Modeling, simulation and experimental validation of a PEM fuel cell system

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\section*{A B S T R A C T}

The aim of this work is the development and experimental validation of a detailed dynamic fuel cell model using the gPROMS modeling environment. The model is oriented towards optimization and control and it relies on material and energy balances as well as electrochemical equations including semi-empirical equations. For the experimental validation of the model a fully automated and integrated hydrogen fuel cell testing unit was used. The predictive power of the model has been compared with the data obtained during load change experiments. A sensitivity analysis has been employed to reveal the most critical empirical model parameters that should be estimated using a systematic estimation procedure. Model predictions are in good agreement with experimental data under a wide range of operating conditions.

\section*{1. Introduction}

Fuel cell (FC) systems have received significant attention in the past 15 years and they are expected to play an important role in future power generation facilities. FC systems are part of a promising environmentally friendly electricity generating technology, which can be used for stationary and mobile applications. The existing categories of FC systems are mainly based on the type of electrolyte and the operating conditions. The choice of the operating region leads to different characteristics for the system regarding its profitability, effectiveness and safety. Lifetime and reliability appear to be important considerations to successfully achieve the commercialization of such systems. In recent years there is an increasing interest in utilizing proton exchange membrane (PEM) fuel cell systems for small portable or stationary applications. This type of FC is currently considered to be in a relative more developed stage. PEMFCs utilize hydrogen and air to produce electricity and water, have high power density, use solid electrolyte, have long stack life, as well as low degradation due to corrosion. The critical operating parameters are mainly the regulation of flow of air and hydrogen feeds, pressure, heat and management of water. The performance of a PEMFC is greatly affected by the operating parameters. Within a PEM fuel cell several processes occur, but those that have the dominant influence on the performance are: (a) the electrochemical reactions in the catalyst layers, (b) the proton transfer in the electrolyte membrane layer and (c) mass transport within all regions. From these processes some management issues arise related to water, heat and gas. To achieve stable and good performance these management issues need to be carefully handled. This can be achieved by optimizing the corresponding operating parameters such as the reactant humidity, the temperature, the gas flow rate and the pressure.

The development of a dynamic model incorporating the above critical parameters should be able to describe the dynamic response of the system to the variation of the values of the input variables. The optimal operation of such a system, which is described by both measured and unmeasured variables, demands for the use of a model based approach of the control problem. The objective of this work is to derive a validated control oriented dynamic mathematical model of the fuel cell, which can be used to predict the system voltage as a function of current demand, taking into consideration operating parameters like temperature, humidity, pressure and reactant mass flows.

This paper is organized as follows: Section 1 presents a literature review of FC modeling following by a description of the system setup. In Section 2 the modeling of the fuel cell is presented, while the subsequent section presents the activation procedure of the system and the response of the system under different operating conditions. Section 4 introduces a parameter estimation procedure followed by an extensive model validation. Concluding remarks are drawn in Section 5.
Nomenclature

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<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tr>
<td>$a$</td>
<td>species activity</td>
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<tr>
<td>$A$</td>
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<td>$c$</td>
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<tr>
<td>$C_p$</td>
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<td>Faraday constant ($C/mol$)</td>
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<td>$y$</td>
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<td>$z$</td>
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Greek letters

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<td>$\varepsilon$</td>
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<td>$\theta$</td>
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<td>$\omega$</td>
<td>humidity ratio or variance model parameter</td>
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Subscripts and superscripts

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<td>generation</td>
</tr>
<tr>
<td>$\text{GDL}$</td>
<td>gas diffusion layers</td>
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1.1. Literature review

Many theoretical works for PEM fuel cell models and review studies can be found in the literature. Cheddie and Munroe (2005) presents a comprehensive review of PEM fuel cell models. An analysis of fuel cell modeling is presented in Haraldsson and Wipke (2004) where the focus is on the evaluation of models. The review by Sousa and Gonzalez (2005) is concerned with modeling at the cell level. More recently, a detailed review of PEM modeling and SOFC modeling is presented in Bavarian (2010). In general, mechanistic modeling has many advantages regarding the thorough investigation of the fuel cell’s insight and increased accuracy on phenomena analysis, but in some cases a model that responds in real time without many internal details is adequate enough. On the contrary, the semi-empirical approach can produce rapidly models able to describe the fuel cell response without the need of insight process details. Therefore they can be used to accurately predict the fuel cell system performance for engineering applications, such as small distributed electrical generation systems, portable electronics and vehicles (Moreira & da Silva, 2009). All of these models are reduced in terms of dimensionality and comprehensiveness.

A pioneering work on PEM fuel cell modeling is presented by Amphlett et al. (1995a, 1995b), where a steady-state model for the Ballard Mark IV fuel cell has been proposed that combines performance losses into parametric equations based on cell operating conditions, such as pressure and operating temperature. Mann et al. (2000) extended that model and presented a generalized steady-state electrochemical model, based also on Springer et al. (1991) and on the experimental data of Buchi and Scherer (1996) for the resistance of the membrane. Amphlett et al. (1996) proposed a transient model to predict efficiency in terms of voltage output and heat losses and includes heat transfer coefficients for the stack and an energy balance.

Golbert and Lewin (2004) developed a transient along-the-channel model for control purposes, which includes mass balances of liquid water and water vapor and heat transfer between the solid, the channels and the cooling water. Pukrushpan et al. (2004) presented a transient dynamic model, which includes the in-compressor flow and inertia dynamics, the manifold filling dynamics, the reactant partial pressures and the membrane humidity. Yerramalla et al. (2003) considered the humidifier and stack pressure. A linear and a nonlinear model were developed and the results showed the risk involved with linearizing the model.

A common simplification in contributions (Khan & Iqbal, 2005; Pukrushpan et al., 2004; Yerramalla et al., 2003) is that the tempera-
ture transient behavior was neglected. Xue et al. (2004) considered the effect of temperature transient behavior and used a three control volume approach to develop a set of dynamic equations that govern the system dynamics. Pathapati et al. (2004) developed a complete fuel cell system-level that include mass and energy balance equations for the gases and the dynamics of flow and pressure in the channels, along with the capacitor effect of charge double layer. Muller and Stefanopoulou (2006) presented a model for the thermal dynamics containing a power section and a humidification section and have compared experimental and theoretical data to validate it.

Lee and Lalk (1998) used an object-oriented approach based on stationary equations and they analyzed the temperature variation and thermal efficiency under regular load fluctuation. The influence of flooding on the dynamic behavior was modeled by McKay et al. (2005). Both gas diffusion layers (GDLs) and gas flow fields have been modeled, considering lumped parameters, by dividing each GDL into three control volumes and each flow field into one. More recently, a simple empirical equation has been introduced by del Real et al. (2007), to model the fuel cell voltage with variations in main variables. The fluid dynamics part of their model is based on (McKay et al., 2005) but the GDL has simpler structure reducing the computational cost.

The aforementioned models describe the evolution of the semi-empirical modeling approach. Although these models do not include many details of the system and they focus on specific operating conditions, in contrast with the analytical and mechanistic CFD models, they are very useful for application to real systems and control studies. A significant modeling effort has been done recently aiming to achieve the proper tradeoff between the usability and the accuracy of the semi-empirical based models. A summary of key contributions from the open literature is presented in Table 1. The enumeration is based on the year of publication. For each work a summary is presented along with the dimensionality and the state.

