Electrochemical Impedance Spectroscopy Study of Membrane Fouling Characterization at a
Conductive Sub-Stoichiometric TiO₂ Reactive Electrochemical Membrane: Transmission Line

Model Development

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Abstract

This work presents a non-invasive and non-destructive electrochemical impedance spectroscopy (EIS) method for studying membrane fouling at a sub-stoichiometric TiO_2 reactive electrochemical membrane (REM). An asymmetric, ceramic, ultrafiltration REM is studied through EIS simulations, that are based on a mathematical transmission line model (TLM). The TLM is developed to interpret EIS data and is shown to be sensitive to fouling at multiple interfaces of the REM (outer surface, active and support layers). Mathematical interpretation of penetration depth of the alternating voltage signal allows a determination of the characteristic frequencies associated with different layers of the membrane. The simulation results of membrane fouling mechanisms, such as monolayer adsorption and pore constriction at either active or support layer, and intermediate pore blockage at the outer surface produce distinguishable EIS spectra. Simulation results suggest that interpreting EIS spectra by the TLM is a useful technique for spatially characterizing membrane fouling and determining prevalent fouling mechanisms at a conductive membrane surface.

Nomenclature

EIS	Electrochemical Impedance Spectroscopy
MWCO	Molecular Weight Cutoff
OCP	Open Circuit Potential
REM	Reactive Electrochemical Membrane
SEM	Scanning Electron Microscopy
TLM	Transmission Line Model
UF	Ultrafiltration

List of Symbols

Symbol	Name	SI Unit
a_s	Stokes radius of the ion	m
C	capacitor	F
C_{ion}	concentration inside the pore	M
C^*	concentration in the bulk solution	M
C_{dl}	double layer capacitance	Farad
$\bar{C}_{dl}$	surface normalized double layer capacitance (60)	$\mu\text{F}\cdot\text{cm}^{-2}$
d	thickness of the oriented solvent layer (2.8×10^{-10})	m
D	diffusion coefficient	$\text{m}^2\cdot\text{s}^{-1}$
e	electronic charge (1.602118×10^{-19})	C
E	total potential	V
E_c	constant potential	V
f	alternating voltage frequency	Hz
F	Faraday constant (96485)	$\text{C}\cdot\text{mol}^{-1}$
i	current	A
j	imaginary unit	dimensionless
k	Boltzmann constant (1.38066×10^{-23})	$\text{J}\cdot\text{K}^{-1}$
$\bar{L}$	active layer length	dimensionless
N_A	Avogadro constant (6.022×10^{23})	mol^{-1}
R	universal gas constant (8.314)	$\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
	resistance	ohm
r	effective pore radius	m
t	time	s
T	absolute temperature	K
Y_0	capacitance constant	$\text{F}\cdot\text{s}^{\alpha-1}$
z	valence of the ion	dimensionless
Z	impedance	ohm

List of Greek Symbols

Symbol	Name	SI Unit
ε_0	permittivity of free space (8.85419×10^{-12})	$J^{-1} \cdot C^2 \cdot m^{-1}$
ε_b	bulk dielectric constant of water (80)	dimensionless
ε_p	pore dielectric constant	dimensionless
ε	dielectric constant of an oriented water layer adsorbed at pore wall (6)	dimensionless
β	steric partition coefficient	dimensionless
ρ	specific solution resistance	ohm·cm
χ	ionic/electronic resistance	ohm
$\Delta\psi_0$	Donnan potential	V
ΔE	amplitude of the potential perturbation	V
ΔW	Born solvation energy	J
τ	ratio of ionic solute radius to pore radius	dimensionless
φ	phase angle	°
ω	angular frequency ($=2\pi f$)	s^{-1}
α	exponential factor	dimensionless
λ	penetration depth	m
κ^{-1}	Debye Length	m

1. Introduction

Membrane filtration utilizing microfiltration or ultrafiltration membranes is a well-recognized technology that is used in a variety of industries (e.g. food processing [1–3], biotechnologies [4–6], wastewater treatment [7–9] and pharmaceutical industries [10–12]). Membrane technologies are able to provide high quality product water, have a small footprint, and require relatively easy maintenance [13]. However, membrane fouling is a common problem, that leads to increased power consumption and reduced membrane life, and causes serious operational and economical challenges for industries utilizing membrane separations (e.g., water and wastewater treatment plants, food and beverage industry, pharmaceutical industry) [14–18]. Early detection of membrane fouling and efficient and sustainable membrane regeneration strategies are necessary in order to optimize operational design, improve the filtration performance, and extend membrane life.

In pressure driven membrane processes, permeate flux and transmembrane pressure (TMP) are the most straightforward indicators of membrane fouling. Under constant TMP operation, the permeate flux decreases due to membrane fouling. Conversely, TMP increases in order to maintain a constant permeate throughput. Membrane fouling can be directly observed using *ex situ* destructive visual methods and *in situ* permeate flux or TMP measurements, but the investigation of the mechanisms associated with membrane fouling is still challenging.

Current methods for studying the mechanisms of membrane fouling have well known limitations. Studying membrane fouling mechanisms by fitting filtration law models to the TMP or permeate flux profile with time during the filtration process is commonly used but is limited to bench-scale testing and cannot be used to identify multiple simultaneous fouling mechanisms [19]. Scanning electron microscopy (SEM) is able to provide visual evidence of fouling, but

preparation of an SEM specimen requires destruction of the membrane [20]. Li et al [21,22] used the ultrasonic time-domain reflectometry method to study membrane fouling and successfully detected cake layer formation, however the ultrasonic wave is unable to penetrate the porous membrane matrix and thus cannot detect fouling mechanisms associated with internal membrane fouling (e.g., pore constriction or plugging mechanisms).

