based combined heat and power system with the use of a system model [125]. A comparison with experimental data suggested that the model was able to predict to an accuracy of ninety percent. Mamlouk *et al.* proposed an integrated HT-PEMFC system and glycerol reformer system model that includes a pseudo two-dimensional model that accounts for the CO poisoning [126]. A system model with the integration between a steam reforming unit and fuel cells is developed. The difference in electric and cogeneration efficiency between using LT-PEMFC and HT-PEMFCs was analyzed [127]. Authayanun *et al.* developed a system model composing of fuel cells and a glycerol steam reformer and compared the performance between its integration with LT-PEMFCs and HT-PEMFCs [128]. Authayunan *et al.* developed a theoretical system model to study the performance and efficiency of a glycerol processing and HT-PEMFC integrated system [129]. Zhang *et al.* developed a unified model for a high-temperature fuel-cell heat-engine hybrid system predicting the performance characteristics and optimal operating regions of key parameters [130].

Pascual and Soler developed a fuel cell-based combined heat and power system using a high temperature proton exchange membrane fuel cell fed with methanol as fuel [131]. Ersöz and

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Sayar investigated a HT-PEMFC incorporated with a fuel processing system, analyzing electrical and fuel processing efficiencies through thermodynamic modelling [132]. Arsalis *et al.* proposed a system model consisting of a heat pump-assisted HT-PEMFC micro-combined heat-and- power system for single-family households to optimize the system net electrical efficiency at a range of varying loads [133]. Perna *et al.* developed a thermodynamic system model investigating an advanced power system based on a HT-PEMFC and an organic Rankine cycle for heating and power production [134]. Najafi *et al.* proposed a configuration for an existing HT-PEMFC based residential micro-cogeneration system to investigate the key parameters of the system through a parametric to comprehend the effects on the performance [135]. Authayanum *et al.* proposed a model to investigate the performance and efficiency of an integrated auto thermal reforming and HT-PEMFC system fuelled by methane [136]. Herdem *et al.* developed a system model to estimate effects of parameters such as the steam-to-carbon ratio (SC), the reformer temperature, the current density of the fuel cell, the fuel cell temperature, the cathode stoichiometric ratio, the hydrogen utilization, and the rate of power production on the reformat gas composition, fuel cell performance, input fuel flow rate, and the heat duties of the system components [137].

These models are indicative that the HT-PEMFC technology has promising potential in energy production for a plant level scale.

2.3.7 Degradation models

Performance degradation refers to the reduction of the output voltage over time due to the reduction in membrane conductivity and catalyst layer activity over time. Several models have been dedicated to integrating degradation concepts to the numerical HT-PEMFC models. These have been important in assessing and increases the lifetime of a HT-PEMFC under operating conditions. Only a handful of publication have been published to date. They

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are as follows. Hu *et al* proposed a one dimensional mathematical model to investigate and compare with degradation/aging tests [138]. Kim *et al.* proposed one-dimensional a model to numerically investigate the effects of operating conditions on the performance degradation of HT-PEMFC with PA-doped PBI membrane, which was validated experimentally [139]. Ubeda *et al.* developed a CFD model to assess the performance degradation due to coalescence of catalyst particles with experimental validation [140]. Pohl *et al.* developed a model to investigate the electrochemical, thermal and degradation effects which is more efficient for long term simulation [141]. Vang *et al.* developed a HT-PEMFC performance degradation model simulate investigate the effect of reactant dynamics on the impedance spectrum [142].

2.3.9 HT-PEMFC membrane models

The unique feature of HT-PEMFC is the membrane, which determines the capability of the fuel cell to be operated in temperatures up to 180 to 200 °C. One of the most common membranes used in HT-PEMFCs is the phosphoric acid doped PBI membrane which serves as the proton transfer medium or electrolyte. Therefore, the uniqueness of modelling of HT-PEMFC greatly lies in the model of the membrane considered. These efforts are summarized below. Zhang *et al.* proposed a one-dimensional theoretical model to understand the hydrogen permeation mechanism in Nafion membranes based HT-PEMFCs. It was concluded from the model that hydrogen permeation is relatively more important to be resolved in Nafion membranes as compared to PBI membranes for enhancing performance [143]. Sharmadina *et al.* developed a simple pseudo two-dimensional analytical model that includes the effect of gas crossover through the membrane. It was concluded that the hydrogen crossover is prevalent at low oxygen stoichiometric flow rate [144]. Siegal *et al.* presented a three-dimensional, steady-state, non-isothermal model of a HTPMEMFC using a (PBI/H₃PO₄) sol-gel membrane, with a key focus on the membrane [145]. Su *et al.* studied

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the effects of PBI loading and operating temperature with the use of a two dimensional numerical model with corresponding experimental validation [146]. Purushothama and Ju proposed a model where oxygen and hydrogen crossover through the PBI membrane was investigated [147]. Chippar *et al.* developed a membrane water transport model for HT-PEMFCs and incorporated it into a three-dimensional HT-PEMFC model to investigate the effects of relative humidity on the performance [148]. Kadzal *et al.* proposed a detailed numerical model of a HT-PEMFC focusing on the phosphoric acid based PBI membrane [149]. Lang *et al.* extended the membrane model and utilized it to investigate the electrolyte loss from the phosphoric acid based PBI membrane of a HT-PEMFC [150].

2.3.9 Other models

There have been a few models that stand aim to extend mathematical modelling to the investigation of other areas such as control, technology integration and others. Some of the works are as follows.

Jensen and Kær developed a model of a blower cooled HT-PEMFC as a strategy to achieve safe dynamic operation [151]. This is a control related model to establish controllability of the dynamic operation. Gao *et al.* presented a numerical model of an exhaust heat recovery system for a HTPEMFC stack [152]. Although the exhaust is a secondary component of the HT-PEMFC, it is a critical part of the whole system which can affect the system efficiency. De beer *et al.* presented an integration model to integrate an emulator system to HT-PEMFC in order to replicate transient phenomena [153].

Salomov *et al.* proposed a pore scale model to investigate the fluid flow through the gas diffusion layers and catalyst layers within a HT-PEMFC [154]. The deterministic model and the stochastic model were considered for the GDL and catalyst layer, respectively, and the permeability was accurately predicted. Yiotis *et al.* proposed a physical model integrating

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heat transfer and desorption kinetics to investigate the thermal coupling potential of HT-PEMFCs with sodium alanate tanks [155].

In addition, a couple of research efforts pertaining to this stress modelling have also been published and are as follows. Chippar *et al.* numerically investigated the effects of gas diffusion layer compression/intrusion on the performance of a phosphoric acid-doped PBI membrane-based HT-PEMFC [156]. Oh *et al.* investigated the thermal stress distributions to simulate the expansion and compression that can be induced during operation and assembly of the fuel cell, with a FEM/CFD no isothermal model [157].

2.4 Summary of literature review

The outline of the literature review has clearly highlighted the several research voids in the existing efforts and the investigation of start-up of HT-PEMFCs is perceived suitable for further research, mainly due to the following reasons. HT-PEMFC technology is a mature one, considering the advances in the area of micro-porous material selection and optimization of material properties that are suitable in the temperature range of 160 to 180 °C. In terms of design, HT-PEMFCs are much more simpler than LT-PEMFCs and thus, HT-PEMFC are much easier to fabricate and maintain. Thus, HT-PEMFCs have a greater potential to be considered as a promising energy source. However, the commercialization of the technology is not as widespread as much as it is desired, considering the benefits and perks of HT-PEMFCs. With respect to the modelling of HT-PEMFCs, several areas where research efforts can be channeled toward are as listed below.

- Thermal degradation - Thermal degradation is a failure mode that can be expected in HT-PEMFCs, especially due to the elevated temperature operation. Operational processes such as start-up, in-operation as well as shut-down can be expected to cause degradation to the components such as the membrane and catalyst layers. Short and

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long term effects as well as fatigue analyses can highlight the limitations of HT-PEMFC operation.

- The HT-PEMFC PBI membrane is modelled as a correlation in most of the HT-PEMFC models. Only a handful of publications have focused on the dynamics of the membrane. This can be investigated further to optimise the chemical composition of the membrane of HT-PEMFCs.
- Pore scale modelling is an appropriate technique to look deeper into the membrane and other micro-scale components. So far, very few publications that relate to pore scale modelling of HT-PEMFCs exists. This could be an area where future research efforts could be channelled towards.
- Another area of interest is start-up, a key process prior to the normal operation of the HT-PEMFC, which can last up to around ten minutes or so. This unsteady process can be further investigated to comprehend typical scenarios of operation considering optimization to achieve energy and time efficiency.
- Furthermore, the unsteady models that are reported in the literature can be further improved by investigating the electrochemical properties that form the model. To be precise, most of the unsteady models have been modelled using steady state properties that do not vary with time. This direction is expected to improve the accuracy of unsteady models.
- Finally, creative ideas to validate the models could be generated. Currently, the most common way of validating mathematical models is by comparing the current-voltage curve. In many cases, the objective of research and the method of validation have been observed to be mildly related. Therefore, for all the potential areas of research highlighted, the method of validation should be in such a way that is closely related to the objective of investigation.

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This thesis will focus on one of the key areas highlighted, which relates to the start-up of HT-PEMFCs. By investigating the area of start-up strategies, methods can be generated to reduce time and energy consumption, and reduce total cost of operating HT-PEMFCs. The existing literature in the field of start-up strategies are focused on ways to improve time and energy management, which considers the heating of the fuel cell by external means. It is considered that these concepts can be further improved and/or fundamentally redefined from scratch. The focus of the thesis will be in this direction.

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Chapter 3. Analytical modelling of boiling phase change phenomenon in high-temperature proton exchange membrane fuel cells during warm-up process

3.1 Introduction

An area that has become popular recently is related to the analysis and optimization of warm-up strategy during the start-up period of a HT-PEMFC [158]. 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) [159-161]. 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 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 [108]. Singdeo *et al.* 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

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distribution enabling the shortest warm-up time [109]. Andreason and Kær also proposed a model for predicting the dynamic temperature of a HT-PEMFC stack as a way to test different thermal control strategies [110]. 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.* recently proposed a numerical model considering the effect of reaction heating when the temperature of the HT-PEMFC reaches 120 °C by external heating [111]. Obviously, the product water in this case was treated as a gas. Apart from this study, there is no other literature to-date considering 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.

This chapter discusses the analytical start-up 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 and 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

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of knowledge on the potential benefits that may exist, especially from an “energy efficiency” point of view [162]. 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.

3.2 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 unsteady behaviour that is divided into the three following phases, typically dominated by the temperature of the fuel cell. This is shown in Fig. 3-1.

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).

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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.

Fig. 3-1 Schematic of expected behaviour phases of temperature, water fraction and cell potential

It can be seen that the cell potential during the phase change period is unknown and will be the focus of this research effort.

All the governing equations were solved analytically through Laplace transform.

3.2.1 Heat and water balance

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

3.2.1.1 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 effective layer that comprises of cathode end plate, cathode bipolar plate and CGDL (Domain 1) and the CCL (Domain 2). The heat transfer equations are shown in Eq. (3:1) and (3:2). The two domains are formed based on thermal symmetry.

$$(V\rho C_p)_1 \frac{\partial T_1}{\partial t} = \dot{Q}_{in} - h_s^{eff} (T_1 - T_2) \quad (3:1)$$

$$(V\rho C_p)_2 \frac{\partial T_2}{\partial t} = \dot{E}_{gen} + h_s^{eff} (T_1 - T_2) \quad (3:2)$$

where

$$\dot{E}_{gen} = IA_{MEA} (E_0 - V_{cell}) \quad (3:3)$$

and

$$h_s^{eff} = h_s A_{MEA} \quad (3:4)$$

where V , ρ , C_p , T , t , $\dot{Q}_{in}$, h_s^{eff} and $\dot{E}_{gen}$ are the volume, density, specific heat capacity, temperature, time, heat input rate, effective thermal conductance and exothermic heat generation rate, respectively. Furthermore, I , A_{MEA} , E_0 and V_{cell} are the current, active area of MEA, reference potential and cell potential, respectively.

Eq. (3:3) stands for the heat generation in the CCL while Eq. (3:4) relates to the effective interfacial thermal resistance between the Domain 1 and 2. The effect of evaporation is

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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, $(E_0 - V_{cell})$ which is a contributor to the heat generation, is shown in Eq. (3:3). This is assumed to be a constant value to avoid 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. (3:5), while “2” refers to the effective thermal mass of the CCL and is given in Eq. (3:6). For simplicity, the effect of water fraction variation on the thermal mass of CCL is assumed to be negligible.

$$(V\rho C_p)_1 = \sum (V\rho C_p) \Big|_{EP+GDL+BP} \quad (3:5)$$

$$(V\rho C_p)_2 = V_{CCL} \left(\varepsilon_{CCL} s_{liq}^{H_2O} (\rho C_p)_{liq} + (1 - \varepsilon_{CCL}) (\rho C_p)_{CCL} \right) \quad (3:6)$$

where V , ρ , C_p , ε and $s_{liq}^{H_2O}$ are the volume, density, specific heat capacity, porosity and liquid water fraction, respectively.

The water fraction is defined as the ratio of the volume of liquid H_2O to the total volume of the pores in the CCL.

The liquid water produced in the CCL can be expressed by Eq. (3:7). The effect of water uptake and electro-osmotic drag in the membrane are assumed to achieve a net zero water transfer for simplicity.

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$$\dot{n}_{prod}^{H_2O} = \frac{IA_{MEA}}{2F} \quad (3:7)$$

Eq. (3:8) shows the liquid water removal rate from the CGDL as follows:

$$\dot{n}_{CGDL}^{H_2O} = \dot{n}_{outflow}^{H_2O} = \xi_c \frac{IA_{MEA}}{4Fr_{O_2}} \frac{p_{sat}}{p_c} \quad (3:8)$$

where $\dot{n}_{prod}^{H_2O}$ and $\dot{n}_{outflow}^{H_2O}$ are the liquid water production and removal rates, respectively.

Furthermore, ξ_c , I , F , r_{O_2} , A_{MEA} , p_{sat} and p_c are the stoichiometric ratio, current, Faradays constant, oxygen content in air, active area of MEA, saturation pressure and cathode pressure, respectively.

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

$$\dot{n}_{acc}^{H_2O} = \dot{n}_{prod}^{H_2O} - \dot{n}_{CGDL}^{H_2O} = I \left(\frac{A_{MEA}}{2F} - \xi_c \frac{A_{MEA}}{4Fr_{O_2}} \frac{p_{sat}}{p_c} \right) \quad (3:9)$$

where $\dot{n}_{acc}^{H_2O}$ is the liquid water accumulation rate.