Fig. 1 illustrates the dimensionality and the system state, along with the existence of temperature and water management subsystems. The presented models can be steady state or dynamic and they study the response of the system to changes and its performance under various conditions. Each work has a specific purpose oriented towards fast development and considers only the required amount of detail needed for the scope of the project involved. It is important to note that these models are either one dimensional or lumped parametric models. When the dimensionality is ignored, usually the temperature variation and the water handling are also ignored and vice versa. The former focuses on simulating the fuel cell polarization curve while the latter generally pays more attention to thermodynamic aspects. These models are used in practical applications and it has been recognized that although a large number of theoretical models have been developed recently, an analogous number of semi-empirical models has been developed too.

Compared to all these models, the model presented in this work is developed for the purpose of on-line control in a power generation unit. As such, it needs to have reduced execution times and enough accuracy for control. It is important to include details regarding the thermal behavior of the system as the regulation of the flow and the temperature are considered. Thus an approach that combines both empirical and mechanistic equations is employed. The proposed model has the potential to couple both the theoretical validity and the inherent simplicity of the empirical application.

### 2. Dynamic model of the PEM FC

The proposed model relies on mass and energy conservation equations combined with equations having experimentally defined parametric coefficients thus resulting in a semi-empirical dynamic model. To model mass transport phenomena a five volume approach was adopted. The model accounts for mass dynamics in the gas flow channels, the gas diffusion layers (GDL) and the membrane. The equation of the voltage as a function of the current and the relationship between the current drawn from the fuel cell and the consumption of the reactants describe the operation of the FC. Finally in this scheme the energy balance equation of the fuel cell was also integrated.
2.1. Structural model analysis and assumptions

To simplify the overall modeling framework and reduce the computational requirements several assumptions have been employed without sacrificing the accuracy of the model. Some of these are theory related and others were derived from the operation of the testing unit. The theory related are:

(a) the ideal gas law holds for gases which are uniformly distributed,
(b) the temperature is uniform at the anode and the cathode side,
(c) each channel is homogeneous in respect to pressure as all channels have a fixed length volume.

The assumptions derived from the operation of testing unit are:

(a) humidified hydrogen and air are fed in the FC,
(b) the produced water is continuously removed through the cathode flow,
(c) the condensed water in the anode channel is dragged by the flow of the unreacted hydrogen.

2.2. Mass dynamics

The model equations consist of material balances of all components whereas every gas follows the ideal gas law. Therefore mass of each gaseous component is described through the partial pressure of each gas in the material balances. The mass balance is applied to the cathode and the anode channel volumes for the respective species. Also the inlet and outlet flows of each channel and the exchange flow between the gas diffusion layers are incorporated. The mass transport throughout each FC volume that has been considered in the model is graphically illustrated in Fig. 2.

2.2.1. Mass balances in cathode and anode channels

The model equations consist of the material balances of each species. Every individual gas follows the ideal gas equation. The concentration of each gas in the channel is calculated based on conservation of mass assuming that the channel is homogeneous with respect to concentration and temperature. Applying mass balance to the cathode channel volume, assessing the inlet and outlet flows of the channel and the exchange flow between the channel and the gas diffusion layer, the following equations are derived (Zioukou, Voutetakis, Papadopoulou, & Georgiadis, 2010):

\[
\frac{dm_{O_2,cach}}{dt} = m_{O_2,cach,in} - m_{O_2,cach,out} - m_{O_2,GDL} \tag{1}
\]

\[
\frac{dm_{N_2,cach}}{dt} = m_{N_2,cach,in} - m_{N_2,cach,out} \tag{2}
\]

\[
\frac{dm_v,cach}{dt} = m_v,cach,in - m_v,cach,out + m_v,cach,GDL + m_{evap,cach} \tag{3}
\]

\[
m_{v,cach,in} - m_{v,cach,out} - m_{evap,cach} = 0 \tag{4}
\]

In order to calculate the inlet mass flow rate of the individual species at the cathode (oxygen, nitrogen, vapor) the ratio of the mass of water vapor to the mass of dry air (\(\omega\)) is used which is also referred as humidity ratio.

\[
\omega_{cach,in} = \frac{m_v,cach,in}{m_{v,cach,in}} = \frac{M_v}{M_a} \frac{\phi_{cach,in}P_{sat}(T_{cach,in})}{\phi_{cach,in}P_{cach,in}(T_{cach,in})} \tag{5}
\]

The relative humidity (\(\phi\)) gives a good representation of the humidity of the mixture as the maximum amount of water that the air can hold (saturation) is included. The saturation pressure (\(P_{sat}\)) is calculated using the equations proposed in Nguyen and White (1993).

![Fig. 2. Structure of the dynamic model.](image)
The mass flow rate of dry air \( (\dot{m}_{a,\text{cach,in}}) \) and vapor \( (\dot{m}_{v,\text{cach,in}}) \) entering the cathode is

\[
\dot{m}_{\text{cach,in}} = \dot{m}_{a,\text{cach,in}} + \dot{m}_{v,\text{cach,in}}
\]

(6)

\[
\dot{m}_{a,\text{cach,in}} = \frac{1}{1 + \alpha_{\text{ca,in}}} \dot{m}_{\text{cach,in}}
\]

(7)

\[
\dot{m}_{v,\text{cach,in}} = \frac{\alpha_{\text{ca,in}}}{1 + \alpha_{\text{ca,in}}} \dot{m}_{\text{cach,in}}
\]

(8)

The mass flow rates of the oxygen and nitrogen to the cathode channel are calculated as follows:

\[
\dot{m}_{i,\text{cach,in}} = x_{i} \dot{m}_{a,\text{cach,in}} = x_{i} \frac{1}{1 + \alpha_{\text{ca,in}}} \dot{m}_{\text{cach,in}}, \quad i = [O_{2}, N_{2}]
\]

(9)

The mass fraction of oxygen \( (x_{O_{2}}) \) and nitrogen \( (x_{N_{2}}) \) in the dry air are defined as:

\[
x_{O_{2}} = \frac{y_{O_{2}} M_{O_{2}}}{M_{a}}
\]

(10)

\[
x_{N_{2}} = (1 - y_{O_{2}}) M_{N_{2}} M_{a}^{-1}
\]

(11)

The molar mass of dry air \( (M_{a}) \) is expressed by the sum of the mass fraction of oxygen and nitrogen and the respective molar masses:

\[
M_{a} = y_{O_{2}} M_{O_{2}} + (1 - y_{O_{2}}) M_{N_{2}}
\]

(12)

The above Eqs. (1)–(12) describe the dependence of masses from the inlet mass flows in the channel and the dynamics in the cathode’s GDL. The outlet mass flows are also required to conclude the description of the dynamics evolving at the cathode. We assumed that no liquid water enters the cathode or the anode channel. Also, the membrane allows only the transport of water in vapor state, due to its waterproof nature. Therefore the liquid water is produced by the reaction inside the cathode and part of it is evaporated or condensed inside the channel. The evaporation/condensation dynamics inside the cathode is expressed by:

\[
\dot{m}_{\text{evap, cach}} = (p_{\text{out}} - T_f c) - \dot{m}_{v,\text{cach}}
\]

(13)

The overall mass balance of the water in liquid phase is:

\[
\dot{m}_{\text{cach,out}} = \dot{m}_{\text{cach,Cond}} - \dot{m}_{\text{evap, ca}}
\]

