Linear sweep voltammetry in flooded porous electrodes at low sweep rates

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Abstract

A theoretical analysis of linear sweep voltammetry (LSV) in flooded-porous electrodes is treated for reversible (Nernstian) and first-order irreversible reactions. At low sweep rates, the ohmic potential drop within the electrode is negligible and concentration gradients are predominantly in the axial direction. The solution to the reversible case is mathematically simple, but the results are presented to understand the influence external mass-transfer resistance has on the voltammogram. For irreversible kinetics, a Green’s function technique is used to obtain an analytical solution to the diffusion equation. An analytical solution for the current as a function of the electrode dimensions, sweep rate and reaction kinetic parameters allows one to predict the voltammogram over a wide range of conditions. The analytical solution is used to develop correlations that enable the kinetic parameters (i.e. exchange current density per unit volume and the transfer coefficient) to be easily extracted from experimental data. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

The industrial application of porous electrodes covers a broad spectrum of areas including batteries, fuel cells, pollution abatement, synthesis of organic chemicals, and hybrid solvent extraction [1]. Porous electrodes reduce the kinetic and mass-transfer resistances accompanying the electrochemical reactions by providing a large interfacial area per unit volume. In situ data analysis is needed to characterize the electrode kinetics for the design and optimization of porous electrodes.

Unfortunately, electroanalytical techniques that work on planar electrodes are not readily adaptable to porous electrodes. For example, controlled hydrodynamic techniques (e.g. rotating disk electrodes) only control the transport of the reacting species external to the porous electrode. In contrast, linear sweep voltammetry (LSV) is appropriate for porous electrodes. However, presently available mathematical methodologies that have been developed to determine the kinetic parameters using LSV on a planar electrode [2–5] and in a thin-layer cell [6–8] are not applicable for a porous electrode except over a narrow range of operating conditions where ohmic resistance and axial diffusion are negligible [9]. For example, at high sweep rates the diffusion layer is small relative to the pore diameter, and when the ohmic resistance is negligible the voltammogram has the characteristics of LSV on a planar electrode. For moderate sweep rates, radial concentration gradients are small, and if the pore is deep, axial concentration gradients are negligible for the major fraction of the pore volume, and consequently, the porous electrode behaves like a thin-layer cell. Weidner and Fedkiw [9] took advantage of these limiting cases to develop a methodology for extracting the kinetic parameters in porous electrodes using LSV. The disad-
vantage of their methodology is that it is valid only for cylindrical pores of uniform and known dimensions. If the pore dimensions and geometry are not cylindrical, or if the pore-size distribution is broad, the voltammograms cannot be interpreted using their methodology.

In this work, LSV in a porous electrode is modeled at low sweep rates where the microstructure of the pores does not affect the voltammogram. Only the electrode thickness and porosity must be known. Also, at low sweep rates, the ohmic potential drop is negligible and axial diffusion dictates the shape of the voltammogram. Therefore, the diffusion equation in the axial direction is solved for reversible (Nernstian) and irreversible (Tafel) kinetics using porous electrode theory [1]. The solution to the reversible case is mathematically simple, but the results are presented to understand the influence that external mass-transfer resistance has on the voltammogram. For irreversible kinetics, an analytical Green’s function technique is used to solve the diffusion equations with constant external mass-transfer resistance. The simulated voltammograms are used to develop correlations that enable the kinetic parameters (i.e. transfer coefficient and exchange current density per unit volume) to be easily extracted from experimental data.

2. Mathematical model

Porous electrode theory is applied to a first-order electrochemical reaction of the form

\[ \text{O} + n\text{e}^\to \to \text{R} \]  

(1)

where O and R are the soluble oxidized and reduced species, respectively and \( n \) is the number of electrons transferred. Fig. 1 is a schematic representation of the porous electrode considered here. The governing equations are solved under the following assumptions:

1. The radial concentration gradients within the pores are negligible.
2. The solid phase and the liquid phase are isopotential.
3. Non-faradaic current is negligible.
4. Diffusion is the dominant mass-transfer mechanism inside the porous electrodes (i.e. convection and migration are negligible).
5. The voltage sweep starts at a potential where the initial current is less than 1% of the peak current.
6. In the presence of a separator, the bulk is well stirred.
7. The concentration profile across the separator is linear.

Weidner and Fedkiw [9] determined the operating conditions where assumptions 1 and 2 are valid. Due to these two assumptions, the concentration is only a function of axial distance, \( x \), and time, \( t \), and the potential is only a function of \( t \). Neglecting the non-faradaic component of the current (assumption 3) places a lower limit on the reactant concentration since only the reaction current decreases with decreasing concentration. However, at low sweep rates this assumption should be valid at reasonable concentrations even for high surface area porous electrodes. Assumption 4 is valid for a well-supported electrolyte. The potential that satisfies assumption 5 depends on the reaction kinetics. For the case of reversible kinetics, the initial potential must be well positive of the formal potential for the initial current to be negligible. For the case of irreversible kinetics, the sweep can start at the formal potential without producing a significant current relative to the peak. The validity of assumption 6 is determined by the experimental conditions. This assumption will be relaxed for the case of reversible kinetics with variable external mass-transfer resistance. Assumption 7 is valid when the characteristic length-of-diffusion is greater than the thickness of the separator (i.e. thin separators or low sweep rates). The numerical values of separator thickness and sweep rate for which this assumption is valid will be presented in Section 3.2.