The development and application of a non-invasive and non-destructive characterization technique to study membrane fouling mechanisms would enable the effectiveness of fouling remediation and cleaning strategies, which is possible by using electrochemical impedance spectroscopy (EIS). Potentiostatic EIS is a frequency domain method where a small-amplitude alternating potential is superimposed onto a constant applied potential between the working and reference electrodes. Its high sensitivity towards interfacial processes and surface geometry makes EIS an ideal tool to evaluate membrane fouling and regeneration [23]. EIS measurements have been made across non-conductive membranes, mostly polymeric reverse osmosis membranes, in order to study membrane fouling. Coster et al. [24,25] employed EIS to characterize the skin layer conductances and capacitances of different layers on an ultrafiltration polysulphone membrane. Chilcott et al. [26] proposed an EIS mathematical model applied to membranes to investigate the conductivity and dielectric permittivity dispersion of the membrane before and after fouling, and they found that fouling along the surface of the membrane was more easily detectable than inside the pore. Gaedt et al [27] adopted the method of Chilcott et al. [26] to a polymeric ultrafiltration membrane that was made conductive by sputtering platinum particles to the membrane surface. The Pt-coated membrane was modeled by the Maxwell–Wagner equation, which characterizes the capacitance and conductance as a function of the sinusoidal voltage wave [27]. However, the limitation of this work is that the Pt coating on the

membrane is not able to represent the true morphology of the membrane, and Pt particles may occlude some of the membrane pores and thus change the membrane morphology [20]. The four-electrode EIS measurement technique has also been applied to membrane fouling studies on reverse osmosis [28], forward osmosis [29] and nanofiltration [30] flat sheet membranes without sputtering a conductive coating. It was found that the layers of an asymmetric membrane were spatially resolved by using EIS, and the measured interfacial dielectric constants were sensitive to membrane fouling.

Recently, a reactive electrochemical membrane (REM), made from a substoichiometric TiO_2 tubular membrane consisting primarily of the Ti_4O_7 Magnéli phase was developed and shown to function as both a membrane and a reactive substrate that could oxidize organic compounds by a combination of direct electron transfer and reactions with hydroxyl radicals ($\text{OH}^\bullet$) produced *via* water oxidation [31–33]. Since REMs are conductive, EIS measurements can be directly implemented without changing the membrane morphology, and therefore can act as a powerful characterization tool for accessing membrane fouling and providing informative suggestions to optimize electrochemical regeneration protocols.

In this study, a transmission line model (TLM) was developed that simulates EIS spectra collected on an asymmetric Magnéli phase, ultrafiltration (UF) REM. The UF REM consists of a thin active filtration layer overlaying a thick porous support layer. The model is used to simulate EIS spectra for the REM as a function of membrane fouling. Common fouling mechanisms are simulated (i.e., pore constriction, monolayer adsorption, and intermediate pore blocking), and changes in the EIS spectra are shown to be unique, indicating the diagnostic power of the technique. Experimental verification of this model is investigated in a separate study [34].

2. Mathematical Model

2.1 Theory. EIS is a powerful characterization technique that can provide detailed information about the electrode-electrolyte interface of an electrochemical system [35]. Potentiostatic EIS is the most common variant of this technique, where a small amplitude sinusoidal potential signal (e) at a given frequency is superimposed onto a constant potential (E_c). The relation for the total potential (E) of the interface under investigation is shown in Equation 1.

$$E = E_c + e = E_c + \Delta E \cdot \sin(\omega t) \quad (1)$$

where ΔE (V) is the amplitude of the potential perturbation, ω (s^{-1}) is the angular frequency ($2\pi f$), and f (Hz) is the alternating voltage frequency. EIS data is usually measured against the open circuit potential (OCP), and therefore for convenience E_c is set to zero.

$$E = \Delta E \cdot \sin(\omega t) \quad (2)$$

The alternating current (ac) response (i) of the electrochemical system is usually out of phase with the potential signal due to the existence of non-faradaic processes (e.g., double layer capacitance) and reaction of adsorbed species, which act as capacitors and inductors, respectively [35]. The ac response is given by Equation 3, assuming that E_c is at the open circuit potential.

$$i = \Delta I \cdot \sin(\omega t + \varphi) \quad (3)$$

where φ represents the phase angle shift between i and E , and ΔI is the amplitude of i .

In the absence of mass transfer limitations and a significant concentration of adsorbed reactive species, the impedance of an electrode-electrolyte interface can be modeled by a resistor (R) and capacitor (C) in parallel, which represent the simultaneous processes of charge transfer and double layer charging, respectively. The total impedance (Z_{total}) of the resistor and capacitor in parallel is given by Equation 4:

$$Z_{total} = \left(\frac{1}{Z_{resistor}} + \frac{1}{Z_{capacitor}} \right)^{-1} = \frac{R}{1 + j\omega RC} \quad (4)$$

where $Z_{resistor}$ and $Z_{capacitor}$ are the impedances of the resistor and capacitor, respectively, and j is the imaginary unit of the complex number. The product of RC represents the characteristic time constant for the system. Impedance is represented as a complex number, where the real component (Z_{real}) is the impedance due to resistance and the imaginary component (Z_{imag}) is the impedance due to capacitance (and inductance if present). Therefore, φ can be calculated from Equation 5:

$$\varphi = \tan^{-1} \frac{Z_{imag}}{Z_{real}} \quad (5)$$

During EIS measurements, Z_{total} is measured as a function of f and the resulting data is often represented on a Nyquist plot ($-Z_{imag}$ versus Z_{real}) or Bode phase plot (φ versus f). When applying EIS to a porous conductive membrane in the presence of a redox active couple in solution, the impedance comes from several simultaneous processes [36]: (1) resistance to electron transport in the conductive membrane, (2) charge transfer resistance between the redox couple and the conductive membrane surface, and (3) the charging of capacitive elements in the high surface area porous structure. Each process has a different RC time constant, which can be determined by interpreting EIS data collected at different values of f [37].

