Investigating the Transient Response of a Low Pt-loaded PEMFC under Various Operating Conditions

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ABSTRACT

Understanding the dynamic behavior of low Pt-loaded proton exchange membrane fuel cells (PEMFCs) subjected to rapid load changes is a prerequisite for ensuring reliable devices suitable for transportation applications. The dynamic cell response requires the coupled solution of all the involved processes. To this end, a multiphase non-isothermal pseudo-three-dimensional (P3D) model coupled with a detailed electrochemical sub-model is adopted for a straight fuel cell portion to evaluate the cell dynamic response under the Galvano-dynamic condition. In addition, the mixed wettability model is incorporated to account for the microstructural properties of different porous layers. The effect of catalyst salient features including Pt-loading, ionomer to carbon weight ratio (I/C ratio), additional bare carbon particles, and CL thickness as well as operating conditions including relative humidity and stoichiometry ratios are studied under load cycling.

Keywords: Proton Exchange Membrane Fuel Cell, Pseudo-Three-Dimensional Model, Dynamic Response, CL Morphology, Low Pt-Loaded Catalysts, Operating Conditions

1. INTRODUCTION

As a promising alternative for power sources in the automotive industry, proton exchange membrane fuel cells (PEMFCs) have attracted significant attention due to high power density, fast start-up, zero to low emissions, low operating temperatures, and high efficiency. Though significant technical challenges have been addressed over the past decades owing to extensive theoretical and experimental research, issues related to durability, cost, and stability require further enhancement. The knowledge of transient response and dynamic characteristics of PEMFCs under load cycling, idling,

startup, and shutdown conditions is necessary to overcome the durability issues. Under actual automotive operation mode, the voltage response delay and voltage undershoot happen due to fuel starvation and transient variations of cell water content [1]. These variations result in adverse dynamic responses including voltage perturbations, uneven distribution of reactants, and flooding causing performance fluctuations and component degradation such as carbon corrosion of the catalytic layer and Pt dissolution [1].

The dynamic response of PEMFCs is a complex phenomenon that strongly depends on operating and controlling parameters. Transient experimental studies mostly focused on slow processes including water accumulation in the gas diffusion layer (GDL) and relaxation of membrane water content [[1]]. Moreover, numerous experimental studies investigated the over/undershooting current and cathodic gas compositions under voltage or current cycling. In this regard, Kim et al. [2] experimentally investigated the transient response of PEMFCs under various air stoichiometry, humidity, and excess ratios. The authors reported increased voltage undershoots with higher step currents due to Ohm's law [2]. In addition, authors represented decreased oxygen concentration and ionic conductivity for lower air stoichiometry and humidity ratios respectively, both resulting in higher voltage drops [2]. The adverse effect of low cathodic humidity ratios both on steady-state and dynamic characteristics of PEMFCs is further confirmed by Yan et al. [3]. The authors reported the positive impact of higher operating pressures under large current steps and high current densities. Furthermore, Cho et al. [4] detailed two stages of time delay for cell response. The first one is caused by through-plane (TP) gas convection and mass transfer limitation, which is in the order of 1 s, while the second one concerns membrane water content recovery taking

about 10 s [4]. The authors concluded that voltage undershoot is mainly caused by oxygen supply delay, non-uniform oxygen distribution, and flooding issues [4]. Recently, Huang et al. [5] represented a notable impact of stoichiometry ratios for low current densities, while a negligible effect is reported for high ones. Authors proposed superior large-scale dynamic behavior upon appropriate initial membrane water content [5].

Several transient models have been proposed to deconvolve the complex transport phenomena investigating the effect of operating conditions, membrane properties [6], and flow field design characteristics [7][8]. Using a three-dimensional (3D) dynamic model, Wang et al. [9] represented the transient response time of 10 s for reaching a new steady-state condition due to the membrane water accumulation. The authors investigated that increased step current under dry operating conditions causes the anode to dry due to electro-osmotic drag [9]. Moreover, Shimpalee et al. [10] reported a significant effect of temperature in modifying the over/undershoot peak, causing the single-phase and isothermal models to overestimate the voltage fluctuations. Furthermore, Goshtasbi et al. [11] proposed a through-plane three-dimensional model for studying the transient response of PEMFCs. The authors suggested the dominance of water redistribution on the transient cell response [11]. Moreover, the authors related the redistribution timescale to the operating conditions, two-phase flow, and membrane water uptake [11].