The relationship between the liquid water fraction in the CCL and the water accumulation rate can be expressed by integrating Eq. (3:10). When $t=0$, the liquid water fraction in the CCL is set as zero.

$$s_{liq}^{H_2O}(t) = \frac{V_{liq}}{V_{void}} = \int_0^t \frac{v_{liq} \dot{n}_{acc}^{H_2O}}{\varepsilon_{CCL} \delta_{CCL} A_{CCL}} dt = \frac{v_{liq} \dot{n}_{acc}^{H_2O}}{\varepsilon_{CCL} \delta_{CCL} A_{CCL}} t \quad (3:10)$$

where $s_{liq}^{H_2O}$, V_{liq} , V_{void} , ε , δ and A_{CCL} are the liquid water fraction, volume of liquid accumulated, volume of void in CCL, porosity of CCL, thickness of CCL and area of CCL, respectively.

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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.

3.2.1.2 Phase (ii)

In phase (ii), the heat transfer for Domains 1 and 2 are expressed by Eq. (3:11) and (3:12), 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. (3:13) represents the rate of liquid water fraction reduction due to the boiling phase change in the CCL and CGDL.

$$(V \rho C_p)_1 \frac{\partial T_1}{\partial t} = \dot{Q}_{in} - h_s^{eff} (T_1 - T_2) \quad (3:11)$$

$$(V \rho C_p)_2 \frac{\partial T_2}{\partial t} = \dot{E}_{gen} + h_s^{eff} (T_1 - T_2) - \varepsilon_{CCL} V_{CCL} L_{lg} \rho_w \frac{\partial S_{liq}^{H_2O}}{\partial t} \quad (3:12)$$

$$\frac{\partial S_{liq}^{H_2O}}{\partial t} = \frac{v_{liq} \dot{n}_{acc}^{H_2O}}{\varepsilon_{CCL} \delta_{CCL} A_{CCL}} - \frac{v_{liq}}{\varepsilon_{CCL} \delta_{CCL} A_{CCL} h_{lg}} (\dot{E}_{gen} + h_s^{eff} (T_1 - T_2)) \quad (3:13)$$

where V , ρ , C_p , T , t , $\dot{Q}_{in}$, $\dot{E}_{gen}$, v_{liq} and L_{lg} are the volume, density, specific heat capacity, temperature, time, heat input rate, effective thermal conductance, exothermic heat generation rate, specific volume of liquid water and latent heat of vaporization, respectively.

Once the temperature reaches the boiling temperature, the liquid water production rate in the porous layers becomes zero because further H_2O produced is in vapour state.

3.2.1.3 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_2O is assumed to be in vapour phase. The heat balance equations are shown in Eq. (3:14) and (3:15).

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$$\left(V\rho C_p\right)_1 \frac{\partial T_1}{\partial t} = \dot{Q}_{in} - h_s^{eff} (T_1 - T_2) \quad (3:14)$$

$$\left(V\rho C_p\right)_2 \frac{\partial T_2}{\partial t} = \dot{E}_{gen} + h_s^{eff} (T_1 - T_2) \quad (3:15)$$

where V , ρ , C_p , T , t , $\dot{Q}_{in}$, h_s^{eff} and $\dot{E}_{gen}$ are the volume, density, specific heat capacity, temperature, time, heat input rate, effective thermal conductance and exothermic heat generation rate, respectively.

3.2.2 Chemical species diffusion

The diffusion of oxygen within the porous layers of the cathode is governed by the general equation shown in Eq. (3:16).

$$\varepsilon_{CCL/CGDL} \frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left(D_{O_2, eff, CCL/CGDL} \frac{\partial c}{\partial x} \right) + S_{O_2} \quad (3:16)$$

Where c , $D_{O_2, eff, CCL/CGDL}$, S_{O_2} and ε are the concentration, effective oxygen diffusion coefficient, the oxygen source term and porosity, respectively. "x" refers to the dimensional notation in the direction of the thickness of the CCCL and GDL.

The approximation as shown in Eq. (3:17) is important for the estimation of the transient period of hydrogen or oxygen diffusion through the porous layers. A closer 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.

$$\tau_{diffusion} = \frac{\delta^2_{CCL/CGDL}}{D_{eff}} \quad (3:17)$$

where $\tau_{diffusion}$, δ and D_{eff} are the diffusion time, thickness of layer and effective diffusion coefficient, respectively.

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This implies that the time taken during transience is very short and thus, Eq. (3:16) can be reduced to Eq. (3:18).

$$\frac{\partial c}{\partial x} \left(D_{O_2} \frac{\partial c_{O_2}}{\partial x} \right) + S_{O_2} = 0 \quad (3:18)$$

where c_{O_2} , D_{O_2} , S_{O_2} are the concentration, effective oxygen diffusion coefficient and the oxygen source term, respectively. "x" refers to the dimensional notation in the direction of the thickness of the CCCL and GDL.

and the source term for the consumption of oxygen is shown in Eq. (3:19).

$$S_{O_2} = -\frac{j}{4F} = -\frac{I}{4F\delta_{CCL}} \quad (3:19)$$

where j , I , F and δ_{CCL} are the volumetric current density, current, Faradays constant and thickness of CCL, respectively.

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 is related to the increase in temperature, which corresponds to a higher diffusion coefficient. The second mechanism is related to the effect of the liquid saturation of the CCL or CGDL that hinders the diffusion of oxygen.

Since the liquid saturation is expected to be different for the three phases, the diffusion of oxygen in the porous layers are assumed to be in the form as shown in Eq.(3:20). When the porous media is saturated with liquid water, the diffusion of oxygen is hindered because the magnitude of diffusion coefficient of oxygen in liquid water is lower by a factor of 10^{-4} , than that in any gas [163]. Therefore, with a given amount of liquid saturation, the diffusion of oxygen is more dominant in the open pores of the porous media. If the porous media is fully

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saturated, then the diffusion of oxygen fully occurs within the liquid water. The following description highlights the mechanisms of oxygen diffusion in the three phases.

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 build-up within the CCL and CGDL. As shown in Eq. (3:20), the diffusion coefficient of oxygen is assumed to behave accordingly [164].

$$D_{O_2,eff,CCL/CGDL} = \varepsilon_{CCL/CGDL}^{1.5} \cdot \begin{cases} \frac{1}{\rho_{eff}} \left(D_{O_2} \rho_{O_2} (1 - s_{liq}^{H_2O}) + \rho_{liq} D_{O_2,liq} s_{liq}^{H_2O} \right), & \text{phase(i) and phase (ii)} \\ D_{O_2,vapor}, & \text{phase(iii)} \end{cases} \quad (3:20)$$

where $s_{liq}^{H_2O}$, $D_{O_2,vapor}$, $D_{O_2,liq}$, ρ_{O_2} , ρ_{liq} , ρ_{eff} and ε are the liquid water fraction, diffusion coefficient of oxygen in vapor, diffusion coefficient of oxygen in liquid, density of oxygen, density of liquid water and effective density of mixture and porosity, respectively.

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. (3:20). 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.

The Bruggeman correlation is considered as one of the several ways of expressing the effective diffusion coefficient within the CL and CGDL [165-167]. The main use of the Bruggeman correlation is to account for the inaccuracy in using the bulk diffusion coefficient

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of the species when porous media flow is concerned. Although, these correlations have variances in accuracy, the difference in accuracy is considered to be of secondary priority for the development of the model, since the main objective of the model is to capture the behaviour trends with respect to the different phases explained in Fig. 3-1. However, it should be noted that the inaccuracy of the effective diffusion coefficient can affect the oxygen mole fraction and the Damköhler number, Da , as expressed in Eq.(3:33), which can affect cell potential. Nevertheless, the fundamental behaviour trends can be formulated and analysed through this model.

3.2.3 Electrochemistry

The cell voltage can be expressed by Eq. (3:21). The transient behaviour of the voltage response is neglected since the extracted current density is constant. In addition, the anode over potential due to HOR is neglected due to its relatively lower effect on the cell voltage [168].

$$V_{cell} = E_o - |\eta_c| - R_{\Omega} I \quad (3:21)$$

where E_o , V_{cell} , η_c , R_{Ω} and I are the reference potential, cell potential, cathode overpotential, ohmic resistance and current, respectively.

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 [169], hence the total ohmic resistance can be expressed as Eq. (3:22)

$$R_{\Omega} = \frac{\delta_{mem}}{\kappa_{mem}} + \frac{\delta_{a,ACL}}{2\kappa_{a,ACL}\epsilon_{ACL}^{1.5}} + \frac{\delta_{c,CCL}}{2\kappa_{c,CCL}\epsilon_{CCL}^{1.5}} \quad (3:22)$$

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Where κ_{mem} , $\kappa_{a,ACL}$, $\kappa_{c,CCL}$, ε and δ are the membrane protonic conductivity, anode electronic conductivity and cathode electronic conductivity, porosity and thickness, respectively.

The reference potential shown in Eq. (3:23) 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 [170].

$$E_0 = \begin{cases} 1.482 - 8.45 \times 10^{-4} T + 4.31 \times 10^{-5} T \ln \left[p_{H_2} p_{O_2}^{0.5} \right], & T < T_{Boiling} \\ 1.18 + \frac{-18.449 - 0.01283T}{F} (T - 298.15) + \frac{RT}{nF} \ln \left[\frac{p_{H_2} p_{O_2}^{0.5}}{p_{H_2O}} \right], & T_{Boiling} \leq T \leq T_{Desired} \end{cases} \quad (3:23)$$

where R , T , F , n , p_{O_2} , p_{H_2} and p_{H_2O} are the universal gas constant, temperature, Faradays constant, number of electrons transferred and partial pressures of oxygen, hydrogen and water respectively.

The cathode over potential can be obtained by relating the oxygen concentration across the cathode to the Butler-Volmer relation shown in Eq. (3:24). It is assumed that oxygen reduction reaction occurs uniformly in the CCL [171, 172].

$$j_c = \frac{I}{\delta_c} = a i_{0,c}^{ref} (1 - s_{liq}^{H_2O}) \left(\frac{c_{O_2}}{c_{O_2}^{ref}} \right) \exp \left(- \frac{\alpha_c F \eta_c}{RT} \right) \quad (3:24)$$

where $s_{liq}^{H_2O}$, $i_{0,c}^{ref}$, a , c_{O_2} , $c_{O_2}^{ref}$, α_c , η_c and δ_c are the liquid water fraction, reference exchange current density, ratio of reaction surface to catalyst layer volume, oxygen concentration, reference oxygen molar concentration, anode transfer coefficient, cathode overpotential and cathode thickness, respectively.

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All other physical, thermal, geometrical, diffusive and electrochemical properties are shown in Table A3:1 (Appendix).

The assumptions of the model are summarized below.

- A lumped thermal model is assumed for heat transfer, for the different domains, even though, a temperature difference of up to 5 °C can be expected in a typical scenario. The justification of this assumption is as follows. The main emphasis of the thermal model is to compare the energy required for the different heating strategies considered, comparing the temperature difference of HT-PEMFCs from room temperature to a desired temperature of 180 °C. As compared to this temperature range, and the energy consumption that is expected, the temperature difference of up to 5 °C within the fuel cell, is considered to be relatively low and thus neglected in the model. Furthermore, another reason for this assumption is simplicity. Since, the solved model uses a purely analytical approach, an ideal system where the temperature is uniform is assumed to capture the fundamental phenomena. Some of the possible effects of assuming uniform temperature throughout the fuel cell, may relate to variations in energy consumption calculations, where the average temperature of the fuel cell is expected to be lower realistically. Furthermore, the different phases as described in Fig. 3-1, might be different in localised regions within the fuel cell. Nevertheless, the fundamental behaviour trends can be formulated and analysed through this idealistic model.
- 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.

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- Once the temperature reaches the boiling temperature, the liquid water production rate in the porous layers is assumed to be zero because further H_2O produced is in vapour state.
- 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.
- An important assumption undertaken 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.
- The electronic resistances are relatively small as compared to the overall resistances, they are neglected in this model [169].
- The OCV shown in Eq. (3:23) 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.
- For simplicity, the effect of water fraction variation on the thermal mass of CCL is assumed to be negligible.
- The effect of water uptake and electro-osmotic drag in the membrane are assumed to achieve a net zero water transfer for simplicity. Electro-osmotic drag is a phenomenon, where liquid water can move from the anode to the cathode due to a potential difference across the membrane. This is expected to transfer liquid water, resulting in the accumulation of water in the CCL and CGDL at a faster rate. Even

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though electro-osmotic drag is neglected in this model, the effects will be discussed in results section.

- The model neglects the contribution of Joule heating (contributed by the electronic and protonic resistances) and anode source due to their relatively low magnitude [173].
- 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.
- All porous media are considered to have uniform pore size distribution. The Bruggeman correlation is assumed to express the effective diffusion coefficient within the CL and CGDL [167].

A list of initial conditions for the model is as follows:

- Lumped Thermal analysis - Initial temperature of the fuel cell is set at room temperature; $T(t=0) = T_{\infty}$.
- Liquid water transport - Initially, the water fraction in the catalyst layer and GDL are at zero because the fuel cell operation starts at $t=0$; $s_{H_2O}^{liq, CL \text{ and } GDL}(t=0) = 0$.
- Oxygen content - The oxygen mole fraction within the catalyst layer at $t=0$, is 1, as the fuel cell has not operated yet; $x_{O_2}(t=0) = 1$.

3.3 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 3.4.2. The next study involves parametric studies pertaining to the warm-up process of the single cell, where

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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. The effects of the system parameters on temperature profile and water fraction in the porous media and overall voltage profile of HT-PEMFC, are analyzed. 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.

