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Journal

Electrochimica Acta, 576

ISSN

0013-4686

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Publication Date

2026-11-01

DOI

10.1016/j.electacta.2026.149697

Supplemental Material

<https://escholarship.org/uc/item/3b51x3j8#supplemental>

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Estimating Kinetic Parameters from the Impedance Response of Proton-Exchange-Membrane Fuel Cells Using Continuum Models

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A mathematical framework for simulating the impedance response of a proton-exchange-membrane fuel cell (PEMFC) was developed to provide insight into the coupled physics and chemistry that influence observed spectra as well as guidance to researchers with similar problems. The model was based on a cell-level continuum model that was linearized and represented in the frequency domain, which allowed for the accounting of coupled transport in a PEMFC and the simulation of full spectra in seconds. Good agreement was observed between experimental and simulated polarization and impedance data. Consistency between steady-state and frequency-domain continuum models was confirmed, which allowed for the extraction of kinetic information from the experimental impedance spectra. The model framework was used to estimate contributions associated with ohmic, charge-transfer, and transport resistances, which was shown to align with power-loss voltage breakdown analyses of steady-state simulations. A proposed equivalent-circuit model facilitated estimates of the low-frequency impedance, which can be used in conjunction with the impedance model to assess properties of the electrochemical cell. Since the model accounted for the effects of coupled physics, pressure impedance transfer functions were simulated, which showed quantitative agreement with experimental observations from literature.

1 List of Symbols

2	Symbol	Descriptions [unit]
3	a	electrochemical active area density [m^2/m^3]
4	C	complex capacitance [$F \cdot cm^{-2}$]
5	C_0	interfacial capacitance [$F \cdot cm^{-2}$]
6	C_2	low-frequency capacitance [$F \cdot cm^{-2}$]
7	C_S	low-frequency surface capacitance [$F \cdot cm^{-2}$]
8	D_{Ψ}^{eff}	effective diffusion coefficient of conserved quantity Ψ
9	d_{Ψ}	transient coefficient of conserved quantity Ψ
10	f	frequency [Hz]
11	i	current density [$A \cdot cm^{-2}$]
12	i_0	exchange current density [$A \cdot cm^{-2}$]
13	j	imaginary number $\sqrt{-1}$
14	L	complex inductance [$H \cdot cm^{-2}$]
15	N_{Ψ}	flux vector of conserved quantity Ψ
16	p_G	gas pressure [Pa]
17	p_L	liquid pressure [Pa]
18	p_R	reactant partial pressure [Pa]
19	R	resistance
20	R_S	low-frequency surface resistance [$\Omega \cdot cm^2$]
21	R_1 and R_2	Havrilia-Negami relaxation resistances [$\Omega \cdot cm^2$]
22	S_{Ψ}	volumetric source of conserved quantity Ψ
23	T	temperature [K]
24	t	time [s]
25	v	velocity vector [$m \cdot s^{-1}$]
26	X	scalar driving force
27	x	x-position [m]
28	Z	impedance transfer function [$\Omega \cdot cm^2$]
29	Z_r	real part of impedance Z [$\Omega \cdot cm^2$]
30	Z_j	imaginary part of impedance Z [$\Omega \cdot cm^2$]
31	Greek	Descriptions [unit]
32	α	constant-phase-element or Havrilia-Negami relaxation parameter
33	β	Havrilia-Negami relaxation parameter
34	η	overpotential [V]
35	κ	protonic conductivity [$S \cdot cm^{-1}$]
36	ζ	pressure impedance [$A \cdot cm^{-2} \cdot Pa^{-1}$]
37	σ	electronic conductivity [$S \cdot cm^{-1}$]
38	Φ_1	electronic potential [V]

1	Φ_2	ionic potential [V]
2	Ψ	variable representing a conserved quantity
3	ω	angular frequency [$rad \cdot s^{-1}$]

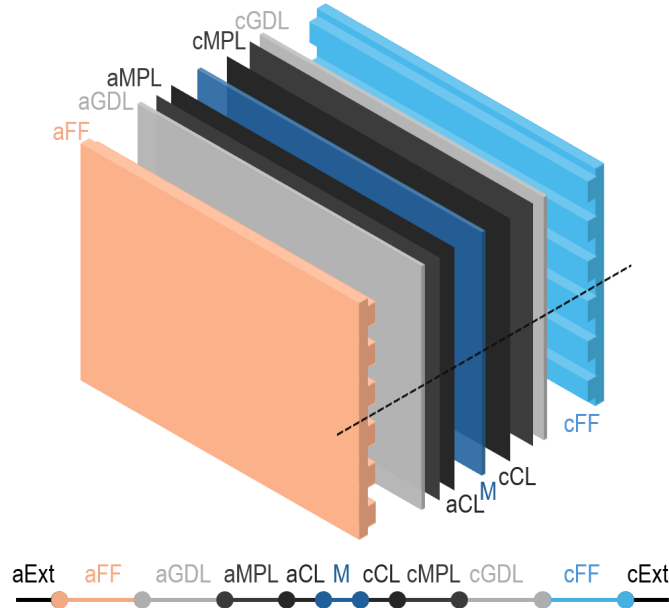
4 1 Introduction

5 The state-of-health of electrochemical energy conversion devices rely on the performance and interpretation
6 of electrochemical characterization techniques that aim to elucidate the relationship between current and potential.
7 Proton-exchange-membrane fuel cells (PEMFCs) are a developing technology where electrical energy is
8 generated from the electrochemical reaction of oxygen and hydrogen. A challenge for the field is the need for
9 controls and development of associated diagnostic tools that yield insight into the cell properties and conditions
10 that dictate cell performance and health.¹

11 Electrochemical characterization techniques are used to probe the potential-current relationship influenced by
12 cell materials and operating conditions, which range from steady-state methods like polarization curves to
13 transient methods like voltammetry. Electrochemical-impedance spectroscopy (EIS) is a transient technique that
14 measures the transfer function between current and potential using a small-amplitude sinusoidal perturbation. The
15 transfer function is commonly referred to as the impedance Z , which is complex and can be expressed as a ratio of
16 the phasors that represent the complex oscillating current $\tilde{i}$ and potential difference $\tilde{V}$ of an electrochemical cell
17 as

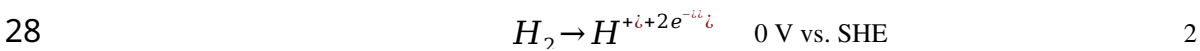
$$18 \quad Z(\omega) = \frac{\tilde{V}}{\tilde{i}} \quad 1$$

19 where ω is the angular frequency of the sinusoidal perturbation. The analysis of electrochemical systems,
20 including but not limited to batteries, fuel cells, corrosion, and sensors, is of high interest due to the non-invasive
21 nature of the analytical technique, which can yield insight into the underlying chemical and physical processes.²⁻⁴

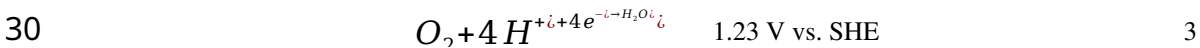


22
23 *Figure 1 Schematic diagram of the simulated modeling domain that is representative of a 1D line segment in the through-plane*
24 *direction of a PEMFC.*

25 As shown in Figure 1, a PEMFC is a layered device that consists of a membrane-electrode assembly (MEA)
26 sandwiched between porous layers that regulate the transport of reactant gases and by-product water. Electricity is
27 generated by the electrochemical reactions of hydrogen oxidation (HOR)



29 and oxygen reduction (ORR)



on Pt-based catalysts contained within the cathode and anode catalyst layers, cCL and aCL, respectively. The electrons travel through an external load, while the protons are transported from the aCL to the cCL using a proton-exchange membrane (M). The membrane and catalyst layers (CLs) are referred to as the MEA. The reactant gases of hydrogen and oxygen are delivered to the aCL and cCL using anode and cathode gas-diffusion layers (aGDL and cGDL) that can be equipped with a micro-porous layer (aMPL and cMPL), respectively. Reactant gases are supplied to the porous layers using channelled graphite plates called flow fields (aFF and cFF).