Most numerical studies consider simplified reaction kinetics neglecting the microstructural characteristics of different layers and anisotropic material properties. However, capturing the most salient feature of cell dynamics, requires a comprehensive transient model to delineate the critical transient phenomena [12] [13]. The CL of PEM fuel cells is a multi-component media, and its microstructural parameters define the cell performance and durability. These design characteristics include the specifications controlled during the CL synthesis such as carbon-supported electrocatalyst nanoparticles enhancing the electronic conductivity and catalytic activity, ionomer content creating a proton conducting pathway, and pore structure facilitating the transport of reactants. Although Platinum (Pt) decrement is a key factor for overcoming cost issues and facilitating the widespread use of PEMFCs, the dynamic behavior of PEMFCs is rarely studied for low Pt-loaded fuel cells.

In this study, a detailed non-isothermal multiphase pseudo-three-dimensional (P3D) model capturing the complex electrochemical kinetics and the microstructural characteristics of porous layers is utilized to investigate the dynamic behavior of PEMFCs. This model was previously proposed to assess the impact of CL microstructural parameters on the steady-state performance of low Pt-loaded PEMFCs [14]. The CL characteristics are found to dramatically affect the steady-state performance of low Pt-loaded CLs [14][15][16], while the dynamic cell response with different CL compositions is not studied. To unravel the effect of CL features on dynamic cell behavior, the cell response is evaluated for different Pt-loadings, Ionomer to Carbon weight percentages (I/C ratio), and additional bare carbon particles (y_{Bare}) considering constant CL thickness. Moreover, further investigation is performed by considering different CL thicknesses upon the addition of bare carbon particles. Furthermore, the impact of stoichiometry and relative humidity ratios of reactants on dynamic response is studied.

2. MATERIALS AND METHODS

2.1 Computational Domain

The modeling domain of interest includes channels and GDLs explicitly while thin CLs and the membrane are included implicitly by the addition of through-plane (TP) fluxes. The computational domain is projected on a single surface and the symmetry causes the channels and ribs to overlap. The reader is referred to Ref. [14] for more information regarding the computational domain.

2.2 Governing Equations

The transient detailed P3D model is used for the analysis of low Pt-loaded PEMFCs in this work. The flow distribution in the channels and GDLs is obtained by solving the time-dependent two-dimensional Brinkman equations simultaneously with Maxwell equations. Moreover, liquid water transport through ionomer is evaluated by considering adsorption, desorption, and water generation processes. Furthermore, the energy equation, liquid water transport through the GDLs, and charge conservation for obtaining the ionic and electric potentials are considered. The time-dependent governing equations are provided in Table 1 while a detailed description of the P3D model alongside the involved sub-models concerning the electrochemical reaction kinetics and water transport is provided in Ref. [14].

2.3 Numerical Implementation

The numerical model is implemented in the commercial finite-element software, COMSOL Multiphysics, with a mapped mesh consisting of 1800

quadrangular linear elements with a double boundary layer at the channel-rib interface. The fully coupled solver is utilized to solve nonlinear equations with Newton iterations. In addition, the linear systems of equations are solved with a PARDISO direct solver at each time step. The backward differentiation formula (BDF) is considered for time stepping with a maximum step size of 500 milliseconds. The simulations were performed on a workstation with a 3.6 GHz quad-core processor and 32 GB RAM.