3.4. Results and discussion

3.4.1 General description, observations and simplifications of the solutions

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

$$T_{CCL} = A + Bt + Ce^{-Dt} \quad (3:25)$$

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 CCL. Thus, neglecting the exponential

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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. (3:26) and (3:27). This simplification also suggests that the temperature difference at any point of time between the CCL and Domain 1 is negligible which is also observed from the original solution. In addition, as shown in Eq. (3:29), the effect of the liquid water phase change, N , 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.

$$B_{phase(i),(iii)} = \frac{\dot{Q}_{in} + \dot{E}_{gen}}{(V\rho C_p)_1 + (V\rho C_p)_2} \quad (3:26)$$

$$B_{phase(ii)} = \frac{(1+M) \cdot (\dot{Q}_{in} + \dot{E}_{gen}) - N}{(1+M)(V\rho C_p)_1 + (V\rho C_p)_2} \quad (3:27)$$

where

$$M = \frac{\varepsilon_{CCL} L_{lg} \rho_w V_{CCL} v_{liq}}{h_{lg} \varepsilon_{CCL} \delta_{CCL} A_{CCL}} = \frac{\rho_w v_{liq}}{M_{H_2O}} = 1 \quad (3:28)$$

and

$$N = \frac{\varepsilon_{CCL} L_{lg} \rho_w V_{CCL} v_{liq}}{\varepsilon_{CCL} \delta_{CCL} A_{CCL}} \dot{n}_{acc} = h_{lg} \dot{n}_{acc} \quad (3:29)$$

The terms V , ρ , C_p , T , $\dot{Q}_{in}$ and $\dot{E}_{gen}$ are the volume, density, specific heat capacity, temperature, heat input rate and exothermic heat generation rate, respectively. Furthermore,

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v_{liq} , L_{lg} , h_{lg} and ε are the specific volume of liquid water, latent heat of vaporization, enthalpy change between liquid water and water vapor and porosity, respectively.

The average concentration drop of oxygen across the CGDL and CCL can be obtained from Eqs. (3:30) and (3:31), respectively. Comparing between the membrane/catalyst interface and the inlet, the average oxygen concentration in the CCL can be obtained as shown in Eq. (3:32).

$$\Delta c_{CGDL}^{O_2} = c_{x_{CGDL}}^{O_2} - c_{x_{CCL}}^{O_2} = \frac{I\delta_{CGDL}}{4FD_{O_2,eff,CGDL}} \quad (3:30)$$

$$\Delta c_{CCL}^{O_2} = \frac{2}{3} \frac{I\delta_{CCL}}{8FD_{O_2,eff,CCL}} \quad (3:31)$$

$$c_{CCL}^{O_2} = c_{x_{CGDL}}^{O_2} - \frac{I\delta_{CGDL}}{4FD_{O_2,eff,CGDL}} - \frac{2}{3} \frac{I\delta_{CCL}}{8FD_{O_2,eff,CCL}} \quad (3:32)$$

The Damköhler number, Da , is a dimensionless measure of the CCL and is given by the ratio of the reaction rate over the mass transport rate, as shown in Eq. (3:33).

$$Da = \frac{I\delta_{CCL}}{8FD_{O_2,eff,CCL}c_{CCL}^{O_2}} = \frac{\text{Reaction rate}}{\text{Mass transport rate}} \quad (3:33)$$

Where $D_{O_2,eff,CCL}$, I , F and δ_{CCL} are the effective diffusion coefficient of oxygen, current Faradays constant and thickness of CCL, respectively.

Finally, the cathode over potential is obtained from the following relationship [171].

$$\eta_c = -\frac{RT}{\alpha_c F} \ln \left(\frac{I}{ai_{0,c}^{ref} \delta_c (1 - s_{liq}^{H_2O})} \frac{c_{O_2}^{ref}}{c_{O_2}} \right) \quad (3:34)$$

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where $s_{liq}^{H_2O}$, $i_{0,c}^{ref}$, a , c_{O_2} , $c_{O_2}^{ref}$, α_c , η_c and δ_c are the liquid water fraction, reference exchange current density, ratio of reaction surface to catalyst layer volume, oxygen concentration, reference oxygen molar concentration, anode transfer coefficient, cathode overpotential and cathode thickness, respectively.

3.4.2 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. 3-2 (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.

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Fig. 3-2 Comparison of temperature vs. warm-up time between different heating strategies for single cell over a temperature range of 295 K (22 °C) to 353 K (180 °C) at 100W (bottom); Comparison of warm-up time and energy consumption vs. heat input rate between different heating strategies for a typical 1-kW stack over a temperature range of 22 °C to 180 °C (top)

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 [108]. 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. 3-2 (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

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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.

3.4.3 Parametric study

3.4.3.1 Effect of heat input rate

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

Fig. 3-3 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 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. (3:35) [108].

$$\dot{Q} = mC_p \frac{\partial T}{\partial t} \quad (3:35)$$

where C_p , T , m , t and $\dot{Q}$ are the specific heat capacity, temperature, mass, time and heat input rate, respectively.

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.

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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.

The effect of electro-osmotic drag which is assumed to be negligible in this model, is expected to increase the level of saturation at a faster rate in the CCL, where the water from the anode side is expected to travel to the cathode side. This can also result in the build-up of the liquid water in the CGDL at a faster time.

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.

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Fig. 3-3 Effect of heat input rate on the temperature and water fraction profiles of the CCL and CGDL with respect to time

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.

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

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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. 3-3. 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 shown in Fig. 3-4, 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.

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Fig. 3-4 Effect of heat input rate on the diffusion coefficient, mole fraction and Damköhler number with respect to time

The Damköhler number as shown in Eq. (3:33), refers to the ratio of the reaction rate over the mass transport rate, and 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

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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.

3.4.3.1.3 Effect of heat input rate on the cathode overpotential and cell voltage

The magnitude of the cathode overpotential is found to decrease with time because the cathode exchange current density increases with temperature as shown in [174]. This mechanism overshadows the direct dominance of temperature on cathode overpotential, which tends to increase the magnitude according to the Butler-Volmer relation. It can be seen that the cathode overpotential 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 overpotential 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 overpotential.

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Fig. 3-5 Effect of heat input rate on the cathode over potential and cell voltage with respect to time

Thus, it can be deduced that the rate of cathode overpotential decrease overshadows 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.

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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. 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.

3.4.3.2 Effect of current density

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

Fig. 3-6 shows the effect of current density on the CCL temperature profile and the water fraction profiles of the CCL and CGDL. The temperature gradients are observed to increase slightly with the increase in the current density from 1000, 2000 to 3000 A m⁻². This is due to the greater dominance of the heat input rate on the temperature gradient where in magnitude, calculated to be a lot more higher than the heat generation rate from 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 with the current density. This is obviously due the linear proportionality of current density with respect to the liquid water generated.

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Fig. 3-6 Effect of current density on the temperature and water fraction profiles of the CCL and CGDL with respect to time

Once the CCL reaches a 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.

The effect of electro-osmotic drag which is assumed to be negligible in this model, is expected to increase the level of saturation at a faster rate in the CCL as the current density is increased. This is due to the direct proportionality of the current density to the liquid water

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flow rate with respect to electro-osmotic drag . This also results in the build-up of the liquid water in the CGDL at a faster time as expected.

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 H_2O 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 the obtained solution.

3.4.3.2.2 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 oxygen diffusion coefficient increases in a similar fashion, as shown in Fig. 3-7, 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

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2000 A m⁻². This is due to the greater level of saturation attained in the CGDL before boiling starts.

Fig. 3-7 Effect of current density on the diffusion coefficient, mole fraction and Damköhler number with respect to time

The mole fraction on the other hand reduces drastically once the diffusion coefficient of oxygen starts reducing. There are two mechanisms that contribute to the reduction of the mole fraction in this study. The first mechanism is related 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

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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 overpotential overshadowing the OCV of the fuel cell.

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 overpotential. 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, which attributes to faster onset of boiling phase change.

3.4.3.2.3 Effect of current density on the cathode overpotential and cell voltage

As shown in Fig. 3-8, the cathode overpotential is found start from a lower magnitude as the current density is increased. This is due to logarithmic relationship between the overpotential and the current density which is in accordance to existing literature [171]. The expected linear decrease in the cathode overpotential with respect to time, can be attributed to the slightly higher temperature gradient observed as the current density is increased. However,

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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 overpotential 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 increases the magnitude of cathode overpotential value along a vertical asymptote just after 200 seconds.

Fig. 3-8 Effect of current density on the cathode over potential and cell voltage with respect to time

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As far as the profile is concerned, the cell voltage is observed to be strongly influenced by the cathode overpotential, 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 overpotential, 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 overpotential.

3.4.3.3 Effect of cathode pressure

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

Fig. 3-9 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 saturation pressure is the increase of the boiling point as depicted by the Antoine equation as expressed in Eq. (3:36) .

$$p_{sat} = 10^{8.1402 - \frac{1810.94}{244.485 + T}} \quad (3:36)$$

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 [173]. Even then, the difference in the accumulation rates for the three cathode pressures is found to be slight. Even though, the electro-osmotic drag is

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neglected in the model, it is expected that the pressure increase has little effect on the water transport due to electro-osmotic drag alone. However, back diffusion of water can occur due to the higher cathode pressure, resulting in the water travelling back to the anode from the cathode, which is neglected in the model. Furthermore, 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, 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.

Fig. 3-9 Effect of cathode pressure on the temperature and water fraction profiles of the CCL and CGDL with respect to time

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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 varies according to the Clausius-Clapeyron relation as shown in Eq. (3:37).

$$\ln\left(\frac{p_1}{p_2}\right) = \frac{H_{lg}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (3:37)$$

where p , ΔH_{vap} , R_u and T are the pressure, enthalpy of vaporization, universal gas constant and temperature, respectively and subscripts "1" and "2" refer to different states corresponding to their respective saturation temperatures and pressures.

3.4.3.3.2 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, which is shown in Fig. 3-10. 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

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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 takes 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.

Fig. 3-10 Effect of cathode pressure on the diffusion coefficient, mole fraction and Damköhler number with respect to time

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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.

3.4.3.3 Effect of cathode pressure on the cathode overpotential and cell voltage

As shown in Fig. 3-11, 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 [175]. 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 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 overpotential 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.

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For the pressures of 2 and 3 bars, the cathode overpotential 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 overpotential starts, and also due to the cathode pressure dependence of the OCV. For all pressures, the cell voltage gradually increases until the time when boiling occurs corresponding to the different pressures. The voltage then suddenly increases at the liquid vapour transition. From then onwards, the voltage gradually increases for the cathode pressure of 1 atm and 2 bars.

Fig. 3-11 Effect of cathode pressure on the cathode over potential and cell voltage with respect to time

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However, as further pressure is applied to 3 bars, voltage is observed to drop. This might be due to the behaviour of the cathode overpotential 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.

3.4.3.4 Effect of cathode stoichiometric flow ratio

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

Fig. 3-12 shows the effect of cathode stoichiometric flow ratio on the temperature profile and the liquid water fraction profiles of the CCL and CGDL. The results show that 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 [173]. 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.

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Fig. 3-12 Effect of cathode stoichiometric flow ratio on the temperature and water fraction profiles of the CCL and CGDL with respect to time

Even though the electro-osmotic drag is neglected in the model, the effect of electro-osmotic drag is expected to increase the rate of liquid water accumulation in the CCL and CGDL at a faster rate as the stoichiometric ratios is increased.

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.

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

As shown in Fig. 3-13, 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 increases 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 delayed 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 profile of the diffusion

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coefficient with respect to 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.

Fig. 3-13 Effect of cathode stoichiometric flow ratio on the diffusion coefficient, mole fraction and Damköhler number with respect to time

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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 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.

3.4.3.4.3 Effect of cathode stoichiometric ratio on the cathode overpotential and cell voltage

As shown in Fig. 3-14, the cathode overpotential 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.

The cell voltage is observed to show slight variation, albeit 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 overpotential. 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 to be in the same manner. This is

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because the OCV and the cathode overpotential 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.

Fig. 3-14 Effect of cathode stoichiometric flow ratio on the cathode over potential and cell voltage with respect to time

3.5 Summary

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 and the electro-kinetics during the warm-up period of a HT-PEMFC were better understood through a parametric study.

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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.

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 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-

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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 focussed towards realizing these benefits through membrane research and the comprehension of the physical effects of boiling on the fuel cell components.

In the next chapter, the investigation of another warm-up strategy that involves the current extraction from a temperature above 100 °C in the presence of CO, will be covered.

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Chapter 4. An analysis of transient carbon monoxide poisoning kinetics during warm-up process of a high-temperature proton exchange membrane fuel cell

4.1 Introduction

In this chapter, the start-up of HT-PEMFC in the presence of CO is investigated with the use of numerical modelling and further extended to sensitivity analysis of typical start-up parameters.

Over the decade, several attempts have been reported that focus on the modelling of start-up, all of which were beneficial in fundamental understanding of the warm-up process, aimed towards minimizing time and energy consumption. These models presented several methods for starting-up the HT-PEMFC. The first method requires the fuel cell to be externally heated up to a temperature above the boiling point of water i.e. around 120°C (at ambient pressure), after which current is extracted from the fuel cell, while still maintaining the applied external heat [176]. Another method involves the same methodology but the only difference is that, the current is extracted at a temperature below the boiling point of water, i.e. from 25 °C [177]. Yet another method disregards the use of current extraction considering the fuel cell as a lump thermal model [178, 179]. Although these models are beneficial in comprehending the basics of start-up process, they could be improved further to incorporate other relevant issues such as the effect of CO on the start-up period of the HT-PEMFC.

The existence of trace amount of CO appears in almost all thermochemical hydrocarbon fuel reforming methods such as steam reforming, partial oxidation, or auto-thermal reforming, making it important to consider the CO electrokinetics in all the theoretical models [89]. The presence of CO in the hydrogen feed has the ability to poison the Pt catalysts at the anode of

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the PEMFC, reducing the active sites available for electrochemical reactions and thus, reducing the CO content becomes necessary [20, 87, 88]. However, the manufacturing of high purity hydrogen gas is expensive, which increases the operating cost of implementing the fuel cell technology. In the context of HT-PEMFCs, the elevated temperature operation allows the use of hydrogen contaminated with high levels of CO [6]. Modelling is a powerful tool in understanding the complex transport and electrochemical phenomena that is exclusive to CO poisoning in fuel cells [93]. Early works focussed on LT-PEMFCs [16, 17, 91, 92]. As far as HT-PEMFCs are concerned, there is only a handful of publications reporting CO poisoning models. Bergmann *et al.* developed a dynamic two-dimensional non-isothermal model that was experimentally validated with a HT-PEMFC and was useful in predicting the dynamic electrochemical performance in the presence of CO [95]. Jiao *et al.* developed a three-dimensional non-isothermal CO poisoning model, which was beneficial in identifying the optimized operational parameters that would generate good performance in the presence of CO [96]. In addition, one of the recent works by Jiao *et al.* extends their numerical model to simulate the effects of varying flow channel dimensions on the CO poisoning effect [99]. Furthermore, Oh *et al.* refined the CO model of Springer *et al.* in order to predict the behaviour of a phosphoric acid based membrane HT-PEMFC [100]. These models enabled better understanding of the effects of CO on HT-PEMFC under the steady-state operation from a modelling point of view. However, it is unknown how CO can affect the electro-kinetics during the transient start-up period, which has not been reported in the literature to-date. Since temperature is the key parameter that affects the CO tolerance and the nature of the transient start-up process is such that temperature increases with time during the warm-up period, an investigation of this phenomenon is highly interesting.

