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Local Oxygen Transport through Ionomer and Water Controls Current Density Overshoot in Proton Exchange Membrane Fuel Cell Cathode Catalyst Layer

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ABSTRACT: Proton exchange membrane fuel cell (PEMFC) is frequently subjected to dynamic loading during practical operation, where delayed oxygen transport in the cathode catalyst layer may induce transient oxygen starvation and accelerate performance degradation. In this study, a refined local mass transport model is developed to investigate how oxygen transport through ionomer and water pathways affects the dynamic response of a PEMFC cathode catalyst layer. The model considers oxygen dissolution at gas-ionomer and gas-water interfaces, oxygen diffusion through ionomer and water films, interfacial resistance near the ionomer-Pt interface, proton transport, and oxygen reduction reactions on the catalyst surface. Particular attention is paid to the effects of ionomer coverage on the catalyst surface, ionomer connection regions between catalysts, loading rate, and loading amplitude. The results show that the magnitude of the transient current density overshoot is directly governed by the local oxygen flux reaching the catalyst surface. As ionomer coverage increases from 10% to 100%, the current density overshoot amplitude rises from 2.1% to 19.4%, mainly because oxygen dissolution and diffusion through ionomer are slower than those through water. Increasing the ionomer connection region favors proton transport but reduces the effective oxygen transport area, leading to a 43.8% decrease in oxygen concentration in the ionomer region at 0.015 s and an increase in overshoot amplitude from 6.6% to 30.8%. Furthermore, reducing the loading rate and loading amplitude effectively suppresses the transient overshoot. These findings reveal the controlling role of local oxygen transport resistance in PEMFC dynamic response. From an engineering perspective, the identified relationships among ionomer distribution, local oxygen transport, and transient response provide a mechanistic basis for catalyst-layer microstructure design and dynamic load-management strategies aimed at mitigating transient oxygen starvation in automotive PEMFCs.

KEYWORDS: Proton exchange membrane fuel cell; cathode catalyst layer; local oxygen transport; ionomer coverage; dynamic loading; current density overshoot

1 Introduction

Proton exchange membrane fuel cells (PEMFCs) are regarded as promising power sources for fuel cell vehicles because of their high energy conversion efficiency, rapid refueling, and zero tailpipe emissions [1–5]. However, durability under automotive dynamic operating conditions remains an important obstacle to their large-scale commercialization [6–10]. During practical vehicle operation, PEMFCs frequently experience load

variations associated with acceleration, deceleration, start-stop events, and changes in power demand [11–14]. When the increase in electrochemical reaction demand exceeds the rate of reactant replenishment, transient oxygen deficiency can occur in the cathode, leading to pronounced voltage or current fluctuations and accelerated performance degradation [15–17]. Therefore, a deeper understanding of oxygen transport under dynamic conditions and its influence on transient electrochemical response is essential for improving PEMFC dynamic performance and durability.

Considerable experimental and numerical efforts have been devoted to investigating the dynamic response of PEMFCs. Kim et al. [18] examined the influence of flow-field configuration on PEMFC transient behavior and found that differences in oxygen replenishment associated with different flow-field designs significantly affect the transient voltage response. Kim et al. [19] further reported that air stoichiometry and humidification conditions influence voltage undershoot through the coupled transport of oxygen and protons. Because PEMFCs involve complex multiphase, multiscale, and multi-physics processes, direct experimental characterization of transient mass transport within the catalyst layer remains challenging [20,21]. Numerical simulation has therefore become an important approach for elucidating the underlying dynamic mechanisms. Wu et al. [22] showed that cathode oxygen transport and water removal are important factors governing transient PEMFC behavior under fully humidified conditions, with a characteristic oxygen transport time of approximately 0.3–1 s. Pei et al. [23] demonstrated that increasing the load accelerates the oxygen reduction reaction, resulting in a rapid decrease in the average oxygen concentration and an increase in the oxygen concentration gradient within the cathode catalyst layer (CCL). Verma et al. [24] further found that oxygen-deficient regions evolve spatially during load transitions and that reducing the load amplitude or slowing the loading rate can improve gas distribution. These studies confirm that oxygen transport is a key factor governing PEMFC dynamic response; however, most previous work has focused on oxygen redistribution at the flow-channel, electrode, or catalyst-layer scale.

At the catalyst scale, oxygen must pass through the local interfacial environment surrounding Pt particles before participating in the oxygen reduction reaction. Because ionomer coverage and distribution over the Pt/C surface are generally nonuniform, different active sites may experience different oxygen and proton transport conditions [25,26]. Recent studies on interface engineering have further shown that regulation of the catalyst/ionomer interface and triple-phase boundary can modify ionomer distribution, oxygen accessibility, and proton transport, thereby affecting local mass-transfer resistance, catalyst utilization, and overall fuel cell performance [13,27–32]. Similar interfacial effects have also been observed in other electrochemical systems. For example, Ni(OH)₂/CeO₂ heterointerface catalysts have been reported to enhance urea electrooxidation through interfacial electronic coupling and oxygen-vacancy-mediated charge transfer [33]. These studies collectively indicate that local interfacial structure can significantly influence electrochemical performance by regulating mass and charge transport.

However, most existing studies have mainly focused on the effects of interface regulation on steady-state transport resistance, catalyst utilization, and overall fuel cell performance, whereas the role of local catalyst interfaces in transient oxygen transport during rapid load changes remains insufficiently understood. In particular, when the Pt surface is only partially covered by ionomer, oxygen may reach the catalyst through different local transport pathways. In ionomer-covered regions, oxygen must first dissolve at the gas-ionomer interface and subsequently diffuse through the ionomer film, whereas in ionomer-free regions, oxygen can be transported to the Pt surface through a local water film. Because oxygen dissolution, diffusion, and interfacial transport characteristics differ between ionomer and water, these two pathways may exhibit different response rates during rapid load changes. Meanwhile, proton transport mainly relies on the connected ionomer phase. Therefore, the transient reaction at the catalyst surface is jointly governed

by local oxygen supply and proton conduction. How ionomer coverage alters these local oxygen transport pathways, and how the resulting delay in oxygen supply further contributes to transient current-density overshoot, have not yet been systematically clarified. In addition, the influence of ionomer connection regions between neighboring catalyst particles on oxygen and proton transport during dynamic operation remains to be further investigated.