Table 1. Transient governing equations

Description	Equation	Eq.
Mass	$\dfrac{\partial(\rho\varepsilon)}{\partial t} + \nabla \cdot (\rho\boldsymbol{u}) = S_{mass}$	(1)
Momentum	$\rho\dfrac{\partial \boldsymbol{u}}{\partial t} + \rho\boldsymbol{u}\cdot\nabla\boldsymbol{u} = -\nabla p + \mu\nabla^2\boldsymbol{u} - \dfrac{\mu}{\kappa}\boldsymbol{u}$	(2)
Species distribution	$\varepsilon\rho\dfrac{\partial w_i}{\partial t} + \nabla\cdot\left(\rho w_i\sum_j D_{ij}\nabla X_j\right) + \rho(\boldsymbol{u}\cdot\nabla)w_i$ $= S_i$	(3)
Electric potential	$\nabla\cdot(-\sigma_s\nabla\phi_s) = S_{\phi s}$	(4)
Ionic potential	$\nabla\cdot(-\sigma_m\nabla\phi_m) = S_{\phi m}$	(5)
Membrane dissolved water	$\dfrac{\partial\left(\frac{\rho_{MEM}}{EW}\lambda\right)}{\partial t} + \nabla\cdot\left(\frac{-\rho_{MEM}}{EW}D_{H2O}^{Naf}\nabla\lambda\right) +$ $\nabla\cdot\left(\frac{-n_d}{F}\sigma_l\nabla\phi_l\right) = S_\lambda$	(6)
Energy	$(\rho C_p)_{eff}\dfrac{\partial T}{\partial t} + (\rho C_P)_{eff}\,\mathbf{u}\cdot\nabla T + \nabla\cdot(-k_{eff}\nabla T)$ $= S_T$	(7)
Liquid water transport	$\dfrac{\partial(\rho\varepsilon)}{\partial t} + \nabla\cdot\left(\frac{\rho_l k_l}{\mu_l}\nabla p_l\right) = S_l$	(8)

3. RESULTS AND DISCUSSION

The non-isothermal two-phase P3D model which is previously validated against systematic experiments [14] is used to reveal the cell dynamic response under various CL compositions namely Pt-loading, Pt/C ratio defined as the weight ratio of platinum in Pt/C electrocatalysts, I/C ratio defined as the weight ratio of ionomer in comparison to the total carbon loading, and the bare carbon mass fraction (y_{bare}). In addition, the cell dynamic behavior is further studied under different inlet relative humidity and stoichiometry ratios.

The inlet gases are assumed to be hydrogen, nitrogen, and water vapor for the anode electrode as well as air consisting of oxygen, nitrogen, and water vapor for the cathode. The base model parameters are provided in Table 2 while the readers are referred to Ref. [14] for more details and the values of the remaining parameters.

Table 2. Operational and geometrical parameter values

Description	Parameter	Value	Unit
Channel length, width, height	L_{ch}, w_{ch}, h_{ch}	50, 1, 1	mm
Land width	w_{rib}	1	mm
Thickness of MEM, CL	$\delta_{mem}, \delta_{CL}$	18, 11	μm
Inlet stoichiometric ratios	st_{ca}, st_{an}	2, 1.2	–
Inlet relative humidity	RH_{ca}, RH_{an}	0.6, 0.6	–
Operation and reference temperature	T, T_0	353, 298	K
Operation and reference pressure	P, P_0	1, 1.5	atm

The result section of this work is separated into two parts including the CL morphology and operating conditions. The former constitutes evaluating the peak under/overshoot using different CL features controlled during the catalyst fabrication process, while the latter concerns comparing low Pt-loaded cells using two different input values for each operating parameter. The Galvano-dynamic approach is utilized for which the current density profile is the model input and is shown in Fig. 1. The magnitude of current steps, especially the middle one, are selected high enough to stimulate the system dynamics.
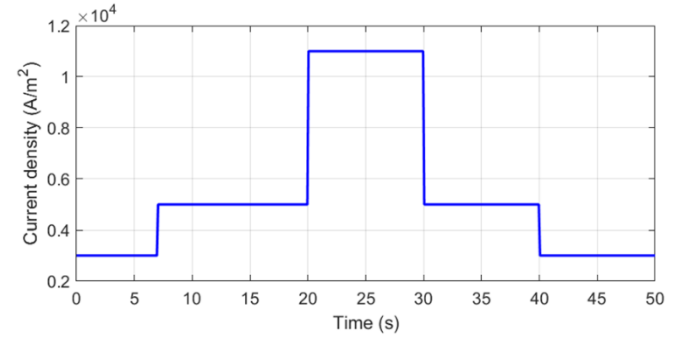