Analyzing EIS data by appropriate mathematical models allows for decoupling of the resistance and capacitance at distinct physical locations of the REM. Therefore, in principle EIS measurements should provide spatial characterization data of electrode fouling. For example, the adsorption of foulants at different locations of the REM (e.g., outer surface versus inner pore) will result in an increase in the resistance to charge transfer (R_{ct}) between the redox couple and electrode, and a decrease of the double layer capacitance (C_{dl}) due to the decreased active surface area of the REM. If the electrode surface is homogeneous and foulants are electrochemically

inert, then fouling of a portion of the surface area will not change the RC time constant due to the inverse relationship that exists between R and C .

In this study, the REM of interest is an asymmetric, ceramic, UF membrane, with a thin active layer overlying a thick, porous support layer, as shown in Figure 1. The morphology of asymmetric membranes varies with respect to the thickness of the layers. The active layer, where filtration takes place, generates significant resistance to flow due to small pores and therefore the thickness is usually $< 100\ \mu\text{m}$. The support layer provides mechanical support to the thin active layer and is usually of mm-scale thickness [19].

Mathematical models for EIS data interpretation must provide a fit to experimental data and represent the physical and electrochemical processes taking place in the electrochemical system under investigation. Park and Macdonald first adopted a TLM to study the dynamic formation of a porous magnetite film on carbon steel during a corrosion process [38]. In their model, a collection of identical cylindrical pores of uniform cross section and finite length is used to represent the overall porous structure, and the total impedance of the system is comprised of ionic, electronic, and interfacial electrochemical impedances. Bisquert et al. applied the TLM to study the electrochemical process on a nanoporous TiO_2 photoelectrode, whose reference point is based on the assumptions that the pore geometry is cylindrical and ion transport is only driven by the alternating voltage [36,39].

Figure 1 Modified transmission line model for a reactive electrochemical membrane with an asymmetric structure.

Applying an EIS model to the REM requires transformation of the three-dimensional porous geometry into one dimension by assuming the REM contains a collection of cylindrical homogeneous pores of uniform radius. In our model we are characterizing the impedance of fluid transport pores, and therefore we define the pore radius as an effective radius (r), which can be determined by interpreting Hg porosimetry or measured flux data as a function of pressure using a Poiseuille flow model. Studies have also developed correlations between membrane pore size and molecular weight cutoff (MWCO) capacities for membranes, which were based on Poiseuille flow models [40–42]. Any of these methods are appropriate for obtaining r for impedance modeling.

As shown in Figure 1, the porous interface is then divided into three distinct regions (outer surface, active layer, and support layer) and the resistances of the solid phase (electronic) and solution phase (ionic) are placed in the direction of current flow, with the interfacial impedances distributed in between. The impedance at each of the three interfaces includes a R_{ct} and constant phase element (CPE) connected in parallel. CPEs are used instead of ideal capacitors in order to

account for the inhomogeneity of the double layers. Double layer inhomogeneity is attributed to ion adsorption, surface roughness of the membrane, and coupling of the solution resistance with the double-layer capacitance; all of which cause a capacitance dispersion at the interfacial region [35]. The impedance of a CPE (Z_{CPE}) can be expressed as:

$$Z_{CPE} = \frac{1}{(j\omega)^\alpha Y_0} \quad (6)$$

where Y_0 is a constant ($F \cdot s^{\alpha-1}$); α is an exponential factor that describes the angle of rotation of a purely capacitive line on the complex plane plots (dimensionless). The non-ideal behavior of the CPE depends on the α value. The CPE represents a pure capacitor when $\alpha = 1$ and a pure resistor when $\alpha = 0$. A rough electrode surface is implied when $0.5 < \alpha < 1.0$ [43].

The model for the total impedance is formulated by considering the potential and current distributions in both electronic and ionic phases, which are obtained by integrating the electronic and ionic currents along the pore depth with suitable boundary conditions. Prior work has shown that the application of a TLM to EIS data collected on a symmetric substoichiometric TiO_2 REM could accurately match experimental data and was used to extract the electroactive surface area of the REM [31]. As for the asymmetric UF REM considered in this study, the morphology has been discussed above and is shown in Figure 1. The pore size of the active layer is much smaller than that of the support layer and the overall active layer has two interfaces experiencing electrochemical reaction and charging processes, which are the outer surface and active layer pore walls, as illustrated in Figure 1. Meanwhile the support layer has only one interface, which exists at the pore walls. Due to the existence of another porous layer (support layer) with a different pore size distribution, previously developed TLMs need to be modified accordingly. The support layer can be assumed as a planar electrode as it possesses more void space compared to the active layer, and this assumption is justified through calculation of the penetration depth

(λ) of the ac signal (see *Section 2.2*). The modification of the TLM was achieved by adding a Randles circuit in series to account for the support layer. The adoption of a serial circuit structure is based on the assumption that the boundary between these two layers can be considered an equipotential plane [44]. The modified TLM is illustrated in Figure 1, with a rail-like transmission line circuit to simulate the active layer, followed by a Randles circuit to simulate the support layer.