To address these issues, a refined local mass transport model is developed in this study to investigate the influence of catalyst-scale oxygen transport on the dynamic response of the PEMFC cathode catalyst layer. The model considers oxygen dissolution at the gas–ionomer and gas–water interfaces, oxygen diffusion through ionomer and water films, interfacial transport resistance near the ionomer–Pt interface, proton transport, and the oxygen reduction reaction on the Pt surface. Particular attention is paid to the effects of ionomer coverage on the catalyst surface and the ionomer connection region between neighboring catalyst particles on local oxygen transport and transient current-density response. The influences of loading rate and loading amplitude are also investigated. By establishing the relationship between local oxygen transport and transient current-density overshoot, this study aims to reveal the catalyst-scale mass-transfer mechanism governing PEMFC dynamic behavior and to provide guidance for cathode catalyst-layer microstructure design and dynamic operating strategies.

2 Model Development

The membrane electrode assembly (MEA) of a PEMFC comprises gas diffusion layers (GDLs), catalyst layers (CLs), and a proton exchange membrane (PEM). Within a typical catalyst layer, Pt/C particles, ionomer, and pore space form a heterogeneous transport and reaction network. As illustrated in Fig. 1a, ionomer coats Pt/C particles to form agglomerates and also connects neighboring particles to provide proton-conduction pathways. Owing to nonuniformity introduced during electrode fabrication, the extent of ionomer coverage varies from particle to particle; Fig. 1b therefore considers both fully and partially covered catalyst surfaces. Here, the ionomer coverage is defined as the fraction of the catalyst surface area covered by ionomer relative to the total catalyst surface area. Therefore, 100% coverage represents a fully ionomer-covered catalyst surface, whereas lower coverage values correspond to partially covered cases, with the remaining surface in contact with the local water film. Since the catalyst surface is hydrophilic and during PEMFC operation oxygen, protons and electrons react to generate water at the active sites on the catalyst surface, liquid water is thought to be present on the area of the catalyst surface that has been uncovered by the ionomer [34]. Therefore, oxygen can transport through both ionomer and liquid water to the three-phase boundary to participate in the oxygen reduction reaction when the catalyst is partially covered by ionomer. In contrast, oxygen can only contribute to the reaction through the ionomer when the catalyst is completely covered, as seen in Fig. 1c.

R_1 is the Pt/C catalyst radius in the model. The carbon particle radius can be utilized to depict the Pt/C catalyst radius because the Pt radius is an order of magnitude smaller than the carbon particle size. d is the thickness of the ionomer on the Pt/C catalyst surface; R_2 is the radius of the agglomerate.

The assumptions in the model are summarized as follows:

- (1) Pt uniformly distribute on the surface of the carbon particle;
- (2) Oxygen reduction reaction occurs uniformly on the carbon particle surface;
- (3) Liquid water in the catalyst surface as a continuous liquid film;
- (4) Water adsorption and desorption processes in the ionomer are ignored.

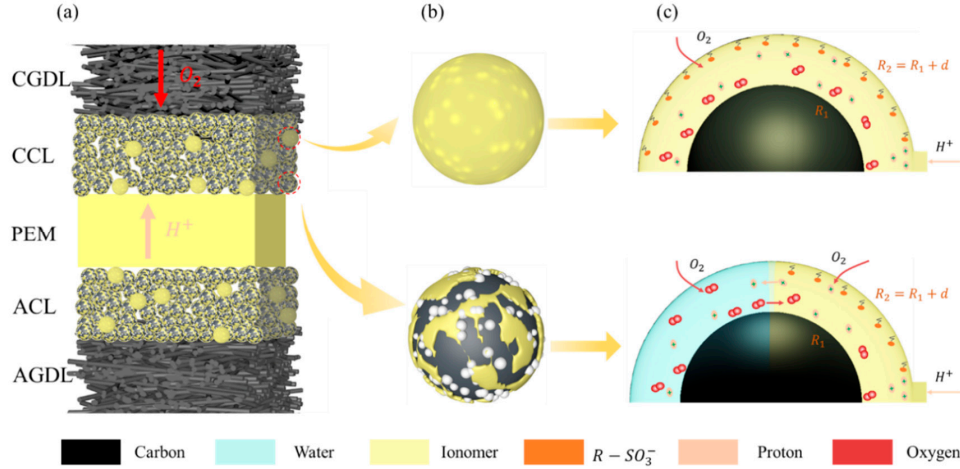


Figure 1: Schematics of (a) MEA, (b) fully and partially covered catalyst, and (c) fully and partially covered computation domain.

2.1 Governing Equations

The Poisson-Nernst-Planck equation is adopted to describe the effect of concentration gradients and electric field on proton transport:

$$\frac{\partial C_{H^+}}{\partial t} + \nabla \cdot (-D_{H^+} \nabla C_{H^+}) + \nabla \cdot \left(-\frac{Z_{H^+} F D_{H^+}}{RT} C_{H^+} \nabla \phi_s \right) = 0 \quad (1)$$

where C_{H^+} is the proton concentration, t is the time, D_{H^+} is the proton diffusion coefficient, Z_{H^+} is the proton charge number, F is the Faraday constant, R is the universal gas constant, T is the temperature, ϕ_s is the potential.

The Poisson equation is solved to obtain the electrostatic field.

$$\nabla \cdot (\epsilon_s \nabla \phi_s) + F Z_{H^+} C_{H^+} + F Z_{-SO_3^-} C_{-SO_3^-} = 0 \quad (2)$$

in which, ϵ_s stand for the dielectric constant of electrolyte, $Z_{-SO_3^-}$ stand for the $-SO_3^-$ charge number, $C_{-SO_3^-}$ stand for the $-SO_3^-$ concentration.

The transport of oxygen is illustrated by Fick's law:

$$\frac{\partial C_{O_2}}{\partial t} + \nabla \cdot (-D_{O_2} \nabla C_{O_2}) = 0 \quad (3)$$

in which, C_{O_2} denotes the oxygen concentration, D_{O_2} denotes the oxygen diffusion coefficient.

2.2 Boundary Conditions and Diffusion Parameters

Oxygen delivery through the ionomer is represented by three consecutive steps: dissolution at the gas-ionomer interface, diffusion across the ionomer film, and transfer across the interfacial region adjacent to Pt. Accordingly, the fully covered case contains three contributions to the local oxygen-transport resistance, as indicated in Fig. 2a. Molecular-dynamics studies suggest that ionomer chains near Pt can bend and pack into a dense interfacial layer, creating an additional barrier to gas transport. No analogous dense layer is assumed at the water-Pt interface; the water pathway is therefore governed only by oxygen dissolution and diffusion through the liquid film. For a partially covered catalyst, oxygen can also diffuse laterally

from water into the neighboring ionomer region. Because the resistance of the water pathway is lower, the oxygen concentration in water remains higher than that in ionomer, as illustrated in Fig. 2b.