2.1. Reversible kinetics

Reversible kinetics means that the potential and concentration at the electrode | electrolyte interface are in equilibrium with one another and related through the Nernst equation as:

\[ \text{CO} = \text{CO}^\circ \]  

Fig. 1. A schematic of the flooded porous electrode considered here. The separator lies between the porous electrode and the bulk electrolyte, which is well stirred. The diffusional flux is zero at the interface of the porous electrode in contact with the current collector (i.e. \( x = 0 \)).
Fig. 2. Effect of \((h_m/\alpha)\) on the voltammograms for a reversible reaction with constant external mass-transfer resistance. The voltammograms are generated using Eq. (6). For \((h_m/\alpha) \geq 1.0\) (i.e. \(\alpha \leq h_m\)) no peaks are observed. As \((h_m/\alpha) \rightarrow 0\), thin-layer behavior is observed.

\[
\frac{c_O}{c_R} = \exp\left[\frac{nF}{RT} (E - E^o)\right] = \exp(E^*_{rev}) \tag{2}
\]

Due to negligible ohmic resistance, the potential is uniform throughout the porous electrode. Reversible kinetics assume that the potential at any point in the porous electrode is in equilibrium with the concentration through Eq. (2). Therefore, if the potential does not vary axially, and no radial concentrations exist, the concentration must also be uniform and vary only with \(t\). Since no diffusion limitations occur inside the porous electrodes, the concentrations of the oxidized and reduced species within the electrode are related to the initial concentration by (assuming only the oxidized species is initially present)

\[
c_O + c_R = c_O^0 \tag{3}
\]

This is the situation that exists in a thin-layer cell when the kinetics are reversible [6,7].

2.1.1. Constant external mass-transfer resistance

The thickness of the external diffusion layer, \(\delta\), is fixed by the thickness of the separator. For a flooded porous electrode in contact with a large reservoir of reactant, the electrode behaves like a thin-layer cell with the addition of material diffusing across the separator from the bulk electrolyte to the electrode surface. To determine this diffusion rate as a function of potential, it is necessary to know a relationship between the oxidized and reduced species. Although Eq. (3) does not hold in the separator, the following equation for the fluxes across the separator can be used in accordance with assumption 7,

\[
N_O = -N_R = -\left(\frac{c_O^0 D_O}{\delta}\right) \frac{1}{1 + \frac{1}{\zeta} \exp(E^*_{rev})} \tag{4}
\]

where \(\zeta = (D_O/D_R)\). The total current is the sum of the contribution from the material initially present in the porous electrode (i.e. thin-layer contribution [6,7]) plus the contribution from material diffusing across the separator, which is given as:

\[
I_{rev} = \frac{n^2 F^2 v \varepsilon V c_O^0}{RT} \left[\frac{\exp(E^*_{rev})}{1 + \exp(E^*_{rev})}\right] + \frac{n F D_O A c_O^0}{\delta} \frac{1}{1 + \frac{1}{\zeta} \exp(E^*_{rev})} \tag{5}
\]

The second term is analogous to the current obtained at a rotating-disk electrode at low sweep rates or high rotation speeds. The current obtained from Eq. (5) does not depend upon the past history of the cell. In other words, Eq. (5) is independent of the initial potential.
When made dimensionless with respect to the peak current for a reversible reaction in a thin-layer cell [6,7], Eq. (5) becomes

\[ I_{\text{rev}}^* = \frac{I_{\text{rev}}}{I_{\text{p,rev,TL}}} = \frac{4 \exp(E_{\text{rev}}^*)}{[1 + \exp(E_{\text{rev}}^*)]^2} \left( \frac{h_m/\sigma}{1 + \xi \exp(E_{\text{rev}}^*)} \right) \]  

(6)

where

\[ I_{\text{p,rev,TL}} = \frac{n^2 F^2 \varepsilon c_0^0}{4RT} \]  

(7)

According to Eq. (6), the dimensionless voltammogram is a function of two dimensionless parameters \((h_m/\sigma)\) and \(\xi\).

### 2.1.2. Variable external mass-transfer resistance

Consider the case where the schematic in Fig. 1 is modified slightly by removing the separator and leaving the bulk stagnant (i.e. no stirring). The thickness of the external diffusion layer grows in time as the experiment proceeds. The parameter \(\delta\) in Fig. 1 can be thought of as a characteristic length-of-diffusion defined as \(\delta \equiv \sqrt{D_0/nf\varepsilon}\). Therefore, as the sweep rate increases, \(\delta\) decreases. Again, the total current is the sum of the contribution from the material present initially in the porous electrode plus the contribution of material diffusing from the electrode reservoir. However, in this case the material diffusing from the bulk to the surface of the porous electrode changes with time. From the perspective of the bulk electrolyte, the surface of the porous electrode is planar. Therefore, the dimensionless current is,

\[ I_{\text{rev}}^* = \frac{4 \exp(E_{\text{rev}}^*)}{[1 + \exp(E_{\text{rev}}^*)]^2} \frac{4 \sqrt{\pi I_{\text{rev}}}}{\varepsilon \sqrt{\sigma}} \]  

