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Bridging Interfacial Properties and Cell Performance: A Multiscale Model for Proton-Exchange-Membrane Fuel Cells

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To elucidate the impact of local interfaces on mass-transport resistance and overall cell performance of low-loading proton-exchange-membrane fuel cells (PEMFCs), we present a multiscale modeling framework incorporating a novel modified agglomerate model. The model considers three distinct Pt-electrolyte interfaces: Pt on the carbon surface covered by either ionomer or water film and Pt inside carbon nanopores. Detailed mass-transport voltage loss breakdowns reveal that coupled agglomerate-interface-scale mass transport dominates the mass-transport loss. The ionomer poisons the exterior-Pt surface through suppressing O₂ adsorption and intrinsic ORR activity, leading to low current-density performance. Conversely, interior-Pt interface enhances the kinetic performance but limits high current-density performance due to its low interfacial permeability. The exterior-Pt/water interface demonstrates superior kinetic performance and mass transport, though its practical implementation requires ensuring proton transport. By coupling the multiscale CL properties with ink parameters, the model identifies an optimal I to C ratio of approximately 0.5, a moderate value where the ionomer content is sufficient to guarantee proton transport without fully covering the Pt surface and forming large agglomeration, thus allowing the utilization of the Pt-water interface and avoiding high mass-transport loss. Overall, the model helps unravel limiting phenomena across different operating regimes and provides routes for optimizing performance.

Introduction

To reduce cost, proton-exchange-membrane fuel cells (PEMFCs) would like to operate with low loadings of precious metals. Even for higher loadings, performance decay due to the loss of catalyst electrochemically active surface area (ECSA) during operation remains a major concern regarding the desired longevity of PEMFCs.[1] This performance decline is largely attributed to the reduction of cathode catalyst-layer (CL) roughness factor (RF) (i.e., ECSA divided by geometric area), which leads to increase in non-Fickian mass-transport resistance occurring near the catalyst surface.[2] To address this challenge, tailoring the cathode CL structure to mitigate this local transport resistance has drawn great research interest in recent years.[3-7] CL structure can be regulated by tuning ink formula, which is typically an alcohol/water mixture composed of catalyst particles supported on carbon and ionomer colloids dispersed in a solvent. The interactions between these ink components determine the CL structure and ultimately the cell performance. However, varying ink parameters simultaneously changes CL structural properties across various scales, such as local ionomer coverage [8-12], agglomeration sizes [13, 14], and CL porosity and tortuosity [8, 15-17]. This multiscale interdependence complicates the identification of direct correlations between ink parameters and cell performance, making ink optimization and CL structure design largely reliant on the empirical trial-and-error process. Additionally, establishing a fundamental understanding of the ink-CL structure-MEA performance correlation requires extensive effort in developing modeled experimental setups and characterization techniques to isolate the effects of structural properties at different lengthscales on cell performance.

O₂ transport resistance is typically separated into pressure-dependent (Fickian) resistance and pressure-independent (non-Fickian) resistance, where the latter can be further broken down into the RF-dependent resistance and the Knudsen diffusion resistance. Alternatively, the multiscale transport phenomena within the CL can be delineated into three distinct scales: layer scale, agglomerate scale, and interface scale (see Figure 1). At the layer scale, O₂ transport occurs in the gas phase outside of the agglomerates, which is governed by macroscopic structural properties such as porosity, tortuosity, CL thickness, and liquid-water saturation. The associated transport resistance is primarily pressure-dependent. While Knudsen diffusion can occur inside the primary pores of CL, state-of-the-art electrodes have effectively mitigated this by employing an

1 appropriate ink process.[15, 18] In contrast, O₂ transport within agglomerates and across the
2 interface is pressure-independent. For low-loading electrodes, the RF-dependent resistance
3 dominates the agglomerate- and interface-scale transport, with the Knudsen diffusion resistance in
4 the secondary pores inside the agglomerates being trivial.[15] This RF-dependent transport
5 resistance further governs the cell performance.[6, 15, 19] Suzuki and coworkers propose
6 attributing part of transport resistance in CL to oxygen dissolution at the gas/ionomer interface
7 instead of the transport within the agglomerates.[20] A later molecular-dynamics (MD) simulation
8 study reveals the presence of free-energy barriers at gas/ionomer and ionomer/Pt interfaces, which
9 respectively leads to reduced oxygen solubility and permeability.[21] This high interfacial
10 transport resistance is further corroborated by experimental studies using microelectrode setups,
11 that the interfacial resistance at Pt/Nafion interface is equivalent to 30 to 70 nm of Nafion thin film,
12 a value significantly higher than typical thin-film thicknesses (<10 nm).[22] Subsequent studies,
13 including thin-film RDE measurements, [23], MD simulations,[24] and MEA studies,[15] further
14 support that the nanoscale Pt/ionomer interfacial region dominates the transport resistance due to
15 its low O₂ permeation. Despite the growing evidence highlighting the critical role of local
16 interfaces, the impact of interfacial resistance on fuel-cell performance remains poorly understood,
17 and mainly studied in isolation of the other cell phenomena. Beyond the most studied Pt/ionomer
18 interface, a realistic CL contains a variety of other interfaces whose combined effects on overall
19 cell performance are unclear. Ionomer coverages on Pt from 30 to 100% have been reported for
20 solid carbon support, with the uncovered Pt surface being electrochemically active when the
21 relative humidity is above 80%, suggesting a Pt/water interface and the need for proton accessible
22 pathways.[25-27] In the case of the mesoporous carbon support, a portion of the catalyst particles
23 are located inside the nanopores, where the local distributions are less defined because of the
24 unknown level of ionomer penetration[28] and complex capillary and other water phenomena.[29]
25 Thereby, these interior catalysts can be covered by either ionomer or water if electrochemically
26 active. However, these interior catalyst interfaces should be distinguished from the exterior
27 catalyst interfaces even if the same electrolyte—whether ionomer or water—is present at the
28 catalyst surface. This distinction arises from the nanoconfinement effects within the nanopores,
29 which alter the electrolyte's molecular structure and can lead to significant deviations from its bulk
30 properties.[28]

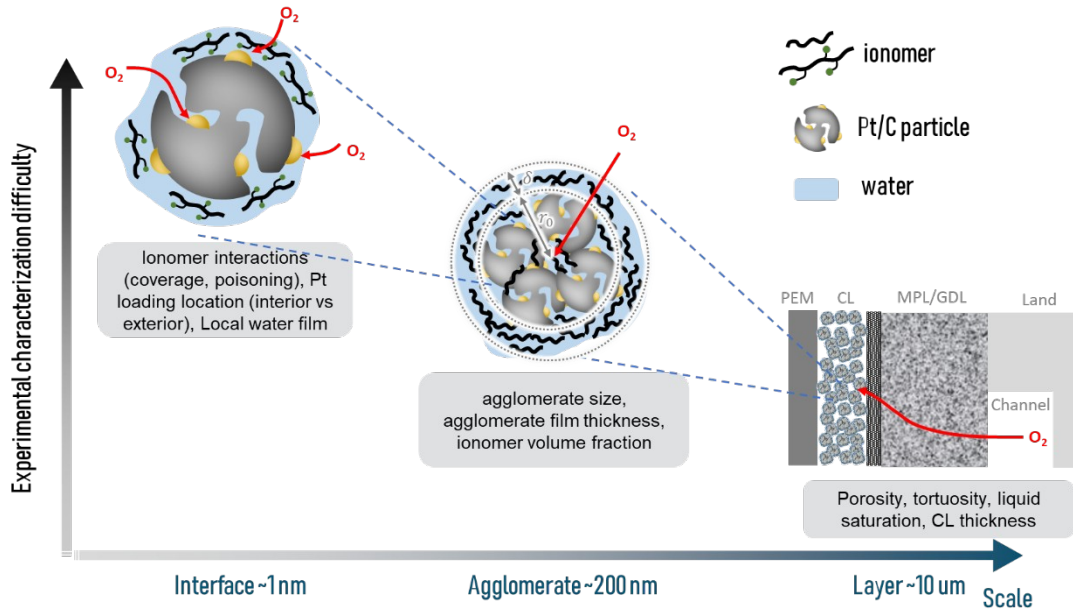


Figure 1. Schematic of the multiscale O_2 transport from flow channel to the reaction site in PEMFCs. The gray boxes list several key properties associated with the transport across different lengthscales, where characterization of the transport becomes increasingly challenging at smaller lengthscales

Advances in nanoscale characterization techniques, such as transmission electron microscopy (TEM) tomography, atomic force microscopy (AEM), small-angle X-ray scattering (SAXS), small-angle neutron scattering (SANS), and nano-computed tomography (nano-CT), [13, 30-32] have provided valuable insights into CL structure. However, these high-cost and labor-intensive experiments are impractical for large-scale screening of CLs fabricated from ink formulations with large parameter matrix. Atomic-scale modeling can directly probe interfacial phenomena, but it is computationally expensive and cannot simulate realistic CL structures and scale up to cell-level performance. Continuum modeling offers a promising alternative by bridging atomistic insights with cell-level performance at a manageable computational cost. The agglomerate model is typically employed to describe the multiscale O_2 transport in CL, with key governing parameters being the agglomerate geometry and O_2 diffusion coefficient. [33-35] However, the conventional agglomerate model does not differentiate the transport resistance contributed from agglomerate scale and interface scale. Consequently, transport loss at the interface is lumped into the agglomerate scale and mischaracterized using agglomeration

properties, leading to unrealistically large agglomerate radii—up to 1 μm —being used in many modeling studies to match experimental data,[20] which does not quantitatively agree with SEM observations [36]. A recent review by Huang *et al.* also points out the diverse agglomerate parameters across the literature, emphasizing the limitations of using the agglomerate model to capture the pressure-independent transport resistance arising from the complex CL microstructure. [37]. Darling developed a modified agglomerate model to capture nanoscale transport resistance, but it was not integrated with cell-level physics and relied on idealized interface assumptions, although did fit observed trends.[38, 39] In this work, we propose a comprehensive multiscale model by coupling a newly developed modified agglomerate model with a 2D MEA cell-level model to account for the effect of different interfaces in the CL, enabling the analysis of local catalyst environments such as ionomer coverage, catalyst particle location, and their influence on cell performance. First, the model framework and parameterization approach is introduced, followed by its application to evaluate performance loss across the scales in MEAs with different interfaces. Then, sensitivity analysis and parametric studies on interfacial properties are conducted and compared with experimental observations. Lastly, the model helps identify ink parameters that optimize cell performance by establishing an ink-structure-performance correlation. The manuscript concludes with key findings and perspectives.

Model Description

A 2D MEA model developed by Pant *et al.* serves as the foundation for simulating the PEMFC, with full details of the physics and model parameters provided in the original work [40]. In brief, the model applies a steady-state multiphase, multiphysics approach using volume-averaged properties, incorporating multicomponent gas diffusion, liquid and gas convection, concentrated-solution proton and water transport in membrane and CL ionomer, electron transport, and heat transport. Modifications were made in modeling the cathode CL to capture the effects of various interfaces on cell performance, as will be introduced later. The integration of O_2 transport in the CL across different scales relies on the following key assumptions:

- Transport at the layer scale occurs in the gas phase and is modeled using Stefan-Maxwell multicomponent diffusion.

- Transport at the agglomerate scale occurs in the ionomer phase. O_2 dissolves into the ionomer phase of the agglomerate from the gas phase with fast equilibrium, and subsequent transport is modeled using Fick's law.
- The interface scale transport governs the O_2 consumption rate as it diffuses through the agglomerate. Transport at the interface scale is modeled using Fick's law, with transport properties dependent on the local interface.
- For the multiscale-transport integration, we first developed the modified agglomerate model to couple the agglomerate- and interface-scale transport. This model yielded an analytical solution describing the current density per volume of CL, which is then incorporated as the source term of the Stefan-Maxwell diffusion equations. These are then directly solved at layer-scale (cell-level).

The model was solved using the finite-element method via the COMSOL Multiphysics software (version 6.3). A stationary study was performed using the direct MUMPS solver with a relative tolerance of 0.001 for convergence. The mesh comprised 936 triangular elements in the land and 10000 quadrilateral elements in the MEA, corresponding to a total element area ratio of 3.24×10^{-5} .

Conventional agglomerate model

First, we briefly introduce the conventional agglomerate model. For detailed derivation, we refer the readers to the original reference.[35] In the conventional agglomerate model, the agglomerate is assumed to be a sphere agglomerate core with radius r_0 covered by an ionomer shell with a thickness of δ (see Figure 1). [35] The agglomerate core is where the oxygen-reduction reaction (ORR) occurs and consists of catalyst/carbon particles bound with ionomer. For convenience, we assume Pt as the catalyst material in the rest of the model description. The current per volume of agglomerate core is given as

$$i_{aggcore} = 4 F R_{O_2} \quad (1)$$

where R_{O_2} is the rate of oxygen consumption per volume of agglomerate core,

$$R_{O_2} = k_{r,aggcore} C_{O_2} \quad (2)$$

1 where $k_{r,aggcore}$ is the apparent volumetric reaction rate at the agglomerate scale and C_{O_2} is the
 2 oxygen concentration within the agglomerate. Here, an ORR reaction order of one is used
 3 according to Parthasarathy *et al.*, [41] which also enables an analytic evaluation. Other ORR
 4 reaction orders have also been reported [42, 43] and its uncertainties have been discussed. [35, 44,
 5 45] $k_{r,aggcore}$ is scaled from the intrinsic ORR reaction rate constant k_r through catalyst layer
 6 porosity ϵ_{CL} , volume ratio of agglomerate core to agglomerate, and the electrochemically active Pt
 7 surface area per volume of catalyst layer $S_{Pt,act}$,

$$k_{r,aggcore} = k_r \left(\frac{S_{Pt,act}}{1 - \epsilon_{CL}} \right) \left(\frac{r_0 + \delta}{r_0} \right)^3 \quad (3)$$

8 where k_r is described using Tafel kinetics:

$$k_r = \frac{i_{ref}}{4 F C_{ref}} \exp \left(\frac{E - E_{ref}}{b} \right) \quad (4)$$

9 where each term has its conventional definition. C_{ref} is 1 mol L⁻¹ and E_{ref} is given as [40]

$$E_{ref} = 1.23 - 9 \times 10^{-4} (T - 298) [V] \quad (5)$$

10 Fick's law is applied to describe the oxygen transport within the agglomerate core:

$$-D_{aggcore} \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dC_{O_2}}{dr} \right) = -R_{O_2} \quad (6)$$

11 where $D_{aggcore}$ is the O₂ diffusion coefficient in agglomerate core and can be approximated using
 12 Bruggeman's relation,

$$D_{aggcore} = D_{film} \epsilon_{aggcore}^{1.5} \quad (7)$$

13 where D_{film} is the oxygen diffusion coefficient in ionomer thin film and $\epsilon_{aggcore}$ is the ionomer
 14 volume fraction in the agglomerate core. The flux of oxygen through agglomerate ionomer film
 15 should equal the total consumption of oxygen in the agglomerate core:

$$-D_{film} \frac{dC_{O_2}}{dr} (4 \pi r^2) = \int_0^{r_0} -R_{O_2} \times 4 \pi r^2 dr \quad (8)$$

1 Analytical solutions can be obtained by applying the boundary conditions:

$$2 \quad C_{O_2} = \frac{P_{O_2}}{H_{film}} \text{ at } r = r_0 + \delta$$

$$3 \quad C_{O_2} \text{ is a finite value at } r = 0$$

4 where P_{O_2} is the oxygen partial pressure and H_{film} is the Henry's constant of oxygen in ionomer
 5 film. After substituting the solution from Equations (6 thru (8) to Equation (1), the expression for the
 6 current per volume of agglomeration core is

$$i_{aggcore} = \frac{4F \frac{P_{O_2}}{H_{film}}}{\frac{1}{k_{r,aggcore} \eta} + \frac{\delta r_0^2}{3(r_0 + \delta) D_{film}}} \quad (9)$$

7

$$\eta = \frac{3}{\phi_L^2} (\phi_L \coth(\phi_L) - 1) \quad (10)$$

8 where ϕ_L is the Thiele's modulus that characterizes the reaction-transport process, defined as

$$9 \quad r_0 \sqrt{\frac{k_{r,aggcore}}{D_{aggcore}}}, \text{ and } \eta \text{ is the effectiveness factor, defined as the ratio of the average reaction rate in}$$

10 the agglomerate core to the reaction rate with no transport loss within agglomerates (*i.e.*, all
 11 catalyst is exposed to outside surface conditions).