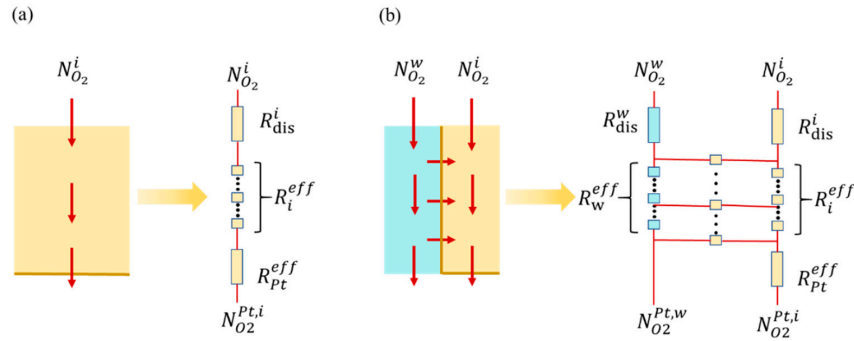


Figure 2: Schematic diagram of local oxygen transport path (a) catalyst completely covered by ionomer, and (b) catalyst partially covered by ionomer.

The equilibrium concentration of oxygen in the ionomer or water is calculated by Henry's law:

$$C_{O_2}^{eq,i/w} = \frac{RT}{H_{O_2}^{i/w}} C_{O_2}^g \quad (4)$$

where $H_{O_2}^{i/w}$ is the Henry constant of oxygen at the ionomer or water surface. $C_{O_2}^g$ is the oxygen concentration in the pores.

The oxygen flux across the ionomer or water surface is calculated by the following equation:

$$N_{O_2}^{i/w} = k_{dis}^{i/w} (C_{O_2}^{eq,i/w} - C_{O_2}^{i/w}) \quad (5)$$

where $k_{dis}^{i/w}$ is the oxygen dissolution reaction rate at the gas-ionomer or gas-water interface, $C_{O_2}^{i/w}$ is the oxygen concentration at the ionomer or water surface.

$$k_{dis}^{i/w} = \frac{1}{R_{dis}^{i/w}} = \frac{D_{O_2,i/w}^0}{k_1 \delta_{i/w}} \quad (6)$$

in which, k_1 is the interfacial resistance coefficient at the gas-ionomer or gas-water interface, $\delta_{i/w}$ is the ionomer or water thickness, $D_{O_2,i/w}^0$ is the oxygen diffusion coefficient in ionomer or water.

In addition, to reflect the interfacial resistance of ionomer to oxygen transport, a thin layer with a low oxygen diffusion coefficient is set in the water-ionomer interface region.

$$D_{O_2,w-i} = \frac{L_1}{k_{dis}^i} \quad (7)$$

Similarly, a thin layer is also set at the ionomer-Pt interface to demonstrate the impact of interfacial resistance on oxygen transport. Therefore, the oxygen diffusion coefficient in the ionomer-Pt region can be calculated by the following equations:

$$R_{Pt}^{eff} = k_2 \frac{\delta_{ion}}{D_{O_2,i}^0} \frac{A_i}{A_{Pt}} \quad (8)$$

$$A_{Pt}^i = 4\pi r_{Pt}^2 \quad (9)$$

$$A_i = \frac{4\pi \rho_{Pt} (r_C + \delta_{ion})^2 r_{Pt}^3}{\rho_C r_C^3} \quad (10)$$

$$D_{o2}^{i-Pt} = \frac{L_2}{R_{Pt}^{eff}} \quad (11)$$

To capture the influence of Pt particle dispersion on oxygen transport, the oxygen diffusion coefficient in the ionomer or water is corrected as follows:

$$R_{i/w}^{eff} = \frac{\delta_{i/w}}{D_{o2,i/w}^0} \frac{A_{i/w}}{A_{Pt}} \quad (12)$$

$$D_{o2}^{i/w} = \frac{\delta_{i/w}}{R_{i/w}^{eff}} \quad (13)$$

where, L_1 is the thickness of the thin layer at the water-ionomer interface, R_{Pt}^{eff} is the effective interface resistance on the ionomer-Pt interface, k_2 is the interfacial resistance coefficient at the ionomer-Pt interface, A_i is the ionomer surface area available for one Pt, A_{Pt}^i is the area of Pt, L_2 is the thickness of the thin layer at the ionomer-Pt interface, D_{o2}^{i-Pt} is the oxygen diffusion coefficient in the ionomer-Pt interface region, $R_{i/w}^{eff}$ is the effective transport resistance of oxygen in ionomer or water.

The consumption fluxes of oxygen and protons at the water-Pt and ionomer-Pt are:

$$N_{H+} = \frac{J_{ORR}}{F} \quad (14)$$

$$N_{O2} = \frac{J_{ORR}}{4F} \quad (15)$$

$$J_{ORR} = J_{ORR}^0 \left(\frac{C_{O2}}{C_{O2}^0} \right)^{\gamma_{O2}} \left(\frac{C_{H+}}{C_{H+}^0} \right)^{\gamma_{H+}} \exp \left(-\frac{\alpha_c F}{RT} \eta_c \right) \quad (16)$$

In which, N_{H+} means the proton flux, N_{O2} means the oxygen flux, J_{ORR} means the ORR current density, J_{ORR}^0 means the exchange current density, γ_{O2} means the oxygen reaction order, γ_{H+} means the proton reaction order, C_{O2}^0 means the reference oxygen concentration, C_{H+}^0 means the reference proton concentration, α_c means the cathode transfer coefficient, η_c represents the signed cathode overpotential, which is negative for the cathode oxygen reduction reaction. For clarity, the positive overpotential values used hereafter represent the magnitude (absolute value) of the cathode overpotential. For ease of description, the term “overpotential” hereinafter uniformly refers to this magnitude.

The ionomer-film thickness and water-film thickness were both set to 5 nm as representative nanoscale local transport layers surrounding the catalyst surface. The same thickness was adopted for the two pathways to minimize the influence of transport-path-length differences, thereby facilitating comparison of the intrinsic oxygen transport characteristics and interfacial resistances of the ionomer and water pathways.

Table 1 shows the relevant parameters of the model.

Table 1: Relevant parameters of the model.