Impedance spectra obtained from a PEMFC contain features that are influenced by operating conditions of the cell (i.e., temperature, pressure, humidity, concentration) and cell-component morphology (i.e., porous structure, catalyst-particle, geometry). The coupled-physics in a PEMFC was presented in a series of works by Schneider *et al.*⁵⁻⁷, where impedance spectra from a segmented PEMFC suggested oscillations in reactant gas concentration pervaded through the porous layers to the channels and to downstream segments. The effect of humidity on the membrane was observed in capacitive features that evolved to a pure resistance when the humidity was increased. Low-frequency inductive features were attributed to oscillating water content in the ionomer, which can be influenced by PtO formation on Pt catalyst in the cCL. A PEMFC was subjected to oscillating reactant gas pressures by Niroumand *et al.*⁸ that resulted in measurable oscillations in cell potential, which demonstrated the probing of the dependencies of cell performance on reactant concentrations. Engebretsen *et al.*⁹ and Shirsath *et al.*¹⁰ developed experimental setups that sinusoidally perturbed the applied backpressure of an operating PEMFC to assess water and reactant transport resistances. The relationship between reactant concentration and electrochemical performance was studied by Sorrentino *et al.*¹¹ through the modulation of reactant-gas pressure. As a possible method to assess reactant and water distributions down the cell channels, Sorrentino *et al.*¹² further developed an experimental method for concentration-frequency-response analysis by imposing oscillations in water-vapor and reactant gas pressure and identified the pressure contribution of the observed total impedance. Subsequent work by Sorrentino *et al.*¹³ examined mass-transport effects and observed the frequency response associated with oscillations in reactant concentration, which can be used for the identification of inadequate humidification of the MEA. Occlusion of the water outlets of the PEMFC was used by Cruz-Manzo *et al.*¹⁴ to induce changes in the impedance spectra related to water accumulation within the cell. Wu *et al.*¹⁵ performed *in-situ* neutron imaging of a PEMFC operated with an oscillating current that allowed for the observation of oscillating water content in the cell, which yielded insight into water transport and aspects of water management.

Analytical tools and methodologies for interpreting spectra strive to relate observed impedance features to physical mechanisms. As in the work by Ren *et al.*¹⁶, analytical methods were developed for analyzing regions of spectra with small phase angles at low frequencies for the purposes of identifying conditions that could increase cell degradation, like insufficient humidification. Frequency-response-analysis methods like distribution of relaxation times (DRT) was used by Schiefer *et al.*¹⁷ to assess the origins of low-frequency inductive features and concluded that ORR kinetics were the primary contribution to low-frequency inductance as opposed to hydration effects. The use of DRT was espoused by Dierickx *et al.*¹⁸ as a powerful analytical tool for the interpretation of impedance spectra from PEMFC. Chandesris *et al.*¹⁹ performed studies using a segmented 8-cell PEMFC for assessing the low-frequency capacitive features in the observed impedance spectra, which was attributed to down-the-channel oxygen transport effects and modeled with a 0D stirred-tank-reactor mathematical model.

Mathematical models describing the coupled transport in the cell can be used to simulate the impedance response of PEMFCs and provide insights into the effects of multiphase transport. In general, the derived governing equations can be solved in transient simulations and transformed into the frequency domain to yield the simulated impedance response or can be transformed into the frequency domain and subsequently solved yielding the impedance. The methods are mathematically equivalent and possess their own challenges associated with numerical stability, implementation, and accuracy.

In foundational work by Springer *et al.*²⁰, a frequency-domain impedance model for the cCL was developed, which suggested that thinner catalyst layers result in higher catalyst utilization and highlighted the sensitivity of the cathode-side impedance to transport limitations of proton conduction, porous permeability of reactant oxygen, and humidification. A continuum frequency-domain model developed by Sun *et al.*²¹ of the cathode side of a PEMFC was used to perform parametric studies exploring the influence of oscillating saturation and transport coefficients, proton conductivity, and oxygen diffusion in the cCL, which suggested that low-frequency inductance resulted from proton conductivity and low-frequency capacitance resulted from oxygen diffusion. In a series of works by Wiezell *et al.* and Holmström *et al.*²²⁻²⁵, PEM-based devices were modeled using a continuum mathematical framework and validated with experimental observations. For PEMFCs, the simulated impedance spectra suggested that the experimentally observed low-frequency inductive features were a result of water

transport that was found to shift to lower frequencies as the thickness of the membrane was increased. Maranzana *et al.*²⁶ assessed the consistency of the low-frequency limit of the experimental impedance and the slope of the polarization curve using observations on a 20-segment PEMFC and a 1D+1 transport model that accounted for advection of the reactant oxygen, which was related to the magnitude of the low-frequency capacitive impedance, which diminished significantly when the reactant oxygen stoichiometry was modulated in coordination with the current-potential oscillation frequencies. Reshetenko *et al.*²⁷ evaluated the performance of Fe-N-C cathode catalyst using a segmented cell and simulated impedance spectra using a 1D down-the-channel frequency-domain continuum model to quantify kinetic and transport losses and reported losses comparable to more commonly used Pt-C based cathodes. In a series of works by Kulikovskiy²⁸⁻³², a continuum mathematical framework was used to derive analytical expressions of various components of the PEMFC total impedance that included oxygen concentration impedance in the cCL, oxygen transport impedance in the cCL, diffusion impedance through the cathode porous layers, cathode faradaic impedance with fast oxygen transport, and concentration impedance of a cCL with low Pt loadings.

In time-domain model simulations by Setzler and Fuller³³, low-frequency inductive features related to PtO formation showed good agreement with experimental observations of low-frequency inductance up to operating current densities of 0.8 A·cm⁻². In a two-part series, Bao and Bessler^{34,35} presented a 2D continuum PEMFC model that accounted for down-the-channel effects associated with water transport, which was used to perform transient simulations with a step-function increase in cell potential that was converted to impedance via a Fourier transform. Simulated impedance spectra exhibited features associated with kinetic activation, ohmic losses, and mass-transport effects. The influence of flow-field geometry was studied with a model by Baricci *et al.*³⁶ that was coupled with computational fluid dynamics to identify oxygen depletion under rib-sections in the flow fields in the simulated spectra, which suggested that interdigitated flow-field geometries yielded lower impedances and that turns in the channel have a minimal effect on cell performance. Futter *et al.*³⁷ developed a non-isothermal 2D model to simulate transient PEMFC operation and generate the impedance from the potential-current response associated with a step change in potential or current density via a Fourier transform. Simulated spectra suggested that low-frequency inductive impedance features were attributed to PtO formation on the ORR catalyst surface. Transient simulations using a 2D PEMFC continuum model performed by Kosakian *et al.*³⁸ replicated low-frequency inductive features attributed to coupled water transport between ionomer and pore spaces. Yuan *et al.*³⁹ simulated the impedance response using a continuum model of a cell subjected to oscillating transient boundary conditions to yield simulated spectra that exhibited mass-transport losses at lower frequencies and attributed low-frequency inductive features to hydration effects. Experimental spectra from a PEMFC were analyzed via the DRT method to correlate model and experimental results.

For practical applications of interpreting impedance spectra, the impedance can be summarily represented in terms of passive circuit elements that represent physical and chemical processes in the cell. An algorithm developed by Lee *et al.*⁴⁰ to simulate the steady-state polarization of a PEMFC, which was used to assess the effective resistances in an equivalent circuit model as a method to relate continuum properties to equivalent-circuit parameters. Wagner⁴¹ used equivalent-circuit models to breakdown ohmic and electrode contributions of the total impedance to quantify losses in PEMFC cell performance.

The use of equivalent-circuit models for diagnostic purposes was advanced by Pattamarat and Hunsom⁴² and Brunetto *et al.*⁴³, which demonstrated model parameterization as a function of cell operating conditions. Niya *et al.*^{44,45} developed an equivalent-circuit process model that showed consistency with ohmic, kinetic, and transport losses that spanned the measurable frequency range of EIS. Chevalier *et al.*⁴⁶ used an impedance equivalent-circuit process model to estimate gas velocities in the air channel as a potential method for monitoring reactant gas distributions in operating PEMFCs. Haimerl *et al.*⁴⁷ used equivalent circuit models to estimate HOR kinetic losses associated with hydrogen starvation as a system monitoring tool.

Hallmarks of PEMFC transport and kinetic mechanisms in the impedance can be assessed using equivalent-circuit models, like in the work by Obermaier *et al.*⁴⁸, who modeled the impedance response of a cCL under H₂-N₂ conditions using a de Levie equivalent circuit for porous electrodes, which related porous-catalyst-layer properties to the observed spectra. Heinzmann *et al.*⁴⁹ assessed consistency of various equivalent-circuit models describing porous-electrode behavior to experimental data and concluded that diffusion, electronic, and ionic transport can be represented using a transmission-line model with fitting performed using DRT to identify line shapes in the spectra. In a subsequent work, Heinzmann and Weber⁵⁰ used impedance fitting methods developed for solid-oxide fuel cells to PEMFCs and showed parameterization of kinetic and transport properties using equivalent-circuit models and the DRT method and noted the necessity for further development in understanding the influence of

water transport on the impedance response in PEMFCs. Low-frequency features in the impedance response of PEMFCs were evaluated by Roy *et al.*⁵¹ and concluded that both hydrogen peroxide and PtO formation in the cCL were plausible mechanisms for low-frequency inductive features, which were subsequently corroborated in characterization of Pt in the cCL and effluent water from accelerated-stress cell testing.⁵² Cruz-Manzo *et al.*⁵³ performed continuum and equivalent-circuit modeling to ascertain the effect of PtO and hydrogen peroxide formation on the impedance response of a PEMFC and concluded that low-frequency inductive features persist when both are taken into account. Pivac *et al.*⁵⁴ amended equivalent circuit models with the addition of two additional low-frequency impedance shapes that represented capacitive and inductive components, which were attributed to oxygen transport, oxygen accumulation, and interfacial phenomena (i.e., interfacial resistance and dissolution). Kwon *et al.*⁵⁵ used EIS to investigate the effects of degradation due to low-humidity operation and observed changes in the impedance response associated with membrane thinning and catalyst coarsening, which was interpreted using an equivalent-circuit transmission-line model.