12

13 **Modified agglomerate model**

14 The modified agglomerate model calculates the current generated from each type of interface
 15 separately and explicitly considers the interfacial transport resistance. We assume three types of
 16 interfaces: exterior-Pt/ionomer, exterior-Pt/water, and interior-Pt, which allows for the description
 17 of the widely used solid carbon and mesoporous carbon catalyst supports. As mentioned above, the
 18 interior-Pt interface is distinguished from the exterior-Pt interfaces, where the latter is further
 19 separated into the ionomer-covered and water-covered portions if the surface is sufficiently

hydrated; something that is currently not able to be visualized and distinguished experimentally. [28] In the following, the interface-dependent parameters are denoted with superscript i , where $i \in \{\text{ext.-Pt/I, ext.-Pt/w, int.-Pt}\}$ to represent the exterior-Pt/ionomer, exterior-Pt/water, and interior-Pt interfaces. Current per volume of agglomerate core generated from interface i is

$$i_{agcore}^i = 4 F R_{O_2}^i \quad (11)$$

where $R_{O_2}^i$ is the rate of oxygen consumption at interface i per agglomerate core volume, which can be described as

$$R_{O_2}^i = k_{r,agcore}^i C_{O_2,s}^i \quad (12)$$

where $k_{r,agcore}^i$ is the interface-dependent volumetric reaction rate at the agglomerate scale and $C_{O_2,s}^i$ is the actual surface concentration at the Pt surface. $k_{r,agcore}^i$ is scaled from the intrinsic ORR reaction rate constant k_r^i through the Pt ECSA per volume of catalyst layer $S_{Pt,act}^i$,

$$k_{r,agcore}^i = k_r^i \left(\frac{S_{Pt,act}^i}{1 - \varepsilon_{CL}} \right) \left(\frac{r_0 + \delta}{r_0} \right)^3 \quad (13)$$

We assume that the intrinsic ORR kinetics are interface-dependent by introducing the interface-specific charge transfer coefficient α^i , as the electrolyte-dependent electrical-double-layer (EDL) structure can affect ORR mechanisms.[46, 47] While a detailed microkinetic model alongside a EDL model could be employed to describe the ORR intrinsic kinetics, both EDL theory and ORR mechanisms remain debated.[46, 48] As an accurate description of ORR kinetics is not the main focus of this work, we account for the interface-dependent kinetics by assuming different fractions of activation energy of the rate-determining-step being reduced by the electrical energy, which is reflected through the parameter α^i .

Similar to the conventional agglomerate model, constitutive equations to describe the O_2 transport at interface i within the agglomerates can be constructed as

$$-D_{aggcore} \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dC_{O_2}^i}{dr} \right) = -R_{O_2}^i \quad (15)$$

$$-D_{film} \frac{dC_{O_2}^i}{dr} (4\pi r^2) = \int_0^{r_0} -R_{O_2}^i \times 4\pi r^2 dr \quad (16)$$

2 where $C_{O_2}^i$ denotes the O_2 concentration in agglomerate. $C_{O_2}^i$ should be distinguished from $C_{O_2,s}^i$
3 due to the additional interfacial transport resistance that is not captured in the conventional
4 agglomerate model. To solve analytically for Equation (15 and (16, $C_{O_2,s}^i$ can be expressed using
5 $C_{O_2}^i$ based on Fick's law. Near the interface i, assuming a linear concentration drop, the O_2 flux
6 should be equal to the rate of consumption:

$$j_{O_2}^i = \frac{\frac{H_{film}}{H^i} C_{O_2}^i - C_{O_2,s}^i}{R^i} = k_r^i C_{O_2,s}^i \quad (17)$$

$$C_{O_2,s}^i = \frac{\frac{H_{film}}{H^i} C_{O_2}^i}{1 + k_r^i R^i} \quad (18)$$

8 where H^i and R^i are interfacial Henry's constant and interfacial diffusion resistance of O_2 at
9 interface i, respectively. R^i can be further expressed by the interfacial diffusion length l^i and
10 interfacial diffusivity D^i : $R^i = \frac{l^i}{D^i}$. MD simulations show that the strong Pt-Nafion and Pt-water
11 interactions both partition the electrolyte film into two distinct regions: a dense molecular layer,
12 typically within 0.5 nm above the Pt surface, and a bulk-like region further away.[21, 24, 49]
13 Therefore, H^i and R^i particularly describe the O_2 transport within the dense layer and whose value
14 should be distinguished from those of either bulk electrolyte or the entire thin film. Grazing-
15 incidence small-angle X-ray scattering (GISAXS) has been conducted for thin films on planar
16 substrates, which shows alignment of domains and denser layers.[50, 51] Also, neutron-
17 reflectometry data has been fit and interpreted to suggest a dense water layer at the
18 catalyst/electrolyte interface at the atomic scale. [52-54] However, direct experimental validation
19 of the dense molecular layer at the sub-nanometer scale remains challenging. Fundamentally, H^i

1 characterizes the oxygen activity at the interface at equilibrium, which is governed by the
 2 adsorption free energy of O₂ at the Pt/electrolyte interface. This parameter influences both apparent
 3 ORR kinetics by determining the maximum surface availability to O₂, given by $\frac{H_{film}}{H^i} C_{O_2}^i$, and the
 4 transport resistance through interfacial permeability. D^i reflects the energy barrier O₂ needs to
 5 overcome to traverse the dense electrolyte layer and reach the Pt surface. By introducing the
 6 adsorption free energy, E_{ads}^i , and diffusion energy barrier, E_a^i , that reference the bulk properties,
 7 H^i and R^i can be expressed by the Henry's constant and diffusion coefficient of O₂ in the bulk
 8 electrolyte, denoted respectively as H_b^i and D_b^i , based on Arrhenius-type relation,

$$H^i = H_b^i \exp\left(\frac{E_{ads}^i}{RT}\right) \quad (19)$$

9

$$R^i = \frac{l^i}{D_b^i \exp\left(\frac{-E_a^i}{RT}\right)} \quad (20)$$

10 where l^i characterizes the thickness of dense electrolyte region at interface i. Substitute Equation
 11 (12(14 and (18 into Equation (15(16 gives

$$R_{O_2}^i = \frac{\frac{H_{film}}{H^i} \left(\frac{S_{Pt,act}^i}{1 - \epsilon_{CL}} \right) \left(\frac{r_0 + \delta}{r_0} \right)^3 k_r^i}{1 + k_r^i R^i} C_{O_2}^i \quad (21)$$

12 If defining a corrected reaction rate constant $k_{r,aggcore}^i = \frac{k}{1 + k_r^i R^i}$, the analytical solution
 13 for $i_{aggcore}^i$ with the same form of Equation (9) can be obtained,

$$i_{aggcore}^i = \frac{4 F \frac{P_{O_2}}{H_{film}}}{\frac{1}{k_{r,aggcore}^i \eta_o^i} + \frac{\delta r_0^2}{3(r_0 + \delta) D_{film}}} \quad (22)$$

1 where the interface-corrected term η_{c}^i and $\phi_{L,*\text{c}}^i$ are

$$\eta_{\text{c}}^i = \frac{3}{\phi_{L,*\text{c}}^i} \quad (23)$$

2

$$\phi_{L,*\text{c}}^i = r_0 \sqrt{\frac{k_{r,aggcore*}^i}{D_{aggcore}}} \quad (24)$$

3 So far, $i_{aggcore}^i$ for each type of interface are defined and can be distinguished by the interface-
 4 dependent parameters $S_{Pt,act}^i$, H^i , R^i , and α^i , where $S_{Pt,act}^i$ is the structural parameter that
 5 characterizes the available area of different types of interfaces and H^i , R^i , and α^i characterize the
 6 intrinsic properties of the interface. Parameterization of these interfacial properties will be
 7 introduced in the next section. Lastly, the current per volume of catalyst layer can be determined as
 8 the sum of the current generated from all types of interfaces,

$$i_{CL} = \left(\frac{r_0}{r_0 + \delta} \right)^3 (1 - \varepsilon_{CL}) \sum_i i_{aggcore}^i \quad (25)$$

9

10 Interfacial properties parameterization

11 **Electrochemically active Pt area for interface i ($S_{Pt,act}^i$).**— CO-stripping voltammetry and
 12 hydrogen-underpotential deposition (H_{UPD}) are widely used to measure ECSA.[55] In electrodes
 13 featuring non-ionomer-covered Pt interfaces, whether they are exterior or interior, ECSA becomes
 14 a function of RH as the Pt not contacting the ionomer can only be electrochemically active at higher
 15 RH when sufficient water or ionomer swelling is present to provide proton-transport pathways.[27,
 16 56, 57] As a result, ECSA measured at high RH approximates the total available active Pt area,
 17 denoted as S_{Pt}^{tot} . The experimental reported ECSA with the unit of area per mass of Pt can be
 18 converted to the model parameters with the unit of area per CL volume by

$$S_{Pt}^{tot} = \frac{L_{Pt} ECSA}{t_{CL}} \quad (26)$$

where L_{Pt} is the Pt loading in the unit of Pt area per MEA area, and t_{CL} is the CL thickness. If not provided in the literature, CL thickness can be estimated based on ink composition and porosity:

$$t_{CL} = \frac{L_{Pt}(1 - \omega_{Pt})}{(1 - \varepsilon_{CL})\omega_{Pt}} \left(\frac{I:C}{\rho_I} + \frac{1}{\rho_C} \right) \quad (27)$$

where ω_{Pt} is the platinum content of Pt/carbon catalyst particle, ρ_I and ρ_C are the densities of ionomer and carbon respectively, and $I:C$ is the I to C ratio. Due to limited data relating CL porosity to ink parameter matrix, ε_{CL} is empirically correlated solely with the I to C ratio based on literature data (Figure S1).[15-17, 58-62]

To decompose S_{Pt}^{tot} into $S_{Pt,act}^i$, we introduce the following parameters: ionomer coverage on exterior-Pt, θ_I , interior-Pt fraction, $f_{\int \omega}$, and the surface utilization for interface i, ξ_{Pt}^i . $S_{Pt,act}^i$ can be fractionated from S_{Pt}^{tot} as

$$S_{Pt,act}^{ext.-Pt/I} = S_{Pt}^{tot} \quad (29)$$

$$S_{Pt,act}^{ext.-Pt/w} = S_{Pt}^{tot} \quad (30)$$

$$S_{Pt,act}^{\int.-Pt} = S_{Pt}^{tot} f_{\int \omega} \xi_{Pt}^{\int.-Pt} \quad (31)$$

The surface utilization factor accounts for the ECSA reduction due to the site-blocking effect of sulfonic-acid moieties for the ionomer-covered interface and the RH-dependent proton accessibility for the non-ionomer-covered interface. For the ionomer-covered interface, sulfonic-acid coverage can be quantified by integrating the displacement current transient as CO gas is introduced to the electrode during potential-hold experiments at 0.5 V, so-called CO-displacement experiments.[10, 12] [63] For the non-ionomer-covered interface, although ECSA's dependence on RH varies across different electrodes,[27, 56, 57] Pt sites achieve the highest ECSA under saturated condition (*i.e.*, RH=100%). Under those conditions, a utilization factor of unity can be assumed. However, one should note that the maximum ECSA utilization under operando

conditions may not always be true, especially at high current densities where proton transport become limiting, a factor beyond the scope of the current study.

Several approaches have been proposed to evaluate the ionomer coverage. Ionomer-covered Pt surface can be distinguished from water-covered Pt surface by measuring ECSA through CO-stripping voltammetry under dry condition or fluorocarbon-fluid-filling condition,[23] where proton transport to non-ionomer-covered Pt surface is inhibited. Other approaches include comparing capacitance current under perfluorohydrocarbon solvent and under nitrogen [25], and analyzing the RH-dependent EDL capacitance from electrochemical-impedance spectroscopy (EIS) [12, 26]. A consistent trend of increasing ionomer coverage with a higher I to C ratio has been reported in literature (see Figure S2 in the Supplementary Materials); however, the values are quantitatively inconsistent. The above characterization techniques have also been applied to Pt/mesoporous carbon electrodes to estimate the interior-Pt fraction, usually under the assumption of no ionomer penetration. However, as there is increasing evidence indicating the presence of ionomer in the pore,[28, 64, 65] the interior-Pt particles should not be equated with non-ionomer-covered Pt. An alternative method is to count the number of interior and exterior-Pt particles identified from comparing scanning-electron-microscopy (SEM) and scanning-transmission-electron-microscopy (STEM) images.[9, 66]

Determination of H^i , R^i , and α^i for exterior-Pt/ionomer interface.— Experimental measurement of interfacial Henry's constant and diffusion resistance for an individual interface requires a controlled experimental system involving only one interface type. Kudo determined O_2 transport resistance by measuring the limiting current density at the Pt/ionomer interface using a microelectrode setup with a Pt disk electrode coated with Nafion films of varying thickness.[22] The film-thickness-independent transport resistance is determined as the interfacial transport resistance by extrapolating the linear relationship between the resistance and film thickness to zero film thickness. This value corresponds to $H^i \times R^i$ for the exterior-Pt/ionomer interface. The expression below, fit from the experimental data reported as a function of RH and temperature, is used in the model (see Figure S3 in the Supplementary Materials):

$$H^{ext.-Pt/I} \times R^{ext.-Pt/I} = (-530.5 a_0 + 1453) \exp\left(\frac{2799[K]}{T}\right) [\text{Pa m}^2 \text{ s mol}^{-1}] \quad (32)$$

where a_0 is the water activity in the ionomer. $H^i \times R^i$ represents the permeation resistance that is inversely proportional to the interfacial permeability and can be separated if either H^i or R^i is known. The assumption underlying the adoption of Equation (32) to describe the transport resistance at exterior-Pt/ionomer interface is that the diffusion resistance at the gas/ionomer interface and in the ionomer film is considered negligible from the overall interfacial resistance. MD simulations have shown that the O_2 permeation flux at the gas/Nafion interface is three orders of magnitude higher than that at the Nafion/Pt interface, indicating negligible resistance at the gas/Nafion interface compared to the Nafion/Pt interface.[21] As for the resistance associated with the ionomer film, both microelectrode and MEA studies have suggested that the local transport resistance for a Pt/Nafion system is insensitive to film thickness within the length scale of the ionomer thin film (e.g. ~ 10 nm).[15, 22] Therefore, at the interface scale, the transport resistance from the ionomer film can be considered minimal compared to the other ones. Alternatively, the model does capture the transport resistance in the ionomer film at the larger agglomerate scale. Jinnouchi and coworkers calculated the dissolution energy of O_2 from the gas phase to the interfacial Nafion ionomer film, denoted as E_{dis} , as a function of water uptake (see Figure S4 in the Supplementary Materials).[21] According to an Arrhenius-type equation, $H^{ext.-Pt/I}$ can be determined as

$$H^{ext.-Pt/I} = RT \exp\left(\frac{E_{dis}}{RT}\right) \quad (33)$$

18 $R^{ext.-Pt/I}$ can be then determined by $\frac{H^{ext.-Pt/I} \times R^{ext.-Pt/I}}{H^{ext.-Pt/I}}$. Lastly, to obtain α^i , the Tafel slope
 19 from ORR voltammetry at the Pt/Nafion interface measured using a microelectrode setup was
 20 used.[41]

21 Rigorously speaking, the above parameters are specific to the Pt/ionomer interface used in
 22 these experiments. For a different ionomer electrolyte, e.g., a hydrocarbon ionomer, different
 23 interfacial parameters may be expected and a precise description of that Pt/ionomer interface
 24 requires additional experimental characterization. Another uncertainty could be the transferability
 25 of findings from the single-crystal Pt/ionomer interface to the realistic interfaces in an MEA, where

factors such as complex polycrystalline catalyst nanoparticles and surface chemistry of catalyst supports come into play.