(8)

where \(\sqrt{\pi I_{\text{rev}}}\) was derived by Nicholson and Shain [4] for current to a planar electrode as

\[ \sqrt{\pi I_{\text{rev}}} = \frac{1}{4\sqrt{\pi}} \int_0^{\xi_{\text{rev}}} \frac{dz}{\sqrt{(\sigma \tau - z) \cosh^2([\ln(\gamma \sqrt{\tau}) - z]/\sigma \tau)}} \]  

(9)

where \(\gamma = (c_{0L}^0/c_{0B}^0)\) and the dimensionless time is \(\sigma \tau = nf(E - E_i)\). For values of \(\gamma\) greater than 100 (i.e. the oxidized species is the dominant species initially), Nicholson and Shain have shown that the voltammogram generated from Eq. (9) is independent of \(\gamma\). Also, Eqs. (8) and (9) are only accurate when the initial potential, \(E_i\), is such that the initial current is less than 1% of the peak current (assumption 5). For a one electron transfer, this corresponds to an initial potential at least 120 mV positive of \(E^0\). Therefore, for \(\xi = 1\), \(\gamma \geq 100\), and an appropriate initial potential, the dimensionless voltammogram generated from Eq. (8) is a function of only one parameter, \(\varepsilon \sqrt{\sigma}\).

### 2.2. Irreversible kinetics—constant external mass-transfer resistance

For a reaction that has kinetic limitations, the concentration will vary in the axial direction. The concentration profile as a function of time can be obtained by solving the following equation
Fig. 4. Comparison of the peak currents from Eq. (25) (solid line) with those from Weidner and Fedkiw [8] (dashed lines) as a function of \( \sqrt{\sigma} \).

The dotted line at small values of \( \sqrt{\sigma} \) is the planar limit based on the projected area, and the dotted lines at large values of \( \sqrt{\sigma} \) are the planar limits based on the internal surface area. The smaller the pores, the larger is the internal surface area. In order to compare the two models, the thickness and porosity of the porous electrode were fixed at \( L = 0.1 \) cm and \( \varepsilon = 0.4 \), respectively.

\[ \frac{1}{\varepsilon} \frac{\partial \theta}{\partial t} = \varepsilon D \frac{\partial^2 \theta}{\partial x^2} - R_O \]

(10)

where \( R_O \) is the rate of consumption of the oxidized species. If the reaction is first-order and irreversible, the rate expression is:

\[ R_O = \frac{a_{fO}}{nF} \frac{c_O}{c_O^0} \exp(-znf(E - E^\circ)) \]

(11)

For convenience in relating the potential to time, the voltage sweep is assumed to start at the formal potential, \( E^\circ \). The results, however, are not affected by the initial potential as long as \( (V_{aj0}) \) is less than 1% of the peak current (assumption 5). In dimensionless form, Eq. (10) may be written as:

\[ \frac{\partial \theta}{\partial \tau} = \frac{\partial^2 \theta}{\partial y^2} - \alpha \sigma \Lambda \theta e^{(x\sigma \tau)} \]

(12)

where \( \theta = (c_O/c_O^0) \). Initially, the concentration in the porous electrode is equal to that in the bulk. Throughout the sweep the flux at the current collector is zero and the flux across the separator is proportional to the gradient at this interface. Mathematically the initial and boundary conditions can be expressed as,

\[ @\tau = 0, \quad \theta = 1, \]

(13)

\[ @y = 0, \quad \frac{\partial \theta}{\partial y} = 0. \]

(14)

\[ @y = 1, \quad \frac{\partial \theta}{\partial y} + h_n \theta = h_m \]

(15)

The governing equation [Eq. (12)] is solved subject to the initial and boundary conditions given in Eqs. (13)–(15). A Green’s function technique is used to solve Eq. (12) analytically [Appendix A]. The solution for the concentration of the oxidized species as a function of time and axial position is:

\[ \theta(y, \tau) \]

\[ = 1 - 2 \sum_{n=0}^{\infty} \left[ \left( \frac{2(\lambda_n^2 + \lambda_n^2)}{(h_m^2 + \lambda_n^2) + h_m^2} \right) \cos(\lambda_n^2) \exp[-\lambda_n^2 \tau] \right. \]

\[ \left. - A \exp(x \sigma \tau) \right] \]

\[ \times \sum_{k=0}^{\infty} \frac{A^{(k+1)}}{k!((i \lambda_n^2/x \sigma) + k + 1)} - 1 \}

(16)

where \( \lambda_n \) is the root of the characteristic equation

\[ \lambda_n \tan(\lambda_n^2) = h_m \]

(17)

The total current is found by integrating the local reaction rate throughout the porous electrode. Therefore, substituting Eq. (16) into the dimensionless form of Eq. (11) and integrating from \( y = 0 \) and \( y = 1 \) gives the following form of the dimensionless current as a function of time.
Fig. 5. Effect of the \( \alpha \sigma \) on the voltammograms for an irreversible reaction with no external mass-transfer resistance. The voltammograms were generated using Eq. (22) (i.e. \( h_m \to \infty \)). The irreversible thin-layer limit was observed at \( \alpha \sigma \to \infty \). Peaks are not observed for \( \alpha \sigma < 20 \) (\( \Lambda = 0.001 \) and \( \alpha = 0.5 \)).