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The effort is divided into two parts. In the first part, a transient isothermal three-dimensional single-channel mathematical model is developed to study the anode electro-kinetics, during a start-up process of a HT-PEMFC, when the HT-PEMFC is fed with CO contaminated hydrogen. The key focus of the study is to assess the effects of start-up parameters such as temperature increase rate, initial start-up temperature, CO concentration and extracted current density on the hydrogen and CO coverage fraction in the anode, leading to the prediction of the anode overpotential and the cell potential during the unsteady-state period. In the second part, the model is intended to study the critical importance of the above mentioned system parameters. These are fundamental steps to better comprehend the heating strategies for HT-PEMFCs, especially when CO contaminated hydrogen (reformed fuels) is used as the fuel.

4.1.1 Part 1 - Physical model and parametric study

4.1.1.1 Model development

A transient three-dimensional isothermal model with a single channel is developed to simulate the start-up process of a HT-PEMFC with the domain dimensions shown in Fig. 4-1. The numerical model consists of the following, as shown in Eqs. (4:1) to (4:4).

Conservation of mass

$$\nabla \cdot \vec{u} = \frac{S_m}{\rho} \quad (4:1)$$

Conservation of momentum (free and porous media)

$$\rho \vec{u} \cdot \nabla \vec{u} = \nabla \left\{ -pI + \mu \left(\nabla \vec{u} + \left(\nabla \vec{u} \right)^T \right) \right\} \quad (4:2)$$

$$\frac{\mu}{\kappa} \vec{u} = \nabla \left\{ -pI + \frac{1}{\varepsilon} \mu \left(\nabla \vec{u} + \left(\nabla \vec{u} \right)^T \right) \right\} \quad (4:3)$$

The notations $\vec{u}$, S_m , ρ , μ , ε and κ are the velocity, source term, density, dynamic viscosity, porosity and hydraulic permeability, respectively.

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The boundary conditions for the mass and momentum conservations which is the average inflow velocity ($U_{inlet} = 0.2 \text{ m s}^{-1}$) positioned at the inlet of the flow channel. Ambient pressure is considered at the exit of the channel.

Conservation of species (hydrogen and CO)

$$\frac{\partial c}{\partial t} + \nabla \cdot (\vec{u} c_i) = \nabla \cdot (D^{eff} \nabla c_i) + S_i \quad (4:4)$$

where $\vec{u}$, c_i , D^{eff} , t and S_i are the velocity, concentration, effective diffusion coefficient, time and the source term, respectively.

The initial volume fractions of hydrogen and CO in the channel are set the same as the inlet conditions as listed in Section 4.1.2.2.

Fig. 4-1 Description of three-dimensional model

The reactions within the anode catalyst layer considered for this study are shown in Eqs. (4:5) to (4:7). These include the adsorption and desorption of hydrogen and adsorption of CO and the electro-oxidation of hydrogen. However, the electro oxidation of CO is neglected because of the absence of water vapour in the fuel supplied to the anode. Based on these reactions,

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Eqs. (4:8) and (4:9) represent the transient hydrogen and CO coverage fraction fractions. Correspondingly, Eqs. (4:11) and (4:12) represent the temperature dependent reactions constants while Eqs. (4:13) refers to the electro-oxidation rate of hydrogen [96].

where "M" refers to the platinum catalyst reaction site.

$$\rho_k \frac{\partial \theta_H}{\partial t} = k_H^{ads} c_{H_2} (1 - \theta_H - \theta_{CO}) - b_H^{ads} k_H^{ads} \theta_H - q_{H-ex} \quad (4:8)$$

$$\rho_k \frac{\partial \theta_{CO}}{\partial t} = k_{CO}^{ads} c_{CO} (1 - \theta_H - \theta_{CO}) - b_{CO}^{ads} k_{CO}^{ads} \theta_{CO} \quad (4:9)$$

The notations ρ_k , k_H^{ads} , k_{CO}^{ads} , θ_H , θ_{CO} , b_H^{ads} , b_{CO}^{ads} and q_{H-ex} refer to the molar density, hydrogen and CO rate constants, hydrogen and CO surface coverage fractions, hydrogen and CO backward forward ratios and the hydrogen electro-oxidation component, respectively.

where

$$\theta_M = 1 - \theta_H - \theta_{CO} \quad (4:10)$$

$$k_i = k_i^0 e^{\left(\frac{E_i^k}{RT} \right)} \quad (4:11)$$

$$b_i = b_i^0 e^{\left(\frac{E_i^b}{RT} \right)} \quad (4:12)$$

$$q_{H-ex} = \frac{i}{\delta_{cl} F} \quad (4:13)$$

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The terms E_i^k , E_i^b , R , T , F , i and δ_{cl} refer to the activation energies of the rate constants and the forward backward ratios, universal gas constant, temperature, Faradays constant, current density and thickness of catalyst layer, respectively.

The initial values of the hydrogen and CO coverage fractions pertaining to Eqs (4:8) and (4:9) are set at zero. The anode and cathode overpotential is calculated by considering Eqs. (4:14) and (4:15) [103, 180], respectively. Eqn. (4:16) represents the total losses due to ohmic resistance, while Eq. (4:17) represents the cell potential. Eqs. (4:18) and (4:19) show the temperature dependant reference potential and the total ohmic resistance, respectively [169, 181].

$$\eta_a = \frac{RT}{\alpha F} \sinh^{-1} \left(\frac{q_{H-ox}}{2k_{eh}\theta_h} \right) \quad (4:14)$$

$$\eta_c = \frac{RT}{\alpha F} \ln \left(\frac{i}{i_{0,c}^{ref}} \right) \quad (4:15)$$

$$\eta_\Omega = iR_\Omega \quad (4:16)$$

$$V_{cell} = E_o - \eta_a - \eta_c - \eta_\Omega \quad (4:17)$$

Where V_{cell} , α , η_a , η_c , η_Ω , R_Ω , $i_{0,c}^{ref}$, i are cell potential, transfer coefficient, anode over potential, cathode overpotential, ohmic loss, ohmic resistance, exchange current density and current density, respectively.

Furthermore,

$$E_o = 1.23 - 9 \times 10^{-4} (T - 298.15) \quad (4:18)$$

$$R_\Omega = \frac{\delta_{mem}}{\kappa_{mem}} + \frac{\delta_{a,CL}}{2\kappa_{a,CL}\varepsilon^{1.5}} + \frac{\delta_{c,CL}}{2\kappa_{c,CL}\varepsilon^{1.5}} \quad (4:19)$$

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where E_0 , κ_{mem} , $\kappa_{a,ACL}$, $\kappa_{c,CCL}$, ε and δ are reference potential, the membrane protonic conductivity, anode electronic conductivity and cathode electronic conductivity, porosity and thickness, respectively.

In addition, Eq. (4:20) is expressed to consider the effects of linear temperature increase with respect to time, which will be applied during a typical start-up process of a HT-PEMFC.

$$T = T_0 + gt \quad (4:20)$$

The initial start-up temperature, T_0 , refers to the temperature of the fuel cell, to which has been heated externally before the current is being extracted. In addition, g , refers to the temperature increase rate of heating which accounts for the external heating and exothermic heat generation from operation. Table A4:1 (Appendix) shows the geometrical, physical and electrochemical properties and correlations used in this study.

The general assumptions of the numerical model are as follows:

1. The gasses at the anode and cathode are incompressible and are assumed to be laminar;
2. The crossover of gasses through the membrane not considered due to negligible electro-osmotic drag in HT-PEMFCs;
3. The presence of water vapour in fuel is neglected;
4. Contact resistances between components is neglected;
5. The fluid velocity is considered as steady state since the transient period of velocity is small as compared to the warm-up process.
6. The temperature increase is assumed to be a linear function with respect to time.

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Table 4.1 summarizes the initial and boundary conditions of the model.

Table 4.1 Initial and boundary conditions

Physics	Initial conditions	Boundary conditions
Conservation of species	$c_{CO}(x, y, z, 0) = c_{CO,inlet}$	$c_{CO}(inlet, t) = c_{CO,inlet}$ Free boundary at the outlet
Adsorption/desorption kinetics	$\theta_{CO}(x, y, z, 0) = 0$ $\theta_H(x, y, z, 0) = 1$	-
Conservation of mass and momentum	-	$U_{inlet} = 0.2 \text{ ms}^{-1}$ $p_{outlet} = p_{atm}$

The HT-PEMFC anode model was solved using finite element-based commercial software, COMSOL Multiphysics. The convergence criteria for mass, momentum, species, adsorption/desorption kinetics calculations residuals were set to 10^{-8} . The grid size independence test is shown in Fig. 4-2. The solution sequence is shown Fig. 4-3.

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Fig. 4-2 Grid size independence test

Fig. 4-3 Solution sequence of numerical simulation

4.1.1.2 Experimental setup

A single cell HT-PEMFC was set up with an active area of 45 cm^2 utilizing a commercial PBI based MEA as purchased from BASF commonly known as CELTEC P1000, shown in Fig. 4-4. The anode and cathode catalysts are made of platinum supported by carbon while

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the gas diffusion layer is manufactured from ETEK. The external heating source were in the form of silicon heaters, applied over the flat areas on both exposed sides of the steel end plates. The whole set up was placed in an oven set to maintain the temperature of the fuel cell at 120 °C before the experiments were run.

The temperatures in the fuel cell were measured using was measured using K-type thermocouples (sheathed and electrically insulated), with a diameter of 150 microns. The tip of the thermocouples were placed on the exposed areas of the GDL and were kept in place by high temperature tapes. A data logger, was used to register the temperature of the fuel cell and the interval between temperature measurements was set at 5 seconds. An electrochemical analyzer was used to measure the cell potential of the fuel cell and the interval between measurements was set at 0.5 seconds. The anode and cathode were fed with hydrogen and oxygen, respectively.

Fig. 4-4 Schematic diagram and experimental setup of the HT-PEM single cell

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4.1.1.3 Design of study

The heating strategy considered for the start-up of the HT-PEMFC is based on the commercially adopted method, i.e. the fuel cell is heated by an external means up to a temperature of above 100°C, after which current is extracted from the fuel cell, while the external heat is still maintained. The final temperature to which the fuel cell is heated is 180 °C.

Then, a fundamental analysis is done with the objective of determining the distribution of variables such as hydrogen and CO coverage fractions and the anode overpotential and the cell potential under baseline conditions (i.e. temperature increase rate of 0.3 K s⁻¹, initial start-up temperature of 120°C, CO volume fraction of 5000 ppm (0.5 %), and extracted current density of 1000 A m⁻²).

Next, a parametric study is carried out to assess the effects of key operational parameters, on the hydrogen and CO coverage fraction and the anode overpotential and the cell potential with respect to time. The operational parameters are as follows:

- **Temperature increase rates: 0.1, 0.3, 0.5 K s⁻¹**
- **Initial start-up temperatures: 110, 120 and 130 °C**
- **CO volume fractions: no CO, 1000 ppm (0.1 %), 5000 ppm (0.5 %) and 10000 (1 %)**
- **Extracted current densities: 1000, 1500 and 2000 A m⁻²**

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4.1.1.4 Results and discussion

4.1.1.4.1 Comparison between experimental data and simulation results

Fig. 4-5 Comparison between experimental data and simulation results

Fig. 4-5 (top) shows the cell potential curves generated by the numerical model and the corresponding experimental data ($i = 1000 \text{ A m}^{-2}$, $v_{\text{CO}} = 30,000 \text{ ppm}$ or 3 % vol.). Fig. 4-5 (bottom) shows the temperature profile from the experimental data. The temperature profile was then used as input for the simulation model to predict the cell potential. The results show that the model is able to predict reasonably well throughout the start-up process. Specifically, the model slightly underpredicts the initial cell potential ($t=0$), with a percentage deviation of 4.45 %. Next, the lowest peak is also found to be under predicted by the model by a percentage deviation of 4.36 %. However, the cell potential at 180 °C is found to be over-predicted by the model, by a percentage deviation of 4.85 %. Furthermore, the rate of change

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of the cell potential predicted by the model, is observed to be greater as compared to the experimental data. This might be due the following reasons.

In actual start-up, non-uniformity of temperature can be expected with respect to time. This means that at any point in time, the measured temperature at the sensor can differ as compared to the other regions of the fuel cell, resulting in a different localised cell performance. This in turn might have caused a lower cell potential increase rate as compared to the model since the model does not account for spatial non-uniformity of temperature.

In summary, model is deduced to be reasonably accurate since the difference of cell potential at any point in time is calculated to be less than 5 %.

4.1.1.4.2 Fundamental analysis

Fig. 4-6 shows the change of hydrogen coverage fraction, CO coverage fraction, anode overpotential and cell potential with respect to time for baseline conditions. The heating profile with an initial temperature of 120°C, while fuel is fed and current is drawn at 1000 A m⁻² during the warm-up period is also shown. Generally, it can be seen that hydrogen and CO coverage fractions start at expected values close to 0.95 and 0, respectively. As soon as contaminated hydrogen (5000 ppm CO) is fed into the fuel cell, CO coverage fraction increases while the hydrogen coverage fraction decreases with time as the temperature increases, until they reach a point in time when attaining their respective peaks (hydrogen coverage fraction minimum peak – 0.34, CO coverage fraction maximum peak – 0.62) at around 40 seconds, which is corresponding to ~131 °C. This is the point when the temperature is high enough to inhibit further adsorption of CO onto the platinum sites and the CO desorbs as the temperature increases further. At the same time, the hydrogen coverage

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fraction restores since the free sites available from CO desorption allows the adsorption of hydrogen.

Fig. 4-6 Variation of hydrogen surface coverage fraction, CO surface coverage fraction, anode overpotential, cell potential and temperature over time for base case conditions

After reaching the maximum and minimum peak points of both CO and hydrogen coverage fraction, respectively, the CO coverage fraction decreases to zero, while the hydrogen coverage fraction increases until reaching a second peak (hydrogen coverage fraction

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maximum peak – 0.7185) at around 115 seconds. This peak is a result of excessive temperature ($\sim 155^\circ\text{C}$) that reduces the tendency of hydrogen adsorption onto the platinum sites. As temperature increases further, the hydrogen coverage fraction drops and finally reaches a plateau at 180°C . In addition, it is also observed that the hydrogen coverage fraction and the CO coverage fraction, at the catalyst layer below the inlet, is generally higher than near the outlet, at any point in time. At $t=0$ and 250 seconds, there is negligible difference between the inlet and outlet. The greatest difference between the inlet and the outlet occurs at $t=40$ seconds (hydrogen coverage fraction, inlet – 0.3702, outlet – 0.344; CO coverage fraction, inlet – 0.6163, outlet – 0.05915) where the hydrogen coverage fraction and the CO coverage fraction reaches its minimum and maximum values, respectively.

