

## Investigation of the Diffusion Impedance for an Irreversible Redox Reaction

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Simple reactant diffusion can be analysed reliably over a finite diffusion layer. The diffusional impedance may be affected by issues arising from homogeneous reactions, variable properties, or ionic migration, and hence more detailed research is needed. The proposed finite-layer impedance model is based on a nonlinear system of equations that includes a nonlinear term related to the diffusion layer's homogeneous reaction. An analytical method is applied to solve the non-steady-state nonlinear equations. The approximate closed-form of analytical expression corresponding to the diffusion-layer impedance has been derived.

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**Keywords:** Impedance, Reaction-diffusion, Nonlinear equations, irreversible homogeneous reaction.

### 1. INTRODUCTION

Diffusion impedance is a critical component of virtually any electrochemical device which involves a solid electrode and a solution [1,2]. Diffusion impedances are studied using electrochemical impedance spectroscopy [1,2,15]. EIS is a valuable method for investigating chemical and physical processes in both solutions and solids. For several years, EIS has been used to analyse various batteries, corrosion mechanisms, and fuel cells.

Electrochemical impedance spectroscopy is a valuable method for classifying different pathways in an electrode process. Diffusional effects may lead to measured impedance in addition to interfacial phenomena. In 1899, the diffusional resistance in the semi-infinite regime (Warburg impedance) was first defined [1]. A suitable model for a phase adjacent to the electrode surface can be used to calculate diffusional impedance [2–5].

Rama Kant et al. [6] discussed second-order perturbation theory for the local electrochemical impedance spectroscopy (LEIS) for a reversible charge transfer system at an electrode with arbitrary surface profile corrugations. Chowdhury and Rama Kant [7] developed a theoretical model for the generalized Gerischer impedance at an irregular interface under quasi-reversible heterogeneous charge transfer reaction.

Diffusion-controlled systems, for example pre-intercalation electrodes for a battery that can be rechargeable, intrinsically conducting polymers, semiconductor  $p - n$  junctions and electrochromic displays, exist in several structures that are both technologically important and scientifically attractive. These processes, including electrochemistry, photoelectrochemistry, solid-state Ionics, and solid-state electronics, are observed in a variety of fields.

Semi-infinite diffusion, as is well known, occurs in the context of the frequency domain. In certain cases, the diffusional impedance's analytical expression can be obtained using Fick's second laws that characterise mass transport due to a concentration gradient [8–10].

$$\frac{\partial n(x, t)}{\partial t} = D \frac{\partial^2 n(x, t)}{\partial x^2} \quad (1)$$

For example, Several groups [11, 12] have studied the diffusion of a reactant to an electrode surface over a thick diffusion layer to obtain the following formula for the Warburg-type impedance:

$$Z(\omega) = R_{D0} \frac{\tanh \sqrt{j\omega}}{\sqrt{j\omega}} \quad (2)$$

where  $R_{D0}$  is the zero- $\omega$ -limit resistance,  $\omega = [\omega \delta^2 / D]$  is the dimensionless frequency,  $\omega$  is the applied-signal frequency,  $\delta, D$  denotes the diffusion layer thickness and the diffusion coefficient respectively and the symbol  $j$  denotes  $\sqrt{-1}$ . Since solution convection creates a mass-transfer boundary layer of finite thickness adjacent to the electrode, the original Warburg expression for liquid electrolytes is less realistic than the finite layer impedance model, which is also appropriate to solid electrolytes and membranes.

If we consider that an irreversible first-order reaction removes the diffusing substance at a known rate  $kn$ , where  $k$  is a constant, the diffusion equation adopts the form [10].

$$\frac{\partial n(x, t)}{\partial t} = D \frac{\partial^2 n(x, t)}{\partial x^2} - kn(x, t) \quad (3)$$

The diffusion-recombination Eq. (3) can be used to model a wide range of conditions, including the diffusion of an ionic species in electrochemical systems coupled with a homogeneous reaction, the transport and recombination of a minority electronic species in solid-state semiconductor devices [13], and electron transport and recombination in nanostructured semiconductor electrodes. In these electrode processes the value of impedance for the absorbing boundary condition is [10]

$$Z(\omega) = R_{D0} \frac{\tanh \sqrt{j\omega + k\delta^2/D}}{\sqrt{j\omega + k\delta^2/D}} \quad (4)$$

For the reflecting boundary the impedance is given by [10]

$$Z(\omega) = R_{D0} \frac{\coth \sqrt{j\omega + k\delta^2/D}}{\sqrt{j\omega + k\delta^2/D}} \quad (5)$$

Various issues, such as concentration-dependent diffusivity, homogeneous reactions, or ionic migration, may influence the mass-transfer resistance at the electrode surface. In general, in transport equations, these complexities introduce non-linear expressions that preclude the creation of detailed analytical results such as Eq. (1).