\[
I_{irrev}^* = \frac{I_{p,irrev,TL}}{I_{p,irrev}} = 2.7184 \left[ 1 - 2 \sum_{n=0}^{\infty} \frac{2(h_m^2 + \lambda_n^2)}{(h_m^2 + \lambda_n^2)/\Lambda} \right] \\
\times \frac{1}{\lambda_n} \exp[-\lambda_n^2 \tau - A \exp(\alpha \sigma \tau)] \\
\times \sum_{k=0}^{\infty} \frac{A^{(k+1)}}{k!} \left[ \exp[\alpha \sigma \tau((\lambda_n^2/\alpha \sigma) + k + 1)] - 1 \right]^{-1} \\
\times \exp(\alpha \sigma \tau) \tag{18}
\]

where the current is made dimensionless with respect to the irreversible current in a thin-layer cell [7,8]

\[
I_{p,irrev,TL} = \frac{z n^2 F^2 \nu_e V C_0^0}{2.718RT} \tag{19}
\]

Eq. (18) is a function of three dimensionless parameters, \( \alpha \sigma, A \) and \( h_m \). As stated earlier, for assumption 5 to be satisfied, \((V\delta h_0) \leq 0.01 \ I_{p,irrev} \). In dimensionless terms this corresponds to \( A \leq 10^{-2} \).

In the limit of \( h_m \) approaching infinity (i.e. negligible external mass-transfer resistance), Eqs. (16)–(18) become

\[
\theta(y, t) = 1 - 2 \sum_{n=0}^{\infty} \frac{\sin(\lambda_n y)}{\lambda_n} \exp[-\lambda_n^2 t - A \exp(\alpha \sigma \tau)] \\
\times \sum_{k=0}^{\infty} \frac{A^{(k+1)}}{k!} \left[ \exp[\alpha \sigma \tau((\lambda_n^2/\alpha \sigma) + k + 1)] - 1 \right]^{-1} \tag{20}
\]

where \( \lambda_n = [\pi(n + 0.5)] \)

\[
I_{irrev}^* = 2.7184 \left[ 1 - 2 \sum_{n=0}^{\infty} \frac{1}{\lambda_n^2} \exp[-\lambda_n^2 \tau - A \exp(\alpha \sigma \tau)] \\
\times \sum_{k=0}^{\infty} \frac{A^{(k+1)}}{k!} \left[ \exp[\alpha \sigma \tau((\lambda_n^2/\alpha \sigma) + k + 1)] - 1 \right]^{-1} \right] \exp(\alpha \sigma \tau) \tag{22}
\]

Again, Eq. (22) is valid for \( A \leq 10^{-2} \). Richardson extrapolation [10] was used to speed the convergence of the series found in Eqs. (16), (18), (20) and (22). Experimentally, the external mass-transfer resistance can be made negligible by removing the separator. For reversible kinetics this leads to an infinite current [see Eq. (6)], but for irreversible kinetics, finite currents are obtained at this limit.

3. Results and discussion

3.1. Reversible kinetics

3.1.1. With constant external mass-transfer resistance

As indicated by Eq. (6), the dimensionless voltammogram is a function of two dimensionless parameters, \( (h_m/\sigma) \) and \( \xi \). In practice, \( D_O \approx D_R \) and therefore the results presented here will be for \( \xi = 1 \). Fig. 2 shows the voltammograms for six different values of \( (h_m/\sigma) \). For \( D_O = D_R, h_m \) is the ratio of electrode thickness to separator thickness. As \( h_m \) increases (e.g. separator thickness decreases), the influence diffusion from the bulk has on the voltammogram increases. The parameter \( \sigma \) can be thought of as the ratio of the axial-diffu-
Fig. 6. The effect of \( h_m \) on the voltammograms for an irreversible reaction. The voltammograms were generated using Eqs. (18) and (22). The influence of axial diffusion increases as \( h_m \) increases. The irreversible thin-layer limit as \( \alpha \sigma \rightarrow \infty \) is shown for comparison (\( A = 0.001 \), \( \alpha = 0.5 \), and \( \sigma = 100 \)).

sion time constant to the experimental time constant. Therefore, at large values of \( \alpha \) (e.g. high sweep rates), the experiment is too short for axial diffusion to influence the voltammogram. As \( \alpha \rightarrow \infty \), the first term in Eq. (6) dominates and thin-layer behavior is observed. The dimensionless peak currents tend to unity and the peak potentials tend to the value of the formal potential (i.e. \( E^* \)). At small values of \( \alpha \) (e.g. low sweep rates), axial diffusion across the separator dominates and no peak is observed. The current plateaus to \( (4h_m/\alpha^2) \) as \( E^* \rightarrow -\infty \). This limit is analogous to the current–voltage response on a rotating electrode [11].