Interest in impedance spectroscopy as a diagnostic tool for electrochemical energy-conversion devices like PEMFCs continues to grow. To advance these efforts, this work aims to develop rapid continuum impedance models for *in-situ* diagnostics of PEMFCs that can be used to extract cell properties from measured spectra, yielding information for performance optimization and improving reliability, which entails the following: (1) validating simulated spectra generated using the framework with experimental spectra and consistency of parameters obtained from steady-state data and models, (2) developing and validating impedance breakdown methodologies that are consistent with established power-loss breakdown analyses, which identify contributions associated with ohmic, kinetic, and transport mechanisms, (3) simulating the impedance signatures of degradation mechanisms, and (4) demonstrating capability of the model framework in predicting the impedance response of other transfer functions that relate key process parameters like pressure, temperature, and concentration to potential/current.

2 Methods

PEMFC impedance spectra were obtained from experimental measurements of a 5 cm² differential cell, which was subsequently modeled using continuum where the interfacial impedance associated with the faradaic reactions were derived from the steady-state continuum model kinetics.

2.1 Experimental

A 5 cm² differential cell was assembled with a Gore MEA (A510 4/M720.18/C510.4) with a Pt catalyst loading of 0.4 mg cm⁻², Sigracet 22BB carbon paper GDL, and 12 mil polyurethane gasket (Merryweather Foam, Anthony, NM, USA), which was contained within a 14-channel serpentine flow field and cell hardware (Fuel Cell Technologies, Albuquerque, NM, USA), as described by Baker *et al.*⁵⁶ Break-in and conditioning was conducted in accordance with the procedure as established by Kabir *et al.*⁵⁷ using a Scribner 850 Fuel Cell Test Station (Scribner & Assoc., Southern Pine, SC, USA) that was equipped with an auto back pressure unit. The cell was operated at 80°C, 1.5 bara, and 100% RH under potentiostatic control using a BioLogic VSP-300 potentiostat with a 20 A booster to obtain a polarization curve ranging from 925 mV to 300 mV in 25 mV increments. At each steady-state potential, the impedance response under potentiostatic control was measured using a 15 mV perturbation amplitude over a frequency range of 100 kHz to 10 mHz.

The linearity of the experimental impedance data was assessed via a measurement model approach as described by Argawal *et al.*⁵⁸, which was used to check consistency with the Kramers-Kronig relations. The measurement-model method uses an arbitrary sum of Voigt elements fit to the impedance spectra using a Levenberg-Marquardt non-linear fitting algorithm for the estimation of effective electrochemical properties of the cell.⁵⁹

2.2 Mathematical Model

The mathematical model for the PEMFC was based on continuum models as developed by Weber and Newman⁶⁰, where the transport of a conserved quantity Ψ_i is governed by

$$d_{\Psi_i} \frac{\partial \Psi_i}{\partial t} + \mathbf{v} \cdot \nabla X_{\Psi_i} = \nabla \cdot \mathbf{N}_{\Psi_i} + S_{\Psi_i} \quad 4$$

where d_{ψ_i} is a transient coefficient, R_{ψ_i} is a volumetric source term, and N_{ψ_i} is the flux, which can be expressed as

$$N_{\psi_i} = -D_{\psi_i}^{eff} \nabla X_{\psi_i} \quad 5$$

with $D_{\psi_i}^{eff}$ is an effective transport coefficient and X_{ψ_i} is the driving force for transport for species i . The generalized transport equations were used to describe the multiphase transport of heat, electrons, ions, liquid and gases as functions of temperature T , electronic potential Φ_1 , ionic potential Φ_2 , liquid pressure p_L , gas pressure p_G , and reactant partial pressure p_R . The volumetric source term R_{ψ_i} represented reactant gas consumption, water production, charge transfer, adsorption of liquid water and water vapor into the ionomer, desorption of liquid water and water vapor out of the ionomer, and heat generation due to water phase changes, electrochemical reactions, and Joule heating. The electrochemical reactions were assumed to adhere to a concentration-dependent Butler-Volmer kinetic expression represented by i_{rxn} , which was applied to HOR and ORR. The water generation and gas consumption rates were related by stoichiometry to the volumetric current density.

The governing equations were converted to the frequency domain by linearization using a Taylor-series expansion about a steady state assuming constant effective diffusion coefficients, where the 2nd order and higher terms were discarded since EIS represents the linear response of the electrochemical system. The independent variables were expressed as the linear superposition of steady-state and transient components

$$\Psi_i = \overline{\Psi}_i + \Re \left\{ \tilde{\Psi}_i e^{j\omega t} \right\} \quad 6$$

with the steady-state part indicated by the overline and the transient part represented as a phasor, where the tilde indicates a complex number.⁴ The generalized oscillating governing equation was given as

$$j\omega d_{\psi_i} \tilde{\Psi}_i = -D_{\psi_i}^{eff} \nabla^2 \tilde{X}_{\psi_i} + \tilde{S}_{\psi_i} \quad 7$$

The oscillating coupled physics described the oscillating behavior in thermal energy $\tilde{T}$, electronic potential $\tilde{\Phi}_1$, ionic potential $\tilde{\Phi}_2$, liquid pressure $\tilde{p}_L$, gas pressure $\tilde{p}_G$, and reactant-gas partial pressure $\tilde{p}_R$. Coupling of oscillating quantities $\tilde{X}_{\psi} = [\tilde{T}, \tilde{\Phi}_1, \tilde{\Phi}_2, \tilde{p}_L, \tilde{p}_G, \tilde{p}_R]$ are enforced via linearized oscillating source terms

$$\tilde{S}_{\psi_i} = \sum_j \frac{\partial R_{\psi_i}}{\partial X_{\psi_j}} \tilde{X}_{\psi_j} \quad 8$$

The impedance at the catalyst surfaces were characterized by an oscillating volumetric current density expression given as

$$\tilde{i}_{CL} = a_{0,CL} \left(\frac{\tilde{\eta}}{Z_0} + \frac{\tilde{p}_R}{R_{p_R}} + \frac{\tilde{T}}{R_T} + \frac{\tilde{p}_G}{R_{p_G}} + \frac{\tilde{p}_L}{R_{p_L}} \right) \quad 9$$

where the resistances were defined as

$$\frac{1}{R_{X_i}} = \frac{\partial i_{rxn}}{\partial X_i} \quad 10$$

and the interfacial overpotential $\tilde{\eta}$ is the difference between the oscillating electronic and ionic potentials.

The impedance associated with electrochemical reactions at the catalyst surfaces was given by the interfacial process model

$$Z_0 = \frac{R_\eta - R_S}{1 + (j\omega(R_\eta - R_S)C_0)^{\alpha_0}} + \frac{R_S}{1 + (j\omega R_S C_S)^{\alpha_s}} \quad 11$$

where the charge-transfer resistance R_η was obtained from Equation and the interfacial capacitance C_0 was fit to agree with the experimental effective capacitance. The terms with the subscript S indicate interfacial effects

associated with side reactions that were used as fitting parameters to describe low-frequency inductive features. Note, that the interfacial impedance model preserves the low-and high frequency limits of the interfacial impedance. At sufficiently low frequencies, the interfacial impedance approaches a limiting value of R_η . For the HOR in the aCL, the value of R_S was set to 0, which yielded a surface impedance that was only associated with HOR. In the case of ORR in the cCL, coupled interfacial reactions associated with PtO and hydrogen peroxide can yield low-frequency inductive features that were represented in terms of the fitting parameters R_S and C_S , which represented interfacial surface charge-transfer resistance and interfacial pseudo-capacitance of the surface-side reactions not associated with ORR, shown in Equation . The values of these parameters were less than zero, which yielded a low-frequency inductive loop. The exponent α parameters were also used to fit the resulting simulated spectra to experimental data. When R_S was set to zero in the cCL, a smaller magnitude low-frequency inductive features were observed, which was due to water adsorption and desorption in the ionomer.