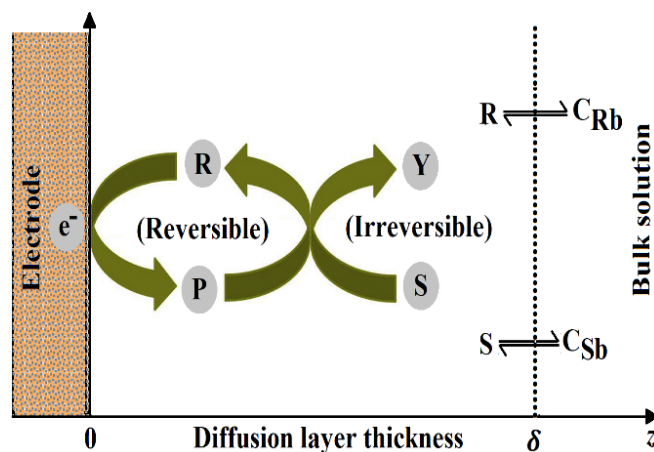
It is also essential for membranes and strong electrolytes. The objective of this paper is to obtain an estimated analytical representation of finite-layer diffusional impedance for the case of an irreversible homogenous reaction.

## 2. MATHEMATICAL FORMULATION OF THE PROBLEM

In a stagnant layer of diffusion, the reaction scheme for a catalytic electrochemical system with diffusion and irreversible second-order reaction is as follows [14]:



The solute  $R$  undergoes oxidation or reduction at the electrode, yielding the soluble substance  $P$ . In the solution,  $P$  responds irreversibly by an irreversible second-order reaction with the reaction rate constant to produce product  $Y$  and to regenerate  $R$  with electrochemically inactive reactant  $S$ , present in the bulk solution. Figure 1 depicts the general scheme for the second-order irreversible homogeneous reaction.



**Figure 1.** Systematic diagram of irreversible homogeneous reaction on finite-layer diffusion impedance.

The boundary value problem that must be solved in this case by ignoring ionic migration can be written in the following form [14, 15]:

$$\frac{\partial c_R(z, t)}{\partial t} = D_R \frac{\partial^2 c_R(z, t)}{\partial z^2} + k_2 c_P(z, t) c_S(z, t) \tag{8}$$

$$\frac{\partial c_P(z, t)}{\partial t} = D_P \frac{\partial^2 c_P(z, t)}{\partial z^2} - k_2 c_P(z, t) c_S(z, t) \tag{9}$$

$$\frac{\partial c_S(z, t)}{\partial t} = D_S \frac{\partial^2 c_S(z, t)}{\partial z^2} - k_2 c_P(z, t) c_S(z, t) \quad (10)$$

where  $c_i$  denotes the concentration of species  $i$ , distance  $z$  across the diffusion layer is measured normal to the electrode surface.  $D_i$  is the molecular diffusion coefficient of species  $i$ ,  $t$  denotes time and  $k_2$  is homogeneous-reaction-rate constant. Assume that all three diffusion coefficients are equal to  $D$  for simplicity. The non-linear differential Eqs. (8)-(10) takes the dimensionless form upon introducing the following dimensionless variables [14].

$$R = [c_R/c_{Sb}], P = [c_P/c_{Sb}], S = [c_S/c_{Sb}], x = z/\delta, \tau = tD/\delta^2, k = [k_2 c_{Sb} \delta^2/D] \quad (11)$$

where  $c_{Sb}$  is the bulk concentration of the substrate  $S$ . Using these parameters, Eqs. (8)-(10) reduces to the following normalized forms.

$$\frac{\partial R(x, \tau)}{\partial \tau} = \frac{\partial^2 R(x, \tau)}{\partial x^2} + k P(x, \tau) S(x, \tau) \quad (12)$$

$$\frac{\partial P(x, \tau)}{\partial \tau} = \frac{\partial^2 P(x, \tau)}{\partial x^2} - k P(x, \tau) S(x, \tau) \quad (13)$$

$$\frac{\partial S(x, \tau)}{\partial \tau} = \frac{\partial^2 S(x, \tau)}{\partial x^2} - k P(x, \tau) S(x, \tau) \quad (14)$$

where  $R, P$  and  $S$  are the dimensionless concentrations of solute, product and the reactant.  $x$  and  $\tau$  denotes the distance and time in dimensionless form respectively,  $k$  is the dimensionless rate constant. The respective initial and boundary conditions are [14]

