Numerical Analysis of the Steady-State Behavior of CE Processes in Rotating Disk Electrode Systems

P. H. M. Leal, O. N. A. Leite, P. R. P. Viana, F. V. V. de Sousa, O. E. Barcia, and O. R. Mattos

1 Laboratory of Non-Destructive Testing, Corrosion and Welding, Federal University of Rio de Janeiro, 21941-596 Rio de Janeiro, Brazil
2 Federal Institute of Education, Science and Technology of Rio de Janeiro, 25050-100 Duque de Caxias, Brazil
3 Physical-Chemistry Department/UQ, Federal University of Rio de Janeiro, 21941-909 Rio de Janeiro, Brazil

This paper presents a numerical analysis of the chemical-electrochemical (CE) mechanism of a rotating disk electrode at steady-state. Two sets of kinetic constants (denominated “fast kinetics” and “slow kinetics”) were used to evaluate how they alter the original concentration profiles and the current response. Comparing the results obtained with those in the literature allows concluding that the range of validity of the reaction layer hypothesis, although able to accurately predict the current density in some cases, is intrinsically limited, because it will always fail for sufficiently high rotation speeds. Hence, a system with “fast kinetics” is merely one in which the hypothesis is applicable for all the rotation speeds that were studied. It was also observed that the range of validity of the reaction layer hypothesis is independent of the equilibrium constant of the chemical process and is determined solely by the absolute values of the kinetic constants.

© The Author(s) 2018. Published by ECS. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, http://creativecommons.org/licenses/by/4.0/), which permits unrestricted reuse of the work in any medium, provided the original work is properly cited. [DOI: 10.1149/2.0501809jes]

Manuscript submitted March 30, 2018; revised manuscript received May 14, 2018. Published June 5, 2018.

One of the great advantages of working with rotating disk electrodes (RDE) is the abundance of literature dedicated to a rigorous assessment of their theoretical bases. Indeed, since the first works by Levich, whose main ideas have been compiled in his seminal book,1 many of the hypotheses of the RDE-system have been revisited to assess their validity and were either confirmed by experimental observation (e.g., the uniform accessibility of the electrode on the limiting current density plateau2,3) or by a numerical proof that the errors they introduced were negligible (e.g., the absence of radial diffusion)4. This adds an extra-layer of confidence for the experimentalist as it is possible to clearly identify deviations from the initial assumptions through a quick analysis of experimental data. More importantly, one can be sure that, when operating under well-defined conditions,5,6 all of these hypotheses are correct within a high degree of confidence.

Unfortunately, such a level of certainty can only be achieved for systems in which neither kinetic complications at the electrode interface nor bulk reactions capable of affecting the concentration profiles occur. Indeed, for the latter, a chemical reaction A ≈ B in the bulk followed by an electrochemical step A + e− → C at the interface was analytically treated, but only under one additional hypothesis: there is a region near the electrode surface, namely the reaction layer, whose thickness (δR) is much smaller than that of the diffusion layer (δD).

As shown in Figure 1, chemical equilibrium is not kept inside the reaction layer because of the consumption of A at the electrode. Outside this layer, and up to the solution bulk, the concentrations of all species involved in reversible chemical reactions are in equilibrium. Consequently, the reaction layer must be thinner than the diffusion layer. This allowed Koutecký and Levich to separate the problem into two regions and derive the steady-state limiting current density of simple CE processes (like the one we describe in this paper) in the case of equal diffusion coefficients for A and B species (iKL).7,8 Later on, Dogonadze extended the same approach to unequal diffusion coefficients (iDKL), thus generalizing the results, whose main features we now present.9,10

\[
\begin{align*}
A & \approx B \\
A + e^- & \rightarrow C
\end{align*}
\]

In these equations, \(i_{KL}\) denotes the limiting current density derived by Koutecký and Levich, \(i_{DKL}\) the one derived by Dogonadze, \(C_A^b\) the molar concentration of species X in the solution bulk (mol m\(^{-3}\)), \(v\) stands for the kinematic viscosity (m\(^2\) s\(^{-1}\)), \(S_{CA} = \frac{\nu}{D}\) for the Schmidt number of species i, \(\Omega\) is the rotation speed of the electrode (Hz), \(D_{eff} = \frac{D_A k_A + D_B k_B}{D_A k_A + D_B k_B}\) and the remaining terms have their usual meaning.