Determination of H^i , R^i , and α^i for exterior-Pt/water interface.— In contrast to the direct measurement of interfacial permeation at the Pt/ionomer interface introduced above, experimental characterization of the interfacial transport at the exterior-Pt/water interface is less straightforward. Takeshita *et al.* found that the ORR specific activity at exterior-Pt/water interface was 4.5 times higher than at Pt/ionomer interface under 80% RH at 0.9 V.[23] Using this correlation with Equation (19, $E_{ads}^{ext.-Pt/w}$ was determined to be -4.9 kJ mol⁻¹. MD simulations calculate adsorption free energy of O₂ on Pt(100), Pt(111), and Pt(110) surfaces in water ranges from -6.4 to +3.5 kJ mol⁻¹. [49] Thereby, the value of $E_{ads}^{ext.-Pt/w}$ reasonably agrees given the mixed facets of realistic Pt nanoparticles. To estimate $R^{ext.-Pt/w}$, we utilized the non-Fickian transport resistance measured from the ionomer-free nanostructured-thin-film (NSTF) electrode, which is 0.187 s cm⁻¹ at a roughness factor of 12.9 cm²_{Pt} cm⁻²_{MEA}. [67] A typical NSTF architecture consists of only catalyst-coated whiskers with the majority of the Pt surface not in contact with the ionomer, except for a small portion of the whiskers that are pushed into the membrane during assembly. [68] Thereby, in the absence of agglomerates and ionomer, the interfacial transport resistance at the exterior-Pt/water interface can be regarded as the sole cause of the non-Fickian transport resistance. Applying Equation (20, $E_a^{ext.-Pt/w}$ was determined as 14.6 kJ mol⁻¹, which falls within the range of free-energy barriers of O₂ adsorption on low-index Pt surfaces in water, calculated as 9.0 to 18.0 kJ mol⁻¹ by MD simulations. [49] $l^{ext.-Pt/w}$ in Equation (20 was approximated as 0.5 nm based on the thickness of high-water-density region above the Pt top atomic layer. [49] We acknowledge the potential uncertainties of $E_{ads}^{ext.-Pt/w}$ arising from the fitting procedure with insufficient characterization of NSTF electrode structure (see Supplementary Materials for detailed fitting protocol). Thus, parametric studies of $E_{ads}^{ext.-Pt/w}$ will be accomplished.

Lastly, to obtain α^i , the Tafel slope from ORR voltammetry measured from rotating-disk electrode (RDE) setups with HClO₄ electrolyte was used. [69]

Determination of H^i , R^i , and α^i for interior-Pt interface.— Harzer and colleagues selectively deposited all Pt particles inside the pores of Ketjenblack (KB) carbon support, providing an ideal

model system for extracting the interfacial parameters to describe the interior-Pt interface.[70] Using their MEA measurements, H^i and R^i were determined by reproducing the kinetic regime of the IR-free polarization curve and the pressure-independent transport resistance, respectively. α^i was fit to the Tafel slope of the kinetic regime from the IR-free polarization curve. Similar to the exterior-Pt/ionomer interface, the values for these interfacial parameters are system-specific, which incorporate the effects of pore-size distribution, level of ionomer penetration, interior-Pt loading, pore-wall surface chemistry, *etc.*, which may not be directly transferable to describe the interior-Pt interfaces in a different electrode although the trends are probably translatable. We suggest that these interfacial parameters might be less appropriate for describing the interior-Pt interfaces in mesoporous carbon pores other than the KB carbon pores, and more experimental data to confirm this is required, as recent studies utilizing novel mesoporous carbon supports have demonstrated improved cell performance;[71, 72] parametric studies are performed in more detail below. A more precise bottom-up approach would involve calculating effective values by integrating pore-property-dependent parameters over all pores; however, the so-far ill-defined pore environment and limited characterization of nanopore-scale O₂ transport limit the practical application of this approach today.

Results and Discussions

Interfacial parameters

Table 1 and Figure 2 summarizes the value of interfacial parameters obtained as discussed above. Details of the fitting protocol are available in the Supplementary Materials. Not surprisingly, the interfacial properties at the Pt/electrolyte interfaces differ from those of the corresponding bulk electrolytes. These deviations arise from either the interfacial interactions between Pt and electrolyte molecules or confined nanopore geometry that create a distinct local environment. The large positive dissolution energy with respect to the gas phase causes a higher interfacial Henry's constant at the Pt/ionomer interface compared to a typical Henry's constant for a recast Nafion membrane under the same conditions (2.95×10^4 Pa m³ mol⁻¹ at 80°C and 100% RH [22]). In contrast, the negative adsorption energy at the exterior-Pt/water interface leads to a lower Henry's constant than that of bulk water (1.25×10^5 Pa m³ mol⁻¹ [73]). Assuming a 0.5 nm-thick interfacial

dense layer, we estimated the interfacial diffusivities to be $9.25 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ and $4.71 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ at exterior-Pt/ionomer and exterior-Pt/water interfaces respectively, which are both notably lower than their bulk values ($6.27 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ for recast Nafion membrane [22] and $6.90 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ for water [73]) due to the additional diffusion energy barriers near the Pt surface due to confinement and structuring of the hydrogen-bond network.

Table 1. Values of interfacial parameters at T=80 °C and RH=100%.

	ext.-Pt/w	ext.-Pt/I	int.-Pt
H^i ($\text{Pa m}^3 \text{ mol}^{-1}$)	2.33×10^4	4.72×10^5	2.27×10^5
R^i (s m^{-1})	10.62	5.41	30.92
$H^i \times R^i$ ($\text{kg m s}^{-1} \text{ mol}^{-1}$)	2.48×10^5	2.55×10^6	7.03×10^6
α^i	1	0.92	0.85

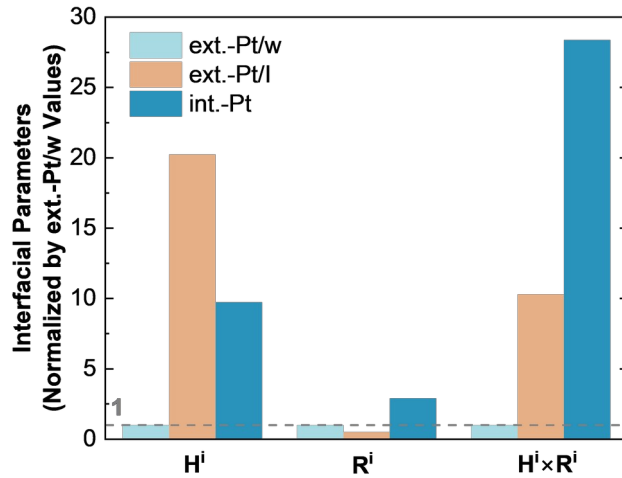


Figure 2. Summary of interfacial parameters. (a) Values of interfacial parameters at T=80 °C and RH=100%. (b) Comparisons between interfacial parameters. All values are normalized by the values for the exterior-Pt/water interface.

Interfacial properties significantly influence macroscopic cell performance (see Equations S6 and S9 in the Supplementary Materials). The interfacial Henry's constant determines the maximum oxygen availability at the catalyst surface, affecting performance across all current densities. At 100% RH, the exterior-Pt/ionomer interface exhibits a Henry's constant

approximately 20 times higher than the exterior-Pt/water interface (Figure 2b). Although this value decreases at lower RH (see Figure S4 in Supplementary Materials), O₂ solubility at the exterior-Pt/ionomer interface remains low. Notably, this trend contrasts with bulk behavior, where O₂ solubility in water is lower than in ionomer,[22, 73] highlighting the disparity between interfacial and bulk properties. The high interfacial Henry's constant at the exterior-Pt/ionomer interface leads to surface oxygen starvation before reaching diffusion limitation, leading to suppressed performance at low current density (lcd) as suggested in Equation S6. Therefore, enhancing O₂ solubility at the exterior-Pt/ionomer interface would benefit cell performance. This is supported by the improved specific ORR activity observed in electrode using a highly oxygen-permeable ionomer (HOPI), where the O₂ solubility at the Pt/HOPI interface was found to be higher than at Pt/Nafion or Pt/Aquivion ionomer interfaces. [24] The highest diffusion resistance was identified to occur at the interior-Pt interface, attributed to the extended transport pathways and reduced diffusivity inside the carbon nanopores. Kikkawa and Kimura found that oxygen diffusion is retarded by 2 orders of magnitude in water-filled pores, and slowed by an additional 1~2 order of magnitude if ionomer is present.[74] The interfacial permeability, which dictates mass transport at high current density (hcd) (see Equation S9 in the Supplementary Materials), is inversely proportional to the product of the interfacial Henry's constant and diffusion resistance. A comparison among the three types of interfaces shows that their interfacial permeabilities follow the trend of interior-Pt < exterior-Pt/ionomer < exterior-Pt/water. The restricted O₂ permeation inside nanopores stems from both low O₂ solubility and high diffusion resistance, whereas the exterior-Pt/ionomer interface benefits from lower diffusion resistance that partially offsets its poor solubility.

Multiscale cell performance diagnostic

Electrochemical impedance spectroscopy (EIS) has been employed to decouple the cell performance loss into various contributions, typically associated with kinetics, ohmic resistance, and mass transport.[75] However, this approach only resolve process with sufficiently distinct times cales, limiting its ability to capture finer mechanistic details.[76-78] For example, the model indicates that O₂ diffusion in gas phase of the catalyst layer and within the agglomerate both exhibit

1 similar characteristic time constants on the order of $\sim 10^{-5}$ s, leading to overlapping impedance
2 features. In contrast, a key advantage of the developed model is its ability to deconvolute
3 performance losses across multiple transport lengthscales and timescales, and identify specific
4 areas for improvement. To demonstrate this capability, MEA measurements from Harzer *et al.*
5 using Pt/KB_{PO} and the Pt/KB_{IW} catalyst—corresponding to electrodes involving only exterior-Pt
6 particles and interior-Pt particles respectively—are used as the reference cases.[70] We assume the
7 exterior-Pt particles in Pt/KB_{PO} are fully covered by ionomer as discussed in the Supplementary
8 Materials. Consequently, the performance difference between the two electrodes reflects the
9 contrasting interfacial properties of the exterior-Pt/ionomer and interior-Pt interfaces.

10 Using the parameters determined previously (Figure 2 and Table S1), the modeled
11 polarization curves at 80°C, 100% RH, 170 kPa, and H₂/10%O₂ channel conditions demonstrate a
12 satisfactory agreement with the experiments (Figure 3a). The voltage-loss breakdowns, analyzed
13 using the power-loss post-processing method detailed by Gerhardt *et al.* [79], suggest that the
14 sluggish ORR kinetics and O₂ mass transport are the two major causes of cell performance loss for
15 both Pt/KB_{PO} and the Pt/KB_{IW} system (Figure 3b and Figure 3c). The model reveals that ORR
16 kinetics is not the only contributor to the performance loss at low current density, and that the O₂
17 mass transport also plays a significant role. Detailed breakdowns (methods provided in
18 Supplementary Materials) of O₂ mass-transport voltage loss demonstrate that the mass-transport
19 loss at low current density originates from O₂ dissolution from the gas phase into the ionomer phase
20 and subsequent interaction with the Pt surface. These processes consistently contribute to the
21 transport losses across the entire current-density range. The transport resistance primarily arises
22 from the agglomerate scale and interface scale (Figure 3d and Figure 3e). At the agglomerate scale,
23 the limiting step of transport within the agglomerate is O₂ dissolution rather than the diffusion
24 resistance in the agglomerate ionomer film and agglomerate core. This observation is likely due to
25 two aspects: first, the O₂ diffusivity in the bulk ionomer film is not exceptionally low compared to
26 that in the dense layer at the interface, as discussed previously; secondly, due to this relatively high
27 O₂ diffusivity and relatively small diffusion length, transport within both the agglomerate film and
28 agglomerate core is insufficient to generate a substantial diffusion resistance. In particular, the
29 thickness of agglomerate film and radius of agglomerate core are 6.76 nm and 84.7 nm,
30 respectively. These values were determined from the I:C ratio based on correlations derived from

1 nano-XCT data (see Equation S10 and Equation S11 in Supplementary Materials), and are
2 considerably smaller than those used in previous modeling studies, where assumed or fitted values
3 were used to describe agglomeration properties.[37] Our finding is consistent with modeling
4 studies that employed similar agglomerate properties that were correlated to TEM and SAXS data
5 as well, which reported uniform O_2 distribution within the agglomerate when interfacial resistance
6 is considered, indicating minimal diffusion resistance within the agglomerate.[80, 81] On the other
7 hand, at the interface scale, the weak adsorption of O_2 at the Pt surface consistently contributes to
8 the transport loss across all operating current densities, while interfacial diffusion becomes limiting
9 at higher current densities.

10 Although diffusion resistance within the agglomeration exhibits minor impact on overall
11 mass transport in the two reference cases, sensitivity analysis suggests the critical role of
12 controlling agglomerate size on diffusion voltage loss at both the agglomerate and interface scales
13 (Figure 4). As the agglomerates become larger, less O_2 can access the inner agglomeration core,
14 which, in turn, reduces the O_2 concentration gradient and diffusive driving force near the interface,
15 further aggravating the interfacial diffusion resistance. Furthermore, given the wide range of
16 agglomeration sizes, ranging from 5 to 5000 nm, used in previous modeling studies [37], one may
17 expect significant discrepancies in dissecting the mass-transport resistance if an unrepresentative
18 agglomerate size is used. These insights underscore the necessity of precise characterization of and
19 accounting for the agglomeration properties to capture the comprehensive multiscale transport
20 phenomena.