The anode overpotential shows very slight increase (by 1.2 %, as compared to the initial anode overpotential) before the hydrogen coverage fraction and CO coverage fraction reach their minimum and maximum peak values, respectively at a temperature of $\sim 131^\circ\text{C}$. However, the reduction in hydrogen coverage fraction after the second peak is found to have negligible effect on anode overpotential because the temperature is high enough to increase the rate constant of hydrogen electro-oxidation, which compensates for the decrease in hydrogen coverage fraction. After this point, the anode overpotential decreases gradually and reaches a low value (0.0034 V) until the external heating ends at 180°C . Consequently, the cell potential is found to remain increase very slightly (by 1.3 %, as compared to the initial cell potential) within the first 40 seconds. After the CO and hydrogen coverage fraction reach their maximum and minimum peaks, respectively, the cell potential starts to increase further and reaches 0.967 V at the end of the heating process. As the temperature increases, the reference potential and the cathode over potential reduces gradually. However, these factors do not significantly dominate the profile of the cell potential because the cell potential is

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strongly affected by the anode overpotential, which decreases with time as shown in Fig. 4-6. In addition, it is also observed that the anode overpotential and cell potential, at the catalyst layer below the inlet, is generally higher than near the outlet, at any point in time. At $t=0$ and 250 seconds, there is negligible difference between the inlet and outlet. The greatest difference between the inlet and the outlet occurs at $t = 40$ seconds (anode overpotential, inlet – 0.1128 V, outlet – 0.1102 V; cell potential, inlet – 0.8393 V, outlet – 0.8367 V), when the anode overpotential and cell potential reaches its minimum and maximum values respectively.

4.1.1.4.3 Parametric study

4.1.1.4.2.1 Effect of temperature increase rate

Fig. 4-7 shows the effect of temperature increase rate on CO coverage fraction, hydrogen coverage fraction, anode overpotential and cell potential. Firstly, the maximum CO coverage fraction peak value is found to reduce as temperature increase rate is increased. This can be expected because a higher heating rate would shorten the residence time available for CO to be adsorbed onto the platinum sites. Hence, the peak is reached at an earlier time with increasing temperature increase rate. In addition, the peaks of CO coverage fractions are found to reduce, in comparison to a case where the temperature increase rate is set at 0.1 K s^{-1} , showing percentage reductions of $\sim 28 \%$ (0.3 K s^{-1}) and $\sim 33 \%$ (0.5 K s^{-1}). In addition, the time that CO coverage fraction reduces to zero, occurs at a faster time as the temperature increase rate is increased (0.1 K s^{-1} – 70 seconds, 0.3 K s^{-1} - 40 seconds and 0.5 K s^{-1} – 25 seconds). This is expected since the maximum peak of CO coverage fraction is lower at higher temperature increase rate, requiring lesser time to reduce it to zero.

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Similarly, the hydrogen coverage fraction follows the same behaviour as that of CO coverage fraction, reaching the minimum peak at the same time when the CO coverage fraction reaches the maximum peak. This is the case for the different temperature increase rates. As the temperature increase rate is increased, the minimum peak value of hydrogen coverage fraction decreases. After this peak point, the hydrogen coverage fraction recovers back to a higher value reaching a second peak. The magnitude of the second peak is the same for different temperature increase rates, however occurring at much earlier time (0.1 K s^{-1} – 350 seconds, 0.3 K s^{-1} - 115 seconds and 0.5 K s^{-1} – 70 seconds) when the temperature increase rate is increased and finally reducing at a faster rate. They reach similar final values (0.52) at the end of the warm-up process, which ends at 180°C .

The anode overpotential initially starts at the same value (0.1194 V) for different temperature increase rates. However, several differences are observed. A maximum peak (0.1623 V, percentage increase of ~36 % compared to initial value) is observed for the temperature increase rate of 0.1 K s^{-1} . For the temperature increase rate of 0.3 K s^{-1} , the anode overpotential shows a plateau (0.1194 V) before which it decreases gradually. While for the case of 0.5 K s^{-1} , the reduction of the anode overpotential is observed right from the start of the warm-up process. For all cases, the anode overpotential reaches zero at similar rates, however at later points in time (when the temperature reaches 180°C).

The cell potential starts off at similar values (0.825 V) for all the three cases and are strongly affected by their respective anode overpotential profiles. Specifically, for the case of 0.1 K s^{-1} , a minimum peak is observed (0.7847 V) which is due to the maximum peak of the anode overpotential reached. For the case of 0.3 K s^{-1} , the cell potential do not reach any minimum peak, while for the case of and 0.5 K s^{-1} , the cell potential gradually increases. For all cases, the cell potentials reach similar values (0.9668 V) since the final temperature reached by the

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Fig. 4-7 Effect of temperature increase rate on the CO surface coverage fraction, hydrogen surface coverage fraction, anode overpotential and cell potential

fuel cell is 180°C for all three cases of temperature increase rates. Most importantly, it should be noted that reduction in the temperature increase rate to a particular level can significantly increase the anode overpotential, and thus, seriously cause a drop in cell potential, resulting in the potential shutdown of the fuel cell.

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4.1.1.4.2.2 Effect of initial start-up temperature

Fig. 4-8 shows the effect of initial start-up temperature on CO coverage fraction, hydrogen coverage fraction, anode overpotential and cell potential. Firstly, the peak CO coverage fraction is highest (0.757) when the initial start-up temperature is set at 110 °C and lowest (0.451), when the initial start-up temperature is set at 130 °C. Specifically, the peaks of CO coverage fractions are found to reduce, in comparison to a case where the initial start-up temperature is set at 110 °C, showing percentage reductions of ~18.3 % (120 °C) and ~40.4 % (130 °C). This is expected because it takes a longer time to reach sufficient temperature (130 ± 5 °C) before CO desorption occurs and thus, results in the build-up of CO adsorption onto the platinum sites. For all cases, the CO coverage fraction value eventually almost zero.

Next, the initial hydrogen coverage fraction values are found to be slightly different for different initial start-up temperatures (110 °C – 0.9649, 120 °C – 0.9557 and 130 °C – 0.9371). Specifically, a comparison with the case where the initial start-up temperature is set at 110 °C shows a percentage reduction of ~0.9 % (120 °C) and ~2.9 % (130 °C). However, the minimum peak values are lower (110 °C – 0.211, 120 °C – 0.34 and 130 °C – 0.4956) and are found to occur at an earlier time, when the initial start-up temperature is decreased. This is due to the same explanation that governs the behaviour of the CO coverage fraction. Next, the magnitude of the second peak is found to be the same (0.7185) for all cases of initial start-up temperatures. After the peaks, the hydrogen coverage fraction gradually reduces and reaching a value of 0.521 for all cases of initial start-up temperatures.

The initial anode overpotential is visibly higher when the initial start-up temperature is lower which can be attributed to sluggish anode kinetics expected at lower temperatures (110 °C – 0.1542 V, 120 °C – 0.1193 V and 130 °C – 0.085 V). These indicate an increase in the initial

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overpotential by 40.3 % (120 °C) and 80.5 % (110 °C) as compared to the case where the initial start-up temperature is set at 130 °C. The anode overpotential remains almost constant up until a certain point of time. This point shifts more towards the right as the initial start-up temperature is increased. Then, the anode overpotential reduces for all cases, occurring at similar rates and reaching zero eventually.

Fig. 4-8 Effect of initial start-up temperature on the CO surface coverage fraction, hydrogen surface coverage fraction, anode overpotential and cell potential

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The initial cell potential is the highest for the initial start-up temperature of 130°C and is the lowest for 110°C (110 °C – 0.7858 V, 120 °C – 0.825 V and 130 °C – 0.8636 V), owing to the temperature dependence of the reference potential and cathode overpotential. These indicate in a decrease in the cell potential by 4.5 % (120 °C) and 9 % (110 °C) as compared to the case where the initial start-up temperature is set at 130 °C. From then onwards, the cell potential for all cases, follows the same profile of the anode overpotential. Specifically, the cell potential for all cases follows the profiles of the anode overpotential. In addition, the cell potential at the end of the start-up process, i.e. at 180°C, reaches similar values (0.9668 V).

4.1.1.4.2.3 Effect of CO volume fraction

Fig. 4-9 shows the effect of CO volume fraction on CO coverage fraction, hydrogen coverage fraction, anode overpotential and cell potential. Firstly, the increased CO volume fraction causes significant increase in CO coverage fraction, which is shown by the increase in the peak values. Specifically, the peaks of CO coverage fractions are found to decrease, showing percentage reduction of ~81.9 % (1000 ppm) and ~32.9 % (5000 ppm), in comparison to a case where the CO volume fraction is set at 10000 ppm,. In addition, they occur at the same time which is due to the similar temperature increase rates for all three cases. Finally, the CO coverage fraction value reduces to zero at similar point of time for all values of CO volume fraction.

Next, the minimum peaks of hydrogen coverage fractions reduce when the CO volume fraction is increased. Specifically, the minimum peaks of hydrogen coverage fractions are found to decrease, showing percentage reduction of ~ 55.3 % (5000 ppm) and ~93 % (10000 ppm), in comparison to a case where the CO volume fraction is set at 1000 ppm. For the case where the volume fraction is set at zero (no CO), no minimum peak is observed.

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Fig. 4-9 Effect of CO volume fraction on the CO surface coverage fraction, hydrogen surface coverage fraction, anode overpotential and cell potential

However, the second maximum peak value is found to be lower when the CO volume fraction is higher. Specifically, the maximum peaks of hydrogen coverage fractions are found to decrease, in comparison to a case where the CO volume fraction is set at 1000 ppm, showing percentage reduction of ~ 12.4 % (5000 ppm) and ~20.5 % (10000 ppm). This is

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expected since there are lesser free sites on the platinum particles for the hydrogen adsorption because of the higher CO coverage fraction. The hydrogen coverage fraction value then reduces until the end of the start-up process where the value reaches 0.5061.

There is no observable change in the initial anode overpotential (0.1195 V) for the different CO volume fractions. However, the peak of the anode overpotential is observed to increase as the CO volume fraction is increased. Specifically, the maximum peaks of anode overpotential are found to increase, in comparison to a case where the CO volume fraction is set at 1000 ppm, showing percentage increase of $\sim 29.9\%$ (5000 ppm) and most importantly, $\sim 101.9\%$ (10000 ppm). Over the time, the anode overpotential reduces at similar point of times (after reaching a temperature of $130 \pm 5^\circ\text{C}$). Next, the cell potential for all cases starts with similar initial values (0.825 V). However, several differences over the time have been observed, which is strongly related to the profile of the anode overpotential as explained. For CO volume fractions of 1000 ppm (0.1 %) and 5000 ppm (0.5 %), the cell potential increases with time albeit having slightly different gradients. However, as the CO volume fraction is increased to 10000 ppm (1 %), the cell potential reduces sharply to 0.7642 V (a percentage reduction of 10.8 % as compared to a case where the CO volume fraction is set at 1000 ppm) around 35 seconds, and then increases further when the temperature increases reaching a final value of 0.9668 V. This is important to note because further increase in CO volume fraction can result in very low cell potential resulting in possible shutdown of the fuel cell.

4.1.1.4.2.3 Effect of extracted current density

Fig. 4-10 shows the effect of extracted current density on CO coverage fraction, hydrogen coverage fraction, anode overpotential and cell potential. Firstly, the CO coverage fraction starts at similar initial values. However, it is found to reach a higher maximum peak value at

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similar point of time when the extracted current density is increased. Specifically, the peaks of CO coverage fractions are found to increase, in comparison to a case where the extracted current density is set at 1000 A m^{-2} , showing percentage increase of $\sim 21.6 \%$ (1500 A m^{-2}) and $\sim 45.6 \%$ (2000 A m^{-2}). After this point, the CO coverage fraction value reduces at similar rates, reaching zero at slightly extended times as the extracted current density is increased. Similarly, the hydrogen coverage fraction reaches a much lower value as the extracted current density is increased. Specifically, the minimum peaks of hydrogen coverage fractions are found to reduce, in comparison to a case where the extracted current density is set at 1000 A m^{-2} , showing percentage reduction of $\sim 40.7 \%$ (1500 A m^{-2}) and $\sim 86 \%$ (2000 A m^{-2}). In addition, the second maximum peak value of hydrogen coverage fraction reduces as the current density is increased, which is attributed to the coverage fraction of CO at that point of time. Specifically, the second maximum peaks of hydrogen coverage fractions are found to reduce, in comparison to a case where the extracted current density is set at 1000 A m^{-2} , showing percentage reduction of $\sim 3.4 \%$ (1500 A m^{-2}) and $\sim 7.5 \%$ (2000 A m^{-2}). Finally, the hydrogen coverage fraction reduces gradually to 0.4667 and is found to have a greater rate of reduction as the current density is increased.

The anode overpotential is found to have a higher initial value when the current density is increased. Specifically, it is found to increase, in comparison to a case where the extracted current density is set at 1000 A m^{-2} , showing percentage increase of $\sim 11.8 \%$ (1500 A m^{-2}) and $\sim 20.4 \%$ (2000 A m^{-2}). In addition, a sharp peak is observed when the extracted current density is the highest (0.2098 V at 2000 A m^{-2}) which is 78.6% higher, as compared to a case where the extracted current density is set at 1000 A m^{-2} . For all three cases, the anode overpotential starts to reduce at the same time, which is ~ 40 seconds, and reaches zero towards the end of the heating process, i.e. 180°C .

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Fig. 4-10 Effect of extracted current density on the CO surface coverage fraction, hydrogen surface coverage fraction, anode overpotential and cell potential

Next, the initial cell potential is found to have a lower value as the extracted current density is increased. Specifically, it is found to decrease, in comparison to a case where the extracted current density is set at 1000 A m⁻², showing percentage reduction of ~6 % (1500 A m⁻²) and ~11.4 % (2000 A m⁻²). The results also indicate that the cell potential at the end of the heating process, reduces with the increase in extracted current density. Specifically, it is found to

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decrease, in comparison to a case where the extracted current density is set at 1000 A m^{-2} , showing percentage reduction of $\sim 4.1 \%$ (1500 A m^{-2}) and $\sim 7.7 \%$ (2000 A m^{-2}). Most importantly, it is observed that at ~ 40 seconds, the cell potential when the extracted current density is set at 2000 A m^{-2} reach the minimum point (0.6717 V). It is to be noted that the further increase in extracted current density may cause the fuel cell to shut down because of excessively high anode overpotential.