(14)

The outlet mass flow rate of the oxygen, nitrogen and vapor in the cathode channel can be determined by:

\[
\dot{m}_{k,\text{cach,out}} = \frac{\dot{m}_{k,\text{cach}}}{\dot{m}_{\text{cach,in}} + \dot{m}_{v,\text{cach}}}, \quad k = [O_{2}, N_{2}, v]
\]

(15)

At the cathode the condensed liquid water is dragged by the air, so the outlet flow is:

\[
\dot{m}_{\text{cach,out}} = K_{\text{cach,out}} (p_{\text{cach}} - p_{\text{out}})
\]

(16)

The partial pressures of the gases in the channel are calculated using the ideal gas law and the overall cathode pressure is determined by the summation of the partial pressure of each species:

\[
p_{k,\text{cach}} = \frac{RT_f}{\dot{m}_{k,\text{cach}}}, \quad k = [O_{2}, N_{2}, v]
\]

(17)

\[
p_{\text{cach}} = p_{O_{2},\text{cach}} + p_{N_{2},\text{cach}} + p_{v,\text{cach}}
\]

(18)

The equations that describe the anode part of the fuel cell are analogous to the ones describing the cathode part. The values of all parameters used for channel dynamics are summarized in Table 2.

### Table 2

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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<tbody>
<tr>
<td>(m_{\text{f,c}})</td>
<td>1.378 kg</td>
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<tr>
<td>(c_{\text{p,c}})</td>
<td>772.57 J/(kg K)^{-1}</td>
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<tr>
<td>(A_{\text{c}})</td>
<td>25 cm^2</td>
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<tr>
<td>(V_{\text{cach}}, V_{\text{cach}})</td>
<td>0.136 x 10^{-4} m^3</td>
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<tr>
<td>(\delta_{\text{cach}}, \delta_{\text{cach}})</td>
<td>1.25 mm</td>
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<tr>
<td>(K_{\text{cach, out}})</td>
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<tr>
<td>(K_{\text{cach, out}})</td>
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<tr>
<td>(K_{\text{cach}})</td>
<td>100 s^{-1}</td>
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</tbody>
</table>

### 2.2.2. Gas diffusion layer (GDL) dynamics

Each gas diffusion layer is considered as a volume with homogeneous properties. A mixture of hydrogen and water vapor flows through the anode GDL, while a mixture of oxygen, nitrogen, and water vapor flows through the cathode GDL. The above gases must diffuse throughout the GDL to reach the membrane. Nitrogen diffusion is neglected since it is an inert gas. The oxygen and hydrogen mass flow rates between the GDL and the cathode and the anode channel respectively are described by:

\[
\dot{m}_{k,\text{GDL}} = A_{\text{f,c}} M_{k} N_{k,\text{GDL}}, \quad k = [O_{2}, H_{2}]
\]

(19)

The molar flux of the vapor that is generated via the electrochemical reaction and the molar fluxes of the reactants are calculated from the electric current and the stoichiometry of the reaction as follows:

\[
N_{e,\text{gen}} = \frac{I}{2F A_{\text{f,c}}}
\]

(20)

\[
N_{O_{2},\text{GDL}} = \frac{I}{4F A_{\text{f,c}}}
\]

(21)

\[
N_{H_{2},\text{GDL}} = \frac{I}{2F A_{\text{f,c}}}
\]

(22)

The water vapor mass flow rate depends on the membrane active area, the vapor molar mass and the vapor diffusion molar flux flow between GDL and anode and cathode:

\[
\dot{m}_{k,\text{GDL}} = A_{\text{f,c}} M_{k} N_{e,k}, \quad k = [an, ca]
\]

(23)

where \(N_{e,k}\) is the molar flow rate per unit area (flux) of the vapor diffusion which is calculated by the effective diffusivity \((D_{eff})\) the thickness of the diffusion channels \((\delta_{\text{GDL}})\) and the concentration gradients \((c_{v,an,\text{GDL}}, c_{v,ca,\text{GDL}})\):

\[
N_{e,k} = -D_{\text{eff}} [H_{2} O] c_{v,k} c_{v,k} - c_{v,\text{GDL}} / \delta_{\text{GDL}}
\]

(24)

As the oxygen is assumed to be in the same pressure with the channel, diffusion will be imposed by the electrochemical reaction. The effective diffusion coefficient that will be used for the calculation of the pressure is a function of the porosity \((\varepsilon_{por})\) of the layer as described in Nam and Kaviany (2003):

\[
D_{\text{eff}} = D_{\text{ref}} \varepsilon_{\text{por}} \left( \frac{\varepsilon_{\text{por}} - \varepsilon_{p}}{1 - \varepsilon_{p}} \right) da
\]

(25)

where \(\varepsilon_{p}\) is a percolation threshold which for porous media is composed of two-dimensional, long and overlapping, random fiber layers, \(\varepsilon_{p}\) is equal to 0.11 and \(da\) is an empirical constant which is 0.785 for cross-plane diffusion (Dutta et al., 2001).

The partial pressure of water vapor in each GDL is calculated through the respective mass balance equation:

\[
\frac{dp_{v,\text{an,\text{GDL}}}}{dt} = RT_f \frac{N_{v,\text{gen}} + N_{v,\text{mem}} - N_{v,\text{ca}}}{\delta_{\text{GDL}}}
\]

(26)

\[
\frac{dp_{v,\text{an,\text{GDL}}}}{dt} = RT_f \frac{N_{v,\text{an}} - N_{v,\text{mem}}}{\delta_{\text{GDL}}}
\]

(27)
Since a uniform diffusion is assumed, the partial pressures of oxygen and hydrogen inside the respective GDL are expressed by:

\[ P_{O_2,GDL} = P_{O_2,cach} - \frac{RT_f \delta_{GDL}}{D_{O_2}} N_{O_2,GDL} \] (28)

\[ P_{H_2,GDL} = P_{H_2,cach} - \frac{RT_f \delta_{GDL}}{D_{H_2}} N_{H_2,GDL} \] (29)

2.2.3. Membrane model

The membrane hydration model calculates the water mass flow rate that crosses the membrane and the water content in the membrane. Given that the membrane only allows the transport of vapour water, the following equations are only considering gaseous water, which is also assumed to be uniformly distributed over the surface area of the membrane. A set of semi-empirical equations are employed from Dutta et al. (2001). The overall mass flow rate of vapour that crosses the membrane is given by:

\[ m_{v,memb} = M_H_2O A_k N_{v,membr} \] (30)

The flow of vapour water through membrane is affected by two phenomena, the electro-osmotic drag \( (N_{v,osm}) \), caused by hydrogen ion drag, and the back diffusion \( (N_{v,diff}) \), caused by water concentration gradient between the cathode and the anode. These two phenomena are mathematically expressed by:

\[ N_{v,osm} = n_d \frac{1}{\delta_{mem}} \] (31)

\[ N_{v,diff} = a_d D_w \frac{c_{v,cach} - c_{v,anch}}{\delta_{mem}} \] (32)

where \( n_d \) is the drag coefficient, \( D_w \) is the diffusion coefficient, \( \delta_{mem} \) is the membrane thickness and \( c_{v,anch}, c_{v,cach} \) are the water concentrations in anode and cathode channel respectively. Based on the combination of those phenomena the net overall molar vapor flow \( (N_{v,membr}) \) across the membrane is expressed by:

\[ N_{v,membr} = N_{v,osm} - N_{v,diff} \] (33)