The height and position of the peaks in Fig. 2 can be determined by differentiating Eq. (6) with respect to \( E^* \), setting the resultant equation to zero, and solving for \( E^* \). The resulting potential is the peak potential, which for \( \alpha = 1 \) is given as

\[
E^*_{p,rev} = \ln \left( \frac{\alpha^2 - h_m}{\alpha^2 + h_m} \right)
\]

Eq. (23) is undefined for \( \alpha \sigma \leq h_m \). This is consistent with the voltammograms in Fig. 2 in that for \( (h_m/\alpha^2) \) greater than 1.0, no peak is obtained. The peak current is determined by substituting the value of \( E^*_{p,rev} \) from Eq. (23) into Eq. (6), giving

\[
I^*_{p,rev} = \left( 1 + \frac{h_m}{\alpha \sigma} \right)^2
\]

At higher sweep rates, the dimensionless peak current approaches one, which indicates the dominance of thin-layer behavior. In practice, the thin-layer limit may not be observed at high sweep rates due to an excessive ohmic potential drop and/or the onset of radial diffusion. For example, to be within 1% of the thin-layer peak, for \( L = 1 \) mm (with values of other physical parameters as given in Table 1) the sweep rate must be greater than 300 mV s\(^{-1}\). A porous electrode 0.1 mm thick would require sweep rates greater than 30 V s\(^{-1}\).

3.1.2. With variable external mass-transfer resistance

As indicated earlier, Eq. (8) is a function of one dimensionless parameter, \( \varepsilon \sqrt{\alpha} \) as long as \( \xi = 1 \) and \( \gamma \geq 100 \). Fig. 3 shows the voltammograms generated for four different values of \( \varepsilon \sqrt{\alpha} \). In this case (i.e. no separator and no stirring), the external diffusion layer grows in time. The parameter \( \delta \) in Fig. 1 can be thought of as a characteristic length-of-diffusion defined as \( \delta \equiv \sqrt{D_G/f_v} \), which makes \( \sqrt{\alpha} = L/\delta \). As \( \varepsilon \sqrt{\alpha} \rightarrow 0 \), the characteristic length-of-diffusion is large relative to the electrode thickness and the voltammogram approaches that obtained on a planar electrode, with the area being that of the projected area. In this limit, \( I^*_{p,rev} \) approaches infinity and, therefore, this limit is not shown in Fig. 3. The peak current on a porous electrode is within 1% of the planar peak current for \( \varepsilon \sqrt{\alpha} \leq 0.02 \). For \( \varepsilon = 0.4 \), \( (\delta/L) \) must be greater than 20 for a porous electrode to behave like a planar electrode. For example, for \( L = 10 \) \( \mu \)m, \( v \) must be less than 0.3 mV s\(^{-1}\) (with the values of other physical parameters given in Table 1). At \( L = 100 \) \( \mu \)m, \( v \) must be less than 0.003 mV s\(^{-1}\). The latter case in particular is not practical because diffusion layers on the order of centimeters are not stable during an experiment that lasts hours.

As \( \varepsilon \sqrt{\alpha} \rightarrow \infty \), the voltammogram approaches that of a thin-layer cell, with the volume being the void volume
Fig. 7. Effect of $h_m$ on the dimensionless peak currents for an irreversible reaction. The symbols result from the use of Eqs. (18) and (22) to calculate the peak currents, while the solid lines represent the empirical correlations that were fit to the calculations (Eqs. (27)–(29)). As $\alpha \sigma \rightarrow \infty$, the dimensionless peak currents approach the thin-layer value of 1.0.

of the porous electrode. The peak current is within 1% of the thin-layer peak current when $e \sqrt{\alpha}$ is greater than 100. At $L = 10$ and $100 \mu m$, the sweep rates would have to be greater than 1200 and 12 V s$^{-1}$, respectively, for the porous electrode to behave like a thin-layer cell. These requisite sweep rates are usually not practical due to an excessive ohmic potential drop. Therefore, LSVs on porous electrodes in the practical sweep rate range of 1 nV s$^{-1}$ to 1 V s$^{-1}$ usually fall outside the planar and thin-layer limits.

The limiting conditions stated above (i.e. planar and thin-layer behavior, as the sweep rate approaches zero and infinity, respectively) is the exact opposite of that reported previously [9]. Weidner and Fedkiw [9] observed thin-layer behavior at low sweep rates and planar behavior at high sweep rates. In order to reconcile this apparent contradiction, the peak-current results from the two studies are plotted in Fig. 4. The solid line in this figure represents the peak values resulting from the solution to Eq. (8), and the dashed lines are from Weidner and Fedkiw [9]. The dimensional peak currents are multiplied by $(e \sqrt{\alpha}/4)$ in order to see more easily the planar limits at the two ends of the sweep rate spectrum. The planar limits are where the peak current is proportional to the square root of the sweep rate, or $I_{p,rev}^* (e \sqrt{\alpha}/4)$ is constant. The thin-layer limit is where the peak current is proportional to the sweep rate, or $I_{p,rev}^* (e \sqrt{\alpha}/4)$ is proportional to $\sqrt{\alpha}$.

Reconciling the two studies only requires a definition of low and high sweep rates. At very low sweep rates (i.e. very small values of $\sqrt{\alpha}$), the voltammogram is governed by material diffusing from the bulk into the porous electrode. Therefore, Eq. (8), which incorporates axial diffusion, approaches the planar limit based on the projected area of the electrode. In contrast, the dashed line was generated assuming axial diffusion is negligible, and therefore it cannot capture this limit. Weidner and Fedkiw [9], however, consider the microstructure of the pores, and therefore their results approach the planar limit at very high sweep rates. At very high sweep rates, the planar area is based on the internal surface area, a value that increases as the pore size decreases. The overlap in the two models at $d = 1$ and $10 \mu m$ indicates that in the absence of ohmic resistance, neither axial diffusion nor microstructure affect the voltammogram. Therefore, either of the two models will accurately predict the peak current over a moderate sweep rate range.