Fig. 1. The applied current profile

3.1 The Effect of CL Morphology

The effect of Pt-loading is investigated considering two different Pt-loadings of 0.2 and 0.05 mg/cm^2 for the cathode electrode, the result of which is shown in Fig. 2(a). Since the rate of cathodic reduction reaction dominates the cell performance, the detailed electrochemical reaction model is only considered for the cathode, while the facile kinetics of hydrogen oxidation reaction (HOR) ensures negligible anode kinetic losses. A constant CL porosity of 0.55 is assumed for all simulation case studies to eliminate the pore volume effect on the cell dynamics.

For studying the effect of Pt loading, the Pt/C weight ratio is modified to adjust the CL thickness keeping the I/C ratio as 1. As demonstrated in Fig. 2(a), as an obvious

result of reduced Pt-loading, the cell voltage decreases. Since the Galvano-dynamic profile is used, the cell water content is not affected by water generation of the electrochemical reaction for different Pt-loadings. Furthermore, constant CL thickness assures consistent heat generation through the cell. Consequently, higher Pt-loading results in a better dynamic response by representing lower voltage undershoot. The lower oxygen transport resistances of higher Pt-loaded CLs cause lower levels of oxygen concentration at the surface of Pt particles, which results in inferior oxygen distribution in the cell.
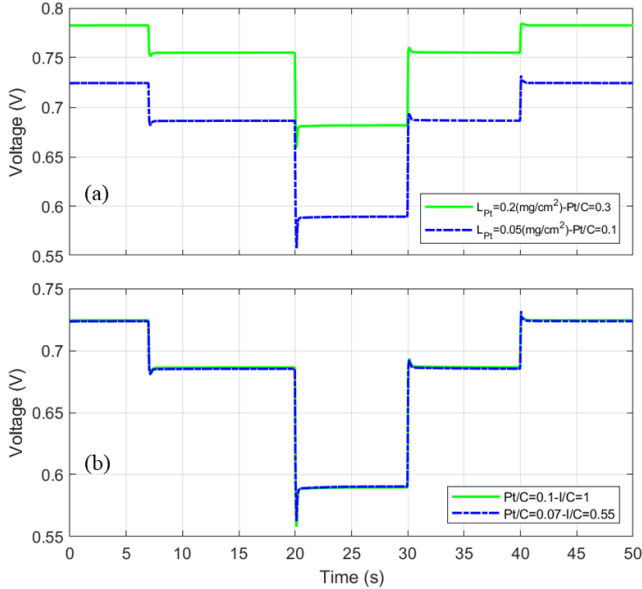

Fig. 2. The comparison of cell dynamic response under constant CL thickness assumption for, (a) Different Pt-loaded CLs and (b) Different I/C ratios

The I/C ratio is another important CL feature providing a proton conduction path for ions to reach the electrochemical active region. A higher I/C ratio produces a thicker ionomer layer causing higher diffusional and interfacial transport resistances since the latter resistance is directly proportional to the former [14]. Conversely, lowering the ionomer content increases the CL ionomer potential loss [14]. The impact of the I/C ratio is investigated using constant Pt-loading of 0.05 mg/cm^2 by varying the Pt/C ratio and I/C ratio simultaneously to ensure constant CL thickness and porosity, and the results are shown in Fig. 2(b). The voltage responses are closely related for two I/C ratios of 0.5 and 1, since the effect of I/C ratio dominates the cell performance only for limiting current density region meaning current density values greater than or close to 2 A/cm^2 as well as for values of I/C ratio below 0.3 [14]. However, a slight positive impact is observed lowering the CL ionomer content under constant Pt-loading and CL

thickness conditions due to the small reduction in voltage undershot. The lower I/C ratio decreases the oxygen transport resistance due to the thinner ionomer layer resulting in higher oxygen concentration on the surface of Pt particles.