The vapor concentration at anode and cathode surfaces \( (c_{v,anch}, c_{v,cach}) \) of the membrane is a function of the water content at these surfaces and it is calculated by the membrane dry density \( n_{mem,dry} \) and the membrane dry equivalent weight \( M_{mem,dry} \):

\[ c_{v,k} = \frac{n_{mem,dry}}{M_{mem,dry}} \lambda_k, \quad k = \{ anch, cach \} \] (34)

To calculate the water content at the membrane surfaces the vapor activity inside each GDL is (Springer et al., 1991):

\[ \lambda_{k,ch} = 0.043 + 17.81 \lambda_k - 39.85 \lambda_k^2 + 36 \lambda_k^3, \quad k = \{ an, ca \} \] (35)

The vapor activity \( (\phi_k) \) is the ratio of the water vapor pressure to the saturation pressure which in case of gas it is equivalent to relative humidity \( (\lambda_k) \) of each GDL channel.

\[ \phi_{GDL} = \frac{P_{v,k,CHDL}}{P_{sat}(T_f)}, \quad k = \{ an, ca \} \] (36)

The relationship between the water content at the anode surface of the membrane and the electro-osmotic drag coefficient \( n_d \) is given by Dutta et al. (2001):

\[ n_d = 0.0029 \lambda_{anch}^2 + 0.05 \lambda_{anch} - 3.4 \times 10^{-19} \] (37)

The water diffusion coefficient \( (D_w) \) is expressed by the membrane water content at the anode surface:

\[ D_w = D_{anch} \exp \left( 24416 \left( 1 - \frac{1}{T_f} \right) \right) \] (38)

<table>
<thead>
<tr>
<th>Table 3</th>
<th>Parameter set.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parameter</td>
<td>Value</td>
</tr>
<tr>
<td>( M_{mem,dry} )</td>
<td>1.1 kg.mol(^{-1})</td>
</tr>
<tr>
<td>( \rho_{mem,dry} )</td>
<td>1.98 × 10(^{-3}) kg.m(^{-3})</td>
</tr>
<tr>
<td>( \delta_{mem} )</td>
<td>8.89 × 10(^{-3}) m</td>
</tr>
<tr>
<td>( \delta_{ca} )</td>
<td>1.9 × 10(^{-3}) m</td>
</tr>
<tr>
<td>( \varepsilon_{par} )</td>
<td>78%</td>
</tr>
</tbody>
</table>

where \( D_{anch} \) is modified based on the relative humidity level that affects the water content at the anode surface \( (\lambda_{anch}) \):

\[ \lambda_{anch} = \begin{pmatrix} 10^{-10} & \lambda_{anch} < 2 \\ 10^{-10}(1 + 2(\lambda_{anch} - 2)) & 2 \leq \lambda_{anch} < 3 \\ 10^{-10}(3 - 1.67(\lambda_{anch} - 3)) & 3 < \lambda_{anch} < 4.5 \\ 1.25 \times 10^{-10} & \lambda_{anch} \geq 4.5 \end{pmatrix} \] (39)

The physical parameters in the membrane model and the GDL dynamics are taken from the fuel cell specifications used on the actual unit. These parameters are summarized in Table 3.

2.3. Energy balance

A dynamic thermal model describes the dynamic behavior of the fuel cell temperature based on the overall energy balance equation of the fuel cell. The amount of energy which is not converted to electrical power is expressed by a set of various energy terms, that are associated with the fuel cell operation:

\[ m_k C_{p,k} \left( \frac{dT_f}{dt} \right) = \Delta H_{an} + \Delta H_{ca} + \Delta H_{chem} + \Delta Q_{R} - \Delta Q_{out} - \Delta Q_{conv} - P_{elec} \] (40)

The above equation takes into account the enthalpy flow rates associated with input and output streams at the anode and the cathode, the rate of energy produced by the chemical reaction, the rate of energy which is released to the environment through radiation, the rate of heat transferred to the cooling system and finally the electric power. The changes of the anode and cathode energy flow rates are given by the changes of enthalpy as follows:

\[ \Delta H_{an} = \dot{m}_{H_2} \Delta H_{H_2} + \dot{m}_{H_2O,an} \Delta H_{H_2O,an} \] (41)

\[ \Delta H_{ca} = \dot{m}_{H_2} \Delta H_{H_2} + \dot{m}_{H_2O,ca} \Delta H_{H_2O,ca} \] (42)

Only a part of the oxygen and hydrogen fed in the inlet channels participate in the reaction. Therefore the remaining amount of energy pass through the system to the outlet. For each gas the enthalpy change is calculated as follows:

\[ \Delta H_{H_2} = \dot{m}_{H_2,anch,in} \Delta H_{H_2,an,in} - \dot{m}_{H_2,anch,out} \Delta H_{H_2} \] (43)

\[ \Delta H_{H_2O,ch} = \dot{m}_{H_2,anch,in} \Delta H_{H_2O,an,in} + \dot{m}_{H_2O,anch,ca} \Delta H_{H_2O,ca} \] (44)

\[ \Delta H_{H_2O,ca} = \dot{m}_{H_2,anch,in} \Delta H_{H_2O,an,in} + \dot{m}_{H_2O,anch,ca} \Delta H_{H_2O,ca} \] (45)

It is assumed that the required energy for the change of water phase is negligible therefore it is not incorporated in the above equations. In order to calculate the enthalpy differences at the anode and the cathode, the changes of mass specific enthalpies with respect to a reference state of the participated gases are used, assuming constant specific heat.

\[ \Delta h_{i,an,in} = C_p(T_{an,in} - T_{ref}), \quad i = [H_2, H_2O, v] \] (46)
\[\Delta h_{\text{ca,in}} = C_p(T_{\text{ca,in}} - T_{\text{ref}}), \quad i = [O_2, N_2, H_2O, v] \]  
(47)

\[\Delta h_i = C_p(T_{\text{fc}} - T_{\text{ref}}), \quad i = [H_2, O_2, N_2, H_2O, I, l, H_2O_l] \]  
(48)

where \(T_{\text{ref}}\) is the reference temperature.

The reaction that converts the chemical energy into electricity and forms liquid water is always exothermic and the produced enthalpy is calculated as the difference between the enthalpy of the produced water and that of the reactants at the anode and the cathode GDL.

\[\Delta H_{\text{chem}} = m_{H_2,GDL}\Delta h_{H_2,an,in} + m_{O_2,GDL}\Delta h_{O_2,ca,in} - m_{H_2O,gen}\left(\Delta H_i(T_{\text{ref}}) - \Delta h_{H_2O,r}\right)\]  
(49)

where \(\Delta H_i\) is the mass specific enthalpy of formation of liquid water.

A part of the produced heat is released to the environment through radiation:

\[Q_{\text{rad}} = \varepsilon_{\text{em}}\sigma A_{\text{cell}}(T_{\text{fc}}^4 - T_{\text{ref}}^4)\]  
(50)

where \(\varepsilon_{\text{em}}\) is the emissivity of the fuel cell body, \(\sigma\) is the Stefan–Boltzmann constant and \(A_{\text{cell}}\) denotes the overall outer surface of the fuel cell.