Impedance-response simulations were performed assuming a sinusoidal potential perturbation with an amplitude of 10 mV, which was enforced by phasor boundary conditions at the anode and cathode external boundaries, $\tilde{\Phi}_{1,a}$ and $\tilde{\Phi}_{1,c}$, that had values of -5 and 5 mV, respectively. The impedance response was independent of the perturbation amplitude, which suggests appropriate linearization of the governing equations. The frequency was swept from 10 kHz to 1 mHz at a rate of ten points per decade. The total cell impedance response was calculated as

$$Z(\omega) = \frac{\tilde{\Phi}_{1,a} - \tilde{\Phi}_{1,c}}{\tilde{i}} \quad 12$$

where the oscillating current density was assessed at either external boundary as

$$\tilde{i} = -\sigma \frac{d\tilde{\Phi}_1}{dx} \quad 13$$

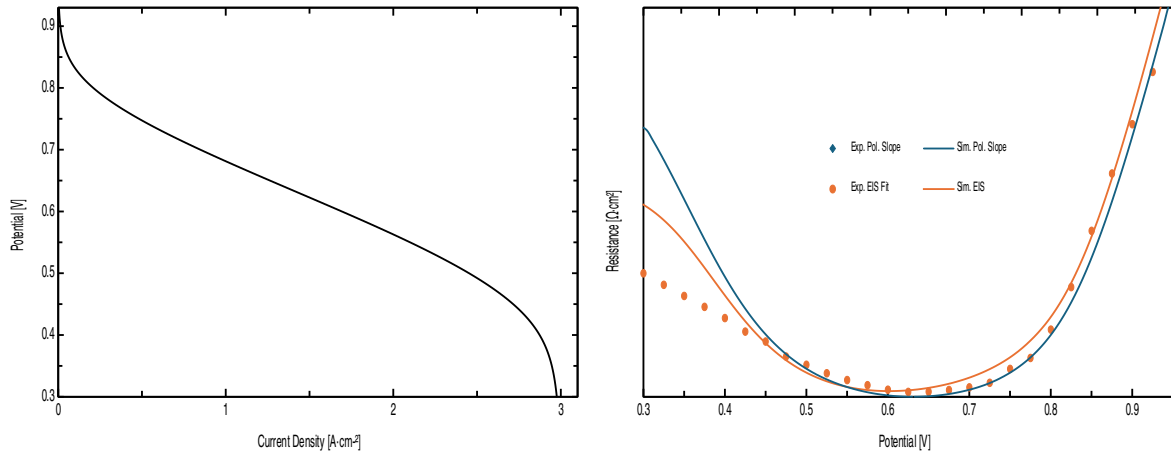
All experimental spectra exhibited a high-frequency inductive behavior, which was considered by the series addition of an inductor with a value of 0.7032 $\mu\text{H}\cdot\text{cm}^{-2}$.

Solutions to the frequency-domain governing equations that describe a PEMFC can be obtained through various numerical methods designed to solve coupled differential equations. Analytical impedance models developed by Kulikovsky²⁸⁻³² provided insight into the impedance signatures associated with reactant limitations to the cCL. Models that contain a greater extent of nonlinear coupling between governing equations may require numerical methods to solve, as demonstrated by Kosakian *et al.*³⁸, where the influence of water transport in a PEMFC on the impedance response was simulated using a transient 2D model that yielded simulated spectra that required simulation times over days using the open-source PEMFC model.⁶¹ Ehlinger simulated the impedance response of a cCL in MATLAB using the BAND(J) subroutine,⁶² which has been a widely used method for simulating electrochemical systems.⁶³⁻⁶⁵ A comparison of numerical approaches for time-domain and both frequency-domain approaches are compared by Ehlinger.⁶⁵

The cell model in this work was implemented in COMSOL Multiphysics® on a Dell Precision T5610 Workstation equipped with an Intel® Xeon® CPU E5-2630 with 64 GB of RAM. Simulation times for the steady-state solutions in 1D and 2D cell models were 30 s and 7 minutes, respectively. The partial derivatives in Equations and , were evaluated based on the results of the steady-state solution and subsequently used to simulate the impedance spectra, which required approximately 14 seconds and 4 minutes in 1D and 2D cell models, respectively. Herein, only results from the 1D simulations are shown. The 2D simulation yielded similar results and did account for in-plane transport processes. The implementation in a 2D geometry was performed to ensure that the mathematical model could be extended to higher dimensions.

3 Results

The mathematical framework was used to simulate the experimental data of a PEMFC operated to 80°C, 1.5 bara, and 100% RH, which is shown in Figure 2a. In Figure 2b, the slope of the polarization curve was compared to the low-frequency limit of the experimental and simulated impedance spectra. The simulated impedance spectra was carried out in two ways, with the first using the same simulation parameters used to generate the polarization curve shown in Figure 2a and the second where the value of R_η was adjusted to replicate experimental spectra.



a

b

Figure 2 Comparisons between experimental and simulated data (a) Experimental polarization data (○) and simulated polarization (line) from a PEMFC operated at 80°C 100% RH at 1.5 bara. (b) Resistance as a function of operation cell potential obtained from the slope of the experimental polarization data (◇), slope of the simulated polarization curve (teal line), low-frequency limit of the experimental impedance (○), and the low frequency limit of the simulated impedance using the same parameters as the simulated polarization curve (orange line). The low-frequency limit of the simulated impedance that was fit to the spectra is not shown because the values were within 0.01% of the experimental low-frequency impedance.

A selection of the simulated impedances is shown in Figure 3, Figure 4, and Figure 5 in comparison to the experimental impedance spectra, the slope of the polarization curve, and the extrapolated low-frequency limiting impedance that was obtained from the measurement-model fitting. All experimental and simulated spectra associated with steady-state potentials ranging from 925 to 300 mV are shown in the Supplemental Information

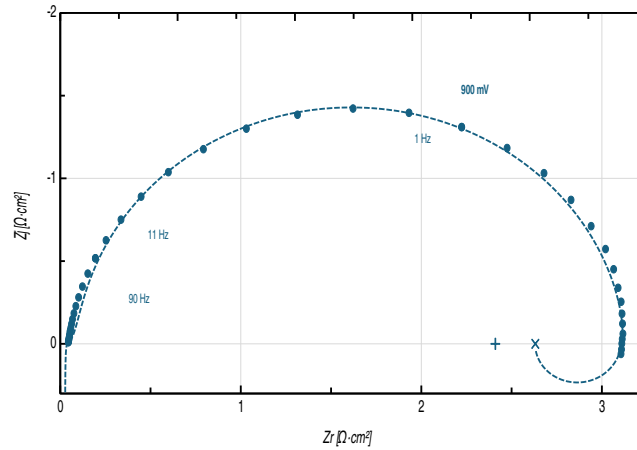
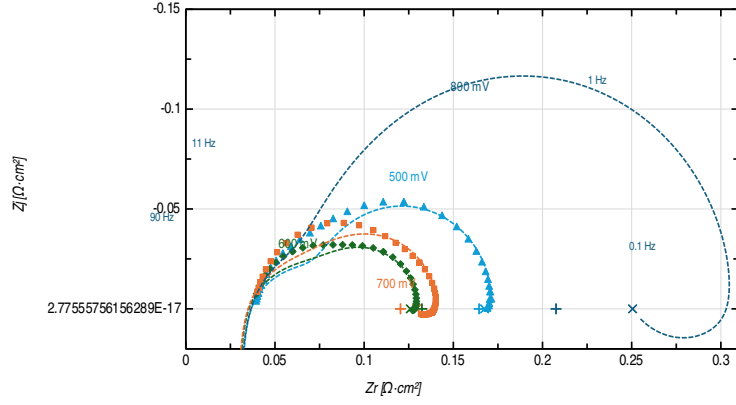
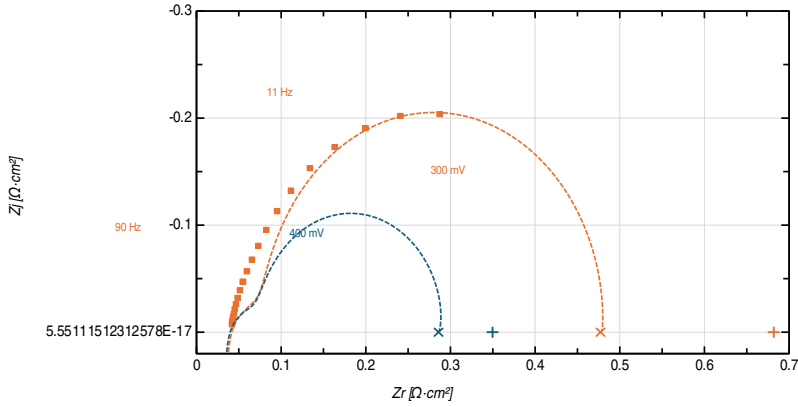


Figure 3 Nyquist plot of the impedance response of a PEMFC operated at 900 mV (○) with the simulated impedance response (dashed line), the low-frequency limit from the measurement model extrapolation of the experimental spectra (×), and the slope of the polarization curve (+).



1

2 *Figure 4 Nyquist plot of the impedance response of a PEMFC with the simulated impedance response (dashed lines), the low-*
 3 *frequency limit from the measurement model extrapolation of the experimental spectra (×), and the slope of the polarization*
 4 *curve (+). The steady-state cell potentials of 800, 700, 600, and 500 mV are shown as a parameter with frequency markers of ○,*
 5 *□, ◇, and △, respectively.*



6

7 *Figure 5 Nyquist plot of the impedance response of a PEMFC with the simulated impedance response (dashed line), the low-*
 8 *frequency limit from the measurement-model extrapolation of the experimental spectra (×), and the slope of the polarization*
 9 *curve (+). The steady-state cell potentials of 400 and 300 mV are shown as a parameter with frequency markers of ○ and □,*
 10 *respectively.*

11 Complex capacitance and inductance representations of impedance spectra served as additional information for
 12 fitting simulated spectra to experimental data. The effective complex capacitance and inductance were obtained by

$$13 \quad C = C_r + jC_j = \frac{1}{j\omega Z} \quad 14$$

14 and

$$15 \quad L = L_r + jL_j = j\omega Z \quad 15$$

16 , respectively. In Figure 6a, the effective interfacial capacitance was observed as a plateau in the real capacitance
 17 when plotted as a function of frequency, which occurred around 10 Hz. In Figure 6b, high-frequency inductance
 18 was observed to be independent of operating current density and potential, which was accounted for by the
 19 addition of a constant inductor added in series to the total impedance shown in Equation .