Based on the description above, the mathematical formulation of the total impedance of the membrane (Z_m) is expressed as:

$$Z_m = R_s + Z_{al} + Z_{sup} \quad (7)$$

where Z_{al} and Z_{sup} are the impedances of the active layer and support layer, respectively, and R_s is the bulk solution resistance. The following TLM is used for Z_{al} [39]:

$$\begin{aligned} Z_{al} = & \frac{1}{\chi_1 + \chi_2} \left[\lambda_{al}(\chi_1 + \chi_2)S_\lambda + (Z_{out} + Z_B)C_\lambda + \frac{1}{Z_{active}(\chi_1 + \chi_2)}Z_{out}Z_BS_\lambda \right]^{-1} \\ & \times \left\{ \bar{L}\lambda_{al}\chi_1\chi_2(\chi_1 + \chi_2)S_\lambda + \chi_1[\lambda_{al}\chi_1S_\lambda + \bar{L}\chi_2C_\lambda]Z_{out} \right. \\ & + \chi_2[\lambda_{al}\chi_2S_\lambda + \bar{L}\chi_1C_\lambda]Z_B + \frac{1}{\chi_1 + \chi_2} \\ & \left. \times \left[2\chi_1\chi_2 + (\chi_1^2 + \chi_2^2)C_\lambda + \frac{\bar{L}}{\lambda_{al}}\chi_1\chi_2S_\lambda \right]Z_{out}Z_B \right\} \end{aligned} \quad (8)$$

where $C_\lambda = \cosh(\bar{L}/\lambda_{al})$; $S_\lambda = \sinh(\bar{L}/\lambda_{al})$; λ_{al} ; χ_l (ohm) is the ionic resistance; χ_2 (ohm) is the electronic resistance; Z_B (ohm) is the boundary impedance, which in this case represents the electronic plane connecting the active and support layers and is set to a low value (e.g., 1×10^{-7} ohm) in the simulation due to sufficient electrical contact between the two layers; $\bar{L}$ is the dimensionless thickness of the electrode active layer; and Z_{out} (ohm) and Z_{active} (ohm) represent the interfacial impedances at the outer surface and active layer, respectively. Each interfacial

impedance contains a time constant characterizing the interfacial response to a variable frequency ΔE signal, as shown in Equations 9 and 10.

$$Z_{out} = \frac{R_{ct,out}}{1 + (j\omega)^\alpha Y_{0,out} R_{ct,out}} \quad (9)$$

$$Z_{active} = \frac{R_{ct,active}}{1 + (j\omega)^\alpha Y_{0,active} R_{ct,active}} \quad (10)$$

The expression for Z_{sup} is given by a Randles circuit model, as follows:

$$Z_{sup} = \frac{R_{ct,sup}}{1 + (j\omega)^\alpha Y_{0,sup} R_{ct,sup}} \quad (11)$$

where $R_{ct,m}$ (ohm) is the charge transfer resistance at interface m ($m = out, active, \text{ or } sup$).

As shown in Equations 9 to 11, there is a unique time constant $(Y_0 R_{ct})^{\frac{1}{\alpha}}$ for each of the three representative interfaces (outer surface, active layer, and support layer). By conducting the EIS measurements over a range of frequencies, each of these time constants is assessed and the specific location of membrane fouling can be characterized. More specifically, fouling is characterized by evaluating the measured electro-active surface area of the REM at each interface, which is determined from the average double layer capacitance ($C_{dl,m}$) of each interface. Therefore the change in the average $C_{dl,m}$ can be used as a measure of membrane fouling. The average $C_{dl,m}$ at a specific interface is determined by the following equation [45]:

$$C_{dl,m} = \left(\frac{Y_{0,m}}{[R_s^{-1} + R_{ct,m}^{-1}]^{1-\alpha}} \right)^{1/\alpha} \quad (12)$$

A surface area normalized $\bar{C}_{dl}$ value of $60 \mu\text{F}\cdot\text{cm}^{-2}$ is assumed to be representative for a metal oxide electrode [46], and $C_{dl,m}$ is divided by this value to calculate the electro-active surface area ($A_{electro}$) of the REM. Although this is a well-accepted value for $\bar{C}_{dl}$, some variation

may occur since the original study calculated this value for a dielectric and not an electrolyte-electrode interface [46].

In order to avoid the complications of electrode polarization effects and drifting of the OCP, an active redox couple is used during EIS measurements, and a small ΔE is superimposed on the OCP of the redox couple. In order to avoid mass transport effects on the EIS measurements, spectra should be collected during convective flow of the solution through the REM pores. To determine if concentration gradients will develop in the REM pores, an analysis of reactive mass transport of the redox species under dc conditions is necessary [47]. A detailed analysis of the redox couple concentration profile and potential distribution with depth into the REM is provided in the Supplementary Information (SI). Results indicate that a concentration gradient of the active redox couple does not develop when ΔE is restricted to small values (≤ 10 mV). The potential decay with depth into the pore is ubiquitous under various operational conditions due to the existence of the solution resistance, but not to the extent that affects the EIS measurement.

2.2 Mathematical Interpretation of Penetration Depth (λ). The prior analysis indicates that a potential drop will occur with depth into the REM pores, which is caused by the solution resistance within the pore and hindered access of ions to the surface [23]. This potential drop affects the λ of the ΔE signal, which is proportional to the inverse of ω . Mathematically the relationship between λ and ω is given by Equation 13 [48].

$$\lambda = \sqrt{\frac{Z}{R}} = \sqrt{\frac{\pi r^2}{2\pi r \rho \omega \bar{C}_{dl}}} = \sqrt{\frac{r}{2\rho \bar{C}_{dl} \omega}} \quad (13)$$

In the calculation, $\rho = 0.08 \, \Omega \cdot \text{m}$ was used to represent a 100 mM ionic strength solution for a symmetric electrolyte. The REM membrane used for measurements is an asymmetric UF membrane with an active layer thickness of $\sim 60.0 \, \mu\text{m}$ and support layer thickness of 2.19 mm.