As stated earlier due to the reaction an excess amount of heat is generated during the operation of the fuel cell since only a part of the produced enthalpy is converted to electrical energy and the rest is converted to thermal energy, resulting in an increase of the temperature. Also as the fuel cell has a different temperature than its environment, heat is lost through convection \(Q_{\text{conv}}\) to its environment. The amount of heat which is transferred to the surroundings consists of a natural convection term and a forced convection term.

\[Q_{\text{conv}} = Q_{\text{amb}} + Q_{\text{ld}}\]  
(51)

The heat loss to the environment caused by natural convection is expressed by:

\[Q_{\text{amb}} = h_{\text{amb}}A\sigma(T_{\text{fc}} - T_{\text{ref}})\]  
(52)

where \(h_{\text{amb}}\) is the natural convection heat transfer coefficient.

A cooling system is used for the removal of the excess heat and to maintain the desired fuel cell temperature. The heat energy removed by the cooling system is expressed by:

\[Q_{\text{ld}} = h_f\sigma A(T_{\text{fc}} - T_{\text{cl}})\]  
(53)

\[h_f = K_{\text{cl}}P_{\text{cl}}^{0.5}\]  
(54)

where \(h_f\) is the forced convective heat transfer coefficient and \(A_f\) is the effective surface for the cooling system. The forced convection heat transfer coefficient is calculated based on two experimentally defined parameters \((K_{\text{cl}}, K_{\text{clG}})\) and the power \(P_{\text{cl}}\) of the fans.

The heat supply for the initial heat up of the fuel cell is expressed by:

\[Q_k = P_kx_k\]  
(55)

where \(P_k\) is the power of the heater and \(x_k\) is the fraction of power used for heating. The parameters used in the energy balance are summarized in Table 4.

### 2.4. Electrochemical equations

Typical characteristics of FC are normally expressed in the form of a polarization curve, which is a plot of cell voltage versus cell current density. To determine the voltage–current relationship of the cell, the cell voltage has to be defined as the difference between an ideal Nernst voltage and a number of voltage losses as it is described in the current section. The main losses are categorized as activation, ohmic and concentration losses. The equation that takes into consideration the above losses expresses the actual cell voltage:

\[V_{\text{cell}} = E_{\text{Nernst}} - V_{\text{act}} - V_{\text{ohm}} - V_{\text{conc}}\]  
(56)

The above equation is able to predict the voltage output of PEM fuel cells of various configurations. Depending on the amount of current drawn the fuel cell generates the output voltage. The electric power produced by the system equals the product of the stack voltage \(V_{\text{cell}}\) and the current drawn \(I\):

\[P = I \cdot V_{\text{cell}}\]  
(57)

The Nernst voltage or open circuit voltage (OCV) falls as the current supplied by the stack increases. The reversible thermodynamic potential is calculated using the Nernst equation and can be expressed:

\[E_{\text{Nernst}} = E^0 + \frac{RT}{2F} \ln(p_\text{H}_2p_\text{O}_2^{1/2}p_\text{H}_2\text{O}^{-1})\]  
(58)

The activation losses are caused by the slowness of the reactions taking place on the surface of the electrodes. A portion of the voltage generated is lost because of the chemical reaction that transfers the electrons to or from the electrodes. The activation losses are described by the Tafel equation (Mann et al., 2000), which can be calculated as:

\[V_{\text{act}} = \xi_1 + \xi_2T + \xi_3T \ln(I) + \xi_4T \ln(c_{O_2})\]  
(59)

This description for the activation overvoltage takes into account the concentration of oxygen at the catalyst layer and various experimentally defined parametric coefficients.

At a later stage of the fuel cell operation, as current density rises, ohmic losses \((V_{\text{ohm}})\) prevail. They are derived from the membrane resistance to the flow of electrons through the material of the electrodes and the various interconnections, as well as by the resistance to the flow of protons through the electrolyte (Pathapati et al., 2004):

\[V_{\text{ohm}} = (\xi_5 + \xi_6T + \xi_7T^2)I\]  
(60)

Finally the mass transport or concentration losses result from the change in concentration of the reactants at the surface of the electrodes as the fuel is used. To calculate the diffusion losses a semi-empirical equation by (Kim et al., 1995) was used:

\[V_{\text{conc}} = \xi_8 \exp(\xi_9I)\]  
(61)

The empirical parameters are related to the conductivity of the electrolyte \((\xi_8)\) and to the porosity of the gas diffusion layer \((\xi_9)\). In the above equations \(K = 1.9\) represent experimentally defined parametric coefficients the value which can vary from stack to stack. The values of these parameters are presented in Table 5. Some of these parameters are defined by the estimation procedure as described in the subsequent Section 4.
Table 5
Electrochemical parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\xi_1$, $\xi_2$, $\xi_3$, $\xi_4$</td>
<td>$1.3205, -3.12 \times 10^{-3}, 1.87 \times 10^{-4}, -7.4 \times 10^{-5}$</td>
</tr>
<tr>
<td>$\xi_5$, $\xi_6$, $\xi_7$</td>
<td>$3.3 \times 10^{-1}, -7.55 \times 10^{-5}, 7.85 \times 10^{-4}$</td>
</tr>
<tr>
<td>$\xi_8$</td>
<td>$3 \times 10^{-5}, 6 \times 10^{-2}$</td>
</tr>
</tbody>
</table>

3. System setup and experimental study

In order to investigate the behavior of the fuel cell it is important to measure a variety of variables. For this purpose a small scale fully automated plant was designed and constructed at the laboratory of Process Systems Design and Implementation at CPERI/CERTH. This unit is able to measure all the necessary input signals, control the appropriate variables and adjust several system parameters. In the current study the operation of a single PEM fuel cell has been tested under a wide range of conditions.

3.1. System description

The unit setup is comprised of a PEM fuel cell working at a constant pressure and a power conversion device capable of controlling the current drawn from the FC. The fuel cell is integrated with several auxiliary components to form a complete system. The developed fuel cell testing unit (FCTU) has two hydrators to maintain proper humidity conditions inside the cell, which is crucial to ensure the optimal operation of the membrane. Two mass flow meters are used for the regulation of the hydrogen and the air flow and a temperature control subsystem for the FC, which includes an air cooling system and a heat up system. To prevent water from condensing in the line between the hydrators and the FC, a line heater with controller was used to maintain the temperature. This unit was designed based on a modular and flexible architecture and a simplified process and instrumentation diagram (P&ID) is depicted in Fig. 3.

The integrated system is equipped also with an electronic load, which simulates the power demands or the power fluctuations that occur in real systems that use fuel cells for power generation, with programmable characteristics depending on the output load requirements. It is operated in two different modes, the constant current (CC) mode and the constant voltage (CV) mode. In CC mode the load current is constant even though the voltage at the terminals of the load changes, while in CV mode the voltage is constant even though the current into the load changes. The activation procedure was performed using the CV mode to avoid any damages to the MEA and to determine the current span, the experiments for model validation were conducted in CC mode. After the determination of the maximum allowable current and since the activation stabilized the underlying system, the electronic load was operated in CC mode. In an application where a DC/DC converter is connected to the fuel cell, the converter requires for a constant current. However other applications might demand for variable voltage and current. Finally a sequence of small current steps was implemented with appropriate programming for the load in order to measure the dynamic response of the fuel cell.