Category	Value	Unit	Refs.
Physical parameters			
Carbon radius	25	nm	[35]
Ionomer thickness	5	nm	
Water film thickness	5	nm	
Pt loading	0.2	mg cm ⁻²	[35]
CCL thickness	3.6	μm	[36]
Pt radius	2	nm	[36]
Pt density	21,450	kg m ⁻³	[37]
Carbon density	1800	kg m ⁻³	[37]
Oxygen diffusion coefficient in ionomer	$0.2 \times 1.14698 \times 10^{-10} \times \lambda^{0.708}$	m ² s ⁻¹	[38]
Proton diffusion coefficient in ionomer	1.5×10^{-9}	m ² s ⁻¹	[39]
Oxygen diffusion coefficient in water	5.3×10^{-9}	m ² s ⁻¹	[40]
Proton diffusion coefficient in water	8.0×10^{-10}	m ² s ⁻¹	[41]
Exchange current density	2.3×10^{-3}	A m ⁻²	[42]
Cathode transfer coefficient	1		[6]
Oxygen reaction order	1		[6]
Proton reaction order	1		
Universal gas constant	8.314	J K ⁻¹ mol ⁻¹	
Faraday constant	96,485	C mol ⁻¹	
Gas-ionomer/water interface resistance coefficient	8.5		[35]
Ionomer-Pt interface resistance coefficient	25		[35]
Oxygen concentration in the pores	2.6	mol m ⁻³	[43]
Proton concentration at ionomer boundary	660	mol m ⁻³	
Henry constant of oxygen at the ionomer or water surface	38.9/43.0		[44]
Oxygen dissolution reaction rate at the gas-ionomer interface	9.25×10^{-3}	m s ⁻¹	[45]
Oxygen dissolution reaction rate at the gas-water interface	3×10^{-1}	m s ⁻¹	
Thickness of the thin layer at the water-ionomer interface	1	nm	
Thickness of the thin layer at the ionomer-Pt interface	1	nm	
Operating conditions			
Temperature	353.15	K	
Reference oxygen concentration	3.39	mol m ⁻³	[6]
Reference proton concentration	1250	mol m ⁻³	[46]

The transient simulations were performed using a time-dependent solver with a time step of 1×10^{-5} s. The relative tolerance was set to 1×10^{-3} to ensure numerical convergence.

2.3 Model Verification

Fig. 3 illustrates the dynamic response of the output voltage to step change in current density. When the current density steps from the initial current density (I_{ini}) to final current density (I_{fin}) (Fig. 3a), the output voltage changes immediately, and decreases to the minimum output voltage (V_{min}). Then the output voltage slowly increases and finally reaches a stable value (V_{stab}) (Fig. 3b). This phenomenon is called output voltage undershoot when current density steps up. In order to well quantify the current density and output voltage variations, the following definitions are made:

$$\Delta I = I_{fin} - I_{ini} \quad (17)$$

$$\Delta V = V_{stab} - V_{min} \quad (18)$$

$$\tilde{\Delta V} = \frac{\Delta V}{V_{stab}} \quad (19)$$

in which, ΔI is the current density step amplitude, ΔV is the undershoot amplitude of output voltage, $\tilde{\Delta V}$ is a dimensionless output voltage undershoot amplitude.

Output voltage undershoot is caused by unstable operating conditions, and the main reasons for this are:

- (i) When the current density steps up, the proton could carry a large number of water molecules from the anode to the cathode. The water absorption rate of the ionomer is much less than the desorption rate, so the anode ionomer water content decreases in a short time, which improves the ohmic voltage loss. The proton conductivity in ionomer and ohmic voltage loss can be expressed as follows:

$$\sigma_m = (0.519\lambda - 0.326)\exp\left[1268\left(\frac{1}{303} - \frac{1}{T}\right)\right] \quad (20)$$

$$\eta_{ohm} = \frac{JLeff}{\sigma_m} \quad (21)$$

where, λ is the ionomer water content, T is the temperature and $Leff$ is the effective proton transport length.

- (ii) When the current density steps up, oxygen transport from the flow channel to the catalyst surface to participate in the reaction takes a certain amount of time, which leads to oxygen starvation on the catalyst surface for a short time, thus increasing the concentration voltage loss.

The object of this study is a catalyst in the CCL and the time scale is of the order of 0.1 ms, while the adsorption and desorption time of water in the ionomer is at 0.1 s, which is three orders of magnitude larger than the time scale of this study, so the water content in the ionomer can be considered constant. The below formulas are used to calculate the rate of water adsorption and desorption in the ionomer [6]:

$$k_{ad} = 1.14 \times 10^{-5} f_v \exp\left[2416\left(\frac{1}{303} - \frac{1}{T}\right)\right] \quad (22)$$

$$k_{de} = 4.59 \times 10^{-5} f_v \exp\left[2416\left(\frac{1}{303} - \frac{1}{T}\right)\right] \quad (23)$$

where, k_{ad} is the water absorption rate, k_{de} is the water desorption rate, and f_v is the water fraction in the ionomer.

In addition, there is no dissolution resistance limiting proton transport at the ionomer interface, so it can be believed that the dynamic response is mainly caused by the slow local oxygen transport. Fig. 3c shows the effect of ΔI on the ΔV . It can be seen that as the ΔI increases, the ΔV also rises gradually. This is mainly attributed to the fact that the larger ΔI , the higher the oxygen flux required in a short time, resulting in a sharp increase in the concentration voltage loss and a decrease in the output voltage. The oxygen in the pores could gradually replenish to the catalyst surface by local transport, and the concentration voltage loss decreases, leading to an improvement in output voltage and eventually to a steady state. Furthermore, Tang et al. [47] theoretically demonstrated that the voltage-undershoot amplitude, ΔV , varies approximately linearly with the current-density step amplitude, ΔI , when the final current density is fixed. As shown in Fig. 3d, the present model reproduces this linear relationship over the investigated range. More importantly, the model predictions agree closely with the experimental data, with only small deviations at individual current-density steps. This agreement indicates that the model can reasonably capture both the characteristic voltage-undershoot behavior following a current-density step and its dependence on the step amplitude. Therefore, the comparison in Fig. 3d provides quantitative support for the capability of the present model to describe the transient local mass-transport response in the CCL.