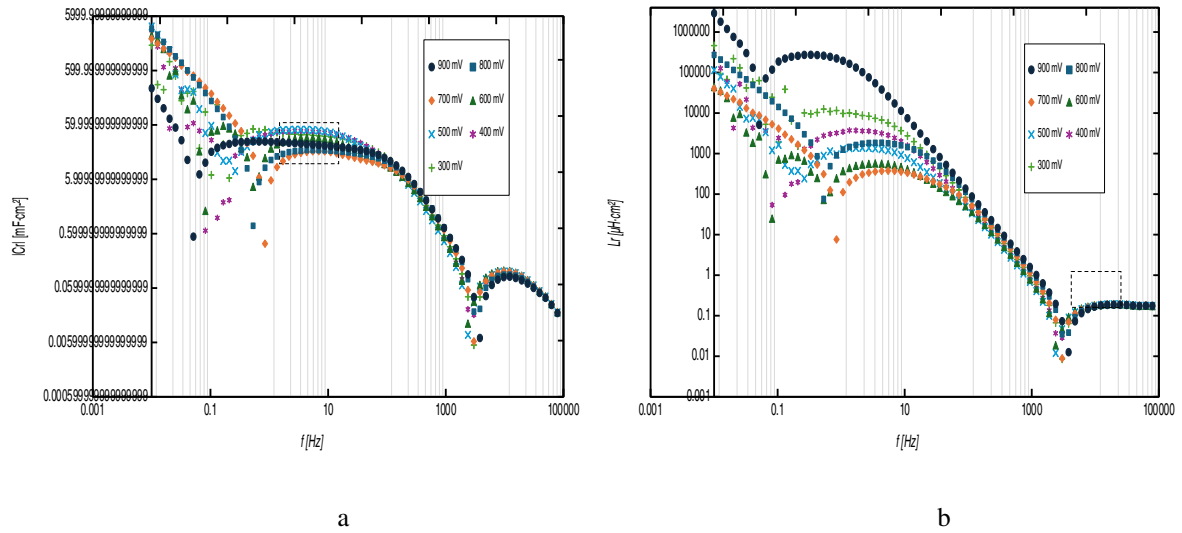


Figure 6 Complimentary forms of the measured cell impedances, capacitance (Equation) and inductance (Equation), as functions of frequency with the cell potential as a parameter. (a) The real part of the complex capacitance yielded information of the interfacial capacitance that was extracted from the plateau region observed at approximately 10 Hz, which is enclosed in the dashed-line rectangle. (b) The real inductance yielded information of a constant high-frequency inductive feature affecting all experimental impedance spectra, which is enclosed in the dashed-line rectangle.

4 Discussion

The model framework allowed for the breakdown of impedance into contributions associated with specific layer components and mechanisms, which facilitated the correlation of layer and cell properties to the total impedance response.

4.1 Parameter Estimation

In Figure 7a, the values of the ORR exchange current density used in fitting the simulated impedance spectra to experimental spectra $\hat{i}_{0,EIS}$ and used in fitting the simulated polarization curve to experimental polarization data $\hat{i}_{0,pol}$, are compared as a ratio of the two values as a function of the cell potential. A larger disparity, evidenced by the deviation of the ratio from unity, was observed to be higher at high cell potentials, which was attributed to the influence of kinetically inhibiting PtO films on the cCL Pt-based catalysts. The fitted fraction of cCL catalyst surface is shown on the secondary y-axis in Figure 7a. Empirically fit coverage factor is consistent with the work of Darling and Meyers⁶⁶, Liu *et al.*⁶⁷, and Wang *et al.*⁶⁸ At lower cell potentials, the ratio of the parameter values of the ORR exchange current densities tend toward unity. Agreement between the values suggests consistency in the intrinsic ORR exchange current density not influenced by surface oxide coverage and reasonable accounting for mass-transport effects of reactant oxygen.

Figure 7b shows estimates of interfacial capacitances obtained from the measurement model fitting and from the parameter values used in the simulated impedance spectra. The interfacial capacitances obtained from the measurement model $C_{0,MM}$ fitting gives insight into the magnitude of the effective interfacial capacitance that influences the HOR and ORR reaction. The interfacial capacitance C_0 used in the impedance simulations were adjusted to yield agreement in the total real capacitance as shown in Figure 6a. The distinction between the two capacitances is that $C_{0,MM}$ is the effective cell capacitance as confirmed by Liao *et al.*⁶⁹, whereas C_0 represents interfacial capacitance at the catalyst-particle interfaces attributed to the presence of an electrical double layer. The fitted values follow similar trends in differential capacitance of Pt surfaces as experimentally observed by Pajkossy and Kolb⁷⁰ and simulations by Shibata *et al.*⁷¹ The effective and estimated double-layer capacitances can yield information of the environment at the catalyst interface like ionic concentrations and pH.

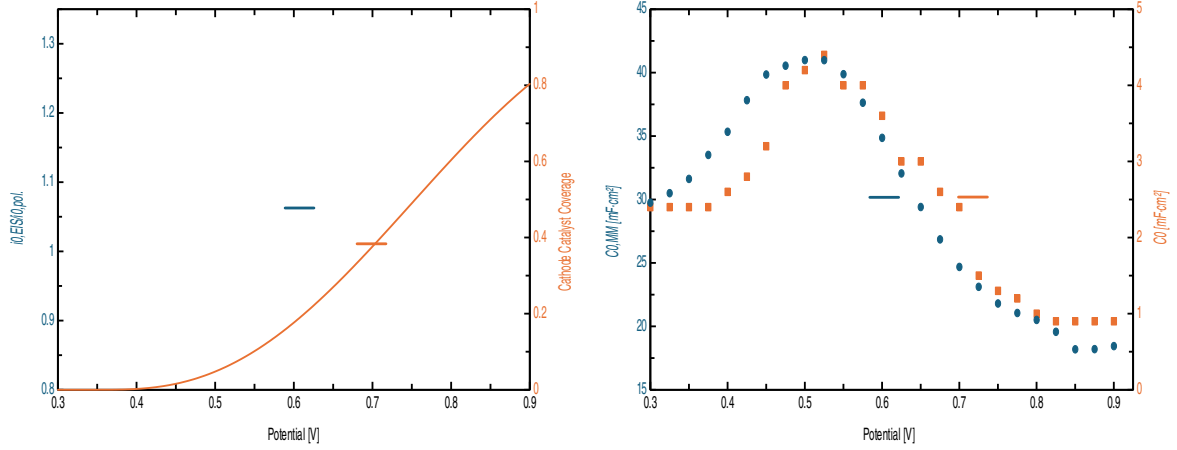


Figure 7 Comparison of the fitted ORR exchange current densities from the impedance spectra and polarization curve and the fraction PtO coverage of the cCL as functions of cell potential. (b) The interfacial capacitance extracted from experimental spectra using the measurement-model fitting $C_{0,MM}$ and fitted interfacial capacitance using the model C_0 as functions of cell potential.

4.2 Impedance Breakdown

The mathematical framework allows for the estimation of impedances associated with a layer or mechanism. The impedance of a region l , represented by Z_l , can be obtained from the potential difference at the boundaries of the region l and the total oscillating current density, which can be expressed as

$$Z_l = \frac{\tilde{\Phi}|_{l,1} - \tilde{\Phi}|_{l,2}}{\tilde{i}} \quad 16$$

The potentials stated in Equation between two points in the simulated cell domain (indicated by the subscript 1 and 2) can be either electronic or ionic potentials. The total impedance shown can be divided into contributions associated with specific layers or series of layers

$$Z = \sum_l Z_l = Z_a + Z_M + Z_c \quad 17$$

where the half-cell impedances associated with the anode and cathode sides of the cell are Z_a and Z_c , which include the FF, GDL, MPL, and CL of the respective side. The membrane impedance Z_M is the impedance of the region between the interfaces of the CLs and M.

The impedance associated with the catalyst interface $Z_{0,CL}$ can be expressed as the average CL overpotential divided by the integral of the volumetric current density.

$$Z_{0,CL} = \frac{1}{\int_{CL} \frac{\tilde{i}_{CL}}{\tilde{\eta}} d\mathbf{x}} \quad 18$$

A non-uniform current density in the CL was observed due to transport effects associated with reactant concentration, fluid pressures and temperature, which underlies the necessity for models that assess spatial distributions of reaction rates.