The asymptotic trends for the solid line in Fig. 4 leads to the following correlation equation for the dimensionless peak currents predicted by Eq. (8).

$$I_{p,rev}^* = \left( \frac{4}{\sqrt{\alpha}} \right) \left( \frac{e \sqrt{\alpha}}{4} \right)^{1.11} + (0.4463)^{1.11}$$

As $\sqrt{\alpha} \rightarrow 0$, $I_{p,rev}^*$ from Eq. (25) approaches the planar limit of $0.4463/(e \sqrt{\alpha}/4)$. As $\sqrt{\alpha} \rightarrow \infty$, $I_{p,rev}^*$ approaches the thin-layer limit of 1.0.

3.2. Irreversible kinetics—constant external mass-transfer resistance

From Eq. (18), the dimensionless voltammograms are a function of the three dimensionless parameters $\alpha \sigma$, $A$, and $h_m$. Figs. 5 and 6 show dimensionless
voltammograms as a function of $\alpha \sigma$ and $h_m$, respectively. For values of $A \leq 10^{-2}$ (i.e. initial currents less than 1% of the peak when the sweep starts at $E^0$), the peak current is independent of $A$. The only effect of $A$ on the voltammogram is to shift the potential by $(1/\alpha n f) \ln(A)$. Therefore, the dimensionless voltammogram is independent of $A$ when the dimensionless potential is defined as

$$E_{p, \text{irrev}}^* = [\alpha n f (E_{\text{irrev}} - E^0) - \ln(A)]$$

(26)

Fig. 5 compares voltammograms at three values of $\alpha \sigma$ with that obtained in a thin-layer cell [7,8] (i.e. $\alpha \sigma \to \infty$). In order to isolate the effect of sweep rate, the external mass-transfer resistance is assumed negligible (i.e. $h_m = \infty$), and Eq. (22) is used to generate the voltammograms. In contrast to the reversible case where no peak is observed for $h_m = 0$, a peak is observed here even in the absence of a separator (i.e. $h_m = \infty$). The peaks in Fig. 5 result from a finite kinetic resistance that prevents an infinite current even when the concentration at the surface of the electrode is equal to that in the bulk. An infinite and finite current in the absence and presence of appreciable kinetic resistance is also predicted at a rotating-disk electrode [11]. As $\alpha \sigma$ decreases, the influence on the voltammogram of material diffusing from the bulk becomes more pronounced. For values of $\alpha \sigma$ below 20, no peaks are observed because the rate of mass transfer from the bulk is sufficient to replenish the reactant consumed in the porous electrode. At higher sweep rates, the voltammogram approaches the thin-layer limit.

Fig. 6 shows voltammograms at three values of $h_m$. The ones at $h_m = 5$ and 50 were generated from Eq. (18), and the one at $h_m = \infty$ was generated from Eq. (22). As $h_m$ increases (e.g. separator thickness decreases), the influence on the voltammogram from material diffusing from the bulk becomes more pronounced.

The effect of $\alpha \sigma$ and $h_m$ on the dimensionless peak currents and peak potentials is summarized in Figs. 7 and 8, respectively. Again, at large sweep rates (i.e. large values of $\alpha \sigma$), the peak values approach those obtained from a thin-layer cell (i.e. $I_{p, \text{irrev}}^* \to 1.0$ and $E_{p, \text{irrev}}^* \to 0.0$). At low sweep rates ($\alpha \sigma < 20$), material diffusing from the bulk dominates and no peak is observed. The influence of axial diffusion is more pronounced as $h_m$ increases. Therefore, at a given value of $\alpha \sigma$, the peak values deviate more from the thin-layer value as $h_m$ increases.

As stated in conjunction with assumption 7, the characteristic length-of-diffusion, $\sqrt{D_0/\alpha n f}$, should be greater than the thickness of the separator, $\delta$, to ensure that the concentration profile across the separator is linear. In dimensionless terms, this translates into $h_m > \sqrt{2\alpha \sigma}$. For example, at $h_m$ equal to 10 and 50, $\alpha \sigma$ should be less than 100 and 2500, respectively, for assumption 7 to hold. Although technically assumption 7 breaks down at high values of $\alpha \sigma$, the simulations should still be accurate over the whole range of $\alpha \sigma$. The reason is that material diffusing from the bulk becomes less significant as $\alpha \sigma$ increases. For example, at $h_m = 10$ and $\alpha \sigma = 100$, material diffusing across the separator in-
creases the peak current by only 7% above the thin-layer current, and at \( h_m = 50 \) and \( \sigma \sigma = 2500 \), the peak current is less than 2% above the thin-layer limit. In practice, therefore, assumption 7 puts a lower limit on \( h_m \), rather than an upper limit on \( \sigma \sigma \). Since a distinguishable peak is not observed for \( \sigma \sigma < 20 \), it is recommended here that \( h_m \geq 5 \) (i.e. the porous electrode should be at least five times thicker than the separator) to ensure a reasonably wide sweep rate range.