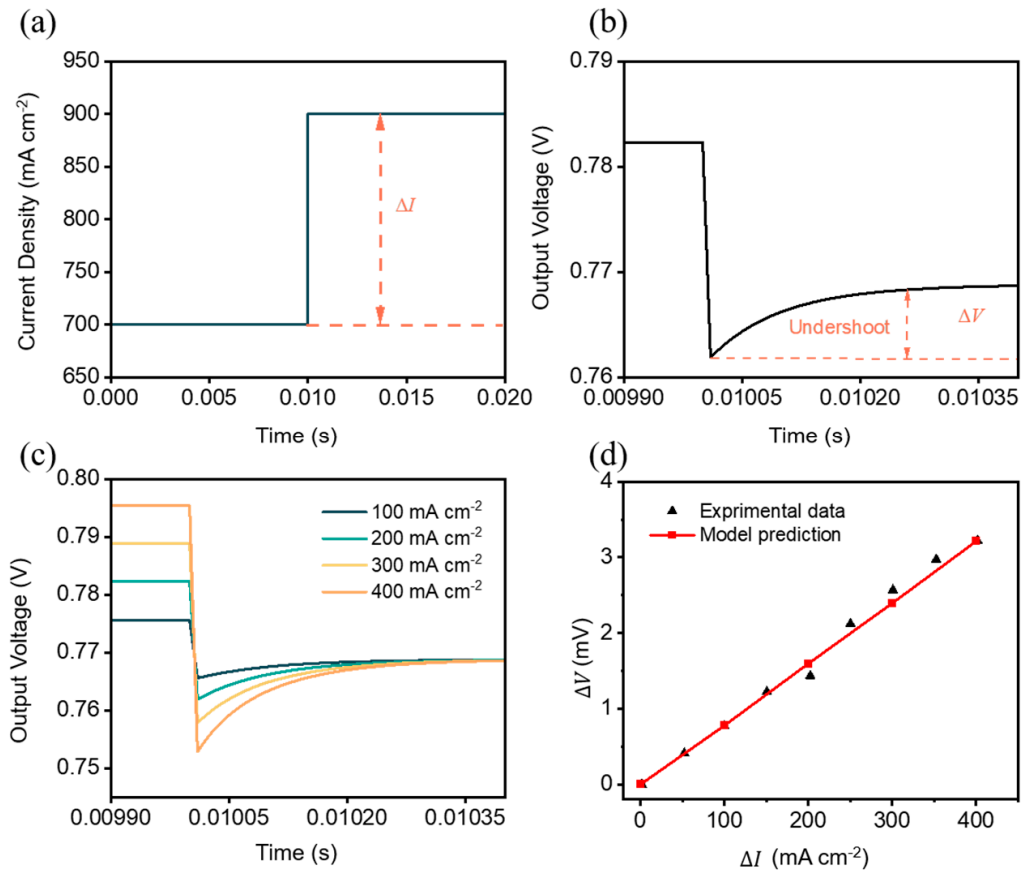


Figure 3: (a) step change in current density, (b) output voltage response, (c) output voltage response at different current density steps, and (d) comparison of experimental data and model predictions for the relationship between current-density step amplitude and voltage-undershoot amplitude.

3 Results and Discussion

3.1 Ionomer Coverage Effects

Most PEMFC transient studies impose a current-density step and monitor the resulting cell-voltage response. In the present catalyst-scale model, however, the ionomer-covered and water-covered portions of a partially coated catalyst can contribute differently to the local current, so the current carried by each region cannot be prescribed independently. Because both regions belong to the same conductive catalyst particle, they share a common electrode potential. An overpotential step is therefore used as the input to examine the transient average current density of a partially covered catalyst. Here, the average current density is defined over the combined ionomer-covered and water-covered portions of the catalyst surface.

At the local catalyst scale considered here, the ohmic loss associated with long-range proton transport is neglected. The imposed overpotential therefore represents the activation loss together with the concentration loss arising from local mass transport. Following a step increase in overpotential, the average current density rises rapidly to a maximum and then relaxes to a steady value; this behavior is termed current-density overshoot. The dimensionless overshoot amplitude is defined by:

$$\Delta\eta' = \eta_{fin} - \eta_{ini} \quad (24)$$

$$\Delta I' = I_{\max} - I_{stab} \quad (25)$$

$$\tilde{\Delta I} = \frac{\Delta I'}{I_{stab}} \quad (26)$$

In which, $\Delta\eta$ is the overpotential step amplitude, η_{fin} is the initial overpotential, η_{fin} is final overpotential, $\Delta I'$ is the overshoot amplitude of average current density, $I_{\max}$ is the maximum average current density, I_{stab} is the stable average current density, $\tilde{\Delta I}$ is the dimensionless average current density overshoot amplitude.

In this study, the overpotential steps from 0.13 V to 0.3 V. Fig. 4a,b exhibits the dynamic response of the average current density on the catalyst surface for different ionomer coverage when the overpotential steps up. It can be seen that as the ionomer coverage increases from 10% to 100%, $\tilde{\Delta I}$ rises from 2.1% to 19.4%. This may be attributed to the slower dissolution rates of oxygen on the ionomer surface than on the water. Oxygen can reach the catalyst surface both through water and ionomer when the catalyst is partially covered by the ionomer. However, water has a much lower resistance to oxygen transport than ionomer, so oxygen mainly transports through the water. As shown in Fig. 5a,b, the oxygen flux transport through the water is $3.73 \times 10^{-14} \text{ mol m}^{-1} \text{ s}^{-1}$, while through the ionomer is $1.13 \times 10^{-14} \text{ mol m}^{-1} \text{ s}^{-1}$ at the time of 0.015 s and the ionomer coverage is 40%. As the ionomer coverage increases, the water area dwindles, which leads to a decline of the effective water area for oxygen transport, and thus improves the oxygen flux through the ionomer. For example, with the ionomer coverage change from 20% to 80%, oxygen flux through the water reduces from $4.75 \times 10^{-14} \text{ mol m}^{-1} \text{ s}^{-1}$ to $2.25 \times 10^{-14} \text{ mol m}^{-1} \text{ s}^{-1}$, while through the ionomer rises from $0.587 \times 10^{-14} \text{ mol m}^{-1} \text{ s}^{-1}$ to $1.96 \times 10^{-14} \text{ mol m}^{-1} \text{ s}^{-1}$ at 0.015 s. When the overpotential steps up, the oxygen consumption increases rapidly, and oxygen via ionomer is slow, so that $\tilde{\Delta I}$ increases gradually with improving ionomer coverage. In particular, when the ionomer completely covers the catalyst, oxygen could only transport through the ionomer, so $\tilde{\Delta I}$ increases significantly (Fig. 4b). Fig. 5c,d illustrates the schematic diagrams of the effect of different ionomer coverage on oxygen transport.