The effective pore radii of these two layers, determined by MWCO studies and Hg porosimetry, are 5.0 nm in the active layer and 1.5 μm in the support layer [34]. These values will be used in Equation 13 to calculate λ . Values for λ were calculated at 4 different characteristic frequencies and the results are shown in Table 1.

Table 1 Penetration depth of ΔE signal at an asymmetric membrane

Characteristic Frequencies (Hz)	λ (μm)
10,000 (r = 5.0 nm)	0.910
1000 (r = 5.0 nm)	2.88
2 (r = 5.0 nm)	64.4
2 (r = 1.5 μm)	1120
0.01 (r = 1.5 μm)	15800

As shown in the Table 1, the ΔE signal in the high frequency range (10,000 Hz to 1000 Hz) is able to penetrate to a depth of 2.88 μm , which accounts for the whole outer surface region. The 60 μm thick active layer is fully penetrated at a frequency of 2 Hz. The ΔE signal in the low frequency range (2 Hz to 0.01 Hz) is able to reach a theoretical depth of 15.8 mm, which is much greater than the thickness of the support layer (2.19 mm). Therefore, at sufficiently low frequencies (0.01 Hz), the electrode surface at the support layer appears to be quasi-planar [49], and the assumption of using a Randles circuit to represent the support layer is justified.

2.3 Modeling Approach. TLMs have been extensively used in studying corrosion of porous structures [50–52] and electrochemical processes in batteries [53–55]. However, this study is the first to utilize EIS interpreted by a TLM to study membrane fouling at a novel asymmetric REM.

A main advantage of the TLM developed in our work, is that it can accurately detect changes in the impedances at the three physical interfaces (outer membrane surface, active and support layers), and therefore is capable of detecting the dominant fouling mechanism (e.g., adsorption at outer, active and support layers, and pore blockage at the outer membrane surface).

In order to illustrate the diagnostic power of the TLM for membrane fouling, EIS simulations were performed on the fouling mechanisms shown in Figure 2. By changing the R_{ct} and Y_0 at one specific interface and holding all other parameters constant at the other two interfaces, the EIS simulations can represent different fouling modes. The R_{ct} and Y_0 are changed by an inverse factor, which results in a constant value for $(Y_0 R_{ct})^{\frac{1}{\alpha}}$, which assumes a homogenous REM surface. The impedance is calculated as a function of frequency, and both Nyquist and Bode phase plots are presented. In the Bode phase plot, φ is presented on a logarithmic scale of frequency to reveal the important behavior seen over a range of frequencies [44].

Figure 2 Schematic diagrams of various fouling mechanisms, (a) monolayer adsorption and (b) pore constriction at the active layer, (c) monolayer adsorption at the support layer, (d) outer surface fouling and (e) intermediate pore blockage.

3. Results and Discussion

3.1 Application of the TLM to Membrane Fouling. EIS Simulations were conducted to represent (1) fouling at either the active or support layers, (2) fouling of the outer membrane surface, and (3) intermediate pore blockage. Simulation parameter values for each of these fouling modes along with that of a clean membrane (background) are summarized in Table 2. The background EIS spectra were obtained from experimental data, and values for α were set to 1.0 for simplicity, although values between 0.8-1.0 are often observed experimentally [34].

Model simulations were conducted over a frequency range of 10 mHz to 10 kHz, where the high frequency range is defined between 1000 Hz and 10 kHz ($\lambda = 0.910$ to $2.88 \mu\text{m}$), mid frequency range between 2 and 1000 Hz ($\lambda = 64.4 \mu\text{m}$), and low frequency range between 10 mHz and 2 Hz ($\lambda > 64.4 \mu\text{m}$). Figure 3 shows a simulated EIS spectrum, where data from each distinct membrane layer is delineated. The outer REM surface is characterized at frequencies between 1000 and 10000 Hz ($\lambda < 3 \mu\text{m}$), which is shown in red. The active layer is characterized at frequencies between 2 and 1000 Hz ($\lambda \sim 3$ to $60 \mu\text{m}$), which is shown in blue. The support layer is characterized at frequencies $< 2\text{Hz}$ ($\lambda > 60 \mu\text{m}$), which is shown in green.

Values of $R_{ct,m}$ and $Y_{0,m}$ were varied while maintaining a constant RC value, and other parameters were held constant: $\bar{L} \sim 1.0$, $\chi_1 \sim 10.0 \text{ ohm}$, $\chi_2 \sim 0.5 \text{ ohm}$, $R_s \sim 0.5 \text{ ohm}$, $\alpha \sim 1.0$, and $Z_B \sim 1 \times 10^{-7} \text{ ohm}$. In the simulated EIS spectrum, three features are taken into consideration during membrane fouling: (1) the increase of Z_{real} over the mid frequency range (active layer), (2) the change in the semi-circle over the low frequency range (support layer), and (3) the change of the ϕ , which is defined by Equation 5.

Figure 3 Illustration of penetration depth on outer surface (red, square), active (blue, circle) and support (green, triangle) layers in a simulated EIS (a) overall and (b) zoomed-in Nyquist EIS spectra, and (c) Bode phase plot of a clean REM. Solid triangles represent the characteristic frequencies of 10 mHz, 2 Hz, and 1 kHz. (Solid line represents piece-wise linear interpolation and is included to guide the readers eye.)