4.1.1.5 Summary

A transient three-dimensional numerical model was developed considering the anode electro-kinetics in the presence of CO in hydrogen during the start-up process of a high-temperature PEM fuel cell. A fundamental analysis of transport and adsorption phenomena, together with the parametric study was conducted in this study. The study shows that parameters such as temperature increase rate, initial start-up temperature, CO volume fraction and extracted current density would significantly affect the anode overpotential and the cell potential. Specifically, a warm-up temperature increase rate that is too low can result in seriously high anode overpotential leading to fuel cell shutdown because when the fuel cell remains at a low temperature for long time, CO coverage fraction would reach an intolerably high level. Similarly, CO volume fraction is a key factor that has to be controlled which can otherwise result in the shut down. Furthermore, the extracted current also needs to be low enough to ensure that the anode overpotential does not reach significantly high that can result in fuel cell shut down. Finally, the initial start-up temperature does increase the anode overpotential when it is set excessively lower. However, it is not observed to cause a sudden shoot up of the anode overpotential based on the set system parameters.

In summary, all of these results indicate that temperature and time are two important factors that govern the CO tolerance, defining whether the transient start-up can be done

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successfully. This is not the same CO tolerance that is assessed where a steady state temperature (usually above 160 °C) is considered. This is a case where both the temperature and CO coverage fraction changes simultaneously with time, and the results (anode over potential and cell potential) have been observed to show unique dynamic behaviour. In all of the results, it can be seen that the anode overpotential reaches almost zero at the end of the warm-up process where the temperature reaches 180 °C. According to existing literature, HT-PEMFCs have no problem handling high concentrations of CO at elevated temperatures (above 160 °C). However, it is the temperature before which the fuel cell becomes tolerant to CO, during the warm-up process that is critical. The model suggests that if the fuel cell reaches 130 ± 5 °C (based on the selected variations in system parameters) before the anode is significantly high, then the fuel cell does not shut down prematurely.

Thus, the model and the relevant studies has been beneficial in providing an understanding of the fundamentals of transient heating strategy which is of critical interest, both from scientific and engineering point of views. The essence of this whole study was aimed at propagating the engineering frontline where CO contaminated fuel can be used, avoiding premature shutdown of the fuel cell during the transient start-up. Thus, this effort is the first step towards this direction. Future works involves sensitivity analysis which further investigates the effects of the above mentioned system parameters. This is expected to improve the comprehension and design of the transient heating strategy of the HT-PEMFC ensuring that it is efficient and at the same time tolerant to traces of CO.

4.1.2 Part 2 - Sensitivity analysis

Next, the developed transient three-dimensional isothermal anode electro-kinetic model is used to further perform sensitivity analysis, assessing operational start-up parameters such as

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the temperature increase rate, initial start-up temperature, CO volume fraction and extracted current density. The following steps were performed for the sensitivity analysis.

1. Select the parameters to be tested.
2. Set the equivalent range for all parameter (kept at + 10 % and - 10 % from base case conditions (in bold) - Table 4:2).
3. Run the numerical model for all the relevant parameters values. This generates a total of 81 (3^4) response curves showing anode overpotential with respect to time temperature.
4. These are then compared against the simulation results obtained for base case conditions according to Eq. (4:21), at the respective temperatures.

$$\text{Percentage deviation} = \frac{\text{Observed value} - \text{Base case value}}{\text{Base case value}} \times 100\% \quad (4:21)$$

Table 4:2 Range of start-up parameters for sensitivity analysis

Parameter	Test range
Temperature increase rate, g (K s^{-1})	0.27, 0.3 (base case) , 0.33
Initial start-up temperature, T_i ($^{\circ}\text{C}$)	108, 120 (base case) , 132
CO volume fraction, v_{CO} (ppm)	4500, 5000 (base case) , 5500
Extracted current density, i (A m^{-2})	900, 1000 (base case) , 1100

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4.1.2.1 Results and discussion

4.1.2.1.1 Analysis of maximum overpotential

Fig. 4-11 shows the compilation of maximum anode overpotential values for all cases of parameter variations. The colours and the shapes represent the variation of current density and CO volume fraction, respectively. This analysis is important because the maximum overpotential is the defining output that determines whether the start-up process can be performed without premature shutdown.

Fig. 4-11 Maximum overpotential values pertaining to the variations of initial start-up temperature, current density, CO volume fraction and temperature increase rate

The results show a distinct gap between cases when initial start-up temperature is varied. Specifically, the anode overpotential values for 132 °C are found to be the lowest, followed

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by 120 °C and finally 108 °C. This is the most important observation which signifies that the initial start-up temperature is the dominating parameter apart from the other parameters. It is also clear that when the initial start-up temperature is low (108 °C) the effects of other parameters are amplified. Specifically, an increase on the anode overpotential is observed as the current density and CO volume fraction are increased, and as the temperature increase rate is reduced.

The effect of temperature increase rate is observed to be low when the initial start-up temperature is set at 120 and 132 °C. However, it can be seen that when the initial start-up temperature is set at 108 °C, a significant increase in the maximum overpotential values can be observed with a lower temperature increase rate. Furthermore, this effect is especially amplified when the current density and CO mole fraction are at their highest values (1100 A m⁻² and 5500 ppm, respectively).

The effect of CO volume fraction is also observed to be the most dominant at the lowest initial start-up temperature of 108 °C, especially at the lowest temperature increase rate (0.27 K s⁻¹) and highest current density (1100 A m⁻²). At lower initial start-up temperatures, a slight increase in maximum anode overpotential can be seen. Finally, the effect of current density is observed to be low at an initial start-up temperature of 120 and 132 °C, clearly showing only a slight increase in maximum anode overpotential as the current density is increased. This behaviour is observable even when the initial start-up temperature is set at 108 °C and the temperature increase rates are set at 0.3 K s⁻¹ and 0.33 K s⁻¹. However, when the initial start-up temperature is set at 108 °C and the temperature increase rate is set at 0.27 K s⁻¹, the effect of CO mole fraction overshadows that of the current density.

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Thus, it can be concluded that the initial start-up temperature is the key dominating parameter that affects the maximum anode overpotential, which in turn determines the success of the start-up process.

Fig. 4-12 Effect of initial start-up temperature on warm-up time (from room temperature) and energy consumption for a typical 1-kW stack

Fig. 4-12 shows the effect of initial start-up temperature (108, 120 and 132 °C) on warm-up time and energy consumption that is considered from a start-up process of a typical 1-kW from room temperature. The formulation of the warm-up time and energy consumption is shown in Eqs. (4:22) and (4:23).

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$$\begin{aligned} \text{Warm-up time}_{T=25 \text{ to } 180^\circ\text{C}} (\text{sec}) &= \text{Warm-up time}_{T=25 \text{ to } T_i} + \text{Warm-up time}_{T=T_i \text{ to } 180^\circ\text{C}} \\ &= \frac{mC_p(T_i - 25)}{P_{ext}} + \frac{mC_p(180 - T_i)}{P_{ext} + IVN_{cell}A_{MEA}} \end{aligned} \quad (4:22)$$

$$\text{Energy consumption (kWh)} = \frac{1}{3600 \times 1000} (\text{Warm-up time}_{T=25 \text{ to } 180^\circ\text{C}} \times P_{ext}) \quad (4:23)$$

Where m , C_p , T , P_{ext} , I , V , N_{cell} and A_{MEA} refer to the mass, specific heat capacity, temperature, externally applied heating power, current, voltage, number of cells and area of MEA, respectively.

Firstly, the results show that there is slight but negligible difference in warm-up time as the initial start-up temperature is varied, especially when the external heat input rate is lower (below 600 W) showing a slightly reduced warm-up time. In addition, it also shows that reducing the initial start-up temperature can reduce the energy consumption calculated for the whole start-up process. This reduction of energy consumption is calculated to be $\sim 7.5\%$ at the lowest heat input rate (200 W) and $\sim 1.5\%$ at higher heat input rates (1200 W onwards). Thus, it can be deduced that having a reduced initial start-up temperature does have its benefits from an energy analysis point of view.

4.1.2.1.2 Sensitivity analysis of parameters at $T_{initial} = 108, 120$ and 132°C

The following results shown in Fig. 4-13, Fig. 4-14, Fig. 4-15 were obtained by comparing the variations of each parameters (temperature increase rate, CO volume fraction and current density) at $+10\%$ and -10% , at initial start-up temperatures of 108, 120 and 132°C , against the base case conditions ($i = 1000 \text{ A m}^{-2}$, $v_{CO} = 5000 \text{ ppm}$ and $g = 0.3$) at that considered initial start-up temperature. The results shown in Fig. 4-13, Fig. 4-14, Fig. 4-15, can be viewed as two parts i.e. (i) from the respective initial start-up temperature (108°C , 120°C or 132°C) to $\sim 135^\circ\text{C}$, and (ii) from $\sim 135^\circ\text{C}$ onwards to 180°C . The first part is most important

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because it is in this phase where premature shutdown of the fuel cell can occur due to high anode overpotential. In the second part, the anode overpotential reduces as the temperature increases further to 180 °C.

Fig. 4-13 Percentage deviation of anode overpotential pertaining to the variations of current density, CO content and temperature increase rate at an initial start-up temperature of 108 °C

Fig. 4-13 shows the percentage deviation of the anode overpotential for the variation in temperature increase rate, CO volume fraction and current density, as compared to the base case condition at 108 °C ($i = 1000 \text{ A m}^{-2}$, $v_{\text{CO}} = 5000 \text{ ppm}$ and $g = 0.3$), over the entire temperature range experienced during the particular start-up process from 108 to 180 °C. For the cases of $i = 900 \text{ A m}^{-2}$, $v_{\text{CO}} = 4500 \text{ ppm}$ and $g = 0.33$, the percentage deviation is calculated to be negative, indicating a reduction in anode overpotential as compared to the base case condition. For effective comparison, the negative deviation curves are mirrored

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onto the positive percentage deviation axis, as shown in Fig.7. The results indicate that the variation of current density (both +10 % and -10 %) has the greatest dominance at 108 °C, showing greater percentage deviation of 1.6 and 1.7 %, respectively, as compared to its base case condition. And as the temperature increases, the percentage deviation gradually

Fig. 4-14 Percentage deviation of anode overpotential pertaining to the variations of current density, CO content and temperature increase rate at an initial start-up temperature of 120 °C

increases. The variation of CO volume fraction (both +10% and -10%) results in a 0 % deviation at 108 °C, which is due to same value of anode overpotential, compared to the base case condition where the initial start-up temperature is set at 108 °C. This is due to same

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value of anode overpotential compared to the base case. As the temperature increases, the percentage deviation for CO volume fractions set at 4500 and 5500 ppm fluctuates between 0 and 2 % as the temperature increases, and finally reduces to almost 0 at 180 °C. Finally, the variation of temperature increase rate (both +10 % and -10 %) results in 0 % deviation at 108 °C, similar to the case where the CO volume fraction is varied. In addition, the percentage deviation for temperature increase rates of 0.27 and 0.33 K s⁻¹, fluctuates between 0 and 2 % as the temperature increases, and finally reduces to almost 0 at 180 °C. This is similar to the case where the CO volume fraction is varied. Fig. 4-14 shows the percentage deviation of the anode overpotential for the variation in temperature increase rate, CO volume fraction and current density, as compared to the base case condition at 120 °C ($i = 1000 \text{ A m}^{-2}$, $v_{CO} = 5000 \text{ ppm}$ and $g = 0.3$), over the entire temperature range experienced during the start-up process from 120 to 180 °C. Firstly, variation of current density (both +10 % and -10 %) has the greatest dominance at 120 °C, showing the greatest percentage deviation ($\sim 2 \%$), from the base case condition, as compared to the variation in CO volume fraction and temperature increase rate which starts at 0 % deviation and gradually increases with temperature. The variation of CO volume fraction (both +10% and -10%) results in 0 % deviation at 120 °C. The CO volume fraction set at 4500 ppm (-10 %) shows a higher peak (peak $\sim 2 \%$), as compared to the case with the CO volume fraction set at 5500 ppm (+10 %)(peak $\sim 1.3 \%$). After the peak, the percentage deviation decreases to almost zero. Finally, the variation of temperature increase rate (both +10% and -10%) results in 0 % deviation which is similar to the case where the CO volume fraction is varied. The peak percentage deviation for the case when the temperature increase rate set at 0.33 K s⁻¹ (+10 %) (peak $\sim 1.5 \%$), is higher than that when it is set at 0.27 K s⁻¹ (-10 %) (peak $\sim 0.9 \%$). After around 135 °C, the percentage deviation reduces to zero.

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Fig. 4-15 shows the percentage deviation of the anode overpotential for the variation in temperature increase rate, CO volume fraction and current density, as compared to the base case condition at 132 °C ($i = 1000 \text{ A m}^{-2}$, $v_{\text{CO}} = 5000 \text{ ppm}$ and $g = 0.3$), over the entire temperature range experienced during the start-up process from 132 to 180 °C. Firstly, variation of current density (both +10 % and -10 %) has the greatest deviation ($\sim 2.2 \%$) at 132 °C, compared to the variation in CO volume fraction and temperature increase rate, which starts with 0 % deviation.

Fig. 4-15 Percentage deviation of anode overpotential pertaining to the variations of current density, CO content and temperature increase rate at an initial start-up temperature of 132

°C

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The current density set at 1100 A m^{-2} (+10 %) and 900 A m^{-2} (-10 %) shows similar percentage deviation profiles and are observed to have no peaks but a gradual increase in percentage deviation as the temperature increases. However, this is not significant because the anode overpotential values observed in this phase are in the order of 10^{-3} , at temperatures above 160°C . The variation of CO volume fraction (both +10 % and -10 %) results in 0 % deviation at 132°C . The CO volume fraction set at 5500 ppm (+10 %) and 4500 ppm (-10 %) shows similar the percentage deviation peaks ($\sim 1\%$). After the peak, the percentage deviation reduces further to zero. The variation of temperature increase rate (both +10 % and -10 %) results in 0 % deviation at 132°C . The temperature increase rate set at 0.27 K s^{-1} (-10 %) and 0.33 K s^{-1} (+10 %) shows similar the percentage deviation peaks ($\sim 0.5\%$). After the peak, at around 135°C , the percentage deviation for the case of the temperature increase rates, set at 0.27 K s^{-1} (-10 %) and 0.33 K s^{-1} (+10 %), reduces further to zero.