It must be emphasized that there is no physical need for \(\delta_D\) being much larger than \(\delta_R\). In fact, there is no easy relationship between the diffusion layer and the reaction layer, because these concepts arise from completely independent physical conditions: the former being related to the region within which species are transported mainly via diffusion, while the latter is related to the region within which reversible reactions are no longer in chemical equilibrium due to the consumption of A at the electrode. Clearly, these definitions do not mandate that the reaction layer must be thinner than the diffusion layer and, therefore, confined within it. In fact, for a given reaction system, it might be either thicker or thinner, depending on the experimental conditions. Indeed, \(\delta_D\) is a function of the rotation speed and might be varied experimentally, while \(\delta_R\) depends solely on the species involved and on the chemical kinetics. Thus, for a given rotation speed \(\Omega\), the inequality \(\delta_D > \delta_R\) might be true but, for a sufficiently higher rotation, the inverse may also be true. Nevertheless, Figure 1 shows that the reaction layer hypothesis assumes that \(\delta_D \gg \delta_R\) is always valid for a

---

\(i_{KL} = \frac{FD (C_A^b + C_B^b)}{\delta_D + K \sqrt{\frac{D}{k_A + k_B}} \frac{1}{\delta_D}} [2]

\(i_{DKL} = \frac{FD_{eff} (C_A^{b} + C_B^{b})}{\delta_{eff} + K \frac{D_B}{D_A} \sqrt{\frac{D_A D_B}{D_B k_A + D_A k_B}} \frac{1}{\delta_R}} [3]

\(\delta_D = \sqrt{\Omega \left[ 1.611(S_{CA})^{-1} + 0.480(S_{CA})^{-1.5} + 0.234(S_{CA})^{-1} \right]} [4]

---

\* Electrochemical Society Student Member.

\(\delta_{eff} = \delta_D (\frac{D_{eff}}{D_A})^{1/3}\) and the remaining terms have their usual meaning.

---

Manuscript submitted March 30, 2018; revised manuscript received May 14, 2018. Published June 5, 2018.
The adoption of the reaction layer hypothesis leads to the conclusion that the reaction layer hypothesis is inconclusive. Besides, given that the reaction layer hypothesis is inconclusive, the rate constant values for which the applicability of the reaction layer hypothesis takes place in a RDE-system, beyond the usual hypotheses necessary to the solution of the Navier-Stokes equations and for the classical RDE-system, the following conditions are imposed,

- Chemical equilibrium is attained at the solution bulk;
- Only the species A is electroactive, i.e.:
  \[ A \leftrightarrow B \]
  \[ k_A \frac{C_B}{C_A} = k_B \]
- Species C does not interact with either A or B;
- The system operates under limiting current conditions;

Under such conditions, we can write the convection-diffusion-reaction equations for both A and B:

\[
\begin{align*}
D_A \frac{d^2 C_A}{dy^2} - v_y \frac{dC_A}{dy} + (k_B C_B - k_A C_A) &= 0 \\
D_B \frac{d^2 C_B}{dy^2} - v_y \frac{dC_B}{dy} - (k_B C_B - k_A C_A) &= 0
\end{align*}
\]

where \( v_y \) corresponds to the electrolyte velocity in the axial direction. We now apply the boundary conditions:

At the solution bulk (\( y \to \infty \)):

\[
\begin{align*}
C_A (y \to \infty) &= C_A^0 \\
C_B (y \to \infty) &= C_B^0 \\
K &= \frac{C_B^0}{C_A^0} = \frac{k_A}{k_B}
\end{align*}
\]

At the electrode surface (\( y = 0 \))

\[
\begin{align*}
C_A (0) &= 0 \\
\frac{dC_B}{dy} \bigg|_{y=0} &= 0
\end{align*}
\]

The limiting current density is calculated as:

\[
i_{lim} = F D_A \frac{dC_A}{dy} \bigg|_{y=0}
\]

The next step involves a change of variables first proposed by von Kármán to solve the Navier-Stokes equations pertinent to this problem:

\[
\xi = y \sqrt{\frac{\Omega}{v_y}}
\]

In doing so, we can also substitute \( v_y \) by a dimensionless function, \( H(\xi) \), whose values in the vicinities of the electrode surface can be accurately described by a power series of \( \xi \):

\[
H(\xi) = -0.5102312k_2^{\frac{3}{2}} + \frac{\xi^3}{3} - \frac{0.615922}{6} \xi^4
\]

\[
v_y = (\nu \Omega)^{\frac{1}{2}} H(\xi)
\]