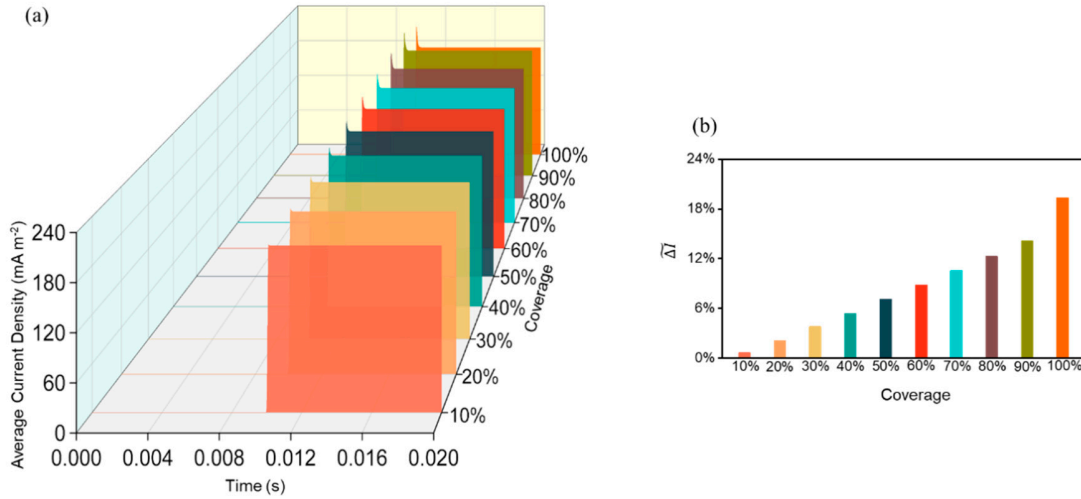


Figure 4: Effect of ionomer coverage on (a) average current density, and (b) overshoot amplitude of average current density.

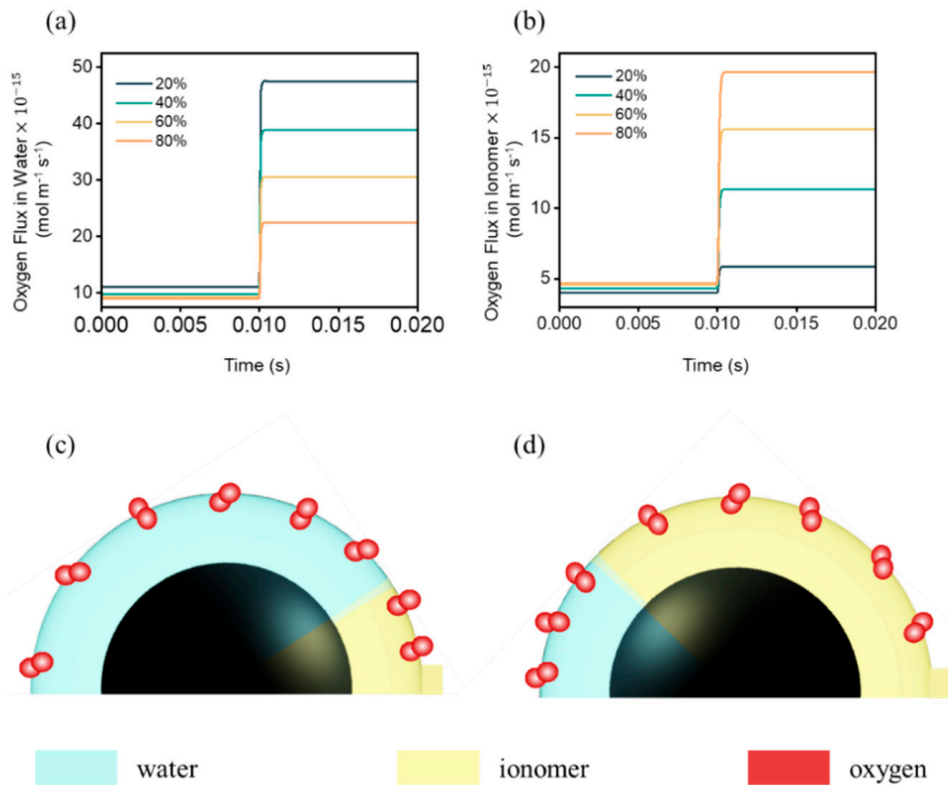


Figure 5: (a) oxygen fluxes via water with different ionomer coverage, (b) oxygen fluxes via ionomer with different ionomer coverage, (c) schematic of oxygen transmission when ionomer coverage is low, and (d) schematic of oxygen transmission when ionomer coverage is high.

3.2 Ionomer Connection Effects

Ionomer interconnects neighboring catalyst particles and provides a pathway for proton transport, while the size of the connection region also affects local oxygen transport. To quantify the relative size of the

ionomer connection region, a dimensionless parameter $\tilde{\theta}_{H+}$ is defined as $\tilde{\theta}_{H+} = \theta_2/\theta_1$, where θ_2 represents the angular extent of the ionomer connection region and θ_1 represents the total angular extent of the ionomer-covered region, as shown in Fig. 6a. Therefore, $\tilde{\theta}_{H+}$ represents the fraction of the ionomer-covered region occupied by the connection region. Fig. 6b,c demonstrates the influence of $\tilde{\theta}_{H+}$ on the dynamic response of the average current density when the overpotential steps up. When the ionomer coverage is constant, $\tilde{\theta}_{H+}$ increases from 6% to 99%, ΔI grow from 6.6% to 30.8%, and cell performance gradually decreases. The inadequate oxygen transport may be to blame for this. As shown in Fig. 7a,b, oxygen transport through the ionomer can be divided into two parts, one is oxygen via the connection region and the other is oxygen via the remaining part. With the increase of the $\tilde{\theta}_{H+}$, the portion of the ionomer not covered by the connection region decreases, which leads to the reduction of the effective area of the ionomer for oxygen transport, and a decrease in the oxygen transport capacity of the ionomer. Thus, as seen in Fig. 7c, the oxygen concentration in the ionomer region decreases from 0.032 mol m^{-3} to 0.018 mol m^{-3} , a decrease of 43.8% when $\tilde{\theta}_{H+}$ rises from 6% to 99% at a time of 0.015 s. In addition, ionomer has a much lower transport resistance to the proton than oxygen. Although the increase in $\tilde{\theta}_{H+}$ is more favorable for proton transport, in this study, the overpotential steps from 0.13 V to 0.3 V, which is sufficiently to provide proton transport even with $\tilde{\theta}_{H+}$ of 6%. Therefore, the proton concentration in Fig. 7d remains constant with increasing $\tilde{\theta}_{H+}$ at 0.015 s.