Table 2 Model parameters for different modes of fouling simulation (Unit: R (Ohm), Y (F·s^{α-1}), C_{dl} (Farad), A (cm²))

Parameter		Background	Outer Surface Fouling			Active Layer Fouling		Support Layer Fouling		Intermediate Pore Blockage
Fouling Factor		0x	5x	10x	5x	10x	5x	10x		
Ionic Resistance	χ_i	1.00×10^1	1.00×10^1	1.00×10^1	1.00×10^1	1.00×10^1	1.00×10^1	1.00×10^1	1.00×10^1	5.00×10^2
Outer Surface	$R_{ct,out}$	1.00×10^1	5.00×10^1	1.00×10^2	1.00×10^1	1.00×10^1	1.00×10^1	1.00×10^1	1.00×10^1	1.00×10^3
	$Y_{0,out}$	1.00×10^{-2}	2.00×10^{-3}	1.00×10^{-3}	1.00×10^{-2}	1.00×10^{-2}	1.00×10^{-2}	1.00×10^{-2}	1.00×10^{-2}	1.00×10^{-4}
Active Layer	$R_{ct,active}$	1.00×10^1	1.00×10^1	1.00×10^1	5.00×10^1	1.00×10^2	1.00×10^1	1.00×10^1	1.00×10^1	1.00×10^2
	$Y_{0,active}$	2.00×10^{-2}	2.00×10^{-2}	2.00×10^{-2}	4.00×10^{-3}	2.00×10^{-3}	2.00×10^{-2}	2.00×10^{-2}	2.00×10^{-2}	2.00×10^{-3}
Support Layer	$R_{ct,sup}$	4.00×10^1	4.00×10^1	4.00×10^1	4.00×10^1	4.00×10^1	2.00×10^2	4.00×10^2	4.00×10^2	4.00×10^2
	$Y_{0,sup}$	5.00×10^{-1}	5.00×10^{-1}	5.00×10^{-1}	5.00×10^{-1}	5.00×10^{-1}	1.00×10^{-1}	5.00×10^{-2}	5.00×10^{-2}	5.00×10^{-2}
Location		Background	Outer Surface Fouling			Active Layer Fouling		Support Layer Fouling		Intermediate Pore Blockage
Outer Surface	$C_{dl,out}$	1.00×10^{-2}	2.00×10^{-3}	1.00×10^{-3}	1.00×10^{-2}	1.00×10^{-2}	1.00×10^{-2}	1.00×10^{-2}	1.00×10^{-2}	1.00×10^{-4}
	A_{out}	1.67×10^2	3.34×10^1	1.67×10^1	1.67×10^2	1.67×10^2	1.67×10^2	1.67×10^2	1.67×10^2	1.67×10^0
Active Layer	$C_{dl,active}$	2.00×10^{-2}	2.00×10^{-2}	2.00×10^{-2}	4.00×10^{-3}	2.00×10^{-3}	2.00×10^{-2}	2.00×10^{-2}	2.00×10^{-2}	2.00×10^{-3}
	A_{active}	3.33×10^2	3.33×10^2	3.33×10^2	6.66×10^1	3.33×10^1	3.33×10^2	3.33×10^2	3.33×10^2	3.33×10^1
Support Layer	$C_{dl,sup}$	5.00×10^{-1}	5.00×10^{-1}	5.00×10^{-1}	5.00×10^{-1}	5.00×10^{-1}	1.00×10^{-1}	5.00×10^{-2}	5.00×10^{-2}	5.00×10^{-2}
	A_{sup}	8.33×10^3	8.33×10^3	8.33×10^3	8.33×10^3	8.33×10^3	1.67×10^2	8.33×10^2	8.33×10^2	8.33×10^2

3.2 Monolayer Adsorption and Pore Constriction. Membrane fouling mechanisms at the active layer consist of monolayer adsorption and pore constriction. In monolayer adsorption it is assumed that foulants only adsorb to the pore walls and do not accumulate as multi-layers (Figure 2a). Pore constriction allows for the formation of multi-layers of the foulants that can result in a decrease in the pore diameter (Figure 2b).

The variation of the pore size can affect the solution conductivity by excluding the electrolyte and redox couple ions. The variation of the average pore dielectric constant (Equation 14) and normalized ion concentration (Equations 15 and 16) are calculated by the methods of Bowen and Welfoot [56].

$$\varepsilon_p = 80 - 2(80 - \varepsilon^*) \left(\frac{d}{r} \right) + (80 - \varepsilon^*) \left(\frac{d}{r} \right)^2 \quad (14)$$

$$\frac{C_{ion}}{C^*} = \beta \exp \left(\frac{-zF}{RT} \Delta\psi_D \right) \exp \left(\frac{-\Delta W}{kT} \right) \quad (15)$$

where ε_p (dimensionless) is the pore dielectric constant, ε^* (dimensionless) is the dielectric constant of an oriented water layer adsorbed at the pore walls, d (m) is the thickness of the oriented solvent layer, C_{ion} (M) is the concentration of ions within the pore, C^* (M) is the concentration of ions in the bulk solution, z (1, dimensionless) is the valence of the ion, R (J·mol⁻¹·K⁻¹) is the universal gas constant, T (298 K) is the absolute temperature, $\Delta\psi_D$ (V) is the Donnan potential, k (J·K⁻¹) is the Boltzmann constant, and β (dimensionless) is the steric partition coefficient of the ion and can be calculated by Equation 16.

$$\beta = (1 - \tau)^2 \quad (16)$$

where τ is the dimensionless ratio of the Stokes radius of the ion to membrane pore radius, and ΔW (J) is the Born solvation energy barrier and is defined as:

$$\Delta W = \frac{z^2 e^2}{8\pi\epsilon_0 a_s} \left(\frac{1}{\varepsilon_p} - \frac{1}{\varepsilon_b} \right) \quad (17)$$

where e (C) is the electronic charge, a_s (2.4×10^{-10} for perchlorate ion, m) is the Stokes radius of the ion, ϵ_b (dimensionless) is the bulk dielectric constant of water, and ϵ_0 ($J^{-1} \cdot C^2 \cdot m^{-1}$) is the permittivity of free space.