$$R = R_{in}, \quad P = 0, \quad S = S_{in} \quad \text{when } \tau = 0 \quad (15)$$

$$R = \gamma + \varepsilon \sin(\omega\tau), \quad \frac{\partial P}{\partial x} = -\frac{\partial R}{\partial x}, \quad \frac{\partial S}{\partial x} = 0 \quad \text{when } x = 0 \quad (16)$$

$$R = \alpha, \quad P = 0 \quad \text{and} \quad S = 1 \quad \text{when } x = 1 \quad (17)$$

where  $\alpha = [c_{Rb}/c_{Sb}]$  and  $\gamma = [c_{R0,SS}/c_{Sb}]$  are the concentration ratios and  $c_{Rb}$  is the bulk solutions of concentrations of  $R$ ,  $c_{R0,SS}$  denotes the concentration of  $R$  at the electrode in steady-state.

### 3. APPROXIMATE ANALYTICAL EXPRESSION OF CONCENTRATIONS AND FLUX

The system of nonlinear equations is represented by equations (8)-(10). Finding the exact solution to these nonlinear equations is extremely difficult. Solving systems of nonlinear equations is perhaps one of the most difficult problems, especially in a diverse range of science and engineering applications. Recently so many approximate analytical methods [16] such as homotopy perturbation method [17–21], Residual method [22], Taylor series method [23–26], AGM method [27–29], new analytical method [30–32] are used to solve the non-linear equations, Here the nonlinear equations (8)-(10) are solved using new analytical method.

Here we can assume that:  $S_{in}P \gg P_{in}S$  which holds for:  $S \gg P(x, \tau)$ . This reduces the homogeneous reaction from a true second order reaction to a pseudo first order reaction with effective rate constant  $k_{eff} = k S_{in}$  and changes the physics to a simple linear diffusion problem, closely related to that of the well-known finite Gerischer impedance. Now the nonlinear term in the differential equations (12)-(14) linearized as follows [14]:

$$PS \approx P_{in}S + S_{in}P - P_{in}S_{in} \approx S_{in}P \quad (18)$$

where  $P_{in}, S_{in}$  are initial values of  $P(x, \tau = 0)(= 0)$  and  $S(x, \tau = 0)$ . Taking the Laplace transform of Eqs. (12)-(14) using above approximation we get

$$\frac{d^2 \bar{R}(x, s)}{dx^2} - s \bar{R}(x, s) + k S_{in} \bar{P}(x, s) + R_{in} = 0 \tag{19}$$

$$\frac{d^2 \bar{P}(x, s)}{dx^2} - s \bar{P}(x, s) - k S_{in} \bar{P}(x, s) = 0 \tag{20}$$

$$\frac{d^2 \bar{S}(x, s)}{dx^2} - s \bar{S}(x, s) - k S_{in} \bar{P}(x, s) + S_{in} = 0 \tag{21}$$

The corresponding boundary conditions in Laplace plane are

$$\bar{R} = \frac{\gamma}{s} + \frac{\varepsilon \varpi}{s^2 + \varpi^2}, \quad \frac{d\bar{P}}{dx} = -\frac{d\bar{R}}{dx}, \quad \frac{d\bar{S}}{dx} = 0 \text{ when } x = 0 \tag{22}$$

$$\bar{R} = \frac{\alpha}{s}, \quad \bar{P} = 0 \text{ and } \bar{S} = \frac{1}{s} \text{ when } x = 1 \tag{23}$$

By solving the Eqs. (19)-(21) using boundary conditions ((22)-(23)) (Appendix A) we can obtain the approximate analytical expression of concentration of species as follows:

$$\bar{R}(x, s) = \frac{R_{in}}{s} - \left( \frac{R_{in} - \alpha}{s} \right) \frac{\cosh(\sqrt{s} x)}{\cosh(\sqrt{s})} - \bar{P}(x, s) \tag{24}$$

$$\bar{P}(x, s) = \left( \frac{R_{in}}{s} - \frac{R_{in} - \alpha}{s \cosh(\sqrt{s})} - \frac{\gamma}{s} - \frac{\varepsilon \varpi}{s^2 + \varpi^2} \right) \frac{\sinh(\sqrt{s + k S_{in}} (1 - x))}{\sinh(\sqrt{s + k S_{in}})} \tag{25}$$

$$\bar{S}(x, s) = \frac{S_{in}}{s} - \bar{P}'(x = 0) \frac{e^{\sqrt{s} x}}{\sqrt{s}} + \left( \frac{1}{s} - \frac{S_{in}}{s} + \bar{P}'(x = 0) \frac{e^{\sqrt{s}}}{\sqrt{s}} \right) \frac{\cosh(\sqrt{s} x)}{\cosh(\sqrt{s})} + \bar{P}(x, s) \tag{26}$$

where  $\bar{P}'(x = 0)$  is given in the equation (27). By measuring the concentration gradient of  $R$  at the electrode, the dimensionless flux was calculated.