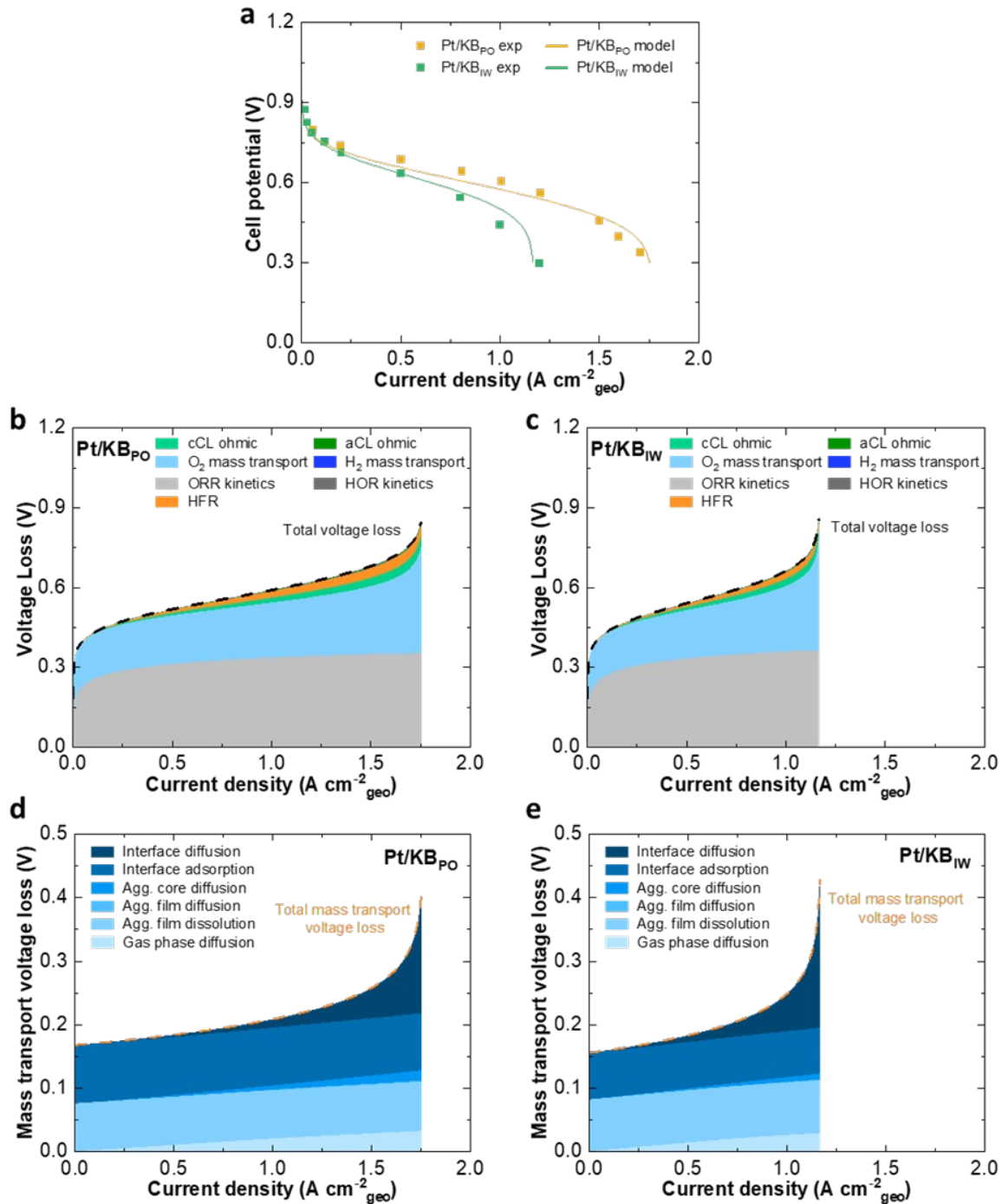


Figure 3. (a) Calculated polarization curves for the Pt/KB_{PO} (all exterior-Pt/ionomer interface) and Pt/KB_{IW} (all interior-Pt interface) catalysts and comparisons with experimental measurements. The operating conditions are 80 °C, 170 kPa, 100% RH, and H₂/10%O₂ feed. (b-c) Voltage-loss breakdowns of Pt/KB_{PO} and Pt/KB_{IW} systems. (d-e) Detailed voltage-loss breakdowns for mass-transport loss of Pt/KB_{PO} and Pt/KB_{IW} cells.

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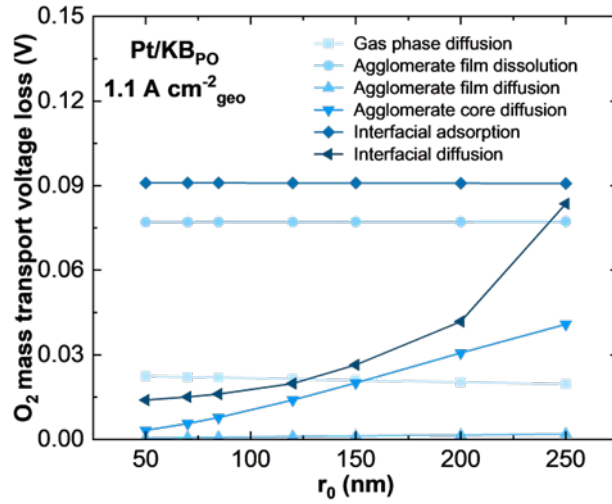


Figure 4. Effect of agglomerate core radius on mass-transport voltage loss at different scales.

3

The influence of interfaces on O₂ mass transport is demonstrated by comparing the Pt/KB_{PO} and the Pt/KB_{IW} cells (Figure 5). At a low current density (0.3 A cm⁻²_{geo}), where diffusion limitation is low, the Pt/KB_{IW} system exhibits smaller mass-transport loss due to the higher interfacial solubility of its interior-Pt interfaces compared to the exterior-Pt/ionomer interface in the Pt/KB_{PO} system (Figure 5a). This trend can be visualized from the computed O₂ concentration profile from the inlet to the Pt surface shown in Figure 5b, which exhibits a more pronounced concentration decrease during interfacial adsorption in the Pt/KB_{PO} system. However, as the current density increases to a higher level (1 A cm⁻²_{geo}), the Pt/KB_{PO} system surpasses the Pt/KB_{IW} system in total mass-transport loss. This reversal is attributed to the lower interfacial diffusion resistance of the exterior-Pt/ionomer interface in the Pt/KB_{PO} system, which compensates for its low interfacial solubility and yields a higher interfacial permeability. This shift corresponds to the changes in O₂ concentration at the interface: at 0.3 A cm⁻²_{geo}, Pt/KB_{PO} system exhibits lower O₂ concentration at Pt interface, but at 1 A cm⁻²_{geo}, it surpasses the Pt/KB_{IW} system due to smaller O₂ concentration drop across the interface. These findings help rationalize the experimental observations that MEAs using porous carbon support—where the majority of catalyst particles reside within nanopores—often exhibit better performance at low current densities but poorer performance at higher current densities compared to MEAs using solid carbon supports.

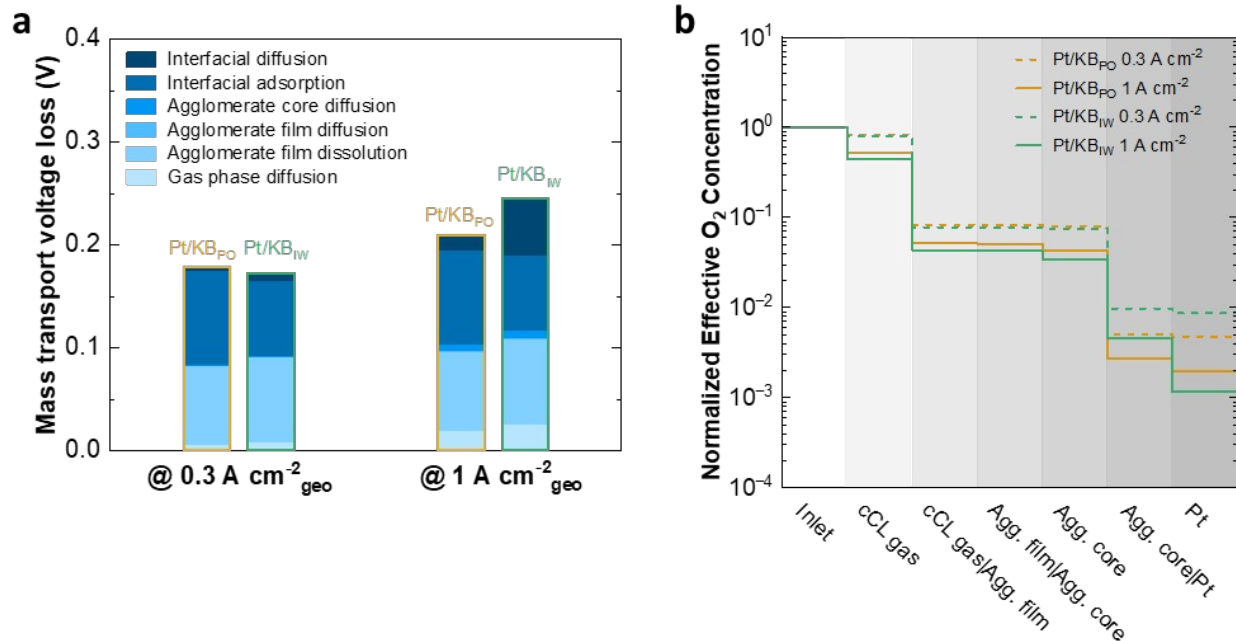


Figure 5. Comparisons between Pt/KB_{PO} and Pt/KB_{IW} systems on (a) mass-transport loss across lengthscales and (b) O₂ concentration profile from inlet to Pt surface at low and high current densities. Concentrations are normalized by the inlet concentration.

Co-effect of different interfaces on cell performance

Beyond diagnosing cell performances, another practical application of the model is to assess how varying the distribution of interfaces affects cell performance. The specific activity at 0.9 V and non-Fickian transport resistance were evaluated for different combinations of interfaces (Figure 6), keeping all other cell parameters consistent with the Pt/KB_{PO} cell. We focus on the scenario of 100% RH, under which both exterior-Pt/water and interior-Pt interfaces are 100% utilized. The highest low-current-density performance is achieved with a 100% exterior-Pt/water interface (Figure 6a), due to its superior interfacial solubility and lowest Tafel slope. This significant advantage suggests that as long as ionomer coverage on exterior-Pt surfaces remains below 100%, low-current-density performance declines with increasing fraction of interior-Pt surface (for the same total ECSA or loading) because of reduced availability of the exterior-Pt/water interface. In this case, using solid carbon support to ensure all Pt particles anchored on the surface of carbon to maximize the exterior-Pt/water interface appears to benefit the low-current-density performance

(Figure 6b). Yang *et al.* observed enhanced specific activity by maximizing Pt/water interface through using a coaxial nanowire electrode, where the triple-phase boundary was separated into a proton-conducting Pt/ionomer interface and an O₂-transport Pt/water interface.[82] However, when the exterior-Pt surface is fully covered by the ionomer, low-current-density performance improves with increasing interior-Pt surface area, indicating that the mesoporous carbon supports become advantageous by ameliorating the performance loss from the Pt particles inside pores (Figure 6b).

The presence of the exterior-Pt/water interface also significantly reduces the non-Fickian transport resistance, as demonstrated in Figure 6c. While non-Fickian transport resistance can be decreased from 0.9 to 0.5 s cm⁻¹ by changing from an electrode with 100% interior-Pt-interface to one with 100% exterior-Pt/ionomer interface, it can be further reduced to 0.3 s cm⁻¹ by introducing only ~10% exterior-Pt/water interface and eventually reach ~0.1 s cm⁻¹ if the electrode is ionomer-free (Figure 6d). Given the uncertainties in interfacial parameters for the exterior-Pt/water interface, parametric studies were carried out by varying the interfacial diffusion energy barrier (Figure S5 in Supplementary Materials). Consistent trends are observed that a small fraction of exterior-Pt/water interface can substantially attenuate the non-Fickian transport resistance. The nonlinear correlation between non-Fickian transport resistance and the areal distribution of the interfaces is likely due to the nature of resistance-in-parallel configuration, implying that the inclusion of a low-resistive interface, even a small portion, can greatly reduce the non-Fickian transport resistance.

The low interfacial transport resistance of the exterior-Pt/w interface can significantly benefit the adoption of cost-saving ultra-low-loaded electrodes, where non-Fickian transport resistance predominantly contributes to performance loss. Figure 7 compares the modeled non-Fickian transport resistance as a function of roughness factor between electrodes with 100% exterior-Pt/water interface (representing an ionomer-free electrode) and 100% exterior-Pt/ionomer interface (representing a conventional ionomer-based Pt/C electrode), with loading below 0.06 mg cm⁻²_{geo}. The model successfully reproduces the inverse relationship between non-Fickian transport resistance and the roughness factor. While quantitative discrepancies exist between the model predictions and experimental data [67], likely stemming from the unknown electrode properties

1 that may not be accurately captured by the model parameters (*e.g.*, agglomeration size and different
2 Pt/electrolyte interactions due to various ink and electrode fabrication processes), the model
3 consistently aligns with the observed trends. The model suggests that the mass-transport resistance
4 of ionomer-free electrodes is far less sensitive to reduced loading. For instance, to achieve the same
5 level of mass transport resistance as a conventional Pt/C electrode, the roughness factor of an
6 ionomer-free electrode can be reduced from 42.7 to 13.1, equivalent to a 70% reduction in Pt
7 loading. Similarly, experiments also indicate that an ionomer-free NSTF electrode with a
8 roughness factor of ~ 12 exhibits non-Fickian transport resistance comparable to that of a
9 conventional Pt/C electrode with a roughness factor of ~ 43 .