The half-cell impedance can further be decomposed into interfacial and non-interfacial effects. An estimate of non-interfacial impedance was obtained by subtracting the catalyst-layer interfacial impedance from the impedance of the respective side of the cell, which is shown for the cathode side as

$$Z_{N0,c} = Z_c - Z_{0,CL} \quad 19$$

An equivalent expression can be written for the anode side of the cell. This impedance is referred to $Z_{N0,a}$ or $Z_{N0,c}$ is the portion of the impedance that is not associated with the reaction surface, but with the ionomer in the CL and the porous-transport layers support the CLs. The high frequency x -intercept of the CL impedance represents the ohmic contribution of the ionomer, electron-conducting support, and contact resistance of the respective side of the cell. The resulting line shape is an asymmetric impedance indicative of transport effects attributed to the porous-electrode morphology of the catalyst, microporous, and gas-diffusion layer

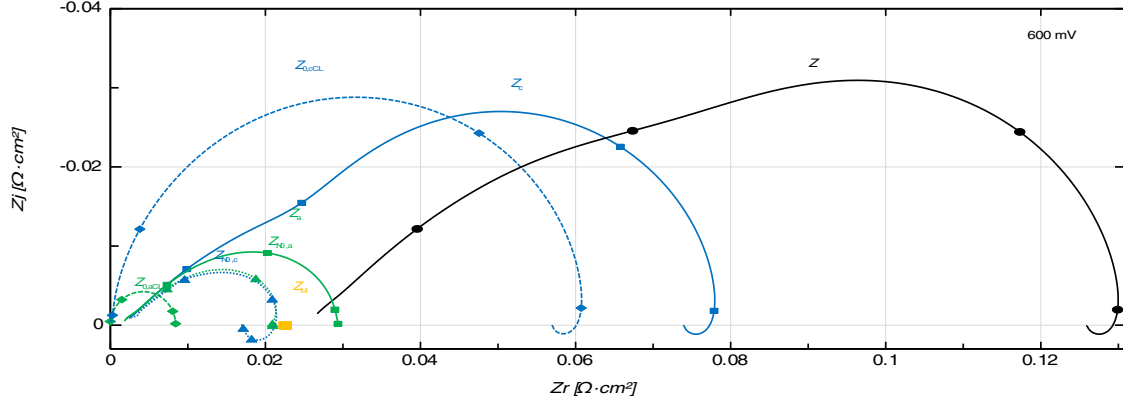


Figure 8 Nyquist plot of the simulated impedance of a PEMFC at an operating potential of 600 mV. The black solid curve is the total cell impedance Z with frequencies marked with $\circ$. The solid blue and orange curves with frequencies marked with $\square$ are the cathode-side and anode-side impedances, Z_c and Z_a , respectively. The membrane impedance Z_M is purely ohmic and indicated by the green $\square$. The interfacial impedances of the cathode $Z_{0,cCL}$ and anode $Z_{0,aCL}$ are indicated by the dotted lines with frequencies marked with $\diamond$. The non-interfacial impedances, $Z_{N0,c}$ and $Z_{N0,a}$, were obtained from the difference between the respective half-cell impedance and the interfacial impedance and are shown with dotted lines with frequencies marked with $\triangle$. The frequencies of 1 Hz, 10 Hz, 100 Hz, and 1 kHz are indicated by increasing opacity from low to high frequency.

A breakdown of the total impedance is shown in Figure 8 at a steady-state cell potential of 600 mV with the series inductor neglected. The total and half-cell impedance exhibited semi-circular low-frequency behavior (i.e. less than 100 Hz), but at high frequency exhibited a porous-electrode behavior with an approximate phase angle of 45°. The complex part of the membrane impedance was negligibly small yielding a near ohmic contribution to the total impedance, which is consistent with observations by Schneider *et al.*⁷ for well-hydrated membranes. The interfacial impedances were near semi-circular. The cCL interfacial impedance expressed a low-frequency inductive loop that was a result of the surface process model shown in Equation with non-zero surface parameters R_s and C_s . The non-interfacial impedances of the cathode and anode are similar in shape at high frequencies (i.e. greater than 100 Hz). But at low frequencies, an inductive loop in the cathode-side non-interfacial impedance was observed, which was attributed to hydration effects in the cCL ionomer. The characteristic frequency of this inductive feature was around 10 Hz, which can be distinguished spectrally from the interfacial inductive loop but became indistinguishable within the total and half-cell impedance.

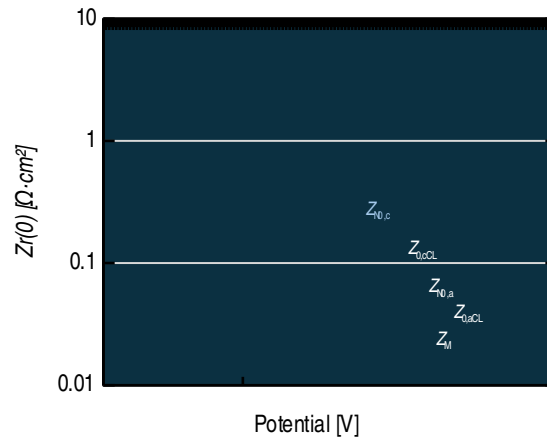


Figure 9 The limiting low frequency real impedances associated with the membrane, interfaces, and catalyst layers obtained from fitting the model to experimental impedance spectra as a function of cell potential.

The low-frequency limit of the real impedance was calculated at each steady-state potential, which was used to generate a breakdown of the contributions as defined by Equations through . The simulated impedances and breakdown were validated by comparing the low-frequency limit of the simulated spectra to the slope of the kinetic overpotentials as obtained from the steady-state model using the power-loss method as described by Gerhardt *et al.*⁷² The low-frequency cathode interfacial impedance was shown to be a reasonable approximation of the kinetic resistances extracted from the steady-state model, which is shown in Figure 10. Additionally, the magnitude of the cathode-side contribution was quantified by calculating fraction of the cathode-side impedance, where the fraction of cathode-side impedance was defined as

$$\frac{Z_c(0) - Z_c(\infty)}{(Z_c(0) - Z_c(\infty)) + (Z_a(0) - Z_a(\infty))} \quad 20$$

The fraction associated with the cathode kinetics from the steady-state model was estimated by

$$\frac{\frac{\partial \eta_{c,kin}}{\partial i}}{\frac{\partial \eta_{c,kin}}{\partial i} + \frac{\partial \eta_{a,kin}}{\partial i}} \quad 21$$

The cathode-side and fraction of cathode-side impedance is shown in Figure 10. Both were observed to be greatest at high cell potentials, which was indicative of ORR kinetic activation. As the cell potential decreased, the fraction of cathode-side resistance decreased, indicating optimal operating conditions for ORR kinetics, which was followed by an increase due to mass-transport effects.

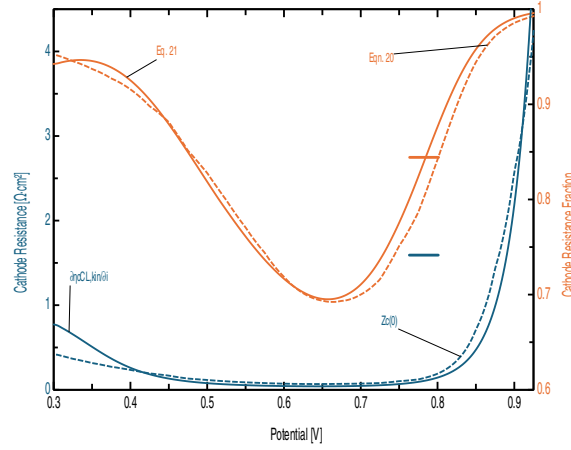


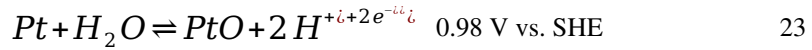
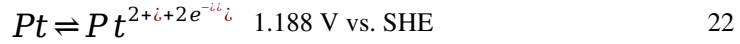
Figure 10 The slope of the cathodic overpotential (teal solid line) and the real low-frequency-limit of the cathode-side impedance (teal dashed line) as functions of the cell operating potential. The cathode resistance fraction, the fraction of the polarization and kinetic resistances of the cathode-side, is shown in orange calculated from the impedance model (dashed) using Equation and the steady-state model (solid) using Equation , which are primarily attributed to ORR kinetics.

The deviation between the curves was attributed to the approximated linearization of the transport equations. Regardless, the agreement between the two simulations suggests that the impedance breakdown can serve as an estimate of layer and mechanistic losses as interpreted from measured spectra.