The additional bare carbon particles in diluted CLs provide insight into the Pt dispersion and utilization in different CLs. The bare carbon particles are added to the CL to increase the thickness using different Pt/C ratios, modifying the number of catalyzed Pt/C particles available for the electrochemical reaction. Since the variation of bare carbon mass fraction (y_{Bare}) modifies the CL thickness affecting the heat generation and water distribution, the effect of dilution is investigated for both constant and varied CL thickness by considering different Pt/C ratios and (y_{Bare}) combinations, and the results are shown in Fig. 3.
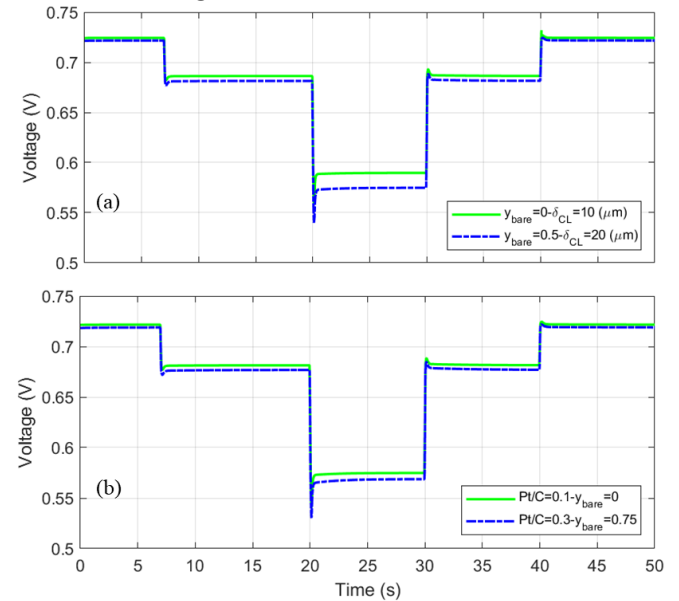

Fig. 3. The comparison of cell dynamic response for, (a) different CL thicknesses and (b) Different bare carbon mass fractions

Higher dilution rates increase both the oxygen transport resistances and the ionomer voltage losses. The CL thickness barely affects the voltage undershoot as demonstrated in Fig. 3(a), while the voltage response deviates for the thicker CL for all the current density steps, especially the third voltage step. Under constant CL thickness conditions, moreover, including more bare carbon particles adversely affects the oxygen transport resistances and results in higher voltage undershoots as demonstrated in Fig. 3(b). Furthermore, the effect of additional bare carbon particles is more intense for high current densities representing more voltage difference between the two cases for the third current density step. It takes 5 s for the thicker cell to reach a new steady state

condition due to the enhanced oxygen transport resistances, while the thinner cell is stabilized after 2 s. However, the voltage response barely deviates for the first and last current density steps with a current density value of 0.3 A/cm^2.

3.2 The Effect of Operating Conditions

The operating conditions of PEM fuel cells including current, voltage, system pressure, temperature, inlet relative humidity, and inlet stoichiometric flow rates define the dynamics of cell response. These parameters serve as the model inputs, which are effectively controlled in an automotive system.

The effect of operating conditions is investigated in this section using a cell with Pt-loading of 0.05 mg/cm^2, Pt/C ratio of 0.1, and I/C ratio of 1. The humidity ratio of reactants is studied considering two values of 1 and 0.6 for both cathode and anode electrodes. The humidity levels of the anode and cathode are not studied separately here. Complex phenomena explain the cell performance under different humidity ratios for anode and cathode electrodes. Higher cathodic humidity elevates the rate of back diffusion from the cathode, while the electro-osmotic drag from the anode exceeds the back diffusion at high current densities [3]. Thus, increasing the anodic relative humidity improves the cell performance by counteracting the back diffusion phenomenon and improves the membrane conductivity [3]. In contrast, higher cathodic relative humidity increases the water vapor fraction in the inlet causing the water flooding and pore blockage in the GDL while increasing the oxygen transport resistance in the CL [3]. As demonstrated in Fig. 4(a), the cell voltage response is closely related for two humidity levels except for the high current density step, for which the higher mass transport resistances deteriorate the cell performance resulting in a lower voltage response for a higher humidity ratio. Moreover, the voltage undershoot is increased for higher relative humidity resulting in an unstable cell response due to lower oxygen concentration.