10 Overall, the presence of the exterior-Pt/water interface (assuming protons can reach the Pt
11 at these lower operating current densities) is pivotal for enhancing both low-current-density and
12 mass-transport-limited performance. The ionomer-free NSTF electrode is one of the pioneer
13 designs to exploit this interface, demonstrating significant improvement in cell performance
14 compared to the conventional ionomer/filled electrodes, albeit with high sensitivity to RH.[82-84]
15 However, effectively leveraging the exterior-Pt/water interface needs a holistic strategy that also
16 accounts for proton conduction and its restricted utilization at lower RH. Promising CL designs
17 include engineering the local ionomer distribution to minimize direct contact with the Pt surface,
18 allowing Pt exposure to the local water phase while maintaining the ionomer network at
19 macroscale to provide sufficient proton conduction.[85, 86] For example, Babu and coworkers
20 developed an array electrode with Pt/C particles supported between the vertically aligned Nafion
21 pillars. These pillars form highly conductive and low-tortuosity proton transport channels,
22 reducing the ionomer required between Pt/C particles and further improving the interfacial mass
23 transport. [87, 88] Developing ionomer-free or low-ionomer electrodes with novel proton-
24 conductive catalyst supports is an alternative approach to leverage the benefits of the Pt/water
25 interface; recent studies have begun exploring such materials and configurations.[89, 90]

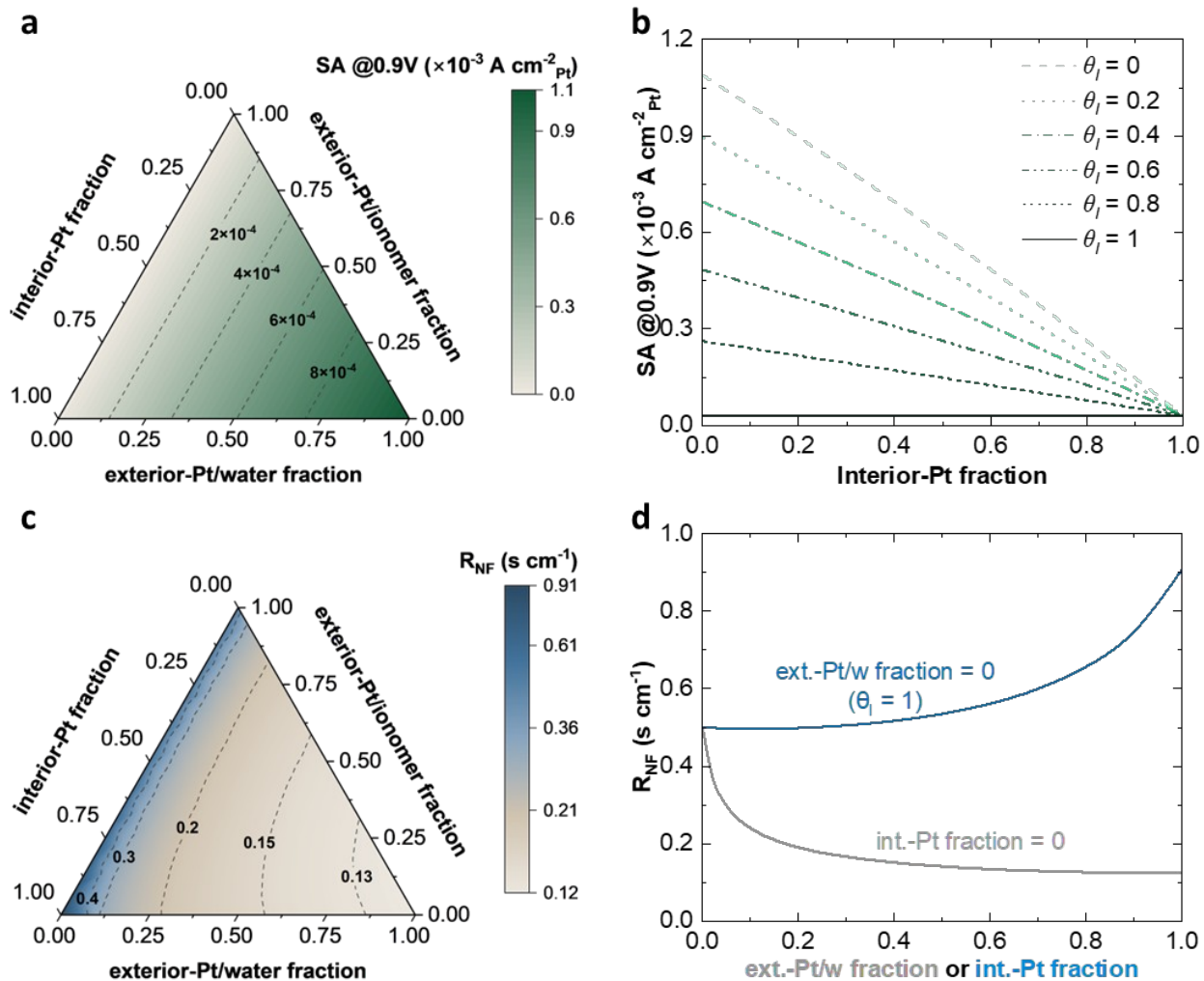


Figure 6. Specific activity (SA) at 0.9 V and non-Fickian transport resistance evaluated with different combinations of interfaces. Specific activity at 0.9 V (a) with different combinations of the three types of interfaces and (b) as a function of interior-Pt fraction with different ionomer coverage θ_I on exterior-Pt interface. Non-Fickian transport resistance (c) with different combinations of the three types of interfaces and (d) as a function of exterior-Pt/water fraction (no interior-Pt) and interior-Pt fraction (no exterior-Pt/water).

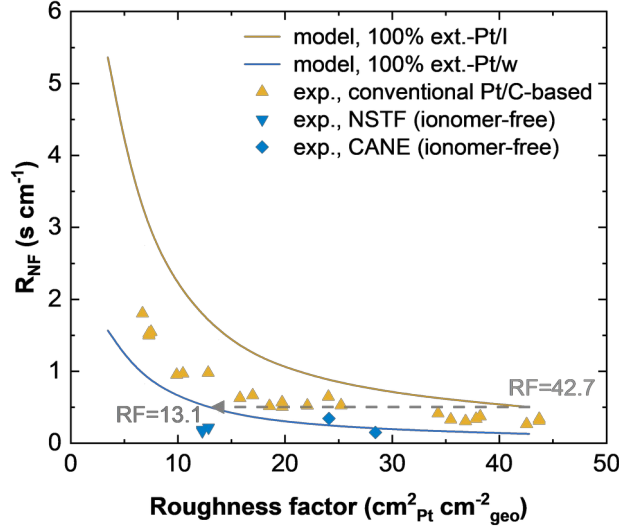


Figure 7. Predicted non-Fickian transport resistance as a function of roughness factor for conventional ionomer-based Pt/C electrode and ionomer-free electrode with ultra-low Pt loading. Calculations were carried out with Pt loading ranging from 0.01 to 0.06 mg cm⁻²geo. Roughness factor was determined by the multiplication of Pt loading and ECSA, which is 69 m² g⁻¹ Pt as used for the Pt/KBPO system. Experimental reference is taken from Kongkanand *et al.* [67].

Effects of carbon-support type

By differentiating interface types, the model can be applied to simulate different types of carbon support. The consistency between interfacial properties and cell performance for porous carbon and solid carbon is demonstrated above, showing that the superior lcd performance and inferior hcd performance of porous carbon aligns with the higher interfacial solubility and slower diffusion at the interior-Pt interfaces. On the other hand, recent breakthroughs in mesoporous carbon development have led to improved electrode performance when using these novel supports, such as specific activity and mass transport, compared to conventional porous- and solid-carbon supports like KB and Vulcan.[71, 72] To reflect these improvements and explore model sensitivity, a parametric study was conducted on changes in interfacial properties of the interior-Pt interface on specific activity and non-Fickian transport resistance (Figure 8a and Figure 8b). In particular, parametric studies on $\alpha^{\text{int-Pt}}$ and $H^{\text{int-Pt}}$ are performed for specific activity, and $H^{\text{int-Pt}} \times R^{\text{int-Pt}}$ for the non-Fickian transport resistance, as these are the effective parameters according to Equation S2 and Equation S9 respectively.

Assuming that all active exterior Pt interfaces are covered by ionomer, which is likely to be a common scenario in a conventional ionomer-based Pt/C electrode, better intrinsic ORR kinetics (larger $\alpha^{f,-Pt}$) or higher O₂ interfacial solubility (smaller $H^{f,-Pt}$) both lead to higher specific activity with more interior-Pt particles. This scenario corresponds to the optimized pore size in the porous carbon support, that pores are sufficiently narrow to block ionomer but large enough to sustain a bulk-like water structure inside. Conversely, if the pore ionomer content is high (e.g., $H^{f,-Pt} = H^{ext,-Pt/l}$), the interior-Pt interface negatively impacts the specific activity and thereby the hcd performance. For the hcd performance, with increasing O₂ permeability inside the pore (smaller $H^{f,-Pt} \times R^{f,-Pt}$), the lowest non-Fickian transport resistance shifts from 0% to increasingly higher interior-Pt fractions, making mesoporous carbon more advantageous than solid carbon. Similarly, when the pore environment approximates bulk water (e.g., $H^{f,-Pt} \times R^{f,-Pt} = H^{ext,-Pt/w} \times R^{ext,-Pt/w}$), mass transport outperforms both conventional mesoporous carbon (baseline case) and solid carbon (interior-Pt fraction = 0%). Finally, it is important to note that $\alpha^{f,-Pt}$, $H^{f,-Pt}$, and $R^{f,-Pt}$ may be interrelated, as changes in the pore electrolyte environment can simultaneously affect ORR kinetics, O₂ adsorption energy, and O₂ diffusion.

Despite the potential for improved mass transport through optimizing mesoporous carbon-pore properties, low RH operation remains a challenge for these electrodes. This is primarily due to the reduced interior Pt utilization from insufficient pore water.[29, 91] Figure 8c illustrates the modeled non-Fickian transport resistance as a function of RH for both Pt/solid carbon and Pt/porous carbon electrodes. Pt/porous carbon is described with 25% exterior-Pt/ionomer interface and 75% interior-Pt interface in the model, with the interior-Pt utilization $\xi_{Pt}^{f,-Pt}$ being implemented as a function of RH (Figure 8d). Both electrodes exhibit higher R_{NF} with decreasing RH. For the Pt/solid carbon electrode, this trend is due to the decreased O₂ permeability at lower RH at the exterior-Pt/ionomer interface and in the agglomerate ionomer phase, with the latter contribution being kept the same between the two electrodes. Notably, Pt/porous carbon electrode demonstrates a more dramatic R_{NF} increase with decreasing RH because of the reduced ECSA at lower RH, indicating greater vulnerability to low RH conditions. Similar trends have been reported in previous modeling [81] and experimental [92, 93] studies.

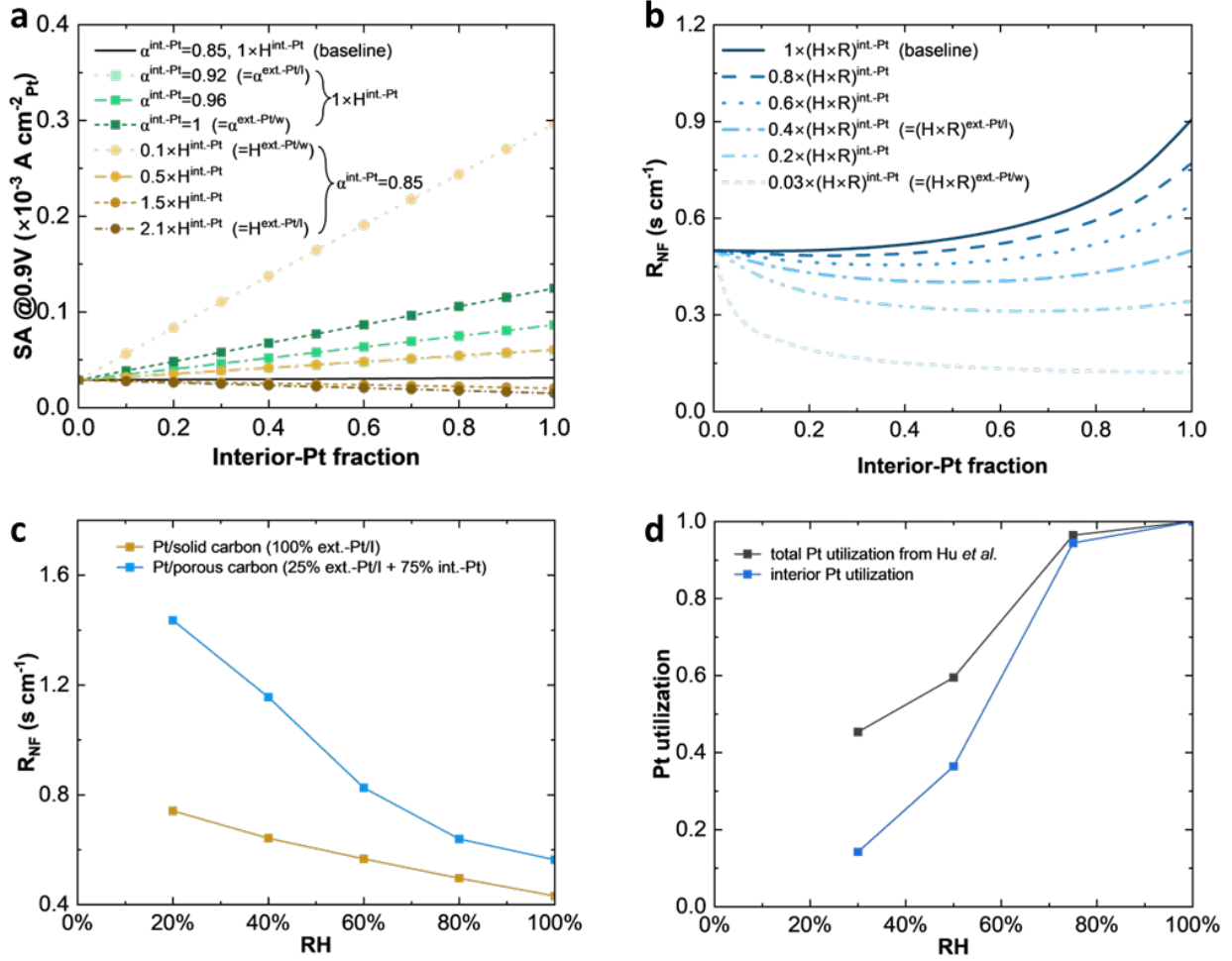


Figure 8. Parametric studies on the interfacial parameters of interior-Pt interfaces to represent different types of carbon supports. (a) Specific activity at 0.9 V and (b) non-Fickian transport resistance evaluated with different combinations of interior-Pt and exterior-Pt/water interfaces, evaluated at RH=100%. (c) RH-dependence of non-Fickian transport resistance for Pt/solid carbon and Pt/porous carbon electrode. (d) Correlation between interior-Pt utilization and RH converted from Hu *et al.* [92]; Pt utilization at RH=30% (dry condition) from Hu *et al.* is assumed to be solely due to the exterior-Pt/ionomer interface, therefore, the rest of the area corresponds to the interior Pt interface that is used to calculate interior-Pt utilization.