$$J_0 = -\left( \frac{d\bar{R}}{dx} \right)_{x=0} = \left( \frac{d\bar{P}}{dx} \right)_{x=0} = \left( \frac{\gamma}{s} + \frac{\varepsilon \varpi}{s^2 + \varpi^2} - \frac{R_{in}}{s} + \frac{R_{in} - \alpha}{s \cosh(\sqrt{s})} \right) \frac{\sqrt{s + k S_{in}}}{\tanh(\sqrt{s + k S_{in}})} \tag{27}$$

### 3.1 Approximate analytical expression of impedance

At the electrode surface, the normalized dimensionless flux impedance is calculated as [33]

$$Z(\varpi) = \frac{\bar{R}(x = 0)}{J_0} = \frac{\frac{\gamma}{s} + \frac{\varepsilon \varpi}{s^2 + \varpi^2}}{\frac{\gamma}{s} + \frac{\varepsilon \varpi}{s^2 + \varpi^2} - \frac{R_{in}}{s} + \frac{R_{in} - \alpha}{s \cosh(\sqrt{s})}} \frac{\tanh(\sqrt{s + k S_{in}})}{\sqrt{s + k S_{in}}} \tag{28}$$

Applying the value  $s = j\varpi$  in Eq. (28) and after simplifying it, we get

$$Z(\varpi) = \frac{\tanh(\sqrt{j\varpi + k S_{in}})}{\sqrt{j\varpi + k S_{in}}} \text{ when } \varepsilon \neq 0 \tag{29}$$

$$= \frac{\gamma}{\gamma - R_{in} + \frac{R_{in} - \alpha}{\cosh(\sqrt{j\varpi})}} \frac{\tanh(\sqrt{j\varpi + k S_{in}})}{\sqrt{j\varpi + k S_{in}}} \text{ when } \varepsilon = 0 \tag{30}$$

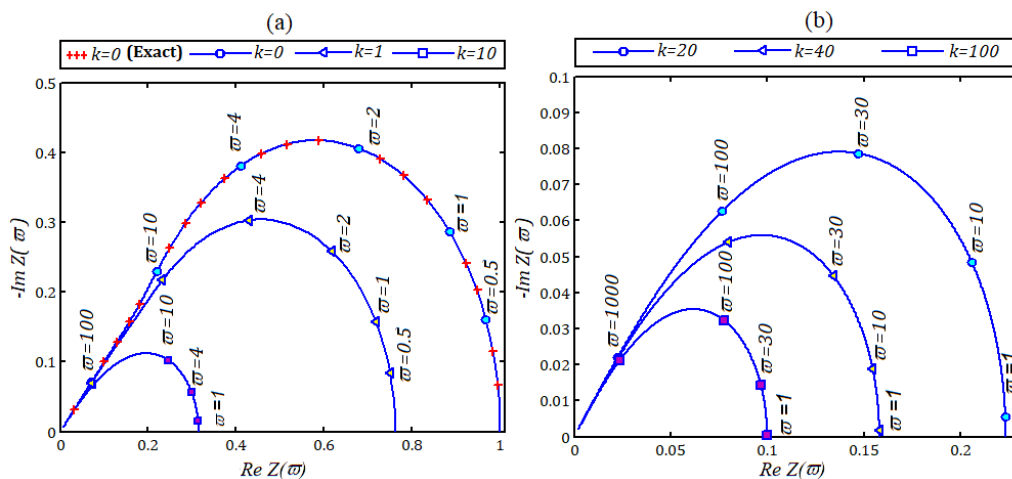
This impedance (Eqn.(29)) is equal to the impedance for absorbing boundary condition [10] and it is same as a finite Gerischer impedance. When  $k = 0$ , we get the diffusion-impedance (Eq.(2)).

Various limiting cases of the Eqs. (29) and (30) with brief discussion is given in Table-1.