Fig. 4(b) represents the comparison of the cell voltage response under two different stoichiometric ratios with values of 1.2 and 2 as low flow rate, and 5 and 6 as high flow rate conditions for anode and cathode, respectively. The inlet stoichiometric flow rate influences the oxygen availability as well as the membrane humidity, which in turn affects the cell total ionic resistance. Decreased mass transport resistances for higher stoichiometric ratios avoid the generation of voltage over/undershoots while it takes 7 s for the system to reach new steady state condition. In contrast,

the channel is easily depleted from oxygen under low flow rate conditions causing a voltage undershoot of 0.05 V for the highest current density step. In addition, the generated cell voltage is enhanced providing a higher inlet stoichiometry ratio for reactants, and this dependency is more intense for high current densities.
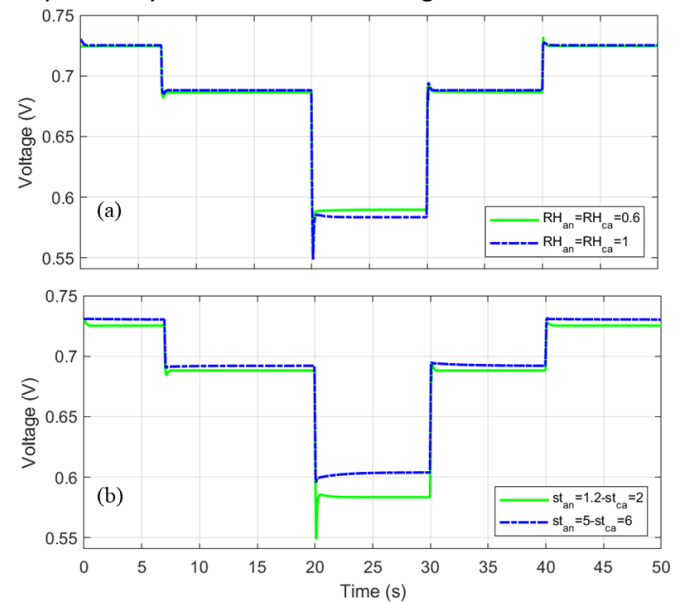

Fig. 4. The comparison of cell dynamic response for, (a) Different relative humidity and (b) Different stoichiometry ratios

4. CONCLUSIONS

The dynamic behavior of PEM fuel cells is dependent on different structural, geometrical, and operational parameters. In this study, the dynamics of fuel cell response are evaluated under different CL compositions and operating conditions considering the Galvano-dynamics approach. To this end, the cell voltage response with straight cathode and anode channels is studied with a non-isothermal multiphase pseudo-three-dimensional (P3D) model considering the microstructural characteristics of the CL and wettability features of different porous layers. The decreased catalyst Pt-loadings cause elevated oxygen transport resistances resulting in higher voltage undershoot. With the considered I/C ratios, the deviation of dynamic behavior is almost negligible, and more elaboration is required on its effect using a more diverse range. Furthermore, a higher voltage undershoot is observed increasing the mass fraction of bare carbon particles under the constant CL thickness condition. However, the voltage undershoot is almost consistent, varying the CL thickness upon the addition of bare carbon particles. A higher stoichiometric flow rate enhances the voltage response by elevating the generated voltage and generating smaller voltage undershoots, especially at

high current densities. Higher relative humidity ratios increase the mass transport resistances and elevate the voltage undershoot. Among all the studied parameters, the effect of the stoichiometry ratio on the cell dynamic response is more dominant.

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DECLARATION OF INTEREST STATEMENT

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. All authors read and approved the final manuscript.

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