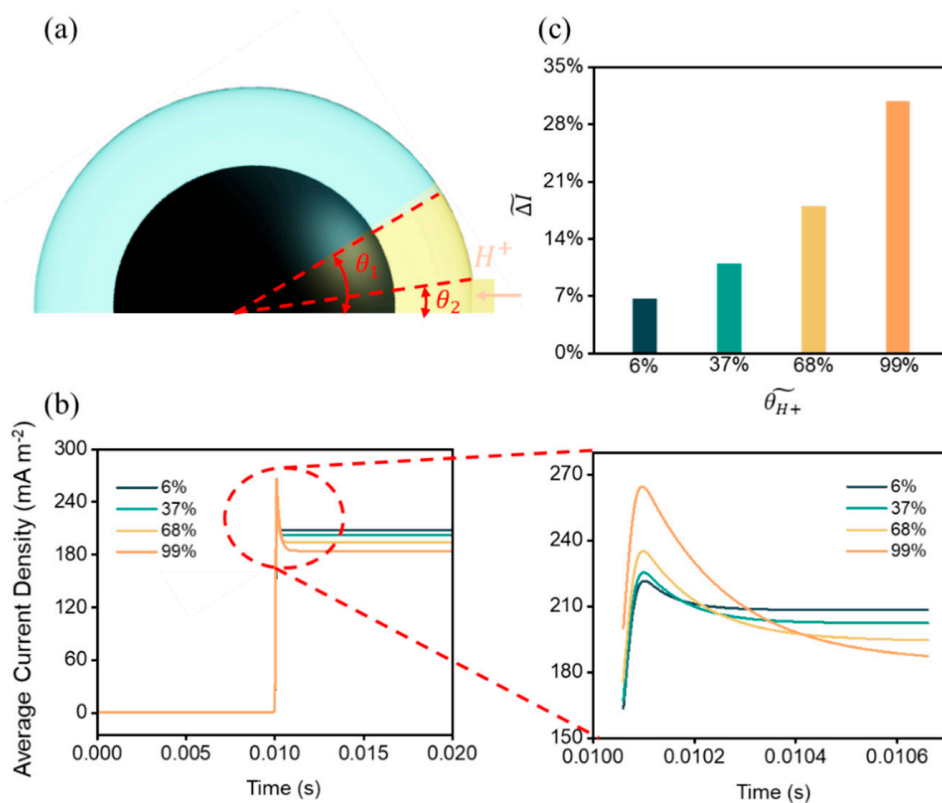


Figure 6: (a) schematic of ionomer connection region between catalysts, (b) effect of ionomer connection region on average current density, and (c) effect of ionomer connection region on overshoot amplitude of average current density.

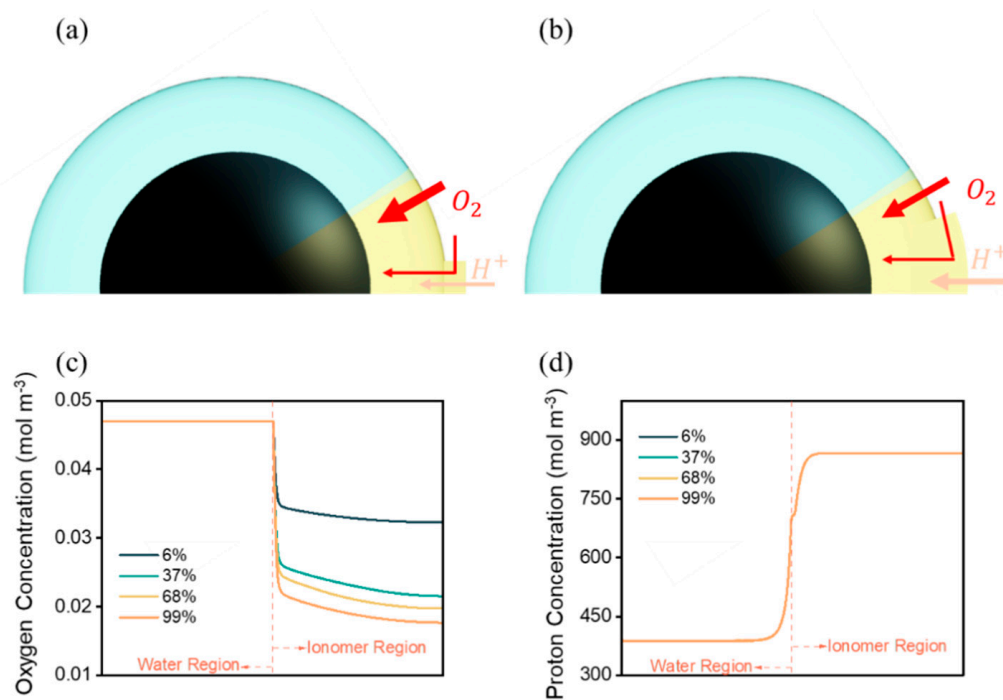


Figure 7: Schematic of oxygen transport through ionomer with (a) small ionomer connection region, (b) large ionomer connection region, (c) oxygen concentration, and (d) proton concentration.

3.3 Loading Rate and Loading Amplitude Effects

The appropriate loading rate and loading amplitude have important implications for optimal control. Fig. 8a shows the dynamic response of average current density with different overpotential loading times of 1×10^{-4} , 5×10^{-4} , 9×10^{-4} , 13×10^{-4} s. It can be found that the overshoot amplitude of average current density decreases with the rise of loading time. To fully analyze the transient behavior of the average current density, the effect of the loading rate on oxygen transport is studied. With a faster loading rate, the average current density rapidly reaches the maximum value, and the oxygen on the catalyst surface is quickly consumed. In contrast, as the loading rate slows down, the oxygen concentration is progressively consumed and the maximum average current density decreases. Therefore, the average current density overshoot amplitude decreases, as seen in Fig. 8a,b. In addition, according to Eq. (5), the oxygen concentration in ionomer and water quickly drops when the loading rate is faster, and the difference between the equilibrium oxygen concentration is larger, so the oxygen flux is larger. Subsequently, the oxygen consumed on the catalyst surface is gradually supplemented, and the oxygen flux reaches a stable value, as seen in Fig. 8c.