The decision to use three terms for the dimensionless velocity profile aims to improve the precision of the calculations. After the change of variables, the initial equations now become:

\[
\begin{align*}
\frac{d^2 C_A}{d\xi^2} - H(\xi) S_B \frac{dC_A}{d\xi} + \frac{S_A}{\Omega} (k_B C_B - k_A C_A) &= 0 \\
\frac{d^2 C_B}{d\xi^2} - H(\xi) S_A \frac{dC_B}{d\xi} - \frac{S_B}{\Omega} (k_B C_B - k_A C_A) &= 0
\end{align*}
\]
With the new set of boundary conditions:
At the solution bulk ($\xi \to \infty$):
\[
\begin{align*}
C_A (\xi \to \infty) &= C_A^b \\
C_B (\xi \to \infty) &= C_B^b \\
K &= \frac{C_B^b}{C_A^b} = \frac{k_A}{k_B} \quad [14]
\end{align*}
\]
At the electrode surface ($\xi = 0$):
\[
\begin{align*}
C_A (0) &= 0 \\
\left. \frac{dC_B}{dx} \right|_{x=0} &= 0 \quad [15]
\end{align*}
\]

This formulation has the immediate advantage of showing the asymptotic limits that the reaction layer hypothesis fails to point out. Indeed, for the limit $\Omega \to \infty$, the term $\pm \frac{\partial C_A}{\partial x} \cdot \frac{k_B C_B - k_A C_A}{\Omega}$ will vanish and the system will behave as if there were no chemical reactions. On the other hand, for the limit $\Omega \to 0$, the equations may be rewritten as:
\[
\begin{align*}
\left( \frac{d^2 C_A}{dx^2} - H (\xi) \frac{\partial C_A}{\partial x} \right) \frac{\partial C_A}{\partial x} + (k_B C_B - k_A C_A) &= 0 \\
\left( \frac{d^2 C_B}{dx^2} - H (\xi) \frac{\partial C_B}{\partial x} \right) \frac{\partial C_B}{\partial x} - (k_B C_B - k_A C_A) &= 0 \quad [16]
\end{align*}
\]

In this scenario, concentration profiles will tend toward equilibrium values except in regions with considerably high gradients (essentially, very close to the electrode surface), which is basically a restatement of the reaction layer hypothesis.

**Discretization procedure.**—The finite difference method was employed to discretize the equations in a linear grid applying derivative approximations of second order.\(^{17}\) This led to the following linearized equations:
\[
\begin{align*}
2 + (S_C A)(\Delta \xi) H^I C_A^{i+1} &= \left[ \frac{2 \Omega (S_C A)(\Delta \xi)^2 k_A}{\Omega (\Delta \xi)^2 + 2 - (S_C A)(\Delta \xi) H} \right] C_A^{i} \\
&+ \frac{k_B (S_C B)(\Delta \xi)^2}{\Omega} C_B^{i} \quad [17]
\end{align*}
\]
where $X^i$ corresponds to the value of $X$ at the node $i$ and $\Delta \xi$ corresponds to the spacing between nodes.

Boundary conditions were considered to apply at points $i = 0$ (for the electrode surface) and $i = N + 1$ (for the solution bulk). After discretization, they can be written as:
At the solution bulk ($i = N + 1$):
\[
\begin{align*}
C_A^{N+1} &= C_A^b \\
C_B^{N+1} &= C_B^b \\
K &= \frac{C_B^b}{C_A^b} = \frac{k_A}{k_B} \quad [18]
\end{align*}
\]
At the electrode surface ($i = 0$):
\[
\begin{align*}
C_A^0 &= 0 \\
C_B^0 &= 4 \frac{C_A^b}{3} - \frac{1}{3} C_B^b \quad [19]
\end{align*}
\]

**Numerical solution.**—The values of the kinematic viscosity ($\nu = 10^{-6} \text{ m}^2 \text{s}^{-1}$) and of the diffusion coefficients ($D_A = 9 \times 10^{-9} \text{ m}^2 \text{s}^{-1}$ and $D_B = 2 \times 10^{-9} \text{ m}^2 \text{s}^{-1}$), were selected according to usual values reported in the literature for aqueous solutions.\(^{14,18,19}\) Rotation speed values varied between 0.5 and 50 Hz and several different $k_A/k_B$ combinations (presented in Table I) allowed $K$ to vary from $10^{-3}$ up to $5 \times 10^4$. The value of $C_A^0$ was fixed at 1 mol m$^{-3}$ and $C_B^0$ was calculated by setting $C_B^0 = \frac{\Delta \xi}{A} C_A^b$.