3.1.1. Control system and data acquisition

The developed unit is fully automated using a supervisory control and data acquisition (SCADA) system that utilizes the industrial software ifiX (GE Fanuc). All system components (pumps, heaters, valves and so forth) are controlled through a computer based system by digital commands and pre-programmed procedures. The various temperatures and pressures are maintained at the required set points by the SCADA system, via decentralized PID controllers, allowing for independent gas conditions to the fuel cell. Furthermore, the automation system allows the executions of predetermined operations, offers safety management and performs data archiving.

3.1.2. Fuel cell specifications

A single PEM fuel cell with an active area of 25 cm$^2$ was used to produce experimental data and to validate the developed mathematic model described in the previous section. The detailed physical specifications of the fuel cell are presented in Table 6.

The unit cell contained parallel serpentine flow channels for gas delivery to both the cathode and anode of the cell. The catalyst layer is made of carbon supported platinum loading. The channel width is 1.25 mm and the depth is 1.72 mm. The membrane electrode assembly (MEA) is sandwiched between two current collectors and then between two non-porous graphite current collectors plates. The graphitic plate and the basic configuration of the fuel cell are presented in Figs. 4 and 5.

![Fig. 3. Fuel cell testing unit.](image)
Table 6
System physical parameters.

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nominal cell voltage</td>
<td>0.6 ± 0.05 V</td>
</tr>
<tr>
<td>Nominal current density</td>
<td>400 ± 50 mA/cm²</td>
</tr>
<tr>
<td>Operating temperature</td>
<td>60–75 ºC</td>
</tr>
<tr>
<td>Total mass</td>
<td>1.378 kg</td>
</tr>
<tr>
<td>Specific heat capacity</td>
<td>772.57 J/(kg K)⁻¹</td>
</tr>
<tr>
<td>Active area</td>
<td>25 cm² (3 cm × 5 cm)</td>
</tr>
<tr>
<td>Channel volume (anode, cathode)</td>
<td>0.136 × 10⁻⁸ m³</td>
</tr>
<tr>
<td>Membrane type</td>
<td>Nafion 1135</td>
</tr>
<tr>
<td>Backing layer catalyst loading</td>
<td>20 wt.% Pt/C</td>
</tr>
<tr>
<td>GDL type</td>
<td>Carbon paper</td>
</tr>
<tr>
<td>Bulk density</td>
<td>0.44 g cm⁻³</td>
</tr>
<tr>
<td>Heater resistance</td>
<td>0.867 kΩ (55.8 W)</td>
</tr>
</tbody>
</table>

3.2. Experimental study

Various experimental studies can be found in the literature exploring the dynamic behavior of a PEM fuel cell system. Each study focuses on a different aspect of the fuel cell operation such as step changes in current with operating temperature (Kim and Min, 2008), start-up behavior (Chen and Zhou, 2008), characterization of the electrical behavior (Kunusch et al., 2010), individual cell behavior (Jang et al., 2008; Sun et al., 2009). In this study the steady state and the dynamic behavior of the single PEM fuel cell system is investigated under various operating conditions. The single cell that was tested during our study was not conditioned, therefore after initial stabilization, the membrane had to be activated. The activation procedure was divided into two stages, the initial activation and the full activation of the membrane. The distinguishing characteristic between these stages was the minimum allowable voltage. Afterwards the performance of the system was tested against various conditions.

3.2.1. Activation procedure

The activation procedure consisted of reading the dynamic response of the cell voltage after the occurrence of small changes in the current load. A series of small fixed length step changes in current load with a specific range were applied, which constitute a cycle. A reference voltage point was set \( V_{ref} = 0.45 \text{ V} \) and used as an indicative point of comparison between each cycle in order to measure the evolution of the membrane activation. The nominal point of operation provided by the manufacturer was 0.40 A/cm² at 0.6 V and it constitutes an indication the membrane is ready for use. During the initial activation the voltage demand was regulated through a ramp procedure and gradually decreased from 1.0 V to 0.45 V and conversely with a step change of 100 mV every 10 s. On Fig. 6 the evolution of the current and power density are presented.

Fig. 6 indicated that the current density was initially steadily increased with time from line A to line D. After a series of cycles it reached a certain point where the response was stable but comparing to the nominal point it could be further improved. Therefore the full activation procedure was employed by applying the same ramp profile with some modification to the step interval (from 10 s to 30 s) and to the hold time at the lowest point (from 4 min to 1 min). The temperature and the pressure were regulated at 65 ºC and 1 Barg respectively, and the hydrogen and air flow were set at 2000 cc/min and 3000 cc/m. Fig. 6 illustrates that after each set of cycles the membrane is further activated, since the current density increases. During the activation stage the excess of hydrogen and of air flow is deliberately kept high to avoid any stressful conditions to the system. The polarization curve illustrates that the system remains at the area where the ohmic losses prevail and the voltage drop is not present due to lack of reactant. Also the current density was very close to the nominal one and after a series of cycles at the same conditions the membrane presented stable behavior (see Fig. 7).

3.2.2. Response of the system under different operating conditions

A detailed experimental study was performed in order to investigate the behavior of the system under different operating conditions. Thus a similar to the above cyclic operation procedure was applied. Furthermore the system was tested under stressful conditions (elevated pressure, low gas flows) in order to explore the boundaries of its performance. To avoid any influence on the measurements from one cycle to the next or between different
conditions, the fuel cell was operated for at least 60 min at nominal steady-state load (0.45 V). For every experiment the flow rate of reactants was kept constant at a flow relative to the maximum theoretical stoichiometric flow predicted by the maximum typical current density of the excess flow ratio is defined by:

\[ \lambda = \frac{\text{flow applied}}{\text{stoichiometric flow at maximum current density}} \]  \hspace{1cm} (62)

The first operating condition that has been tested was the fuel cell temperature at four different levels (50 °C, 60 °C, 65 °C, 70 °C). The hydration temperature was fixed at 70 °C, the system operated at ambient pressure (0 Barg) and the excess flow ratio for anode and cathode flows were 2.3 and 1.5 respectively. Figs. 8 and 9 illustrate the effect of temperature on the performance of the fuel cell in terms of delivered power and versus current density and voltage versus current density.

The lower operating temperature provided by the membrane manufacturer was 60 °C. At the low temperature (50 °C) a significant decrease in maximum power and current density was observed, which indicated that the full capacity of the fuel cell was not utilized. Between 60 °C and 65 °C the performance was similar up to the maximum delivered power but after that, the power at the elevated temperature was decreased at higher current densities. Finally a small difference exists between 65 °C and 70 °C and although the operation at higher temperature could deliver more power, to preserve the lifetime of the membrane, the chosen temperature for the experiments was 65 °C.

The second testing condition was the change of the hydration temperature at 65 °C, 80 °C and 90 °C, for both anode and cathode electrodes. The performance was improved for hydrotreated temperature up to 80 °C due to the increase of humidity which results in a decrease of the internal resistance. However the performance is decreased at 90 °C due to flooding phenomena. Since the suggested operating temperature from the previous experiment is 65 °C the hydrator temperature is chosen to be 5 °C to 10 °C higher. This results to avoid flooding and at the same time the membrane was adequately humidified.