4.1.2.1.3 Sensitivity analysis of parameters at different T_{initial}

Fig. 4-16 shows the percentage deviations of the anode overpotential for the variation in current density, as compared to their respective base case conditions at different initial start-up temperatures. The results show that as the initial start-up temperatures is set at higher values, the initial percentage deviation at the respective initial start-up temperatures, are higher. Apart from that, the increase in percentage deviation compared between the three cases is observed to be similar in magnitude, after 135°C onwards to 180°C . Thus, it can be concluded that having a high initial start-up temperature, can reduce the sensitivity of current density at critical temperature range (108 to 135°C), which in turn improves the controllability of the anode overpotential. This is important since high anode overpotential can result in premature shutdown of the fuel cell during start-up.

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Fig. 4-16 Percentage deviation of anode overpotential pertaining to the variation of current density at different initial start-up temperatures

Fig. 4-17 shows the percentage deviations of the anode overpotential for variation in CO volume fraction, as compared to their respective base case condition at different initial start-up temperatures. The results show that as the initial start-up temperatures is set at higher values, the initial percentage deviation at the respective initial start-up temperatures, remains at zero. However, the maximum peak deviation is found to reduce with the increase in initial start-up temperatures, 108, 120 °C and 132 °C. Specifically, it can be seen that the maximum peak deviation is the lowest when the initial start-up temperature is set at 132 °C.

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Fig. 4-17 Percentage deviation of anode overpotential pertaining to the variation of CO volume fraction at different initial start-up temperatures

Fig. 4-18 shows the percentage deviations of the anode overpotential for variation in temperature increase rate, as compared to their respective base case condition at different initial start-up temperatures. The results show that as the initial start-up temperatures are set at higher values, the initial percentage deviation at the respective initial start-up temperatures, start from zero. However, the peak deviation is found to reduce with the increase in initial start-up temperatures, 108, 120 °C and 132 °C. Specifically, it can be seen that at 132 °C, the peak percentage deviation is lesser than that for the case of 108 and 120 °C.

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Fig. 4-18 Percentage deviation of anode overpotential pertaining to the variation of temperature increase rate at different initial start-up temperatures

4.1.2.2 Summary

In this part of the study, the operational start-up parameters such as initial start-up temperature, current density, CO volume fraction and temperature increase rate were assessed for sensitivity with respect to the temperature of the fuel cell.

The results indicate that the initial start-up temperature greatly affects the maximum anode overpotential as compared to other parameters. In addition, the results also indicate that having a low initial start-up temperature is the key reason that makes the other parameters such as the current density, CO volume fraction and temperature increase rate, sensitive.

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Apart from the initial start-up temperature, the current density is the second most critical parameter (followed by CO volume fraction and temperature increase rate), as it is found to show the highest sensitivity, especially at low initial start-up temperature of 108 °C. In addition, a temperature range of 130 ± 5 °C is most critical as the sensitivity is found to reach a peak for all parameters at the three considered initial start-up temperatures. In addition, a system level energy analysis considered for the start-up process of a 1-kW stack, suggests the potential benefits of having low initial start-up temperature, which are reduced warm-up time and energy consumption.

Thus, it can be deduced that the initial start-up temperature is the main parameter that has to be kept in strict control which can affect the sensitivity of the other parameters. Specifically, having an increased (preferably above 130 °C) initial start-up temperature can prevent high anode overpotential. However, having a lower initial start-up temperature can reduce warm-up or start-up time and energy consumption of the start-up process, which are the potential benefits concluded from energy analysis. In addition, since the anode overpotential is particularly sensitive at the critical range, minor fluctuations in temperature can cause shoot-up of the anode overpotential. Thus, it is important to keep the initial start-up temperature controlled at a critical temperature range of 130 ± 5 °C for effective start-up.

In the next chapter, the investigation of the transient evolution of OCV that is expected to occur in a typical start-up process will be studied.

Chapter 5. Experimental investigation of open circuit voltage during warm-up process of HT-PEMFCs

5.1 Introduction

In this chapter, the transient evolution of OCV, during a start-up process of a HT-PEMFC is experimentally investigated. This effort is dedicated to improving the accuracy of transient start-up models that consider the temperature to vary with respect to time. Over the decade, several models on start-up have been published. Andreason and Kær proposed a dynamic stack temperature lumped model to predict the energy required to heat up the HT-PEMFC to above 120°C from room temperature by comparing the different heating methods [182]. Singdeo *et al.* compared different warm-up methods through numerical modelling and the results were validated with experimental data from a HT-PEMFC stack and concluded that coolant heating gives the better uniformity in temperature distribution and enables the shortest warm-up time [178]. Andreason and Kær also proposed a model for predicting the dynamic temperature of a HTPEMFC stack as a way to test different thermal control strategies [179]. All of these models consider the heating strategy that totally disregards the extraction of current during start-up, with a lumped thermal mass that is transiently heated.

Recently, heating strategies that includes the current extraction during start-up has been investigated. Wang *et al.* recently proposed a numerical model considering the effect of reaction heating after the temperature of the HTPEMFC reaches 120°C by external heating [176]. Also in one of our previous efforts, the heating strategy involved the consideration of extraction of current from room temperature [177]. In both of these models, the OCV which is one of the critical electrokinetic variables, were assumed to be governed by the Nernst equation. The Nernst equation has been reported to have good predictive capability of the

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OCV for steady state fuel cell operation and have been used for a considerable period of time. However, in scenarios such as start-up of a HT-PEMFC where the temperature increase rate can be high, its accuracy in predicting the OCV is still unclear. This is especially important because achieving faster start-up time, strongly depends on the contribution of exothermic heat that is governed by the OCV. Therefore, in order to move towards optimization of the start-up strategy of the HT-PEMFC, accurately predicting the OCV under a thermal gradient is necessary. Thus, the objective of this effort is to highlight the limitations of the Nernst equation, focusing on the responsiveness of the OCV to transient increase in temperature that is experienced during start-up or warm-up process of a HT-PEMFC.

5.2 Experimental

A single cell HT-PEMFC was set up with a purchased phosphoric acid doped PBI-based MEA (CELTEC P1000) with an active area of 45 cm^2 . Fig. 5-1 shows the experimental setup of the HT-PEM single cell. Steel was used for the end plates. Variable power control silicon heaters were pasted on to the exposed sides of the end plates for dynamic heating.

Fig. 5-1 Schematic diagram and experimental setup of the HT-PEM single cell

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The conventional oven was used to maintain the fuel cell at the 140°C before the dynamic heating was introduced to the fuel cell. The temperature was measured by securely placing K-type thermocouples (sheathed and electrically insulated, diameter - 150 microns) onto the exposed areas of the GDL.

A data logger was used to sense the temperature of the fuel cell with a time measurement interval of 5 seconds while an electrochemical analyzer was used to measure the OCV of the fuel cell with a measurement interval of 0.5 seconds.

5.3 Design of study

The study involves the transient heating of the fuel cell at various input heat flux, to investigate the effect of heat input flux on the (V_o) OCV. The initial temperature of the fuel cell is set at 140 ± 2 °C with the use of a conventional oven. The OCV is ensured to have reached a steady state value prior to the start of the experiment.

Next, the heat input flux is set at desired values with the use of the power controller. At $t = 0$, the heat input is supplied to the fuel cell, while the temperature and electrochemical measuring data loggers are turned on. Once the fuel cell reaches 180 ± 2 °C, the heat input flux is turned off.

The heat input flux is varied between 55 W, 110 W, 192.5 W, 275 W, 412.5 W and 550 W over an area 169 cm^2 ($13 \text{ cm} \times 13 \text{ cm}$) inclusive of both sides of the anode and cathode end plates.

Table 5:1 shows conversion between heat input and heat input flux. For simplicity, the heating power will be expressed as a percentage of the maximum heating power supplied by the external heating elements.

Table 5:1 Conversion between heat input and heat input flux

Heating power as a percentage of maximum value (550 W)	Heating power (W)	Effective area (cm ²), both sides	Heating power flux (W cm ⁻²)
10 %	55	13 × 13 × 2	0.1627
20 %	110		0.3254
35 %	192.5		0.5695
50 %	275		0.8136
75 %	412.5		1.2204
100 %	550		1.6272

5.4 Time and temperature lag analysis

In order to have a quantitative sense of accuracy of the measured temperature, the time difference or time lag is estimated between the point when the external heat source (silicon heaters) is introduced, and the point when the temperature is sensed at the thermocouple, and the temperature at the centre of the MEA. This time lag is expected because the sensor is located at a distance away from the silicon heaters. Furthermore, it is also expected that a time lag will exist between the temperatures at the sensor and the centre of the MEA. The temperature at centre of the MEA is the most reliable indication of the fuel cell operational temperature because the catalyst layers (which are very close to the membrane) are where the electrochemical performance is defined. However, measuring the temperature at the centre of the MEA can pose a problem because the thermocouple has to be inserted into the MEA, which may damage the MEA.

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Thus, a simple 1-dimensional transient model of the HT-PEMFC is developed to compare the temperature measured at the sensor and predict the temperature at the centre of the MEA. Thus, the time lag between the sensor and the centre of the MEA can be estimated. Fig. 5-2 shows the modelling domain of the numerical model.

Fig. 5-2 Description of transient 1-dimensional model

The main purpose of this section is to show that the time lag or difference in reaching the same temperature between the sensor and the centre of the MEA is sufficiently low, ensuring that the accuracy of the measured temperature with respect to the centre of the MEA is within tolerable values.

The conservation of energy is used to predict the temperature with respect to time at the thermocouple. The general equation is shown in Eq. (5:1).

$$\rho C_p \frac{\partial T}{\partial t} + \nabla \cdot (\rho C_p \vec{u} T) = \nabla \cdot (k^{eff} \nabla T) + S_e \quad (5:1)$$

Where ρ , C_p , T , $\vec{u}$, k^{eff} , t and S_e refer to the density, specific heat capacity, temperature, velocity, effective thermal conductivity, time and energy source term, respectively.

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The densities, heat capacities, thermal conductivities and thickness of the components of the MEA used in the numerical model are as follows.

- Density, ρ , *end plate, bipolar plate, GDL, CL, mem* (kg m^{-3}) - 7750, 2266,, 1800, 21450, 1300
- Heat capacity, C_p , *end plate, bipolar plate, GDL, CL, mem* ($\text{J kg}^{-1} \text{K}^{-1}$) - 502, 1580, 710, 3300, 1650
- Thermal conductivity, k , *end plate, bipolar plate, GDL, CL, mem* ($\text{W m}^{-1} \text{K}^{-1}$) - 16 , 20, 1.2, 1.5, 0.95
- Thickness, δ *end plate, bipolar plate, GDL, CL, mem* (m) - 0.017, 2e-3, 380e-6, 50e-6, 100e-6

Eq. (5:2) refers to the initial condition where T_∞ stands for the temperature set at 140 °C. Eq. (5:3) is a boundary condition, suggesting the external heat input at the edge of the end plate. Eq. (5:4) is the other boundary condition which refers to the thermal symmetry along the centre of the single cell.

$$T(x, 0) = T_\infty \quad (5:2)$$

$$-k \frac{\partial T}{\partial x}(0, t) = \dot{q}_{in} \quad (5:3)$$

$$-k \frac{\partial T}{\partial x}(L, t) = 0 \quad (5:4)$$

The transient one-dimensional model was solved numerically using finite element-based commercial software COMSOL Multiphysics. The convergence criteria for temperature calculations were set to 10^{-8} . The solution sequence is shown in Fig. 5-3.

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Fig. 5-3 Solution sequence of numerical simulation

Fig. 5-4 shows the simulated temperatures at the sensor and the centre of the MEA and compared against experimentally measured temperature at the sensor, at a set percentage heating power of 35 %, for the first 100 seconds. Firstly, the experimentally measured temperature at the sensor shows that the initial time lag between the point in time when the external heat input is introduced at $t = 0$ s, and the time when the temperature at the sensor starts increasing, is close to 5 seconds. This is compared against results of the numerical model and is found to be almost similar. Thus, the model can be used to predict the temperature at the centre of the MEA. The results shows that the time lag between the sensor and the centre of the MEA is close to 4 seconds. This means that the centre of the MEA

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reaches the same temperature at the sensor after 4 seconds, which also means that the steady temperature difference at any point in time, is around 0.5°C . In comparison to the whole heating process which takes around 650 seconds, the total time lag of 9 seconds (initial lag + steady lag) is negligible (percentage difference = 1.38 %). Another perspective also suggests that a steady temperature difference of 0.5°C as compared to the whole temperature range of 140 to 180°C , is negligible (percentage difference = 1.25 %). Therefore, this analysis suggests that the temperature measured at the sensor is a reliable indication of the fuel cell temperature, and the OCV measured at any point is that which is at the sensed temperature.

Fig. 5-4 Time and temperature lag analysis

5.5 Results and discussion

5.5.1 Temperature and OCV vs. time

Fig. 5-5 (a), (b) and (c) shows the measured temperature profile, measured OCV and the fitted OCV, with respect to time, respectively. Initially, the temperature (Fig. 5-5 (a)) remains almost constant till when the time reaches around 20 seconds.

Fig. 5-5 (a) Measured temperature, (b) measured OCV and (c) fitted OCV, vs. time

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This has been clearly explained in Fig. 5-4. From then onwards, the temperature increases from 140 to 180 °C in a curvilinear manner. In addition, as expected, the time it takes to heat up the fuel cell from 140 to 180 °C, increases as the heating power percentage is reduced from 100 to 10 %.

Next, the measured voltage is shown in Fig. 5-5 (b). This is simultaneously measured along with the temperature of the fuel cell. It can be seen that measured OCV is irregular in profile and is thus, fitted to a 4th order polynomial as shown in Fig. 5-5 (c). It can be seen that the fitted OCV reduces almost linearly with time when the heating power is set at 10 %. As the heating power percentage increased to 20 %, a slight bend is noticed when $t \approx 250$ seconds.

As the heating power percentage is increased further, it can be seen that the curvature of the voltage profile becomes greater. Thus, an effect of the temperature profile (i.e. heating power percentage) on the voltage profile is shown. In order to compare this with the Nernst Equation, the voltage and temperature profiles with respect to time are mathematically manipulated to obtain a voltage profile with respect to temperature. This is shown in the next section.