Origins of ionomer poisoning effect

What's been embedded in the previous discussion is the consideration of ionomer poisoning. Ionomer poisoning has been widely used to explain the suppressed kinetic performance of MEAs involving the catalyst/ionomer interface, with sulfonic-acid moiety adsorption identified as the primary cause. Sulfonic-acid group adsorption directly leads to ECSA loss by blocking active sites,

1 while its indirect effects include hindering O₂ adsorption [24] and altering the electronic state of
2 catalyst particles [94]. Consequently, the origins of ionomer poisoning remain unclear, as these
3 outcomes of sulfonic-acid group adsorption all influence the kinetic performance but in distinct
4 ways. Sulfonic-acid group coverage is typically used as a descriptor to characterize the level of
5 poisoning; [10, 12, 24] however, it is only quantitatively associated with the ECSA loss and is
6 typically reported to be below 20% [10, 12, 24]. On the other hand, MD simulations suggest that
7 sulfonic-acid adsorption not only decreases ECSA, but also brings additional poisoning moieties,
8 such as the ether in the sidechain, resulting in a denser ionomer molecular layer that can further
9 alters the interfacial Henry's constant by an order of magnitude.[24] Additionally, the electronic
10 structure regulated by sulfonic-acid group adsorption may modify the EDL structure and
11 subsequently influence the ORR intrinsic kinetics as reflected in terms of the Tafel slopes. For
12 example, Shao *et al.* regulated the sulfonic-acid adsorption via sulfur-doping and observed a shift
13 in Tafel slopes of the polarization curves from 79.1 to 88.6 mV dec⁻¹ across MEAs with different
14 doping levels.[95] Sambandam and Ramani also found that polarization curves measured from
15 MEAs employing ionomer with different equivalent weights exhibited Tafel slopes ranging from
16 80 to 90 mV dec⁻¹ for PFSA-based systems, and from 100 to 120 mV dec⁻¹ for hydrocarbon-based
17 systems.[96] As a result, an approximate 20 mV dec⁻¹ change in Tafel slope appears to be a
18 reasonable estimate of the impact arising from the different sulfonic-acid adsorption.

19 In the model, however, the above-discussed co-effects arising from sulfonic-acid group
20 adsorption are not explicitly correlated, and instead are embedded in the values of low-current-
21 density-performance-related parameters for the exterior-Pt/ionomer interface—namely, surface
22 utilization, interfacial Henry's constant, and Tafel slope. To differentiate the individual
23 contributions of ECSA loss, interfacial solubility reduction, and intrinsic kinetic changes to the
24 overall poisoning effect, we performed a sensitivity analysis on these parameters, as shown in
25 Figure 9. We consider the case of Pt/mesoporous carbon assuming that the exterior-Pt particles are
26 fully covered by ionomer. Current densities at 0.9 V were determined for different areal
27 distributions of exterior-Pt/ionomer interface and interior-Pt interface at different levels of ionomer
28 poisoning on the exterior-Pt/ionomer interface. The effect of ECSA loss was evaluated by
29 calculating the true specific activity and apparent specific activity, where the cell current density
30 was normalized by either the effective Pt area or the total Pt area with the area blocked by sulfonic-

acid moieties being included (Figure 9a and b). The results show that the true specific activity is insensitive to the ECSA loss. The performance gains from increasing interior-Pt surface remain consistent regardless of how much Pt area is blocked—even up to an unrealistic 80%, suggesting that contribution from the site-blocking effect to the ionomer poisoning effect is trivial. In contrast, the apparent specific activity is more responsive to the sulfonic-acid coverage, demonstrating greater performance gain when Pt particles are deposited inside the pores. Such discrepancy suggests that when comparing specific activities to identify the ionomer-poisoning effect, normalizing cell current density by experimentally measured ECSA is likely to underestimate the true specific activities, as both CO-stripping and H_{UPD} determine ECSA after the exclusion of sulfonic-acid adsorption and tend to overestimate the true ECSA. On the other hand, specific activity demonstrates much greater sensitivity to changes in interfacial Henry's constant and Tafel slope (see Figure 9c and Figure 9d). The benefit of loading Pt particles inside pores disappears when the exterior-Pt/ionomer interface achieves better ORR kinetics or higher interfacial solubility. Under such conditions, a lower fraction of interior-Pt interface leads to improved specific activity.

Interestingly, while the ECSA loss has negligible effect on the specific activity, it plays a more substantial role in the non-Fickian transport resistance. The minimum non-Fickian transport resistance occurs at a higher interior-Pt fraction as the utilization of the exterior-Pt/ionomer interface decreases. As shown in Figure 9e, a configuration with no interior-Pt interface is optimal for minimizing the non-Fickian transport resistance in the case of no ECSA loss for the exterior-Pt/interface. However, a 20% increase in site blocking shifts the minimum non-Fickian transport resistance to a configuration with 20% of interior-Pt particles. This observation is attributed to the significant dependence of non-Fickian transport resistance on the roughness factor in low-loaded electrodes ($0.062 \text{ mg cm}^{-2}_{\text{geo}}$); such sensitivity is expected to be more pronounced as the loading continues to decrease.

To summarize, ionomer poisoning impacts both low- and high-current-density performance, but through different mechanisms. While previous studies correlate the suppressed low-current-density performance with the site-blocking effect, the associating ECSA loss does not quantitatively correlate to changes in performance. Instead, the underlying mechanism appears to

1 be the poorer intrinsic kinetics and lower O₂ solubility at the exterior-Pt/ionomer interface that
2 coming with the adsorption of sulfonic-acid moieties; a more quantitative correlation between
3 sulfonic-acid coverage and other interfacial properties, rather than ECSA alone, should be
4 established to thoroughly unveil the ionomer poisoning effect. On the other hand, the reduced
5 roughness factor resulting from the site blockage negatively affects the high-current-density
6 performance through increasing mass-transport resistance. This effect is expected to become more
7 concerning as the loading is decreased either by design or degradation.

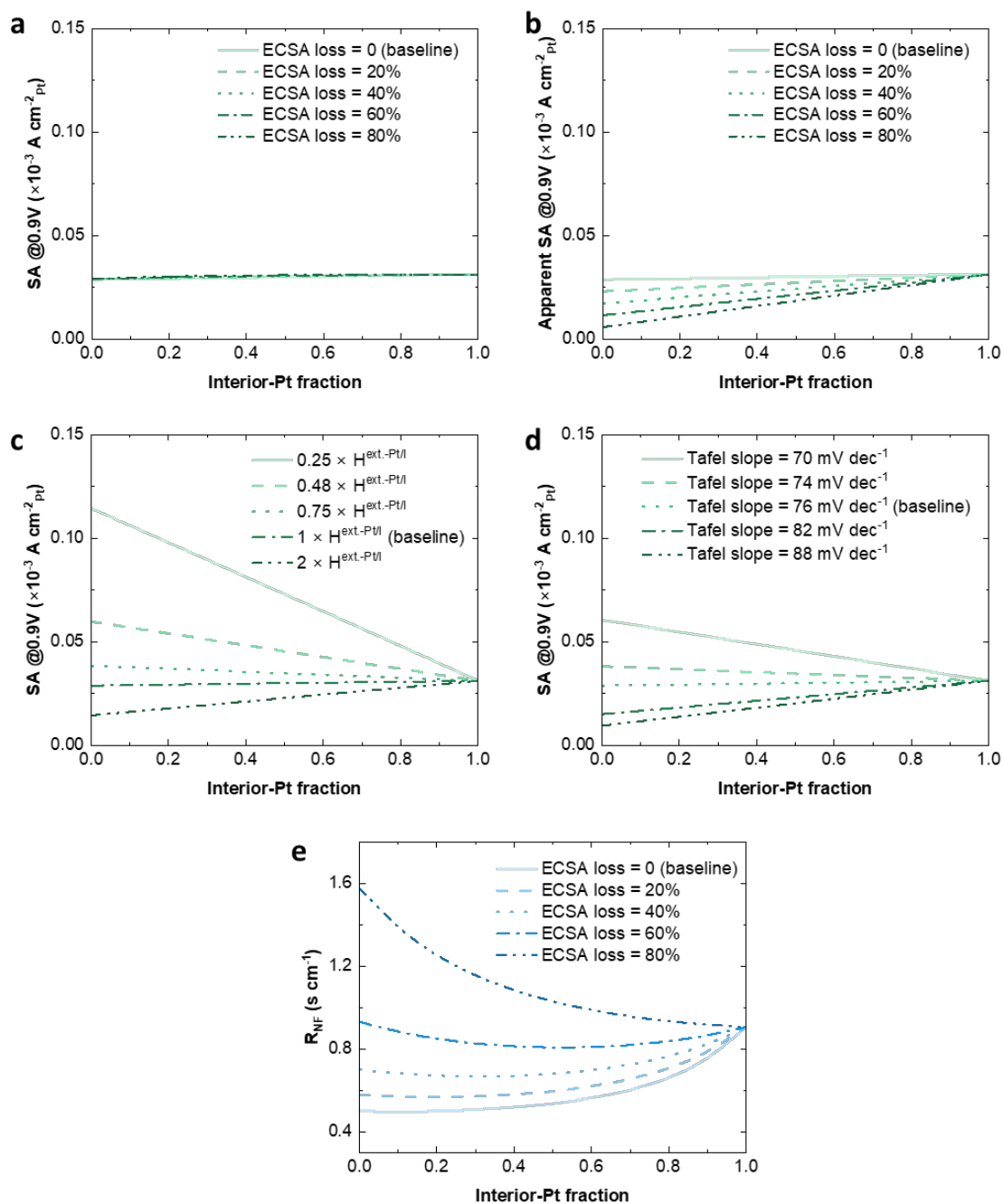


Figure 9. Specific activity or apparent specific activity as a function of interior-Pt fraction with different (a) ECSA loss, (b) interfacial Henry's constant, and (c) ORR Tafel slopes for the exterior-Pt/ionomer interface. (d) non-Fickian transport resistance as a function of interior-Pt fraction with different ECSA loss for the exterior-Pt/ionomer interface. Baseline values were determined with the original cell parameters for Pt/KB_{PO} given in Table S1.

Ink-performance correlations

While both exterior-Pt/ionomer and interior-Pt interfaces have their respective pros and cons, the exterior-Pt/water interface outperforms them in terms of both kinetics and O₂ mass transport. However, in a realistic cell, a CL fabricated from only Pt supported on carbon particles to introduce exterior-Pt/water interfaces exhibits poor performance,[97] due to high proton resistance to the catalyst site in the absence of ionomer. Therefore, when tuning ink parameters to design beneficial local interfaces, one should expect simultaneous changes in other CL properties that may negatively affect cell performance. We evaluate these tradeoffs with our model framework by constructing an ink-structure-performance roadmap, which helps identify the performance-determining CL properties and their correlation with ink parameters. Key CL properties across the scales, including thickness, porosity, agglomeration size, ionomer coverage, and effective proton conductivity, are correlated to ionomer to carbon (I:C) ratio based on experimental characterizations [8-17] (see Figure S6 in Supplementary Materials). Given the quantitative discrepancies reported in various experimental measurements (see Figure S1, Figure S2, and discussions in Supplementary Materials), we aim to capture the qualitative trends in how cell performance responds to variations in ink parameters. The scattered experimental data are likely due to the dependence of these properties on other ink parameters such as primary particle loading [62], ink alcohol content [12, 98] , and carbon support [99], as well as discrepancies in characterization methods and fabrication processes. However, these uncertainties could be addressed with broader ink studies and integrating sub-models describing ink interactions [100, 101] and CL formation (e.g., drying process) [102]. For simplicity, we use the I:C ratio as the only ink parameter variable and assume Pt/solid carbon (*i.e.*, no interior-Pt interface).

The polarization curves predicted by the model with different I:C ratios are illustrated in Figure 10. At zero or low I:C ratio, the performance gain brought by the presence of exterior-Pt/water interface is largely overshadowed by the poor proton conduction in the CL, resulting in poor cell performance. As the I:C ratio increases, e.g., from 0.3 to 0.5, the improved proton conduction due to the higher ionomer content facilitates better utilization of the CL and ECSA and thus improved cell performance. Although the simultaneously increased ionomer coverage begins to poison the Pt surfaces, leading to reduced low-current-density performance,

this performance loss can be compensated by the continuously enhanced proton transport and thereby achieves better performance at higher current densities. When the ionomer content is sufficient to cover fully the Pt surfaces, e.g., I:C = 0.7, the cell performance is somewhat suppressed across the entire operating current because of the lower O₂ solubility and permeability at the exterior-Pt/ionomer interface, despite sufficiently fast proton conduction through the CL. Further increasing the I:C ratio continues to harm cell performance, with transport in the consequent larger agglomerates becoming the primary performance-limiting factor (see Figure 4). Overall, a moderate I:C ratio appears to maximize the cell performance. Under this condition, the ionomer content is high enough to guarantee sufficient proton transport without excessively poisoning the Pt surfaces and forming large agglomerates. On the other hand, if an ionomer-free electrode can achieve the same level of proton conduction as the ionomer-filled design, the cell performance can be greatly improved for low-Pt-loading MEAs (dash line in Figure 10).

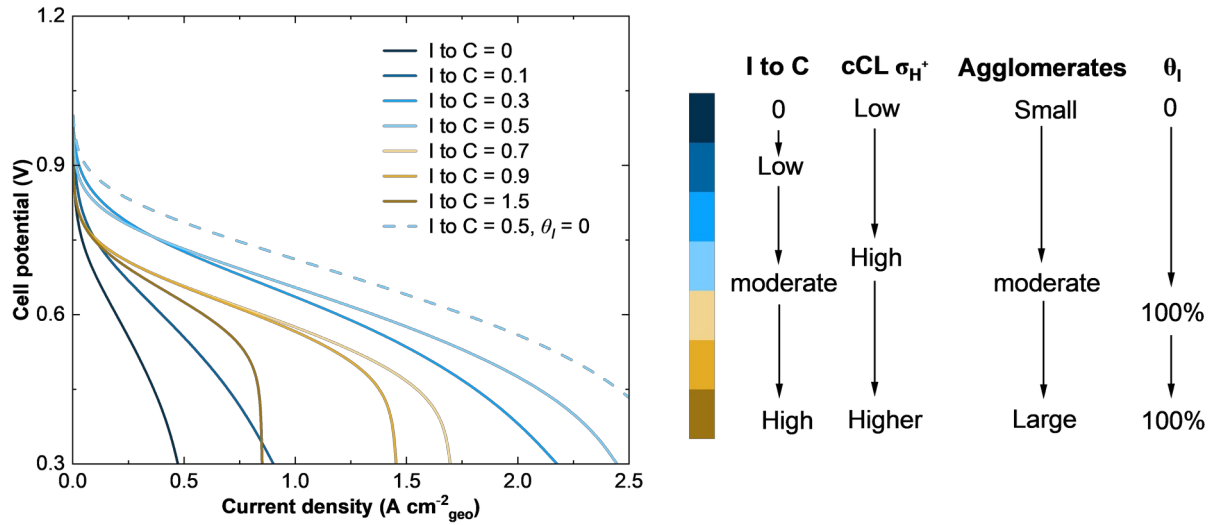


Figure 10. Predicted polarization curves with different I:C ratio. The color scale bar suggests how CL properties at different lengthscales change with the I:C ratio. Other cell parameters are kept consistent with the Pt/KB_{p0} system (parameters give in Table S1). The polarization curves were calculated under 80 °C, 100% RH, 170 kPa, and H₂/10%O₂ feed.