After the investigation of the temperature and the humidity effect the flow rate and the pressure are investigated. For every case, the mass flow rates of reactants were determined by the excess flow coefficient (Eq. (62)). The tested excess ratios were for air 1, 2, 4, 6 which were translated to flow rates of 500 cc/min, 1000 cc/min, 2000 cc/min and 3000 cc/min respectively. At low excess ratio the oxidant is not sufficient and even at low current densities a fluctuation at the produced voltage is observed. Also after the maximum power point a sharp voltage drop appears which indicates a lack of oxidants in the channels probably due to flooding. On the other case side at high excess ratio (\( \lambda = 6 \)) the produced power was lower than the one with ratio 2 and 4. The water removal rate is analogous to the air flow rate which causes drying of the membrane and an increase to the electrical resistance. Therefore any ratio between 2 and 4 can deliver satisfactory results. The hydrogen flow rate had very limited influence on the performance and it was set to a stoichiometric ratio of 2.3 (500 cc/m) to maintain sufficient reaction.

Finally, the pressure is an important parameter for the fuel cell, since it affects the homogeneity and the partial pressure of the reactants in the channels, the inlet gas compositions and the diffusivities of the gases through diffusion layers and rate of electrochemical reaction. The pressure was maintained at a certain level by two pressure regulators at the outlet lines. At Figs. 10 and 11, a series of polarization curves are presented at different operating pressures (0–2 Barg). It can be observed that the elevated pressure is beneficial for the performance. Even at low current densities a noticeable improvement is observed as the activation overpotential decreases with an increase of the pressure. Between 1.5 Barg
and 2 Barg there was no apparent improvement. Furthermore at 1.5 Barg, the inlet pressure at the cathode side was increased and consequently the pressure difference was increased between the anode and the cathode. This is an unsafe operating condition which should be avoided for lifetime and safety issues. Therefore the preferred pressure was between 0 Barg and 1 Barg.

Fig. 12 illustrates the produced voltage after two current step changes for different pressure levels. The first change was from 8 A to 4 A and after 120 s a second change occurred, from 4 A to 6 A. It is observed that the voltage increases as the pressure increases and the system has the same fast dynamic response to current changes, regardless the pressure level.

This investigation was also carried out for different temperature, excess of reactants and humidity levels and it revealed the fast dynamic nature of the experimental system.

It is clearly derived from the results that the temperature and pressure have a predominant effect in the system. Also proper gas and water management are essential to achieve and maintain high power output. The increased gas flow rate is beneficial to fuel cell operation if the positive effects of increased availability of oxygen offset the negative effects of membrane dehydration. This study aims to determine the operating conditions window for safe and reliable operation of the system under consideration as summarized in Table 7.

The aforementioned experimental study will provide a baseline for the determination of the values of certain empirical parameters of the model.

4. Parameter estimation and model validation

In order to assess the validity of the developed model, the FC testing unit described in the previous section, was used to generate experimental data under various conditions. Power load profiles up to the maximum point have been used for the estimation of model parameters and for the experimental validation of the model. There are two sets of model parameters: physical or estimated. The physical parameters are based on the fuel cell hardware specifications and listed in Tables 2, 6 and 7 along with their values. The estimated parameters are the ones that cannot be physically determined. For this reason a formal systematic parameter estimation technique was employed in order to find the optimal values for the parameters. The purpose of this formal technique is to minimize the deviation between the model predictions and the experimental data, in that sense the resulting values are optimal.

The aforementioned model, which is used to derive the polarization curve, describes voltage as a function of the current, temperature and partial pressures. The polarization curve resulting from a set of electrochemical equations includes a few parameters, some of which are unknown, depending on the operating conditions, while others have been taken from the open literature.

When an experiment is executed, to obtain the polarization curve, the voltage (dependent variable) is measured directly, but the parameters not. The model response is sensitive to changes in the values of some of these parameters. The estimation of these critical parameters is a procedure which increases the predictive power of the model. The estimation procedure results in the determination of the optimal values for these parameters. After the adjustment of the model to the optimal values, a validation procedure was performed under different operating conditions to assess the model accuracy.

Table 7  
Selected operating conditions.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure (anode and cathode)</td>
<td>0 Barg</td>
</tr>
<tr>
<td>Temperature: fuel cell</td>
<td>65 °C</td>
</tr>
<tr>
<td>Temperature: hydrators/line</td>
<td>70 °C/120 °C</td>
</tr>
<tr>
<td>H2/air flow rate</td>
<td>500 cc/min/750 cc/min</td>
</tr>
</tbody>
</table>
4.1. Procedure and representative set of data used

Various experiments were conducted which revealed that according to the literature the change of the current is a critical input variable of the system which can therefore be used as a manipulated variable for the fuel cell system. The technique that was followed for the parameter estimation relies on the variation of current, which is directly connected to the actual power demand and affects the temperature and the partial pressures of the reactants in the fuel cell. Consequently the change of the current affects voltage according to the polarisation curve. Thus, the focus of the parameter estimation procedure is on the semi-empirical equations that describe the voltage losses. The estimation of critical voltage drop coefficients was made with using measurements allowed the optimal tuning of the semi-empirical model.

The experimental procedure consists of reading the dynamic response of the cell voltage and cell power after the occurrence of small successive changes in the load demand. This experimental procedure intended to derive the fuel cell polarization curve and acquire data from the overall operational range. Two sets of experiments were conducted for the generation of data for the parameter estimation procedure. More specifically, in each experiment 11 different load levels were requested from the fuel cell. The duration of each request was set to 2 min which is sufficient enough to obtain a steady-state voltage. The requested load varied from 0 A to 20 A with a step change of 2 A. The varying operating condition was the pressure, 0 barg and 1 barg. The FC temperature was kept constant at 65 °C and the humidification temperature was 75 °C. The air flow was 2000 cc/min and the hydrogen flow 500 cc/min. The reproducibility of the experimental procedure and the accuracy of the results were ensured by the two above mentioned sets of experiments, consisting of four experiments at each condition.

4.2. Parameter estimation and results

The developed model has been implemented in the gPROMS modeling environment (PSE Ltd., 2010). Once the model is constructed, a sensitivity analysis has been performed to identify the most critical model parameters which are further optimally selected. A detailed sensitivity analysis based on simulation results revealed the most critical parameters to be estimated. Thus comparing the prediction of the model to the experimental data a major deviation was observed at the beginning of the polarization curve, the area where the activation losses appear. Therefore a parameter related to the activation losses equation was selected for the estimation procedure. Another important deviation was observed in the slope of polarization curve at the area of the ohmic losses. This indicates that the parametric coefficients at the ohmic losses should optimally be estimated. Finally the area of the concentration losses was not taken into consideration, as it should be avoided during normal operation, in order to avoid system failure.

A nonlinear regression technique with a constant variance model defining a maximum likelihood estimation problem was employed to determine the optimal values for the selected parametric coefficients. For the scope of the estimation procedure the model parameters (ξ1, ξ2) are expressed as (θ1, θ2) representing the estimated variables used in the maximum likelihood problem.

In the estimation procedure the parameters can be fitted independently or simultaneously. Although the independent parameter estimation is numerically more reliable, it cannot represent the coupling between the parameters; therefore the simultaneous approach is used. The data acquisition of the system variables is performed by various sensors. Each variable is associated with one sensor, which introduces an uncertainty in the data measurements or otherwise stated a measurement error. When solving an estimation problem the measurement errors (ξi) are modeled by a variance model. In the aforementioned testing unit the measurement errors are assumed to be statistically independent and normally distributed with zero mean and therefore a constant variance model was used:

$$\sigma^2 = \sigma^2(z, B) = \omega^2(z^2 + \varepsilon)$$ (63)

where $z$ is the model prediction of the measured quantity, $\omega$ is a parameter of the variance model and $\varepsilon$ is a small but non-zero constant that ensures that the variance is still defined for predicted values that are equal to zero or very small (see Table 8).