5.5.2 OCV vs. Temperature

Fig. 5-6 (a) shows the OCV profile with respect to temperature, $V_0 = f(T)$ which has been mathematically treated with $T = f(t)$ and $V_0 = f(t)$ that were measured experimentally. Fig. 5-6 (b) shows the fitted voltage profile with respect to temperature. The results show that for all cases of heating power percentage, the OCV is clearly decreasing in a curvilinear manner as the fuel cell temperature is increased. As the heating power percentage is increased, the curvature of the voltage profile is greater. At a glance, it is very clear that the behaviours

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presented is very much different from the ones that has been used so far in existing literature.

These are derived from the Nernst equation to fit the application of HT-PEMFC operation.

Fig. 5-6 (a) Measured OCV and (b) fitted OCV, vs. Temperature

Eqs. (5:5) shows the Nernst equation while Eq. (5:6) shows the derived theoretical potential for a hydrogen/oxygen fuel cell, and is plotted in Fig. 5-7, together with the steady state OCV that was measured experimentally using the purchased MEA (CELTEC P1000).

$$V_0 = E_{rev}^0 + \left(\frac{\Delta S}{nF} \right)_p (T - 298) + \frac{RT}{2F} \ln \frac{p_{H_2} p_{O_2}^{1/2}}{p_{H_2O}} \quad (5:5)$$

$$V_0 = 1.185 - 2.3 \times 10^{-4} (T - 298.15) \quad (5:6)$$

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Fig. 5-7 OCV vs. steady state temperature

It can be seen from Fig. 5-7 that the OCV profiles presented by the Nernst equation are perfectly linear. A comparison between the commercial MEA, CELTEC P1000 (experimental- steady state) and the Nernst equation is done. It shows that the baseline value of the OCV measured experimentally (CELTEC P1000) is lower than the that predicted by the Nernst equation which is expected because gas crossover can occur reducing the OCV. However, the reduction gradient, dV_o/dT of the OCV of CELTEC P1000 (experimental) is very much similar to the Nernst equation showing a value of $\sim -2.3 \times 10^{-4} \text{ V/}^\circ\text{C}$. Thus, it is clearly shown that the OCV when measured under steady state thermal conditions remains perfectly linear, thus indicating an almost fixed reduction gradient, dV_o/dT . In the next section, it can be clearly seen that the reduction gradient, dV_o/dT , varies under a temperature gradient.

5.5.3 dV_o/dT vs. Temperature

Fig. 5-8 shows the reduction gradient with respect to the fuel cell temperature, dV_o/dT . This is the first order derivative of the fitted OCV profile, $V_o = f(T)$ as previously shown in Fig. 5-8 (b). Firstly, the reduction gradient, dV_o/dT , starts with a zero gradient at 140 °C for all cases of heating power percentages. As the temperature increases the reduction gradient, dV_o/dT , increases in magnitude. For a heating power percentage of 10 %, the reduction gradient decreases steadily till around 145 °C after which the rate of change is lower, finally reaching a magnitude of close to -9×10^{-4} V/°C.

Fig. 5-8 OCV reduction gradient, dV_o/dT , with respect to temperature

For a heating power percentage of 20 %, the magnitude of the reduction gradient increases almost in a linear manner. For all the other cases, the magnitude of the reduction gradient increases in a parabolic manner. All of the value reach close to $-7.5 \sim -9 \times 10^{-4}$ V/°C. This is in contrast with the results obtained and presented in Fig. 5-7, showing an almost fixed

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reduction gradient of $-2.3 \times 10^{-4} \text{ V/}^\circ\text{C}$ (at any temperature from 140 to 180 $^\circ\text{C}$) using the same experimental setup in this case. Thus, it is clear from the results that the reduction gradient, dV_o/dT , varies when subjected to a temperature gradient.

5.6. Summary

An experimental study consisting of a PBI based HT-PEMFC single cell was conducted. The main aim of the study is to identify the limitations of using the Nernst equation to predict the OCV, in cases where the temperature of the fuel cell is increased with respect to time. Such a scenario exists during the start-up of a HT-PEMFC. The effect of increasing the temperature transiently on the OCV in the temperature range of 140 to 180 $^\circ\text{C}$ was observed, by external application of a heating source with constant heat input rate. The temperature and OCV that was measured with respect to time, was then mathematically treated to show the behaviour of OCV with respect to temperature. This was then compared against the Nernst equation.

The results indicate that the OCV exhibits non-linear behaviour as it reduces with respect to temperature, when the fuel cell is subjected to a constant heating power applied externally. Specifically, the behaviour under a constant heating power shows curvilinear reduction of the OCV as the temperature increases. This behaviour is clearly in contrast with the Nernst equation, which considers the temperature as steady state. In addition, it was also observed that as the external heating power is increased, the degree of curvature of the OCV profile is greater. Furthermore, the reduction gradient of OCV, dV_o/dT , is found to increase negatively with temperature in a nonlinear manner. This is also in contrast with the Nernst equation suggesting a constant OCV reduction gradient ($\sim -2.3 \times 10^{-4} \text{ V/}^\circ\text{C}$) which was experimentally (commercial MEA) measured under steady state temperatures. Therefore, this study clearly indicates that it is not an accurate way to predict the OCV in cases where the temperature of

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the fuel cell is steady. Thus, for thermal start-up models where the temperature increase is expected to be unsteady, a non-linear behaviour should be considered for better accuracy.

Chapter 6. Conclusion and Future works

6.1 Conclusion

In conclusion, this thesis explores several novel ideas to address issues related to the important problem of start-up of HT-PEMFC technology.

Firstly, an analytical model was conceptualized as a way to explore new heating or start-up strategies. Specifically, a start-up where current is extracted from the fuel cell from room temperature was proposed. This method was compared against existing start-up strategies and is found to be energy and time efficient. The novelty about this investigation is the mathematical model itself which includes the concept of boiling phase change i.e. an inherent phenomena that is expected in the proposed start-up method. Parameters such as Damköhler number and the cell performance were observed, in the context to start-up, from the results based on the analytical model.

Next, an experimentally validated, transient three-dimensional numerical model was developed as a way to simulate the start-up of a HT-PEMFC supplied with hydrogen supply that has traces of CO. This is a highly likely situation in HT-PEMFC technology which has been overlooked. This work is novel in two perspectives. Firstly, in terms of experimentally obtaining a transient response in the presence of CO, is novel by itself. Secondly, and most importantly, the three-dimensional model that was developed, considered a case where the adsorption kinetics of hydrogen and CO vary with time and temperature, simultaneously, which has not been considered so far, from a mathematical point of view. The model generated novel results such as hydrogen and CO surface coverage fractions under a transiently varying temperature profile. Thus, a new term "transient CO tolerance" was conceived that describes the tolerance of a HT-PEMFC in successfully starting up without

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premature shutdown due to high anode overpotential that results from the presence of CO. Furthermore, the use of the model was extended to identify the sensitivity of system parameters such as temperature gradient, initial start-up temperature, CO mole fraction and extracted current density, on the anode overpotential. The results showed that the initial start-up temperature is the dominating factor that can shoot up the anode overpotential, causing a negative cell potential, which results in shut down of the HT-PEMFC. This whole study is considered as one of the key contributions in this thesis because of two reasons. Firstly, the concept and mathematical model is novel from a knowledge point of view. Secondly, the sensitivity analysis ensures that the problem is viewed from a system-level perspective, where several practical guidelines pertaining to start-up were drawn.

Finally, experiments that relates to the transient evolution of OCV under a varying temperature, with respect to time, were conducted. This effort is solely dedicated to improve the accuracy of HT-PEMFC models that aim to simulate start-up ,where current extraction (apart from the external heat input) is done at a temperature above 100 °C. The novelty of this work relates to the observation that the OCV is non-linear when subjected to varying temperature with respect to time, which is in contrast with the linear Nernst equation. Thus, this work is perceived to be a minor contribution in the domain of start-up modelling of HT-PEMFC.

Thus, the ideas presented in this thesis can help spur further development in HT-PEMFCs. In addition, these ideas contributed towards broadening the boundaries of existing scientific knowledge and at the same time to practical engineering aspects.

6.2 Future works

Future works that stem from the ideas explored from this thesis are expected to be related to start-up of HT-PEMFCs. Firstly, the start-up strategy that involves current extraction from a temperature above 100 °C, in the presence of CO, can be further improved by considering a control strategy that adjusts the extracted current density according the registered cell potential. This experimental concept is expected to make use of the exothermic heat generated from the current extraction, especially at low initial start-up temperatures while avoiding shutdown to due high anode overpotential.

Secondly, modelling efforts relating to stress analysis of HT-PEMFCs during start-up would be valuable. Stress analysis has been popular in modelling of PEMFCs. Transient heating of the HT-PEMFCs can results in sudden hot spots which can cause localised stress build-up within the MEA if the rate of temperature increase in relatively high. Modelling this phenomenon can help draw guidelines that can aid in the design of heating configuration of the fuel cell.

List of publications

During Ph.D candidature

1. Abdul Rasheed, R.K., S.M.M. Ehteshami, and S.H. Chan, Analytical modelling of boiling phase change phenomenon in high-temperature proton exchange membrane fuel cells during warm-up process. *International Journal of Hydrogen Energy*, 2014. **39**(5): p. 2246-2260.
2. Abdul Rasheed, R.K. and S.H. Chan, Transient carbon monoxide poisoning kinetics during warm-up period of a high-temperature PEMFC – Physical model and parametric study. *Applied Energy*, 2015. **140**(0): p. 44-51.
3. Kamal, R. and S.H. Chan, Sensitivity analysis of anode overpotential during start-up process of a high temperature proton exchange membrane fuel cell. *Electrochimica Acta*, 2015. **176**: p. 965-975.
4. Abdul Rasheed, R.K. and S.H. Chan, Experimental investigation of open circuit voltage during start-up process of HT-PEMFC. *Electrochimica Acta*, 2015. **186**: p. 353-358.

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Appendix

Table A3:1 List of multi-physical properties and parameters

Property/Parameter	Correlation/ Value
Thermal	
Initial Temperature	$T_1(0) - 295 \text{ K}, T_2(0) - 295 \text{ K}$
Heat capacity, ρC_p	CL - $1.69 \times 10^6 \text{ J K}^{-1} \text{ m}^{-3}$, GDL - $5.68 \times 10^5 \text{ J K}^{-1} \text{ m}^{-3}$ EP - $3.82 \times 10^6 \text{ J K}^{-1} \text{ m}^{-3}$
Molar volume of liquid water	$18.015 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$
Molar mass of H_2O	$18.015 \times 10^{-3} \text{ kg mol}^{-1}$
Interfacial thermal resistance, h_s	$1 \text{ W K}^{-1} \text{ m}^{-2}$
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	$7 \times 10^{-5} \text{ m}^3$
Density of species, ρ	$\rho_i = \rho_{i,0} (1 + \beta_i (T - T_0))^{-1} \text{ kg m}^{-3}$
Geometric	
Thickness, δ	CL - $50 \times 10^{-6} \text{ m}$, GDL - $260 \times 10^{-6} \text{ m}$, Membrane - $120 \times 10^{-6} \text{ m}$
Active area of MEA, A_{MEA}	0.0045 m^2
Porosity, ε	CL - 0.2, GDL - 0.6
Diffusive	
Diffusion coefficient of oxygen	$D_{O_2} = 3.2 \times 10^{-5} \left(\frac{T}{295} \right)^{\frac{3}{2}} \left(\frac{101325}{p} \right) \text{ m}^2 \text{ s}^{-1}$
Diffusion coefficient of oxygen in liquid H_2O	$D_{O_2,liq} = 2.2 \times 10^{-9} \left(\frac{T}{298} \right)^{\frac{3}{2}} \left(\frac{101325}{p} \right) \text{ m}^2 \text{ s}^{-1}$
Diffusion coefficient of oxygen in water vapour	$D_{O_2,vapor} = 2.82 \times 10^{-5} \left(\frac{T}{308.1} \right)^{\frac{3}{2}} \left(\frac{101325}{p} \right) \text{ m}^2 \text{ s}^{-1}$
Electrochemical kinetics	
Conductivity, κ	Membrane - 9 S m^{-1} , Catalyst layer - 300 S m^{-1}
Transfer coefficient, α	Anode - 1

Appendix

Cathode - 1	
Effective catalyst area per unit volume × Cathode exchange current density	$ai_{0,c}^{ref}(T) = ai_{0,c,353.15K}^{ref} \exp \left[-\frac{E_{a,cathode}}{R} \left(\frac{1}{T} - \frac{1}{353.15} \right) \right]_{p_c=1atm}$ $ai_{0,c}^{ref}(p) = 1724.5 \exp \left[2.06 \frac{p_c}{101325} \right]$ $ai_{0,c,353.15K}^{ref} = 1 \times 10^4 \text{ A m}^{-3}$

Appendix

Table A4:1 Geometrical, physical and electrochemical properties and correlations

Parameter	Correlation/ Value
Geometric properties	
δ (CL and GDL)	$50 \times 10^{-6}, 380 \times 10^{-6} \text{ m}$
ε (CL and GDL)	0.3, 0.4
Diffusive properties	
Binary diffusion coefficient of hydrogen and CO	$D_{H_2-CO} = 1.305 \times 10^{-4} \left(\frac{T}{403.15} \right)^{1.75} \text{ m}^2 \text{ s}^{-1}$
Electrochemical kinetics	
κ (anode, cathode and membrane)	300, 300 and 9 S m^{-1}
α_a	Anode - 1
$i_{0,c}^{ref}$ [180]	$i_{0,c}^{ref}(T) = i_{0,c,353.15K}^{ref} \exp \left[-\frac{7900}{R} \left(\frac{1}{T} - \frac{1}{353.15} \right) \right]_{p_c=1atm}$
$i_{0,c,353.15K}^{ref}$	1 A m^{-2}
$k_{H,ads}^0$	5960 s^{-1}
$b_{H,ads}^0$	$4.18 \times 10^8 \text{ kmol m}^{-3}$
$E_{H,ads}^k$	$1.04 \times 10^7 \text{ J kmol}^{-1}$
$E_{H,ads}^b$	$8.79 \times 10^7 \text{ J kmol}^{-1}$
$k_{H,eox}^0$	$1.2 \times 10^{17} \text{ kmol s}^{-1} \text{ m}^{-3}$
$E_{H,eox}^k$	$1.45 \times 10^8 \text{ J kmol}^{-1}$
$E_{CO,ads}^k$	$4.73 \times 10^7 \text{ J kmol}^{-1}$
$b_{CO,ads}^0$	$3.57 \times 10^{21} \text{ kmol m}^{-3}$
$E_{CO,ads}^b$	$1.96 \times 10^8 \text{ J kmol}^{-1}$
$k_{CO,ads}^0$	$6.02 \times 10^6 \text{ s}^{-1}$