Since one of the boundary conditions was set at infinity, the total length of the $x$-axis had to be long enough to allow attainment of asymptotic concentrations. A trial-and-error procedure indicated that setting the maximum distance as three times the largest diffusion layer thickness (either $A$'s or $B$'s) met this requirement.

The discretized equations constituted a tridiagonal system of $N$ linear equations that was solved using the Thomas algorithm.\(^{17}\) The system was solved iteratively, with the initial guess for $C_A$ being its concentration profile in the absence of volume reactions and that of $C_B$ set to 1, except on the boundaries. The main stopping criterion was the maximum difference between any two successive iterations ($\varepsilon$), which had to satisfy the inequality:
\[
\varepsilon = \max_{1 \leq i \leq N} \left| C_A^{i+1} - C_A^i \right| \leq 10^{-15} \quad [20]
\]
Alternatively, on occasions in which the algorithm was incapable of bringing the error down to this margin, the loop stopped after $\varepsilon$ repeated its value 1000 times (not necessarily in sequence).

Finally, the limiting current density ($A \text{ m}^{-2}$) was calculated as follows:
\[
i_{\text{lim}} = F D_A \left( \frac{4 C_A^b - 3 C_A^b - 3 C_A^b}{2 \Delta \xi} \right) \sqrt{\nu} \quad [21]
\]

**Validation of the numerical scheme.**—To validate the methodology, we simulated two different systems; one with no volume reactions and another with very low rate constants (with an equilibrium constant of $10^{-3}$), so as to make the effects of chemical reactions negligible. These results should agree very closely with analytical calculations using the well-known Levich equation ($i_{\text{lim}} = \frac{F D_A C_A^b }{b \nu}$). Figure 2 shows the close agreement between both analytical and numerical solutions.

![Figure 2](image-url)
of the RDE system with and without reaction, thus proving the adequacy of the procedure.

Convergence was assessed in three different ways, following the criteria established by Katelhön and Compton. On the extremes of either very high or very low reaction rate constants, simulated current densities obtained for a set of different grid spacings were compared to the analytical expressions. Figure 3 shows that convergence was attained for both cases, but since the value of $\delta K$ decreased remarkably with the increase of the reaction rate constants, a subsequent decrease of $\Delta \xi$ was necessary to properly assess the derivative at the electrode surface, which also means a huge increase of node points. For nearly absent homogeneous reactions, convergence was attained for a grid of as few as 100 nodes ($\Delta \xi \approx 10^{-2}$). On the other hand, for extremely fast kinetics, e.g. $k_A = 1.5 \times 10^5$ and $k_B = 3$, at least 50000 nodes were used ($\Delta \xi \approx 2 \times 10^{-5}$). In the case of intermediary reaction rate constant values, no analytical solutions are available, so our approach was to reduce $\Delta \xi$ to a range in which there was minimal ($< 0.1\%$) variation of the current density with further refining of the grid. Typically, values of $\Delta \xi$ varied between $10^{-3}$ (1000 nodes) and $2 \times 10^{-5}$ (5000 nodes) as depicted in Figure 4. Lastly, we also evaluated the total number of molecules ($n_A + n_B$) for different grid spacings (see Figure 5). The values of $n_A$ and $n_B$ were obtained via integration of the concentration profiles along the $\xi$-axis. It is clear that a refinement of the grid leads to a constant value of molecules, which serves as additional evidence of the convergence of the numerical scheme.

**Fast kinetics.---** As Figure 6 shows, rate constants of the order of $10^2$ s$^{-1}$ are high enough to justify the use of the reaction layer hypothesis and an excellent agreement between analytical and numerical results was found. Also, it is worth noticing that the curves for $K = 1$ and $K = 10$, Figures 6a and 6b, could be mistaken for a system without chemical reactions. As a matter of fact, when subject to linear regression with intercept at the origin, both curves showed $R^2 > 0.999$. This demonstrates how careful one must be when making inferences about the behavior of a system based on fitting procedures and linear regressions. A linear relation between the limiting current density and $\Omega^{1/2}$ in an unknown system does not imply the absence of chemical reactions and that a simple classical diffusion-convection process is taking place.

This large agreement is better understood with the additional data of normalized $C_A/C_B$ values throughout the solution. Indeed, Figure 7 shows that chemical equilibrium is attained within a few steps from the electrode and at distances much smaller than the diffusion layer thickness, validating the reaction layer hypothesis.