The Debye length κ^{-1} of the electric double layer inside the pore is obtained by Equation 18 and is equal to 1.0 nm for the pores with 5.0 nm radius ($\epsilon_p = 71.94$) and 100 mM bulk ionic strength condition (decreased to 77.0 mM in pores with $r = 5.0$ nm as shown in Figure 4), which indicates the electric double layer does not overlap within the pore, and thus ion exclusion is due to the increase of ion solvation energy and the Donnan effect is neglected ($\Delta\psi_D = 0$).

$$\kappa^{-1} = \sqrt{\frac{\epsilon_p \epsilon_0 kT}{2000 N_A e^2 C_{ion}}} \quad (18)$$

where N_A (mol^{-1}) is the Avogadro constant.

The calculated results for the perchlorate ion (ClO_4^-) using Equations 14 and 15 are shown in Figure 3. The values of ϵ_p and C_{ion} are similar to the bulk solution values when $r > 30$ nm, which indicates the pores in the support layer ($r = 1.5 \mu\text{m}$) do not affect ion transport. The pore dielectric constant and ion concentration inside the pore change significantly when the pore radius is smaller than 10 nm (hollow points). The 5 nm pore radius at the active layer is able to cause ion exclusion and reduces the ion concentration and dielectric constant inside the pores to 77% and 72% of the bulk solution values, respectively, which affects the ion movement inside the pore and causes χ_I to be higher than R_s [57]. Since the pore size of the support layer is much greater than the active layer, the ionic resistance in the support layer is equal to that of the active layer. At the active layer, fouling modes, such as pore constriction and pore blockage, are able to change the pore size due to the adsorption of foulants on the pore wall or deposition of foulants

at the pore orifice, which result in an ionic resistance increase due to the decrease in pore dielectric constant and ion concentration inside the pores.

Figure 3 Variation of averaged pore dielectric constant and normalized ion concentration inside the pore. Hollow points are at 5 nm in pore radius. (Solid line represents piece-wise linear interpolation and is included to guide the readers eye.)

The simulation of monolayer adsorption at the active layer is conducted by increasing $R_{ct,active}$ by 5 and 10 times and decreasing Y_0 by 5 and 10 times of background values, in order to maintain a constant RC time constant (Table 2). The simulated EIS spectra are represented as Nyquist plots in Figure 4a for the overall frequency range and 4b for the high and mid frequency data. Figure 4c shows the effect of f on ϕ (Bode phase plot). The characteristic features associated with monolayer adsorption at the active layer are an increase of Z_{real} in the mid frequency data points (2 – 1000 Hz) (Figure 4a and 4b), and a shift in ϕ at mid and low frequencies (Figure 4c). The values for ϕ are shifted to more negative values at frequencies characteristic of the active layer and less negative values at frequencies characteristic of the support layer (Figure 4c). Changes to ϕ at the active layer are attributed to fouling of this region,

and changes to φ at the support layer are due to the increase in Z_{real} from superposition of active layer fouling. The φ value approaches zero at the high frequency limit due to the influence of the solution resistance R_s . The φ at high frequencies (Figure 4c) and the magnitude of semi-circle over the low frequencies do not change (Figure 4a).

Figure 4 Simulated Nyquist plot from TLM in the case of monolayer adsorption at active layer over (a) all frequencies and (b) high and mid frequencies, and (c) Bode phase plot. Unfilled symbols represent characteristic frequencies at 10 mHz, 2 Hz and 1 kHz. (Solid line represents piece-wise linear interpolation and is included to guide the readers eye.)

Figure 5 Simulated Nyquist plot from TLM in the case of pore constriction at active layer over (a) all frequencies and (b) high and mid frequencies, and (c) Bode phase plot. Unfilled symbols represent characteristic frequencies at 10 mHz, 2 Hz and 1 kHz. (Solid line represents piece-wise linear interpolation and is included to guide the readers eye.)

The simulation of pore constriction at the active layer is achieved by increasing $R_{ct,active}$ and decreasing $Y_{0,active}$ 100-fold and increasing the ionic resistance 2-fold and 10-fold. Figure 2b shows a schematic for pore constriction of the active layer. The simulated EIS spectra are shown in Figure 5a for the overall frequency range and Figure 5b contains only the high and mid frequency data. A control simulation, which accounts for only monolayer fouling (100-fold) at the active layer, without changing the ionic resistance is shown in yellow in Figure 5. Pore constriction at the active layer causes an increase of Z_{real} in the mid frequency data points (2 — 1000 Hz) compared to the background spectrum (Figure 5a and 5b). Due to the pore size shrinkage, the dielectric constant within the pore decreases which also decreases ion solvation and leads to a lower concentration of both the background electrolyte and redox couple in the

pore. This process increases Z_{al} significantly and results in a shift in φ to more negative values at the active layer. According to equation (5), the negative shift in φ indicates Z_{imag} is affected to a greater extent than Z_{real} (Figure 5c). Comparing results in Figures 4 and 5, indicate Z_{al} is more sensitive to changes in χ_l than changes to $R_{ct,active}$ and $Y_{0,active}$. Therefore, pore constriction and monolayer adsorption at the active layer have unique EIS spectra and should be distinguishable using the TLM. Furthermore, pore constriction at the active layer shifts φ to less negative values at the support region, due to an increase in Z_{real} from superposition of active layer fouling. Neither φ values at high frequencies (Figure 5c), nor the magnitude of the semi-circle at low frequencies (Figure 5a) change significantly as a result of pore constriction fouling at the active layer.