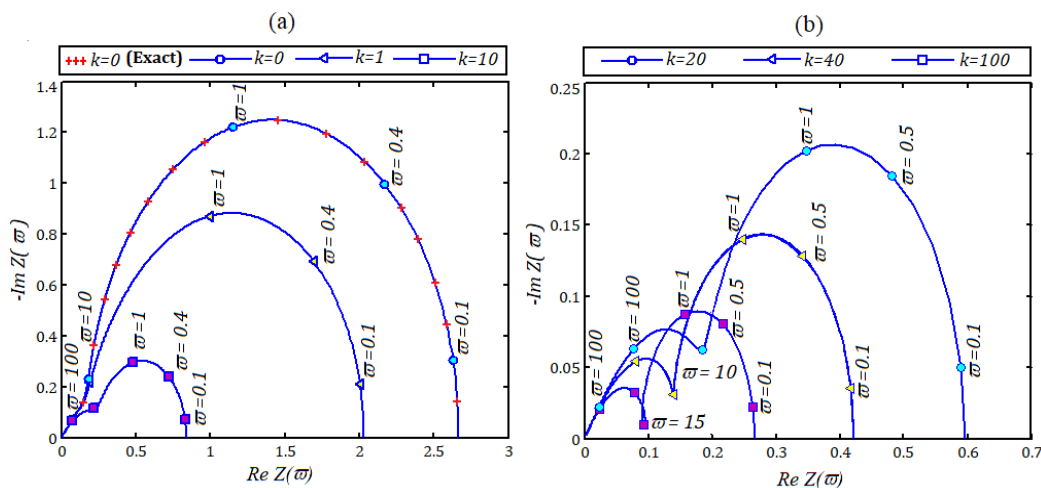
**Table 1.** Various limiting cases of homogeneous reaction Impedance

Limiting cases		Impedance	Discussion
$k = 0 \ \& \ \varepsilon \neq 0$		$Z(\omega) = \frac{\tanh(\sqrt{j\omega})}{\sqrt{j\omega}} \quad (31)$	<p>Eq. (31) is the dimensionless diffusion impedance in the absence of homogeneous reaction. <b>For low-frequency limit</b> [33], i.e electrode dimension is small compared to the penetration depth, <math>\omega \ll 1</math> or <math>\omega \rightarrow 0</math>, this becomes</p> $Z(\omega) \simeq 1 - \frac{j\omega}{3} - \frac{2\omega^2}{15} \simeq 1.$ <p>This is also called steady-state Nernstian diffusion impedance.</p> <p><b>For high-frequency limit</b> [33], i.e <math>\omega \gg 1</math> or <math>\omega \rightarrow \infty</math>, eqn.(31) becomes</p> $Z(\omega) = \frac{1}{\sqrt{j\omega}}$ <p>This is referred to as the Warburg impedance consistent with semi-infinite diffusion.</p>
$k = 0 \ \& \ \varepsilon = 0$		$Z(\omega) = \frac{\gamma}{\gamma - R_{in} + \frac{R_{in} - \alpha}{\cosh(\sqrt{j\omega})}} \frac{\tanh(\sqrt{j\omega})}{\sqrt{j\omega}} \quad (32)$	Impedances in the absence of homogeneous reaction and small perturbation amplitude.
$k \neq 0, \ \varepsilon \neq 0$	$\omega \rightarrow 0$	$Z(\omega) = \frac{\tanh(\sqrt{kS_{in}})}{\sqrt{kS_{in}}} - j\omega \left( \frac{\tanh(\sqrt{kS_{in}})}{2(kS_{in})^{3/2}} + \frac{\tanh^2(\sqrt{kS_{in}}) - 1}{2kS_{in}} \right) \quad (33)$	It is an impedance response with a low-frequency limit and the amplitude effect for combined homogeneous reaction and diffusion.
$k \neq 0, \ \varepsilon \neq 0$	$\omega \rightarrow \infty$	$Z(\omega) = \left( \frac{1}{\sqrt{j\omega}} + \frac{kS_{in}\sqrt{j\omega}}{2\omega^2} \right) \tanh \left( \sqrt{j\omega} + \frac{kS_{in}}{2\sqrt{j\omega}} \right) \quad (34)$	This represents the impedance for coupled homogeneous reaction with high-frequency limit and the amplitude effect.
$k \gg 1, \ \varepsilon \neq 0$		$Z(\omega) = \frac{1}{\sqrt{j\omega + kS_{in}}} \quad (35)$	<p>This is the Gerischer impedance obtained for high influence of the homogeneous reaction rate constant</p> $k \gg 1 \text{ or } \sqrt{\frac{D}{k_2 c_{Sb}}} \ll \delta.$ <p>At the highest frequencies, the Gerischer impedance becomes <math>Z(\omega) = \frac{1}{\sqrt{j\omega}}</math></p>
$k \ll 1, \ \omega \gg k, \ \varepsilon \neq 0$		$Z(\omega) = \frac{\tanh(\sqrt{j\omega})}{\sqrt{j\omega}} \quad (36)$	<p>This represents the diffusion impedance with high frequency and low homogeneous reaction rate i.e <math>\sqrt{\frac{D}{k_2 c_{Sb}}} \gg \delta.</math></p>
$k \ll 1, \ \omega \ll k, \ \varepsilon \neq 0$		$Z(\omega) = \frac{\tanh(\sqrt{kS_{in}})}{\sqrt{kS_{in}}} \quad (37)$	This equation represents real impedance with low frequency (which approach to zero) and low homogeneous reaction rate.