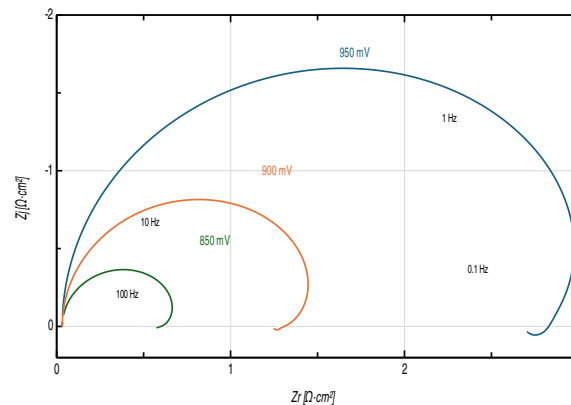
4.3 Mechanistic Models

4.3.1 Pt Dissolution

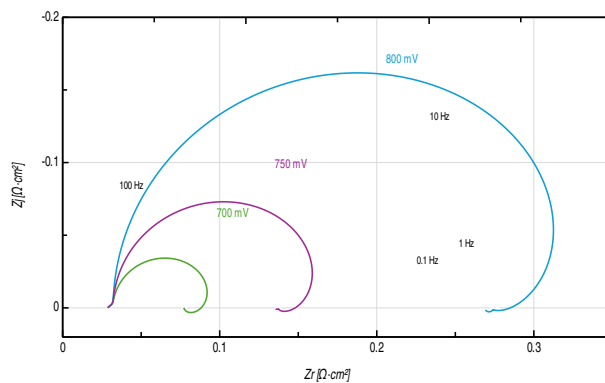
The mathematical approach was applied to the kinetic Pt-dissolution model proposed by Darling and Meyers⁶⁶, where the following reaction mechanism was assumed to occur on the cCL Pt catalyst



Simulated spectra using the Pt-dissolution model yielded low-frequency inductive features consistent with previous PtO kinetic models^{33,37}, which are shown in Figure 11.



a



b

Figure 11 Nyquist plots of simulated impedance for a PEMFC at operating steady-state cell potentials of (a) 950, 900, and 850 mV, and (b) 800, 750, and 700 mV using the mathematical method described in this work and applied to the PtO formation model as developed by Darling and Meyers⁶⁶. PtO formation can yield low-frequency inductive features.

The magnitude of the inductive feature was estimated by subtracting the low-frequency real impedance from the maximum real impedance as an estimate of the low-frequency resistor-inductor behavior, which was also performed on the experimentally obtained spectra. A comparison of the low-frequency inductance is shown in Figure 12, which suggests good agreement between simulation and experimental observation for cell potentials down to 700 mV. At potentials below 700 mV, the PtO model overpredicted the real impedance, which may be dominated by water transport in the ionomer as reported by previous models for low-frequency inductive features in PEMFC spectra.^{20,33,38}

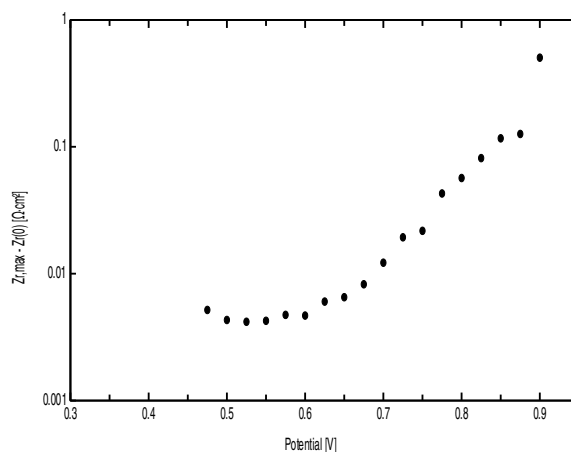


Figure 12 Magnitude of the low frequency-inductive feature, which is characterized by the difference between the maximum real impedance and the low-frequency real impedance. The line was obtained from the Pt-PtO impedance simulations. The data points were obtained from the measurement model fit of the experimental data.

Thus, the interpretation of low-frequency inductance may be a result of multiple mechanisms like the water transport in the ionomer and reactions involving adsorbed intermediates like PtO formation and hydrogen peroxide formation and contain information applicable to estimating degradation mechanisms and rates of the MEA.

Impedance of a Degraded Cathode Catalyst Layer

The model framework was used to simulate the effects of degradation with a cCL that assumed a Tafel-kinetic model for ORR. The influence of decreasing active catalyst surface area per unit volume and decreasing ionic conductivity of the ionomer within the cCL on the impedance response were simulated to estimate the effect of catalyst and ionomer degradation. The EIS response from the frequency-domain modeling approach are shown in Figure 13a. A low-frequency semi-circle was observed, which became smaller as the potential decreased. The high-frequency behavior observed is a skewed-right semi-circle, which is a function of the proton conductivity in the membrane. The high-frequency impedances superposed, which suggests that the high-frequency behavior is a

result of the same mechanism. The low-frequency impedance is shown to be a function of the applied steady-state potential.

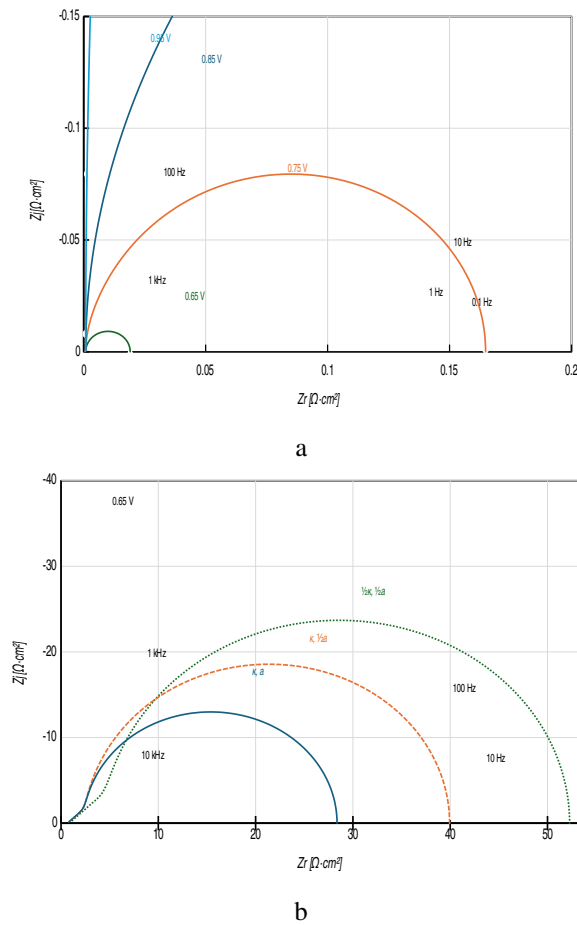


Figure 13 Simulated impedance response of a PEMFC cCL operating at 353.15 K, 50% relative humidity, and 1 bara pressure air. (a) Nyquist plot of simulated spectra with the applied potential as a parameter at steady-state potentials of 0.95, 0.85, 0.75, and 0.65 V. (b) Impedance spectra at 0.65 V influenced by a 50% decrease in ionomer conductivity and a 50% decrease in electrochemically active specific surface area indicated by $1/2\kappa$ and $1/2a$, respectively. The simulated impedances under nominal material parameters are indicated by κ and a .

Typical signs of degradation include loss of membrane conductivity due to membrane degradation and a decrease in catalyst-layer specific interfacial surface area due to catalyst particle coarsening and dissolution.⁷³⁻⁷⁹ Simulated results in Figure 13b illustrate how impedance spectra at beginning-of-life and end-of-life might differ by performing a parametric study where the ionomer conductivity and specific surface area were decreased by 50%. A decrease in catalyst surface area, which are labeled with $1/2a$, yield spectra with increased charge-transfer resistance indicating a decrease in kinetic activity. The high-frequency impedance remained unchanged. When the ionomer conductivity was decreased by 50%, indicated by $1/2\kappa$, the overall impedance increased as well. But an increase in the high-frequency impedance was observed, which suggested larger transport resistance in the cCL, which underlies the need for treating the coupled effects of degradation.

4.4 Equivalent-Circuit Model

Equivalent-circuit models have been developed to link experimental observations to physical mechanisms and exist as initial surrogate models for interpreting EIS spectra. Extraction of the low-frequency impedance is important for the impedance breakdown given a sufficiently accurate continuum model. In this work, simulated spectra exhibit kinetic and transport impedance signatures that occur in the 1 to 100 Hz range, which makes the isolation of specific impedance line shapes challenging. For numerical fitting in the current model, accurate estimates of the limiting low-frequency impedance were observed to be crucial for extracting kinetic parameters. The measurement model approach, where a finite sum of Voigt elements, can be used to fit experimental data and yield effective properties of the electrochemical cell exhibited good agreement between experimental polarization

curves and impedance spectra.^{58,69} The separation of impedance features occurring at similar characteristic frequencies is challenging even for DRT-based methods.¹⁸ The consistent observation of low-frequency inductive features in PEMFC impedance spectra is a barrier for DRT-based methods due to the integral form that prevents the assessment of overlapping inductive and capacitive features.

A simple equivalent-circuit model that was inspired by Havrilia and Negami⁸⁰, given as

$$Z = j\omega L + R_e + \frac{R_1}{\left(1 + (j\omega R_1 C_0)^{\alpha_1}\right)^{\beta_1}} + \frac{R_2}{1 + (j\omega R_2 C_2)^{\alpha_2}} \quad 25$$

yielded good agreement with the low-frequency extrapolations using fewer parameters for the purpose of expedient fitting to observed impedance spectra as a surrogate model for analytical methods using machine learning. For experimental datasets where high-frequency inductance is observed, a preceding inductor in series was included in Equation , which can be discarded when high-frequency inductance is not observed. The effective ohmic resistance is represented as R_e . The third term on the RHS in Equation represents the effective charge transfer resistance R_1 and interfacial capacitance C_0 , with the fitting parameter exponents α_1 and β_1 . The last term on the RHS represents low-frequency inductive features with R_2 is a negative resistance and C_2 is a negative capacitance, which yields inductive behavior. The equivalent circuit was fit to experimental data sets are shown in Figure 14.