Summary

This study introduces a comprehensive multiscale cell-level model that integrates a modified agglomerate model to account for the effects of various interfacial properties, enabling detailed analysis of cell performance and identification of voltage loss from nanoscale to macroscale. For a

low-loaded electrode, mass-transport loss from the coupled agglomerate-interface-scale transport plays a significant role in the total voltage loss. The O_2 dissolution from the CL gas phase to the agglomerate ionomer domain and O_2 adsorption on the Pt surface influence the polarization curve across the entire range of operating current density, with the interfacial transport resistance becoming more pronounced at higher current densities. Comparisons between the three typical Pt-electrolyte interfaces: Pt particles on the carbon surface covered by either ionomer or water film, and Pt particles deposited inside carbon nanopores, reveal that the exterior-Pt surface is prone to ionomer poisoning because of the weak O_2 adsorption or reduced intrinsic ORR activity at the Pt-ionomer interface, which limits the low-current-density performance. On the other hand, the large diffusion resistance near interior-Pt particles results in low interfacial permeability and negatively impact the high current-density performance. The presence of the exterior-Pt/water interface is promising for advancing both performance and mass transport; however, practical utilization of electrodes with only exterior-Pt/water interfaces requires novel design strategies to guarantee sufficient proton transport through the layer and thus catalyst utilization. For a conventional ionomer-filled electrode, the ink-structure-performance correlations predicted by the model suggest that the optimal cell performance is achieved at a moderate I:C ratio, where the ionomer content is sufficient to facilitate proton transport without fully covering the Pt surface, thereby utilizing the Pt/water interface while avoiding high mass-transport losses associated with large agglomerates.

Despite the model's ability to capture key qualitative trends in PEMFC performance, several limitations remain particularly in terms of providing precise quantitative prediction. Scarcity of reliable interfacial parameters in current literature affects the accuracy of model predictions and limits the model's predictive ability to electrodes with different ionomers. While fundamental understandings of catalyst-electrolyte interfaces have been continuously advanced, knowledge from these studies may not be directly transferrable to the realistic interfaces in an MEA, as the surface chemistry of catalyst support and catalyst particle structures alter the interfacial behavior in the catalyst layer. Additionally, the empirical correlations utilized to establish the ink-structure-performance correlation overlook the influences of other ink parameters and fabrication processes. This simplification, originated from limited data on ink-structure correlations, further constrains the model's predictive capability. However, these uncertainties

could be addressed with broader experimental characterizations of diverse interfaces and integrating sub-models developed from emerging ink modeling and process modeling studies. Lastly, the influence of operating conditions, particularly lower RH, on multiscale transport behavior requires further investigation. While adequate water content can be assumed in CL under saturated conditions, water distribution across the scales becomes complex at undersaturated conditions, which affects the multiscale transport. For instance, liquid saturation in macroscopic pore affects gas phase transport; water activity in the ionomer phase influences O₂ transport within agglomerates and at ionomer-covered catalyst interface, and interfacial water impacts the utilization of non-ionomer-covered catalyst. To address this, a quantitative correlation between water content at different scales and local RH, temperature, and pressure is essential. Overall, despite these limitations, the model provides a powerful tool for fuel cell diagnostics and offers strategic guidance for optimizing ink formulations and electrode design.

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References

- [1] D.A. Cullen, K.C. Neyerlin, R.K. Ahluwalia, R. Mukundan, K.L. More, R.L. Borup, A.Z. Weber, D.J. Myers, A. Kusoglu, New roads and challenges for fuel cells in heavy-duty transportation, *Nature energy*, 6 (2021) 462-474.
- [2] A.Z. Weber, A. Kusoglu, Unexplained transport resistances for low-loaded fuel-cell catalyst layers, *Journal of Materials Chemistry A*, 2 (2014) 17207-17211.
- [3] Y. Sun, S. Polani, F. Luo, S. Ott, P. Strasser, F. Dionigi, Advancements in cathode catalyst and cathode layer design for proton exchange membrane fuel cells, *Nature communications*, 12 (2021) 5984.

- [4] M.N. Islam, A.B. Mansoor Basha, V.O. Kollath, A.P. Soleymani, J. Jankovic, K. Karan, Designing fuel cell catalyst support for superior catalytic activity and low mass-transport resistance, *Nature Communications*, 13 (2022) 6157.
- [5] S. Liu, S. Yuan, Y. Liang, H. Li, Z. Xu, Q. Xu, J. Yin, S. Shen, X. Yan, J. Zhang, Engineering the catalyst layers towards enhanced local oxygen transport of Low-Pt proton exchange membrane fuel cells: Materials, designs, and methods, *Int. J. Hydrogen Energy*, 48 (2023) 4389-4417.
- [6] P.A. García-Salaberri, P.K. Das, A.M. Chaparro, Local oxygen transport resistance in polymer electrolyte fuel cells: origin, dependencies and mitigation, *Frontiers in Energy Research*, 12 (2024) 1357325.
- [7] J. Gao, H. Wang, Z. Zhang, Y. Chen, D. Li, M. Zhou, M. Chai, Y. Li, Semi-ordered catalyst layer with ultra-low Pt loading for proton exchange membrane fuel cells, *J. Power Sources*, 606 (2024) 234516.
- [8] H. Ishikawa, Y. Sugawara, G. Inoue, M. Kawase, Effects of Pt and ionomer ratios on the structure of catalyst layer: A theoretical model for polymer electrolyte fuel cells, *J. Power Sources*, 374 (2018) 196-204.
- [9] S. Ott, A. Orfanidi, H. Schmies, B. Anke, H.N. Nong, J. Hübner, U. Gernert, M. Gliech, M. Lerch, P. Strasser, Ionomer distribution control in porous carbon-supported catalyst layers for high-power and low Pt-loaded proton exchange membrane fuel cells, *Nature materials*, 19 (2020) 77-85.
- [10] S. Minami, S. Kajiya, H. Yamada, K. Shinozaki, R. Jinnouchi, Measurement of ionomer coverage on carbon and Pt in catalyst layer of polymer electrolyte fuel cells by electrochemical impedance spectroscopy, *Electrocatalysis*, 14 (2023) 522-533.
- [11] R. Sun, Z. Xia, X. Xu, R. Deng, S. Wang, G. Sun, Periodic evolution of the ionomer/catalyst interfacial structures towards proton conductance and oxygen transport in polymer electrolyte membrane fuel cells, *Nano Energy*, 75 (2020) 104919.
- [12] T. Van Cleve, S. Khandavalli, A. Chowdhury, S. Medina, S. Pylypenko, M. Wang, K.L. More, N. Kariuki, D.J. Myers, A.Z. Weber, Dictating Pt-based electrocatalyst performance in polymer electrolyte fuel cells, from formulation to application, *ACS applied materials & interfaces*, 11 (2019) 46953-46964.
- [13] F.C. Cetinbas, R.K. Ahluwalia, N.N. Kariuki, D.J. Myers, Agglomerates in polymer electrolyte fuel cell electrodes: Part I. structural characterization, *J. Electrochem. Soc.*, 165 (2018) F1051.
- [14] F.C. Cetinbas, R.K. Ahluwalia, Agglomerates in polymer electrolyte fuel cell electrodes: Part II. Transport characterization, *J. Electrochem. Soc.*, 165 (2018) F1059.
- [15] K. Shinozaki, S. Kajiya, S. Yamakawa, N. Hasegawa, T. Suzuki, M. Shibata, R. Jinnouchi, Investigation of gas transport resistance in fuel cell catalyst layers via hydrogen limiting current measurements of CO-covered catalyst surfaces, *J. Power Sources*, 565 (2023) 232909.
- [16] T. Suzuki, S. Tsushima, S. Hirai, Effects of Nafion® ionomer and carbon particles on structure formation in a proton-exchange membrane fuel cell catalyst layer fabricated by the decal-transfer method, *Int. J. Hydrogen Energy*, 36 (2011) 12361-12369.
- [17] P. Gode, F. Jaouen, G. Lindbergh, A. Lundblad, G. Sundholm, Influence of the composition on the structure and electrochemical characteristics of the PEFC cathode, *Electrochim. Acta*, 48 (2003) 4175-4187.
- [18] D.R. Baker, D.A. Caulk, K.C. Neyerlin, M.W. Murphy, Measurement of oxygen transport resistance in PEM fuel cells by limiting current methods, *J. Electrochem. Soc.*, 156 (2009) B991.

- [19] W. Yoshimune, Dependence of oxygen transport properties of catalyst layers for polymer electrolyte fuel cells on the fabrication process, *Results in Chemistry*, 5 (2023) 100738.
- [20] T. Suzuki, K. Kudo, Y. Morimoto, Model for investigation of oxygen transport limitation in a polymer electrolyte fuel cell, *J. Power Sources*, 222 (2013) 379-389.
- [21] R. Jinnouchi, K. Kudo, N. Kitano, Y. Morimoto, Molecular dynamics simulations on O₂ permeation through nafion ionomer on platinum surface, *Electrochim. Acta*, 188 (2016) 767-776.
- [22] K. Kudo, R. Jinnouchi, Y. Morimoto, Humidity and temperature dependences of oxygen transport resistance of nafion thin film on platinum electrode, *Electrochim. Acta*, 209 (2016) 682-690.
- [23] T. Takeshita, Y. Kamitaka, K. Shinozaki, K. Kodama, Y. Morimoto, Evaluation of ionomer coverage on Pt catalysts in polymer electrolyte membrane fuel cells by CO stripping voltammetry and its effect on oxygen reduction reaction activity, *J. Electroanal. Chem.*, 871 (2020) 114250.
- [24] R. Jinnouchi, K. Kudo, K. Kodama, N. Kitano, T. Suzuki, S. Minami, K. Shinozaki, N. Hasegawa, A. Shinohara, The role of oxygen-permeable ionomer for polymer electrolyte fuel cells, *Nature communications*, 12 (2021) 4956.
- [25] K. Ikeda, N. Nonoyama, Y. Ikogi, Analysis of the ionomer coverage of Pt surface in PEMFC, *ECS Trans.*, 33 (2010) 1189.
- [26] H. Iden, A. Ohma, An in situ technique for analyzing ionomer coverage in catalyst layers, *J. Electroanal. Chem.*, 693 (2013) 34-41.
- [27] K. Shinozaki, H. Yamada, Y. Morimoto, Relative humidity dependence of Pt utilization in polymer electrolyte fuel cell electrodes: effects of electrode thickness, ionomer-to-carbon ratio, ionomer equivalent weight, and carbon support, *J. Electrochem. Soc.*, 158 (2011) B467.
- [28] N. Kikkawa, R. Jinnouchi, Does an ionomer penetrate a carbon mesopore? Free-energy analysis using molecular dynamics simulations, *The Journal of Physical Chemistry C*, 126 (2022) 11518-11528.
- [29] A. Chowdhury, C.J. Radke, A.Z. Weber, Relative-humidity dependence of electrochemically active surface area in porous carbon catalyst layers, *J. Electrochem. Soc.*, 170 (2023) 114525.
- [30] F. Chabot, J. Lee, F. Vandenberghe, L. Guetaz, G. Gebel, S. Lyonnard, L. Porcar, S. Rosini, A. Morin, Detailed catalyst layer structure of proton exchange membrane fuel cells from contrast variation small-angle neutron scattering, *ACS Appl. Energy Mater.*, 6 (2023) 1185-1196.
- [31] F.C. Cetinbas, R.K. Ahluwalia, N. Kariuki, V. De Andrade, D. Fongalland, L. Smith, J. Sharman, P. Ferreira, S. Rasouli, D.J. Myers, Hybrid approach combining multiple characterization techniques and simulations for microstructural analysis of proton exchange membrane fuel cell electrodes, *J. Power Sources*, 344 (2017) 62-73.
- [32] D. Kulkarni, S.J. Normile, L.G. Connolly, I.V. Zenyuk, Development of low temperature fuel cell holders for Operando x-ray micro and nano computed tomography to visualize water distribution, *Journal of Physics: Energy*, 2 (2020) 044005.
- [33] F. Jaouen, G. Lindbergh, G. Sundholm, Investigation of mass-transport limitations in the solid polymer fuel cell cathode: I. mathematical model, *J. Electrochem. Soc.*, 149 (2002) A437.
- [34] J. Itonen, F. Jaouen, G. Lindbergh, A. Lundblad, G. Sundholm, Investigation of mass-transport limitations in the solid polymer fuel cell cathode: II. Experimental, *J. Electrochem. Soc.*, 149 (2002) A448.
- [35] M. Moore, P. Wardlaw, P. Dobson, J. Boisvert, A. Putz, R. Spiteri, M. Secanell, Understanding the effect of kinetic and mass transport processes in cathode agglomerates, *J. Electrochem. Soc.*, 161 (2014) E3125.

- [36] T.A. Greszler, D. Caulk, P. Sinha, The impact of platinum loading on oxygen transport resistance, *J. Electrochem. Soc.*, 159 (2012) F831.
- [37] J. Huang, Z. Li, J. Zhang, Review of characterization and modeling of polymer electrolyte fuel cell catalyst layer: The blessing and curse of ionomer, *Frontiers in Energy*, 11 (2017) 334-364.
- [38] R.M. Darling, A hierarchical model for oxygen transport in agglomerates in the cathode catalyst layer of a polymer-electrolyte fuel cell, *J. Electrochem. Soc.*, 165 (2018) F571.
- [39] R.M. Darling, S.F. Burlatsky, Modeling oxygen transport in high surface area carbon supports for polymer-electrolyte fuel cells, *J. Electrochem. Soc.*, 167 (2020) 104506.
- [40] L.M. Pant, M.R. Gerhardt, N. Macauley, R. Mukundan, R.L. Borup, A.Z. Weber, Along-the-channel modeling and analysis of PEMFCs at low stoichiometry: Development of a 1+ 2D model, *Electrochim. Acta*, 326 (2019) 134963.
- [41] A. Parthasarathy, S. Srinivasan, A.J. Appleby, C.R. Martin, Temperature dependence of the electrode kinetics of oxygen reduction at the platinum/Nafion® interface—a microelectrode investigation, *J. Electrochem. Soc.*, 139 (1992) 2530.
- [42] K. Neyerlin, W. Gu, J. Jorne, H.A. Gasteiger, Determination of catalyst unique parameters for the oxygen reduction reaction in a PEMFC, *J. Electrochem. Soc.*, 153 (2006) A1955.
- [43] M. Moore, A. Putz, M. Secanell, Investigation of the ORR using the double-trap intrinsic kinetic model, *J. Electrochem. Soc.*, 160 (2013) F670.
- [44] A.Z. Weber, J. Newman, Modeling transport in polymer-electrolyte fuel cells, *Chem. Rev.*, 104 (2004) 4679-4726.
- [45] W. Yoon, A.Z. Weber, Modeling low-platinum-loading effects in fuel-cell catalyst layers, *J. Electrochem. Soc.*, 158 (2011) B1007.
- [46] P. Li, Y. Jiao, J. Huang, S. Chen, Electric double layer effects in electrocatalysis: insights from ab initio simulation and hierarchical continuum modeling, *JACS Au*, 3 (2023) 2640-2659.
- [47] M.S. Shibata, Y. Chen, A. Zagalskaya, T. Ogitsu, A.T. Pham, Y. Morimoto, A.Z. Weber, I. Zenyuk, Impact of Double Layer on Electrochemical Kinetics via Bottom up Multiscale Modeling Approach, *ECS Meeting Abstracts*, 2024, pp. 4090-4090.
- [48] C.M. Schott, P.M. Schneider, K.-T. Song, H. Yu, R. Götz, F. Haimerl, E. Gubanova, J. Zhou, T.O. Schmidt, Q. Zhang, How to assess and predict electrical double layer properties. implications for electrocatalysis, *Chem. Rev.*, 124 (2024) 12391-12462.
- [49] S. Wang, E. Zhu, Y. Huang, H. Heinz, Direct correlation of oxygen adsorption on platinum-electrolyte interfaces with the activity in the oxygen reduction reaction, *Sci. Adv.*, 7 (2021) eabb1435.
- [50] A. Kusoglu, D. Kushner, D.K. Paul, K. Karan, M.A. Hickner, A.Z. Weber, Impact of substrate and processing on confinement of Nafion thin films, *Adv. Funct. Mater.*, 24 (2014) 4763-4774.
- [51] A. Chowdhury, A. Bird, J. Liu, I.V. Zenyuk, A. Kusoglu, C.J. Radke, A.Z. Weber, Linking perfluorosulfonic acid ionomer chemistry and high-current density performance in fuel-cell electrodes, *ACS applied materials & interfaces*, 13 (2021) 42579-42589.
- [52] D. Wood, J. Chlistunoff, E. Watkins, P. Atanassov, R. Borup, Elucidation of PEMFC electrocatalyst-layer surface and interfacial phenomena via neutron reflectivity, *ECS Trans.*, 3 (2006) 1011.
- [53] W. Yoshimune, N. Kikkawa, H. Yoneyama, N. Takahashi, S. Minami, Y. Akimoto, T. Mitsuoka, H. Kawaura, M. Harada, N.L. Yamada, Interfacial distribution of nafion ionomer thin films on nitrogen-modified carbon surfaces, *ACS Applied Materials & Interfaces*, 14 (2022) 53744-53754.