The dimensionless peak currents shown in Fig. 7 were correlated to the dimensionless parameters \( \sigma \sigma \) and \( h_m \) using the following empirical relationships

\[
I_{p,irrev}^* = \exp[m_1(\sigma \sigma)^m_3]
\]  
(27)

where

\[
m_1 = \exp[0.255 \exp(-0.0093 h_m) + 0.72]
\]

(28)

and

\[
m_2 = \left[ -0.55 - \frac{4.944}{9.846 + h_m} \right]
\]

(29)

Similarly, the dimensionless peak potentials shown in Fig. 8 were correlated to the \( \sigma \sigma \) and \( h_m \) to give

\[
E_{p,irrev}^* = m_3(\sigma \sigma)^m_4
\]  
(30)

where

\[
m_3 = [1.802 \exp(-0.128 h_m) - 4.682]
\]

(31)

and

\[
m_4 = \left[ -0.642 - \frac{4.048}{11.89 + h_m} \right]
\]

(32)

The parameters \( m_1 \) through \( m_4 \) were found by least-squares fit of the peak values obtained from Eqs. (18) and (22). Forty values of \( \sigma \sigma \) ranging from 10 to \( 10^5 \) at each of the 36 values of \( h_m \) ranging from 5 to \( \infty \) were used to establish these correlations. Figs. 7 and 8 also show the results of applying the above dimensionless correlations juxtaposed with the actual model simulations. The peak currents and peak potentials predicted by the correlations differed from those obtained from the model by 1 and 2%, respectively.

3.3. Methodology to extract the kinetic constants of an irreversible reaction

In this section, a methodology is developed that will serve two purposes; (a) test the correlations developed in the previous section, and (b) illustrate how the correlations can be used in practice to extract the kinetic parameters from experimental data. To this end, Eqs. (27) and (30) are made dimensional to give

\[
I_{p,irrev} = \left( \frac{z n^2 F c v V_c \alpha^0}{2.718} \right) \exp\left[ m_1 \left( \frac{z n f v L^2}{D_\Omega} \right)^{m_2} \right]
\]

(33)

and

\[
E_{p,irrev} = E^0 + \frac{1}{z n f} \ln \left( \frac{a_{\Omega}}{z n^2 F c v V_c^0} \right) + m_3 \left( \frac{z n f v L^2}{D_\Omega} \right)^{m_4}
\]

(34)

Using the parameter values in Table 1, and the \( \sigma \) and \( a_{\Omega} \) combinations in Table 2, peak-current and peak-potential data were simulated using Eq. (22) for sweep rates ranging from 0.5 to 8 mV s\(^{-1}\). The parameters \( \sigma \) and \( a_{\Omega} \) were then found by least-squares fit of Eqs. (33) and (34) to this simulated data. The error in the estimation of \( \sigma \) is always less than 3.5% while the error in the estimation of \( a_{\Omega} \) is less than 2%. The results of these fits are summarized in Table 2, and the peak values and the best fit curve for \( \sigma \) and \( a_{\Omega} \) of 0.5 and \( 10^{-6} \) A cm\(^{-3}\), respectively, are shown in Figs. 9 and 10. For comparison purposes, the corresponding thin-layer line is shown in Figs. 9 and 10. The results in Table 2 and Figs. 9 and 10 demonstrate the validity of using the above correlations to extract the kinetic parameters.

4. Conclusions

A theoretical analysis of LSV in flooded-porous electrodes is treated for reversible (Nernstian) and first-order irreversible reactions. Reversible kinetics were used to understand the influence external mass-transfer resistance has on the voltammogram. For irreversible kinetics, it was shown how the Green’s function analytical technique was employed to solve the governing equations in terms of electrode dimensions, sweep rate and density.
the reaction kinetics. The analytical solution is used to develop correlations that enable the kinetic parameters (i.e. exchange current density per unit volume and the transfer coefficient) to be easily extracted from experimental data. The methodology to extract the kinetic parameters was developed and demonstrated. It was shown that, under ideal conditions, \( \alpha \) and \( \alpha_j \) can be obtained within 3.5 and 2\%, respectively. Experimental error will increase this uncertainty, but the methodology proposed here is superior to relying on analyses developed for planar electrodes and thin-layer cells.

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**Appendix A**

In this appendix the steps leading to the solution given by Eq. (16) are provided. For further details on the Green technique see Ref. [12]. The first step is to apply the adjoint linear operator and the bilinear comitant to the governing equation to obtain the following Green’s function problem

\[
-\frac{\partial \tilde{G}}{\partial \tau} + A \pi \sigma \tilde{G} \exp(z \sigma \tau) - \frac{\partial^2 \tilde{G}}{\partial y^2} = \delta(y - y_0) \delta(\tau - \tau_0)
\]  

subject to the following initial and boundary conditions

\[
\begin{align*}
@ \tau = 0, & \quad \tilde{G} = 0 \\
@ y = 0, & \quad \frac{\partial \tilde{G}}{\partial y} = 0 \\
@ y = 1, & \quad h_m \tilde{G} + \frac{\partial \tilde{G}}{\partial y} = 0
\end{align*}
\]  

where \( \delta(\tau - \tau_0) \) and \( \delta(y - y_0) \) represent the Dirac delta functions. The concentration is related to the Green’s function solution by

\[
\theta(y, \tau) = 1 - \int_0^\tau \int_0^y A \pi \sigma \exp(z \sigma \tau) \tilde{G}(y, t; y_0, \tau_0) \, dy_0 \, d\tau_0
\]  