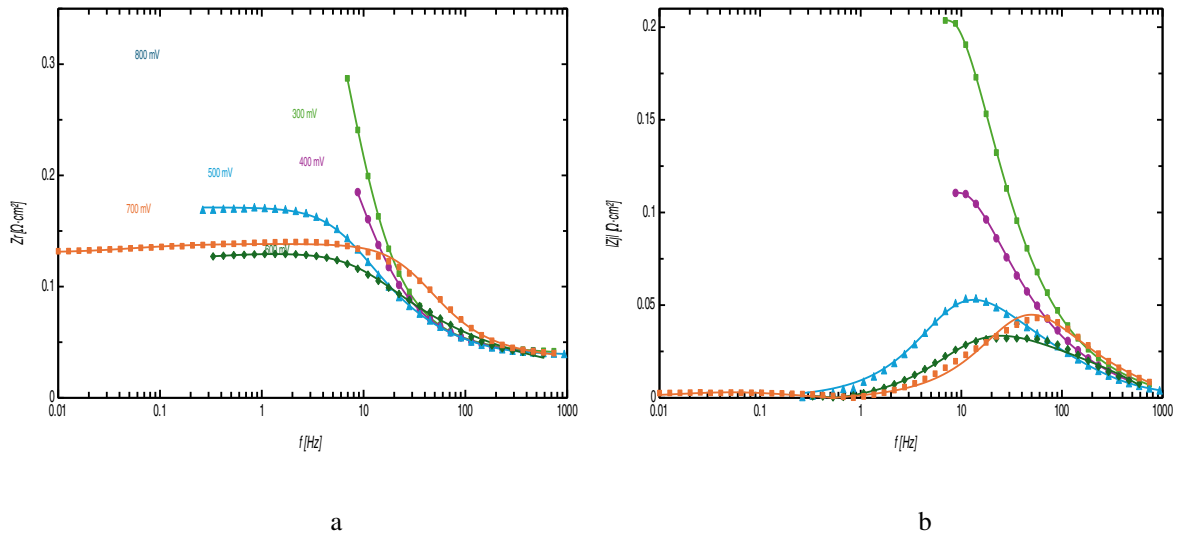


Figure 14 (a) Real and (b) imaginary impedances as functions of frequency of the experimental data with the lines generated from the fitting of the equivalent-circuit model given in Equation to the experimental spectra with the steady-state cell potential as a parameter.

The fitting was performed using a Levenberg-Marquardt nonlinear fitting algorithm with modulus weighting.

Low-frequency limiting values of the impedance using the measurement model approach and the Equation are shown in Figure 15, which show parity between the two extrapolation methods.

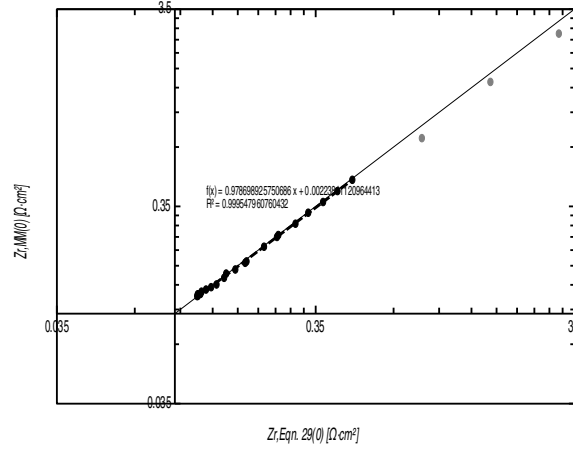


Figure 15 A parity plot that compares the impedance extrapolated to low-frequency for the Voigt-element model and the equivalent circuit model inspired by Havrilia-Negami relaxation. The agreement was best for the black data points which corresponded to cell potentials of 825 mV and lower.

Effective parameter estimation was best for operating cell potentials of 825 mV and lower due to the absence of low-frequency impedance features, which may require additional fitting parameters like in the measurement model approach. For more operationally relevant cell potentials, Equation was found to be sufficient.

4.5 Simulation of Other Transfer Functions

The isolation of the linear response of a PEMFC to perturbations in operational parameters other than current and potential has been performed to improve the understanding of the coupled physics within the cell.^{8,10,11-13} Simulation of a pressure-current density transfer function ζ

$$\zeta = \frac{\dot{i}}{\tilde{p}_R} \quad 26$$

was performed where the model boundary conditions were changed to enforce a sinusoidal perturbation in reactant-oxygen partial pressure with an amplitude of 2 kPa. With the same parameters used to generate the simulated impedance spectra shown in Figure 3, Figure 4, and Figure 5, the pressure-current density transfer function was simulated, which is shown in Figure 16.

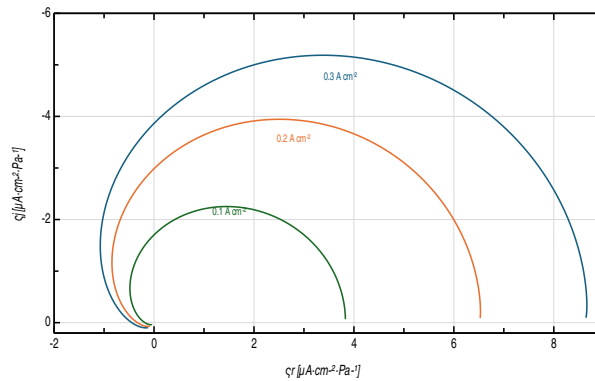


Figure 16 Reactant-pressure-current-density transfer function simulated using the impedance model, which are agreement with experimental observations in literature.^{11,32}

The spiraling pressure-current density transfer function generated using the present model yielded spectra that duplicated the spectra observed experimentally by Sorrentino *et al.*¹¹ and Kulikovsky³², which suggests adequate coupling of physical transport mechanisms presented in this work and allows for the simulation and interpretation of other transfer functions of a PEMFC. The modulation of parameters other than potential or current yield information on the coupled coefficients expressed in Equation , which are derived from the time-domain continuum model. Assuming that the linear response of the system is preserved experimentally, effective transport

properties associated with heat and mass transport can be isolated via a generalized frequency response analysis. Focusing on a specific modulating independent variable can enhance the observation of the associated resistance as described by Equation .

Conclusions

The mathematical framework that accounted for coupled physics and chemistry within proton-exchange-membrane fuel cells (PEMFC) yielded simulated polarization curves and impedance spectra that were consistent with experimental observations and allowed for the parallel extraction of ORR kinetic parameters from both steady-state polarization and impedance measurements. The analysis also showed that the limiting low-frequency impedance was primarily a function of the ORR kinetics regardless of low-frequency inductive features in the total impedance spectra. Extraction of electrochemical cell properties from impedance spectra can advance the use of impedance as an *in-situ* diagnostic tool for the real time monitoring of critical process parameters associated with cell health and performance for hydrogen-based energy conversion devices. An impedance breakdown was demonstrated that parsed layer-specific contributions to the total impedance that was confirmed to be consistent with steady-state polarization potential-loss analyses via a power-loss method. Ohmic, kinetic, and transport resistances were extracted from simulated spectra that were fit to experimentally measured spectra. Analysis of experimental spectra was also performed using an equivalent-circuit model inspired by Havrilia-Negami relaxation, which yielded estimates of the zero-frequency impedance for the estimation of the effective polarization resistance.

The model framework was extended to simulate other aspects that influence cell performance. A frequency-domain kinetic model of the impedance response associated with PtO films on the surface of cathode electrocatalysts was performed, which showed good agreement with experimental low-frequency inductive features for cell potentials down to 0.7 V or cell current densities up to 1 A·cm⁻². The frequency response to oscillations in reactant-oxygen partial pressure was simulated, which demonstrated agreement with experimental pressure-current transfer functions of PEMFCs in literature, and can be used for the analysis of physio-electrochemical transfer functions. Overall, the model and analysis forms a framework and methodology towards approaching these kinds of data and problems.

CRedit authorship contribution statement

Arthur Dizon - Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Validation, Visualization, Writing – original draft, Writing – review & editing. **Victoria M. Ehlinger** - Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Validation, Visualization, Writing – original draft, Writing – review & editing. **Rangachary Mukundan** - Conceptualization, Funding acquisition, Methodology, Project administration, Resources, Supervision, Writing – review & editing. **Adam Z. Weber** - Conceptualization, Funding acquisition, Methodology, Project administration, Resources, Supervision, Writing – review & editing.

Conflicts of interest

There are no conflicts to declare.

Acknowledgement

This work was supported by M2FCT Consortium under U.S. Department of Energy's Office of Critical Minerals and Energy Innovation (CMEI) under the Alternative Fuels and Feedstocks Office, formerly the Hydrogen and Fuel Cell Technologies Office, under Contract DE-AC02-05CH1123.

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