4. DISCUSSION



**Figure 2. (a-b).** Plot of impedance results obtained for various values of  $k$  over a range of dimensionless frequencies  $\omega$  from 0.1 to 1000 using Eq. (29). (+ + +) symbol indicate exact solution for impedance computed for  $k = 0$  when  $\varepsilon \neq 0$ .



**Figure 3. (a-b).** Plot of impedance results obtained for various values of  $k$  over a range of dimensionless frequencies  $\omega$  from 0.1 to 1000 using Eq. (30) for experimental values [14] of parameters  $\alpha = 0.5, \gamma = 0.8, R_{in} = 0, S_{in} = 1$ . (+ + +) symbol indicate exact solution of impedance computed for  $k = 0$  when  $\varepsilon = 0$ .

Eqs. (29) to (30) represent the new approximate analytical expression of impedances for a catalytic EC mechanism in which the electrode process is coupled with a homogeneous reaction in the diffusion layer. And various limiting cases of impedance is given in Table 1.

From Figs. 2 and 3, it is detected that the effect of the diffusional impedance decreases with the value of the reaction rate constant. These are acceptable since, near the electrode surface, the homogeneous reaction regenerates reactant R and reduces the diffusional resistance.

From Fig. 2, it is observed that when  $\varepsilon \neq 0$ , the impedance increasing when dimensionless frequency  $\omega$  increases until it reaches its peak, then drops to zero. The dimensionless frequency was defined as  $\omega = [\omega\delta^2/D]$ . For a stirred solution, a standard value of  $\delta$  might be 0.01 cm, and  $D$  is on the order of  $10^{-5} \text{ cm}^2\text{s}^{-1}$ . In the Figs. 2 (a-b), the all  $k$ -Nyquist curve reaches zero when  $\omega >$

100 Hz ( $\omega > 1000$ ). The maximum  $Z(\omega) = 0.4602 - 0.3039j$  in the one- $k$  Nyquist curve occurs at  $\omega = 0.36$  Hz. The maximum impedance in the 100- $k$  Nyquist curve occurs at  $\omega = 1.67$  Hz is  $Z(\omega) = 0.1772 - 0.1680j$ . An applied frequency of corresponds to one- $k$  and 100- $k$  Nyquist curve is  $f = 0.06$  Hz, 0.26 Hz respectively. On comparing various- $k$  Nyquist curve, the impedance is higher for the zero- $k$  Nyquist curve and corresponding impedance is  $Z(\omega) = 0.5882 - 0.4172j$ .

From the Fig. 3 (a-b), when  $\varepsilon = 0$ , it was found that when  $k > 20$  the computed impedance began to rise again with increasing  $k$ . This limitation holds because the concentration profiles become stiffer at increasing rate constants, with the dimensionless concentrations product and solute tending to zero inside the diffusion layer in a thin reaction region.

## 5. CONCLUSION

In this work, we suggest a simple approximate approach to solve the system of nonlinear equations in irreversible homogeneous reaction for finite diffusion. Non-linear effects in a diffusion layer can influence the apparent diffusional impedance, as seen in this process. The estimated solution can be considered to investigate the impacts of multiple system parameters such as bulk concentration ratios, diffusion coefficients, and the reaction rate constant. The findings presented here can be used to explore membrane-transport experiments and other ionic transport cases in semiconductors and other solids.