Using separation of variables, the eigen functions are determined by assuming \( \tilde{G}(y, \tau) = X(y)T(\tau) \). Therefore, the Green’s function problem is rewritten as,

\[
-\frac{T'('}{T(')} + A \pi \sigma \exp(z \pi \tau) \frac{X''(y)}{X(y)} = -\lambda^2
\]  

where the prime and double prime represent the first and second derivatives, respectively. Since the left-hand side is a function only of \( \tau \), and the right-hand side is a function only of \( y \), \( \lambda \) must be a constant. Therefore, the
two differential equations can be integrated individually to give

\[ T(\tau) = A_1 \exp[\lambda^2 \tau + \lambda x \sigma \exp(\lambda x \sigma)] \]  
\[ X(y) = B_1 \sin(\lambda y) + B_2 \cos(\lambda y) \]  

The boundary condition at \( y = 0 \) requires \( B_1 = 0 \). The non-trivial solution to the boundary condition at \( y = 1 \) gives the eigen values, \( \lambda_n \), as the roots to the following equation:

\[ \lambda_n \tan(\lambda_n) = h_m \]  

Combining Eqs. (A7) and (A8) gives the solution to the partial Green’s function as

\[ \tilde{G}(y, \tau) = \sum_{n=0}^{\infty} A_n \exp[\lambda_n^2 \tau + \lambda x \sigma \exp(\lambda x \sigma)] \cos(\lambda_n y) \]  

(A10)

The product of the two constants \((A_1B_2)\) has been replaced by the infinite set of constants \(A_n\). Applying the initial condition and the properties of orthogonality gives the following expression for the remaining set of constants \(A_n\):

\[ A_n = \frac{(\lambda_n^2 + h_m^2) + h_m}{2(\lambda_n^2 + h_m^2)} \]  

(A11)

The above process is repeated for the dummy variables, \( y_0 \) and \( \tau_0 \) so that the respective Dirac delta functions satisfy the relation,

\[ \int_0^\infty \delta(\tau - \tau_0) \, d\tau_0 = 1 \quad \text{and} \quad \int_0^\infty \delta(y - y_0) \, dy_0 = 1 \]  

(A12)

This yields the Green’s function solution found in Eq. (A5) as

\[ \tilde{G}(y, \tau | y_0, \tau_0) = \sum_{n=0}^{\infty} A_n u(\tau_0 - \tau) \exp[\lambda_n^2 (\tau - \tau_0)] \cos(\lambda_n y_0) \cos(\lambda_n y) \]  

(A13)

where \( u(\tau - \tau_0) \) is the unit step function. Substituting Eq. (A13) into Eq. (A5) results in an integral of the form \( \int \exp(at + e^{bt}) \, dt \). Since this cannot be integrated analytically, the following identity

\[ \exp(e^{bt}) = \sum_{k=0}^{\infty} \frac{\exp(kbt)}{k!} \]  

(A14)

is used to get Eq. (16).

**Appendix B. Nomenclature**

- \( a_{j_0} \): exchange current density per unit volume, A cm\(^{-3}\)
- \( A \): electrode area, cm\(^2\)
- \( c_i \): concentration of species \( i \), mol cm\(^{-3}\)
- \( c_i^0 \): initial concentration of species \( i \), mol cm\(^{-3}\)
- \( d \): pore diameter, cm
- \( D_i \): diffusion coefficient of species \( i \), cm\(^2\) s\(^{-1}\)
- \( D_i' \): effective diffusion coefficient of species \( i \), cm\(^2\) s\(^{-1}\)
potential difference between working and reference electrode, V
formal potential, V
equilibrium potential, V
dimensionless potential, \( \eta F(E - E^o) \)
dimensionless potential (see Eq. (26))
\( F/RT \), V \(^{-1} \)
Faraday’s constant, 96487 C mol\(^{-1} \)
dimensionless mass-transfer coefficient, \( (D_O L/D_O \delta) \)
current, A
dimensionless current, \( (I/I_{TL}) \)
electrode length, cm
number of e\(^-\) in redox couple
flux of species \( i \), mol cm\(^{-2} \) s\(^{-1} \)
universal gas constant, 8.314 J mol\(^{-1} \) K\(^{-1} \)
rate of consumption of O, mol cm\(^{-3} \) s\(^{-1} \)
time, s
temperature, K
volume of porous electrode, cm\(^3 \)
axial distance in the pore, cm
dimensionless axial distance in the pore, \( (x/L) \)
cathodic transfer coefficient
initial concentration ratio, \( (c_O^0/c_R^0) \)
external diffusion layer or separator thickness, cm
porosity of electrode
dimensionless concentration, \( (c_O^0/c_R^0) \)
eigen values

v
\( \eta \)
\( \sigma \)
\( \tau \)
\( \sqrt{\pi}/\lambda_{irrev} \)
sweep rate, Vs\(^{-1} \)
diffusion coefficient ratio, \( (D_O/D_R) \)
dimensionless sweep rate, \( (\eta F L^2/D_O) \)
dimensionless time, \( (tD_O/L^2) \)
dimensionless planar peak current, \( I/\eta F c_O^0/\eta F v D_O \)
irreversible kinetics
oxidized species
value at peak of voltammogram
planar value
reversible kinetics
reduced species
value of parameter at pore mouth
thin-layer value

References