Similarly, the simulation of membrane fouling at the support layer is achieved by increasing $R_{ct, sup}$ 5 and 10 times and decreasing Y_0 accordingly under a constant RC (Table 2). Membrane fouling at the support layer does not affect the ionic resistance because of the large pore size. Figure 2c shows a schematic for fouling of the support layer pores, which results in a significant growth of the semi-circle at low frequencies (< 2 Hz) (Figure 6a). As shown in Figure 6a, the Nyquist plot primarily shows one large semi-circle and hides the characteristics of the other two time constants. Figure 6c also shows that pore constriction of the support layer results in a shift of φ to more negative value in the whole frequency range, which is a direct result of the superposition of the large semi-circle shown in the Nyquist plot on other features of the EIS spectra.

Figure 6 Simulated results from TLM in the case of membrane fouling at support layer over (a) all frequencies and (b) high and mid frequencies, and (c) Bode phase plot. Unfilled symbols represent characteristic frequency at 10 mHz, 2 Hz and 1 kHz. (Solid line represents piece-wise linear interpolation and is included to guide the readers eye.)

3.3 Fouling of Outer Membrane Surface. Adsorption of foulants at the outer membrane surface was simulated using the parameters shown in Table 2. Figure 2d shows a schematic for membrane fouling at the outer surface, which leads to an increase in Z_{real} at the mid frequency data (2 Hz to 1000 Hz) (Figures 7a and 7b), and a unique shift of ϕ as a function of f (Figure 7c). A shift of ϕ to more negative values at high frequencies is associated with an increased fouling at the outer surface. The fouling of the outer surface masks the characteristic ϕ profile of the active layer, such that only two time constants are evident. Meanwhile the magnitude of the semi-circle at low frequencies does not change in the Nyquist plot (Figure 7a), but the shift of ϕ to less

negative values in this frequency range is due to the superposition of the outer surface fouling at the support (Figure 7c).

Figure 7 Simulated results from TLM in the case of membrane fouling at outer surface over (a) all frequencies and (b) high and mid frequencies, and (c) Bode phase plot. Unfilled symbols represent characteristic frequencies at 10 mHz, 2 Hz and 1 kHz. (Solid line represents piece-wise linear interpolation and is included to guide the readers eye.)

3.4 Intermediate Pore Blockage. Fouling at the outer surface represents the initial stage of membrane flux decline [58] during the filtration of large aggregates and particles. In this stage, the outer electro-active surface area is reduced, but the membrane is still permeable to fluid flow. As the membrane surface becomes more densely fouled, some aggregates deposit as multi-layers while other aggregates block the membrane pore, which leads to membrane permeability decrease. This fouling mode is defined as intermediate pore blockage [59]. Intermediate pore

blockage requires a dense fouling layer at the outer surface, and results in a reduction of the ionic current due to reduced accessibility to ionic solutions (i.e. the resistance for ions entering the pore will increase). To simulate this fouling mode the EIS simulation, $R_{ct, out}$ was increased from 10 to 1,000 ohm, $Y_{0, out}$ was decreased from 0.1 to 0.001 F, and χ_I was increased from 10 to 500 ohm. Due to reduced accessibility to ion solutions, 10x fouling is set to both active and support layers. Figure 2e shows a schematic for pore blockage at the outer surface, which results in the formation of an additional semi-circle at high to mid frequencies (Figure 8a). The semi-circle spanning the high and mid frequency ranges represents the outer surface, which tends to be planar compared to the porous structure due to pore blockage, and the semi-circle at the lower frequencies represents the quasi-planar support layer. The intermediate pore blockage increases the Z_{real} at all three representative areas of the REM, which leads to a shift in ϕ to less negative values over nearly the entire frequency range (Figure 8b).

Figure 8 Simulated (a) Nyquist and (b) Bode plots from TLM in the case of intermediate pore blockage. Unfilled symbols represent characteristic frequency at 10 mHz, 2 Hz and 1 kHz. (Solid line represents piece-wise linear interpolation and is included to guide the readers eye.)

3.5 Calculation of $A_{electro}$ Table 2 also contains values for $A_{electro}$ before and after fouling at each specific location (*outer surface, active layer, and support layer*), which was calculated from

the double layer capacitance (Equation 12). This estimate assumes that the fouling layer is not redox active, and thus the $A_{electro}$ value decreases in response to membrane fouling, and can be used as a surrogate of membrane fouling in experimental studies.

4. Conclusions

This study has established the fundamentals of a TLM, which can be used to spatially characterize membrane fouling and regeneration at an asymmetric REM. Different areas of the asymmetric REM (outer surface, active layer, support layer) can be assessed at different characteristic frequencies, which is due to the relationship between the penetration depth of the sinusoidal voltage wave and voltage frequency. Membrane fouling mechanisms, such as monolayer adsorption, pore constriction, and intermediate pore blockage are studied through Nyquist and Bode phase plots based on TLM simulations. The EIS simulations developed here show that the EIS data produces distinct signatures of membrane fouling at different locations on the membrane surface, and will be used in future studies to characterize REM fouling after experimental fouling and regeneration treatments [34].

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Transmission Line Model for Asymmetric Membrane

Electrochemical Impedance Spectra of Asymmetric Membrane