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## NOMENCLATURE

Symbols	Description	unit
$c_R$	Concentration of solute	$\text{mol cm}^{-3}$
$c_P$	Concentration of product	$\text{mol cm}^{-3}$
$c_S$	Concentration of reactant	$\text{mol cm}^{-3}$
$c_{Rb}, c_{Pb}, c_{Sb}$	Bulk solutions of concentrations of R, P and S	$\text{mol cm}^{-3}$
$c_{R0,SS}$	Steady - state concentration of R at the electrode	$\text{mol cm}^{-3}$
$k_2$	Reaction - rate constant	$\text{cm}^3/\text{s mol}$
$D_R, D_P, D_S$	Diffusion coefficient of R, P and S	$\text{cm}^2 \text{s}^{-1}$
$z$	Distance from electrode surface	cm
$\delta$	Diffusion layer thickness	cm



$t$	Time	s
$\omega$	Dimensional frequency	s <sup>-1</sup>
$f = \omega/2\pi$	Applied frequency	Hz
$\varepsilon C_{Sb}$	Amplitude	cm
$R$	Dimensionless concentration of solute	none
$P$	Dimensionless concentration of product	none
$S$	Dimensionless concentration of reactant	none
$x$	Dimensionless distance from the electrode	none
$\tau$	Dimensionless time	none
$k$	Dimensionless rate constant	none
$\varpi$	Dimensionless frequency	none
$Z$	Dimensionless Impedance	none
$\alpha = [c_{Rb}/c_{Sb}]$	Concentration ratio	none
$\gamma = [c_{R0,ss}/c_{Sb}]$	Concentration ratio	none
$R_{in}, P_{in}, S_{in}$	Dimensionless concentration at t=0	none
$J_0$	Dimensionless Flux	none
$j$	Imaginary number ( $\sqrt{-1}$ )	none
$s$	Laplace variable	none

APPENDIX A: Approximate analytical expression of concentration of species  $\bar{R}(x, s)$ ,  $\bar{P}(x, s)$  and  $\bar{S}(x, s)$

A.1 Concentration of species  $\bar{R}(x, s)$

Adding Eqs. (19) & (20), we get

$$\frac{d^2(\bar{R} + \bar{P})}{dx^2} - s(\bar{R} + \bar{P}) + R_{in} = 0 \tag{A. 1}$$

The boundary conditions for the above differential equations is obtained from Eqs.(22)-(23) as follows:

$$\frac{d(\bar{R} + \bar{P})}{dx} = 0 \quad \text{when } x = 0, \quad \bar{R} + \bar{P} = \frac{\alpha}{s} \quad \text{when } x = 1. \tag{A. 2}$$

By solving Eq. (A. 1), we get

$$\bar{R}(x, s) + \bar{P}(x, s) = \frac{R_{in}}{s} + a_0(s)e^{-\sqrt{s}x} + b_0(s)e^{\sqrt{s}x} \tag{A. 3}$$

where  $a_0(s) = b_0(s) = \frac{-(R_{in}-\alpha)}{s(e^{\sqrt{s}}+e^{-\sqrt{s}})}$  are constants obtained using the boundary condition (A. 2).

Hence the relation between the concentration  $\bar{R}(x, s)$  &  $\bar{P}(x, s)$  is obtained as

$$\bar{R}(x, s) + \bar{P}(x, s) = \frac{R_{in}}{s} - \left(\frac{R_{in} - \alpha}{s}\right) \frac{e^{\sqrt{s}x} + e^{-\sqrt{s}x}}{e^{\sqrt{s}} + e^{-\sqrt{s}}} \tag{A. 4}$$

And so, the value of concentration species  $\bar{R}(x, s)$  is given as follows

$$\begin{aligned} \bar{R}(x, s) &= \frac{R_{in}}{s} - \left(\frac{R_{in} - \alpha}{s}\right) \frac{e^{\sqrt{s}x} + e^{-\sqrt{s}x}}{e^{\sqrt{s}} + e^{-\sqrt{s}}} - \bar{P}(x, s) \\ &= \frac{R_{in}}{s} - \left(\frac{R_{in} - \alpha}{s}\right) \frac{\cosh(\sqrt{s}x)}{\cosh(\sqrt{s})} - \bar{P}(x, s) \end{aligned} \tag{A. 5}$$

A.2 Concentration of species  $\bar{P}(x, s)$ 

Approximate solution of  $\bar{P}(x, s)$  by solving Eq. (20) is

$$\bar{P}(x, s) = a_1(s) e^{-\sqrt{s+kS_{in}}x} + b_1(s) e^{\sqrt{s+kS_{in}}x} \quad (\text{A. 6})$$

where  $a_1(s)$ , and  $b_1(s)$  are constants. Substituting  $x = 0$  and  $\bar{R}(x = 0, s) = \frac{\gamma}{s} + \frac{\varepsilon \omega}{s^2 + \omega^2}$  in Eq.