The effect of overpotential loading rate on the average current density dynamic response is analyzed previously. In addition, the step amplitude of overpotential also has an important impact on the dynamic response when the loading rate is constant. The initial overpotential of 0.13 V is kept constant in this study, and the final overpotential is 0.32, 0.30, 0.28, 0.26 V, so the range of $\Delta\eta'$ is 0.19 V to 0.13 V. As shown in Fig. 9a,b, $\tilde{\Delta I}$ decreases from 9.8% to 2.5% as $\Delta\eta'$ reduces from 0.19 V to 0.13 V. The oxygen concentration on the catalyst surface remains constant at the moment of overpotential steps up, and the higher overpotential is, the larger the average current density is, which also means the higher $I_{\max}$. Subsequently, the oxygen on the catalyst surface is consumed and it takes some time to reach a steady state due to the limitations of ionomer and water surface dissolution rates. By Eq. (5), the larger the overpotential is, the more oxygen flux is required, so the lower oxygen concentration on the catalyst surface, in Fig. 9c,d.

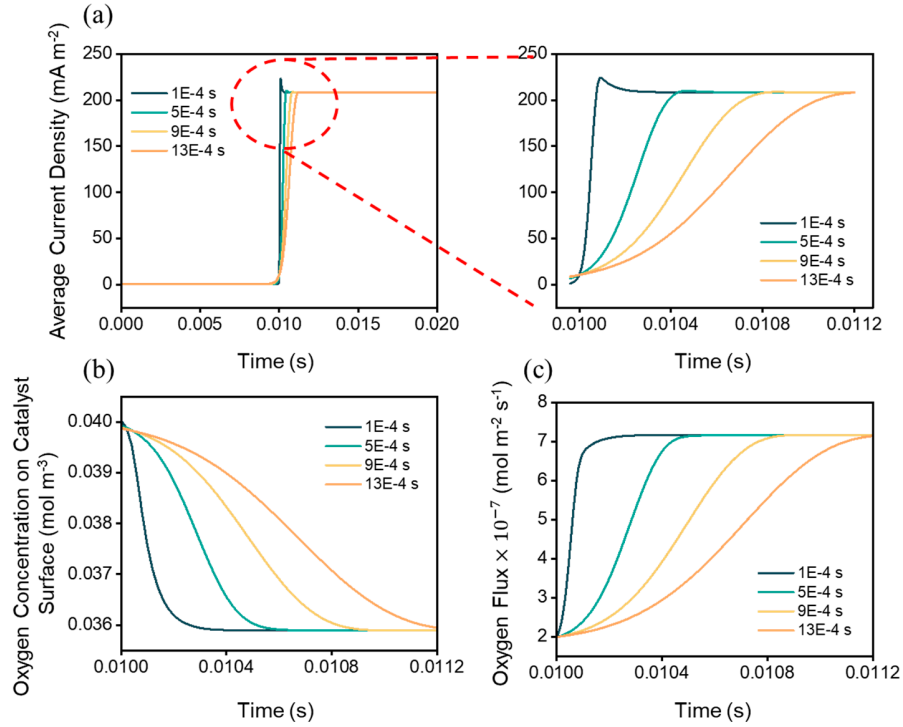


Figure 8: Effect of overpotential loading rate on (a) average current density dynamic response, (b) oxygen concentration on catalyst surface, and (c) oxygen flux.

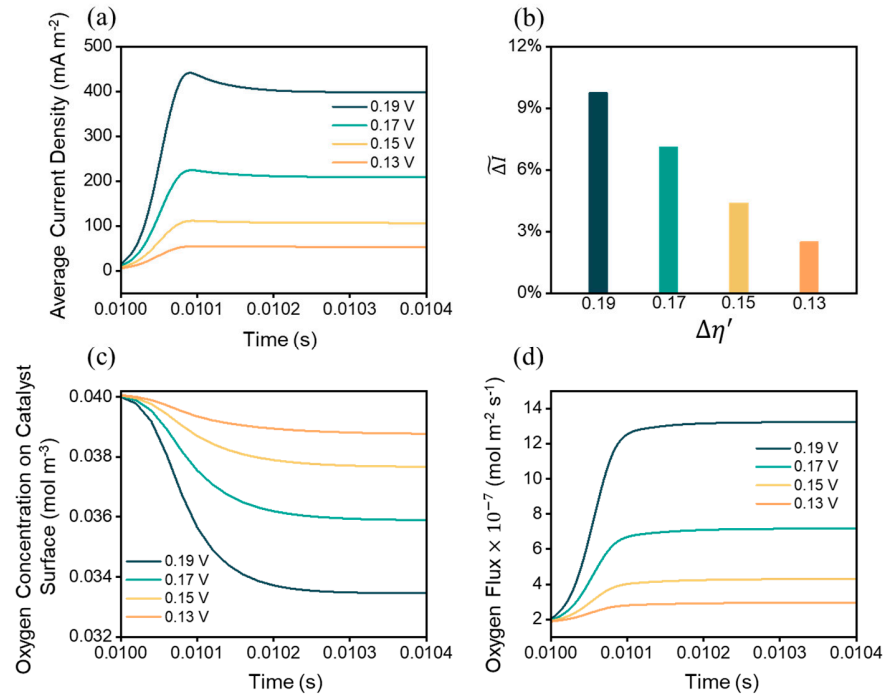


Figure 9: Effect of various overpotential step changes on (a) average current density dynamic response, (b) overshoot amplitude of average current density, (c) oxygen concentration on catalyst surface, and (d) oxygen flux.

4 Conclusion

A refined catalyst-scale mass transport model was developed to investigate the effects of local oxygen transport through ionomer and water on the transient response of PEMFC cathode catalyst layers. The results show that ionomer coverage strongly regulates the local oxygen transport pathway. As the ionomer coverage increases, the effective water-mediated oxygen transport area decreases and oxygen transport becomes increasingly dependent on the higher-resistance ionomer pathway, resulting in an increase in the current-density overshoot amplitude from 2.1% to 19.4%.

The ionomer connection region between neighboring catalyst particles also plays an important role in local oxygen transport. Although a larger connection region facilitates proton conduction, it reduces the effective area available for oxygen transport through the ionomer. Consequently, the oxygen concentration in the ionomer region decreases by 43.8%, while the current-density overshoot amplitude increases from 6.6% to 30.8%. These results demonstrate that, under the conditions considered here, transient response is primarily governed by local oxygen transport rather than proton transport.

In addition, reducing the loading rate and loading amplitude effectively suppresses the transient current-density overshoot. Overall, controlling ionomer coverage and connection morphology to maintain efficient local oxygen transport provides a useful basis for catalyst-layer microstructure design and dynamic operating strategies in PEMFCs.

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