- [54] C.R. Randall, L. Zou, H. Wang, J. Hui, J. Rodríguez-López, M. Chen-Glasser, J.A. Dura, S.C. DeCaluwe, Morphology of Thin-Film Nafion on Carbon as an Analogue of Fuel Cell Catalyst Layers, *ACS Applied Materials & Interfaces*, 16 (2024) 3311-3324.
- [55] N.C. Röttcher, Y.-P. Ku, M. Minichova, K. Ehelebe, S. Cherevko, Comparison of methods to determine electrocatalysts' surface area in gas diffusion electrode setups: a case study on Pt/C and PtRu/C, *Journal of Physics: Energy*, 5 (2023) 024007.
- [56] P. Schneider, A.-C. Scherzer, B.D. Storey, M. Klingele, N. Zamel, D. Gerteisen, The effect of ionomer to carbon ratio and relative humidity on cathode catalyst degradation in PEM fuel cells, *J. Electrochem. Soc.*, 170 (2023) 104505.
- [57] X. Wang, D. Li, Y.-T. Pan, K. Chen, K. Burns, Y.S. Kim, G. Wu, J. Watt, J.S. Spendelow, Effect of the catalyst metal content and the carbon support on proton-exchange membrane fuel cells performance and durability, *Electrochim. Acta*, 512 (2025) 145490.
- [58] Y. Liu, C. Ji, W. Gu, D.R. Baker, J. Jorne, H.A. Gasteiger, Proton conduction in PEM fuel cell cathodes: effects of electrode thickness and ionomer equivalent weight, *J. Electrochem. Soc.*, 157 (2010) B1154.
- [59] H. Yu, J.M. Roller, W.E. Mustain, R. Maric, Influence of the ionomer/carbon ratio for low-Pt loading catalyst layer prepared by reactive spray deposition technology, *J. Power Sources*, 283 (2015) 84-94.
- [60] P. Schneider, M. Batool, A.O. Godoy, R. Singh, D. Gerteisen, J. Jankovic, N. Zamel, Impact of platinum loading and layer thickness on cathode catalyst degradation in PEM fuel cells, *J. Electrochem. Soc.*, 170 (2023) 024506.
- [61] R. Alink, R. Singh, P. Schneider, K. Christmann, J. Schall, R. Keding, N. Zamel, Full parametric study of the influence of ionomer content, catalyst loading and catalyst type on oxygen and ion transport in PEM fuel cell catalyst layers, *Molecules*, 25 (2020) 1523.
- [62] S.A. Berlinger, A. Chowdhury, T. Van Cleve, A. He, N. Dagan, K.C. Neyerlin, B.D. McCloskey, C.J. Radke, A.Z. Weber, Impact of platinum primary particle loading on fuel cell performance: insights from catalyst/ionomer ink interactions, *ACS applied materials & interfaces*, 14 (2022) 36731-36740.
- [63] T.R. Garrick, T.E. Moylan, V. Yarlagadda, A. Kongkanand, Characterizing electrolyte and platinum interface in PEM fuel cells using CO displacement, *J. Electrochem. Soc.*, 164 (2016) F60.
- [64] V. Yarlagadda, M.K. Carpenter, T.E. Moylan, R.S. Kukreja, R. Koestner, W. Gu, L. Thompson, A. Kongkanand, Boosting fuel cell performance with accessible carbon mesopores, *ACS Energy Lett.*, 3 (2018) 618-621.
- [65] Y.-C. Park, H. Tokiwa, K. Kakinuma, M. Watanabe, M. Uchida, Effects of carbon supports on Pt distribution, ionomer coverage and cathode performance for polymer electrolyte fuel cells, *J. Power Sources*, 315 (2016) 179-191.
- [66] G. Ferro, C. Roiron, H. Wang, J. Braaten, B.M. Stühmeier, C. Johnston, L. Cheng, I.V. Zenyuk, P. Atanassov, Designer Electrocatalysts for the Oxygen Reduction Reaction with Controlled Platinum Nanoparticle Locality, *Adv. Energy Mater.*, (2024) 2403165.
- [67] A. Kongkanand, M.F. Mathias, The priority and challenge of high-power performance of low-platinum proton-exchange membrane fuel cells, *The journal of physical chemistry letters*, 7 (2016) 1127-1137.
- [68] M.K. Debe, A.K. Schmoeckel, G.D. Vernstrom, R. Atanasoski, High voltage stability of nanostructured thin film catalysts for PEM fuel cells, *J. Power Sources*, 161 (2006) 1002-1011.

[69] D. Sepa, M. Vojnovic, A. Damjanovic, Reaction intermediates as a controlling factor in the kinetics and mechanism of oxygen reduction at platinum electrodes, *Electrochim. Acta*, 26 (1981) 781-793.

[70] G.S. Harzer, A. Orfanidi, H. El-Sayed, P. Madkikar, H.A. Gasteiger, Tailoring catalyst morphology towards high performance for low Pt loaded PEMFC cathodes, *J. Electrochem. Soc.*, 165 (2018) F770.

[71] T. Takeshita, K. Yano, K. Kodama, Effect of the Pore Size of Mesoporous Carbon Supports for Cathode Catalysts on the Cell Performance of Polymer Electrolyte Fuel Cells, *ACS Catalysis*, 15 (2025) 13549-13557.

[72] V. Yarlagaadda, N. Ramaswamy, R.S. Kukreja, S. Kumaraguru, Ordered mesoporous carbon supported fuel cell cathode catalyst for improved oxygen transport, *J. Power Sources*, 532 (2022) 231349.

[73] R. Mann, J. Amphlett, B. Peppley, C. Thurgood, Henry's Law and the solubilities of reactant gases in the modelling of PEM fuel cells, *J. Power Sources*, 161 (2006) 768-774.

[74] N. Kikkawa, M. Kimura, Comprehensive Molecular Dynamics Study of Oxygen Diffusion in Carbon Mesopores: Insights for Designing Fuel-Cell Catalyst Supports, *Langmuir*, 40 (2024) 1674-1687.

[75] J. Wu, X.Z. Yuan, H. Wang, M. Blanco, J.J. Martin, J. Zhang, Diagnostic tools in PEM fuel cell research: Part I Electrochemical techniques, *Int. J. Hydrogen Energy*, 33 (2008) 1735-1746.

[76] A. Kulikovsky, Analytical impedance of two-layer oxygen transport media in a PEM fuel cell, *Electrochem. Commun.*, 135 (2022) 107187.

[77] S. Cruz-Manzo, Further understanding of uncertainties in the impedance spectrum of the polymer electrolyte fuel cell due to inductive effects and oxygen diffusion time constant, *Journal of Energy and Power Technology*, 2 (2020) 1-21.

[78] A. Kulikovsky, A model-based analysis of PEM fuel cell distribution of relaxation times, *Electrochim. Acta*, 429 (2022) 141046.

[79] M.R. Gerhardt, L.M. Pant, J.C. Bui, A.R. Crothers, V.M. Ehlinger, J.C. Fornaciari, J. Liu, A.Z. Weber, Method—Practices and Pitfalls in Voltage Breakdown Analysis of Electrochemical Energy-Conversion Systems, *J. Electrochem. Soc.*, 168 (2021) 074503.

[80] L. Hao, K. Moriyama, W. Gu, C.-Y. Wang, Modeling and experimental validation of Pt loading and electrode composition effects in PEM fuel cells, *J. Electrochem. Soc.*, 162 (2015) F854.

[81] F.C. Cetinbas, R.K. Ahluwalia, N.N. Kariuki, V. De Andrade, D.J. Myers, Effects of porous carbon morphology, agglomerate structure and relative humidity on local oxygen transport resistance, *J. Electrochem. Soc.*, 167 (2019) 013508.

[82] G. Yang, S. Komini Babu, W.P. Liyanage, U. Martinez, D. Routkevitch, R. Mukundan, R.L. Borup, D.A. Cullen, J.S. Spendelow, Coaxial nanowire electrodes enable exceptional fuel cell durability, *Adv. Mater.*, 35 (2023) 2301264.

[83] M.K. Debe, Nanostructured thin film electrocatalysts for PEM fuel cells—a tutorial on the fundamental characteristics and practical properties of NSTF catalysts, *ECS Trans.*, 45 (2012) 47.

[84] M.K. Debe, R.T. Atanasoski, A.J. Steinbach, Nanostructured thin film electrocatalysts—current status and future potential, *ECS Trans.*, 41 (2011) 937.

[85] G. Yang, C. Lee, X. Qiao, S.K. Babu, U. Martinez, J.S. Spendelow, Advanced electrode structures for proton exchange membrane fuel cells: current status and path forward, *Electrochemical Energy Reviews*, 7 (2024) 9.

- [86] G. Zhang, Z. Qu, W.-Q. Tao, Y. Mu, K. Jiao, H. Xu, Y. Wang, Advancing next-generation proton-exchange membrane fuel cell development in multi-physics transfer, *Joule*, 8 (2024) 45-63.
- [87] K.M. Rod Borup, Adam Weber, FC-PAD: Fuel Cell Performance and Durability Consortium, DOE Fuel Cell Technologies Office Annual Merit Review, 2018.
- [88] S. Komini Babu, X. Wang, L.M. Pant, R. Mukundan, A.Z. Weber, R.L. Borup, J.S. Spendelow, Meso-Structured Polymer Electrolyte Fuel Cell Electrode, *Electrochemical Society Meeting Abstracts 237*, The Electrochemical Society, Inc., 2020, pp. 1634-1634.
- [89] R. Yoshihara, D. Wu, Y.K. Phua, A. Nagashima, E. Choi, S.M. Jayawickrama, S. Ishikawa, X. Liu, G. Inoue, T. Fujigaya, Ionomer-free electrocatalyst using acid-grafted carbon black as a proton-conductive support, *J. Power Sources*, 529 (2022) 231192.
- [90] J. Yang, H. Xu, J. Li, K. Gong, F. Yue, X. Han, K. Wu, P. Shao, Q. Fu, Y. Zhu, Oxygen-and proton-transporting open framework ionomer for medium-temperature fuel cells, *Science*, 385 (2024) 1115-1120.
- [91] T. Soboleva, K. Malek, Z. Xie, T. Navessin, S. Holdcroft, PEMFC catalyst layers: the role of micropores and mesopores on water sorption and fuel cell activity, *ACS applied materials & interfaces*, 3 (2011) 1827-1837.
- [92] L. Hu, T. Van Cleve, H. Yu, J.H. Park, N. Kariuki, A.J. Kropf, R. Mukundan, D.A. Cullen, D.J. Myers, K.C. Neyerlin, Electrochemical characterization of evolving ionomer/electrocatalyst interactions throughout accelerated stress tests, *J. Power Sources*, 556 (2023) 232490.
- [93] G.-R. Zhao, W.-Z. Fang, H. Ling, K.-B. An, Y.-H. Lu, W.-Q. Tao, Boosting performance of PEMFCs via optimization of oxygen transport resistance in catalyst layers using mesoporous carbons, *ACS Appl. Energy Mater.*, 8 (2025) 3732-3744.
- [94] K. Kodama, R. Jinnouchi, T. Suzuki, H. Murata, T. Hatanaka, Y. Morimoto, Increase in adsorptivity of sulfonate anions on Pt (111) surface with drying of ionomer, *Electrochem. Commun.*, 36 (2013) 26-28.
- [95] P.-Y. Shao, M. Ma, W. Ye, Z.-G. Zhao, Q. He, L.-X. Shen, Y.-L. Zhang, L. Zhao, Z.-B. Wang, Optimizing ionomer distribution for constructing efficient Pt/ionomer interfaces: Research on improving the performance of low-platinum-loading hydrogen fuel cells, *J. Colloid Interface Sci.*, 689 (2025) 137197.
- [96] S. Sambandam, V. Ramani, Influence of binder properties on kinetic and transport processes in polymer electrolyte fuel cell electrodes, *PCCP*, 12 (2010) 6140-6149.
- [97] A.D. Modestov, A.V. Kapustin, V.B. Avakov, I.K. Landgraf, M.R. Tarasevich, Cathode catalyst layers with ionomer to carbon mass ratios in the range 0–2 studied by electrochemical impedance spectroscopy, cyclic voltammetry, and performance measurements, *J. Power Sources*, 272 (2014) 735-742.
- [98] S.A. Berlinger, B.D. McCloskey, A.Z. Weber, Inherent acidity of perfluorosulfonic acid ionomer dispersions and implications for ink aggregation, *The Journal of Physical Chemistry B*, 122 (2018) 7790-7796.
- [99] M. Harada, H. Kadoura, S.-i. Takata, H. Iwase, S. Kajiya, T. Suzuki, N. Hasegawa, A. Shinohara, S. Kato, Equation Elucidating the Catalyst-Layer Proton Conductivity in a Polymer Electrolyte Fuel Cell Based on the Ionomer Distribution Determined Using Small-Angle Neutron Scattering, *ACS Applied Materials & Interfaces*, 15 (2023) 42594-42602.
- [100] H. Srivastav, A.Z. Weber, C.J. Radke, Colloidal Stability of PFSA-Ionomer Dispersions Part II: Determination of Suspension pH Using Single-Ion Potential Energies, *Langmuir*, 40 (2024) 6666-6674.

- 1 [101] H. Srivastav, A.Z. Weber, C.J. Radke, Colloidal Stability of PFSA-Ionomer Dispersions.
2 Part I. Single-Ion Electrostatic Interaction Potential Energies, *Langmuir*, 40 (2024) 6654-6665.
3 [102] P.E. Santangelo, M. Romagnoli, M. Puglia, An experimental approach to evaluate drying
4 kinetics and foam formation in inks for inkjet printing of fuel-cell layers, *Exp. Therm Fluid Sci.*,
5 135 (2022) 110631.

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