(A. 4), we get

$$\bar{P}(x = 0, s) = \left( \frac{R_{in}}{s} - \frac{2(R_{in} - \alpha)}{s(e^{\sqrt{s}} + e^{-\sqrt{s}})} - \frac{\gamma}{s} - \frac{\varepsilon \omega}{s^2 + \omega^2} \right). \quad (\text{A. 7})$$

Then the constants  $a_1(s)$  and  $b_1(s)$  are obtained using Eq. (A. 7) and the boundary condition  $\bar{P}(x = 1, s) = 0$ , as follows

$$a_1(s) = \left( \frac{R_{in}}{s} - \frac{2(R_{in} - \alpha)}{s(e^{\sqrt{s}} + e^{-\sqrt{s}})} - \frac{\gamma}{s} - \frac{\varepsilon \omega}{s^2 + \omega^2} \right) \frac{1}{1 - e^{-2\sqrt{s+kS_{in}}}}, b_1(s) = -a_1(s) e^{-2\sqrt{s+kS_{in}}}$$

Substituting above values in Eq. (A. 6) we have

$$\begin{aligned} \bar{P}(x, s) &= \left( \frac{R_{in}}{s} - \frac{2(R_{in} - \alpha)}{s(e^{\sqrt{s}} + e^{-\sqrt{s}})} - \frac{\gamma}{s} - \frac{\varepsilon \omega}{s^2 + \omega^2} \right) \frac{e^{-\sqrt{s+kS_{in}}x} - e^{\sqrt{s+kS_{in}}(x-2)}}{1 - e^{-2\sqrt{s+kS_{in}}}} \\ &= \left( \frac{R_{in}}{s} - \frac{R_{in} - \alpha}{s \cosh(\sqrt{s})} - \frac{\gamma}{s} - \frac{\varepsilon \omega}{s^2 + \omega^2} \right) \frac{\sinh(\sqrt{s+kS_{in}}(1-x))}{\sinh(\sqrt{s+kS_{in}})} \end{aligned} \quad (\text{A. 8})$$

And the derivative of the concentration  $\bar{P}(x, s)$  at  $x = 0$ , is given by

$$\bar{P}'(x = 0) = \left( \frac{\gamma}{s} + \frac{\varepsilon \omega}{s^2 + \omega^2} - \frac{R_{in}}{s} + \frac{R_{in} - \alpha}{s \cosh(\sqrt{s})} \right) \frac{\sqrt{s+kS_{in}}}{\tanh(\sqrt{s+kS_{in}})}$$

A.3 Concentration of species  $\bar{S}(x, s)$ 

Subtracting Eqs. (20) & (21) we get

$$\frac{d^2(\bar{S} - \bar{P})}{dx^2} - s(\bar{S} - \bar{P}) + S_{in} = 0 \quad (\text{A. 9})$$

Solving the above equation, we get,

$$\bar{S}(x, s) - \bar{P}(x, s) = \frac{S_{in}}{s} + a_2(s) e^{-\sqrt{s}x} + b_2(s) e^{\sqrt{s}x} \quad (\text{A. 10})$$

Using the boundary conditions (Eq.(22)-(23)), we can obtain the constants

$$a_2(s) = \left( \frac{1}{s} - \frac{S_{in}}{s} + \frac{\bar{P}'(x=0)e^{\sqrt{s}}}{\sqrt{s}} \right) \frac{1}{e^{\sqrt{s}} + e^{-\sqrt{s}}} \quad \text{and} \quad b_2(s) = -\frac{\bar{P}'(x=0)}{\sqrt{s}} + a_2(s).$$

Then Eq. (A. 10) becomes

$$\begin{aligned} \bar{S}(x, s) &= \frac{S_{in}}{s} - \bar{P}'(x = 0) \frac{e^{\sqrt{s}x}}{\sqrt{s}} + \left( \frac{1}{s} - \frac{S_{in}}{s} + \bar{P}'(x = 0) \frac{e^{\sqrt{s}}}{\sqrt{s}} \right) \frac{e^{\sqrt{s}x} + e^{-\sqrt{s}x}}{e^{\sqrt{s}} + e^{-\sqrt{s}}} + \bar{P}(x, s) \\ &= \frac{S_{in}}{s} - \bar{P}'(x = 0) \frac{e^{\sqrt{s}x}}{\sqrt{s}} + \left( \frac{1}{s} - \frac{S_{in}}{s} + \bar{P}'(x = 0) \frac{e^{\sqrt{s}}}{\sqrt{s}} \right) \frac{\cosh(\sqrt{s}x)}{\cosh(\sqrt{s})} + \bar{P}(x, s) \end{aligned} \quad (\text{A. 11})$$

where  $\bar{P}(x, s)$  is given in the Eq. (A. 8).

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