The proposed non-linear regression technique attempts to model the relationship between the measured data and the response of the model by fitting a quadratic equation to observed data. The estimation procedure is based on a maximum likelihood formulation which provides simultaneous estimation of parameters in the dynamic model of the fuel cell and the variance model of the measuring sensors. The maximum likelihood goal can be expressed by the objective function:

$$J_b = N \ln(2\pi) + 2 \min_{\omega, \varepsilon} \sum_{i=1}^{N} \sum_{j=1}^{m} \left[ \ln(2\pi) + [z_{ij} - z_{ij}]^2(\omega^2 + \varepsilon) \right]$$ (64)

where $N$ is the total number of measurements taken during all experiments, $\theta$ are the model parameters to be estimated, constrained between a lower and an upper bound, $nE$ are the number of experiments performed ($nE = 8$), $nVi$ are the number of variables measured in the $i$th experiment ($nVi = 2$) and $nMij$ are the number of measurements of the $j$th variable in the $i$th experiment ($nMij = 60$). The solution of the maximum likelihood problem determines the values for the uncertain physical and variance model parameters, $(\xi_1, \xi_2)$. These values maximize the probability that the dynamic model will predict the measurement values obtained from the experiments. The measured variables ($\hat{z}_1, \hat{z}_2$) are the produced voltage and power, having a sample time of 2 s and ($z_1, z_2$) are the model predicted values. The variation of the load is handled as a piecewise constant term during the estimation procedure, using the same interval duration (2 min) as described in the experimental procedure. After the solution of the aforementioned problem in gPROMS the estimated parameter values are summarized in Table 9.

The estimation results have sufficient accuracy and therefore the values of the parameters can be applied to the model for its validation. This is justified by the fact that the standard deviation is more than two orders of magnitude lower than the estimated value. Also a clear indication of this accuracy is the 95% t-values of both estimated parameters which are larger than the reference t-value.

Besides the 95% confidence interval of each estimation parameter, another measure that indicates that the parameters are optimally defined is the confidence ellipsoid. It takes into account the correlation between the estimates of $\theta_1$ and $\theta_2$. The individual 95% confidence intervals are appropriate to validate the possibility of specifying the range for each parameter under consideration independently of the value of the other parameter. The confidence ellipsoid interprets these intervals simultaneously.

<table>
<thead>
<tr>
<th>Table 8: Parameters for estimation.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model prediction</td>
</tr>
<tr>
<td>$z_1$</td>
</tr>
<tr>
<td>$z_2$</td>
</tr>
</tbody>
</table>

This alternative significance test is considered in Fig. 13 and it is based on whether the elliptically shaped area representing the joint confidence region encloses the optimal point at its center neighborhood. The joint confidence region illustrates that the parameters are known with the same precision and that the estimated point is optimal for both of them.
Table 9

Results of parameter estimation.

<table>
<thead>
<tr>
<th>Variables</th>
<th>Est. value</th>
<th>Up bound</th>
<th>Low bound</th>
<th>Std. dev.</th>
<th>95% Conf. Int.</th>
<th>95% t-value</th>
<th>Ref. t-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \theta_1 )</td>
<td>1.3205</td>
<td>1.4</td>
<td>0.954</td>
<td>1.04 ( \times ) 10(^{-3} )</td>
<td>2.04 ( \times ) 10(^{-3} )</td>
<td>6.464 ( \times ) 10(^2 )</td>
<td>1.645</td>
</tr>
<tr>
<td>( \theta_2 )</td>
<td>7.85 ( \times ) 10(^{-4} )</td>
<td>4.3 ( \times ) 10(^{-3} )</td>
<td>1.1 ( \times ) 10(^{-6} )</td>
<td>4.12 ( \times ) 10(^{-6} )</td>
<td>8.1 ( \times ) 10(^{-6} )</td>
<td>0.969 ( \times ) 10(^4 )</td>
<td></td>
</tr>
</tbody>
</table>

![Fig. 13. Confidence ellipsoid.](image)

Another measure which indicates that the estimation was performed successfully is the examination of the residuals using a corresponding diagram which illustrates the distribution of the observed error against time. Fig. 14 illustrates a horizontal band of residuals which is indicative that a long-term effect is not influencing the data. Also the observed error between the experimental and the predicted data is independent and it is randomly distributed. There are no significant outliers present which confirms that the applied regression technique provided accurate results.

This accuracy is better depicted by the corresponding polarization and power curves in Figs. 15 and 16. Model predictions are in a very good agreement with the experimental data for both conditions. It is found that the mean square-root difference between the experimental and the predicted voltage is about 0.03892 V with a maximum difference of about 0.01987 V. Thus, the optimal parameters provide to the model the accuracy to properly describe the behavior of the output voltage.

The optimal values for parameters \( \xi_1(\theta_1) \) and \( \xi_2(\theta_2) \) are presented in the second column of Table 9. It is not possible to fairly compare these parameters with those from other fuel cells units, since they are related to the specific system and they are empirical in nature. This is clearly illustrated in both the statistical metrics (Table 9, Figs. 13 and 14) and the comparison against experimental data (Figs. 15 and 16).

4.3. Model validation

To perform a comprehensive model validation study, the model with the optimal parameters was simulated concerning step changes of the input variable (current). In this section in order to validate the accuracy of the derived model (which incorporates...
the optimal parameter values), we compare its predictive power with new experimental data at various operating conditions. These conditions are different from the ones used for the parameter estimation procedure. An indicative set of experiments are presented to demonstrate the accuracy of the model. The varying condition between the validation experiments is related to the pressure at two different levels, 0.5 Barg and 1.5 Barg. Figs. 17 and 18 illustrate a comparison between model prediction and experimental data. Again a good agreement is achieved.

It is clear that under different pressure conditions the model response is very close to the experimental behavior for the whole range of current variation. Fig. 19 further illustrates the accuracy of the model with respect to response in two step changes in current (6 A, 8 A). The sampling time is 500 ms and the duration of each step is 120 s. A good agreement is observed between the measurements and the model predictions with a maximum error of 0.0027 V.

During step changes in current an adequate voltage prediction is achieved by reproducing both the steady-state behavior between the step change and the dynamic behavior due to the instantaneous increase in current. In summary the proposed model demonstrates an excellent behavior both at steady and transient conditions and therefore it can be used both in startup and during variable load changes.

5. Conclusions

This work presents a dynamic model of a PEM fuel cell system which relies on mass and energy conservation equations combined with equations having experimentally defined parametric coefficients thus resulting in a semi-empirical dynamic model. A formal estimation procedure was employed, to determine the values of the most critical empirical parameters. The experimental data were provided by a real fuel cell testing unit. The methodology that was followed in the underlying experimental study and the model-based validation was implemented in a way that it can be extended to different fuel cell stacks, after proper adjustment of the physical parameters. It is also shown that the model predictions are in a very good agreement with experimental data under different operating conditions. Current work focuses on the use of the developed model for deriving flexible design options and real-time control policies. Extensions to integrate the model into a larger dynamic subsystem, to complete a power generation process are also under way.

References