We also compared our results with the limiting current density derived by Koutecký and Levich, i.e., assuming equal diffusion coefficients for both species. Even though we already expected different results, we hoped a graphical comparison would provide important qualitative information. Two scenarios were considered and consisted in assigning either the previous value of $D_A$ or that of $D_B$ to both species (Figure 8). As expected, the results with unequal coefficients are bounded by those with equal ones and all three curves behave very
Figure 6. $i_{\text{lim}}$ vs $\Omega^{1/2}$ for a system with fast kinetics: a) $K = 1$; b) $K = 10$; c) $K = 100$; d) $K = 5 \times 10^4$.

Figure 7. Normalized values of $C_A/C_B$ vs $\xi$ for different values of $K$ ($\Omega = 10$ Hz).

Figure 8. $i_{\text{lim}}$ vs $\Omega^{1/2}$ for different diffusion coefficients but equal kinetic parameters. Results from our procedure are presented with black marks. ($k_A = 5 \times 10^2$ s$^{-1}$, $k_B = 5 \times 10^2$ s$^{-1}$).

Figure 9. $(i_{\text{lim}})^{-1}$ vs $\Omega^{-1/2}$ for the system presented at Figure 5 with two different diffusion coefficients.

Similarly, hence, it seems it is not possible to tell if the assumption of equal coefficients is valid just by looking at the data and a fitting procedure should be employed.

Another error that must be avoided is assigning a physical meaning to extrapolations of the inverse of the current density toward the ordinate axis. For instance, if we use the same data presented in Figure 8 to draw a graph for $(i_{\text{lim}})^{-1}$ vs $\Omega^{-1/2}$, we see a line whose intercept is close but not equal to zero (see Figure 9). However, adding new data for higher rotation speeds readily shows that there is a change of the slope in the curve (see Figure 10). This new region, whose extrapolation intercepts the graph’s origin, represents a transition to a concentration profile independent of chemical reaction effects.
Slow kinetics.— The results seen in Figure 11 show good agreement between numerical and analytical solutions for low rotation speeds. These results were not unexpected because it was already outlined that lowering the rotation speed increases the diffusion layer thickness while leaving the reaction layer unaltered, therefore the latter will be eventually thinner than the former. On the other hand, doubling or tripling the rotation speed may be enough to invert this scenario, causing the deviations observed. The numerical solution also shows, for high rotation speed, the classical Levich behavior - as seen for fast kinetics. However, systems of slow kinetics exhibit this transition at low $\Omega$ values. In this case, the plot of $(i_{\text{lim}})^{-1} \propto \Omega^{-1/2}$ does not always display a straight line with non-zero intercept at the ordinate axis and the use of any approximate theory to describe the whole curve is doubtful.

The difference in behavior between fast and slow kinetics is clear in the results presented in Figure 12 for equilibrium constant with equal values. The agreement between the numerical and analytical results in the case of fast kinetics ($k_A = 500 \text{ s}^{-1}$) is maintained up to high rotation speeds. As for systems with slow kinetics ($k_A = 5 \text{ s}^{-1}$), deviations occur at much lower rotation speeds.

Conclusions

We have successfully developed a numerical procedure to calculate steady-state concentration profiles of CE processes in the RDE-system. Results were validated in both asymptotic limits, i.e., in cases in which the chemical step is negligible (Levich theory) and in cases of high interference of the chemical processes on the concentration profile (reaction layer hypothesis).

It was shown that the reaction layer hypothesis fails to describe the limiting current density in the limit of high rotation speeds because it neglects convection effects which help to create concentration gradients in the diffusion layer that surpass those in the reaction layer. In this sense, a system with “fast kinetics” is one in which the theory of the reaction layer remains valid up to very high rotation speeds. Under these conditions, the plot $(i_{\text{lim}})^{-1} \propto \Omega^{-1/2}$ obtained from experimental data will always show the presence of a line that does not intercept the origin. However, this extrapolation to infinite rotation speeds does not have a real physical meaning, because the fundamental hypothesis of the reaction layer theory, ($\delta_D \gg \delta_R$), is no longer valid. Indeed, the thickness of the reaction layer becomes larger than that of the diffusion layer. In the case of slow kinetics, the reaction layer theory
fails in a range of rotational speeds that are usually experimentally accessible and, hence, no proper fitting can be performed.

Acknowledgments

P. H. M. Leal and P. R. P. Viana thank the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) for their doctoral scholarships. N. A. Leite thanks the Fundação Carlos Chagas Filho de Amparo à Pesquisa do Estado do Rio de Janeiro (FAPERJ) for her postdoctoral scholarship.

List of Symbols

| Symbol | Description |
|--------|-------------|
| $C_i$  | Molar concentration of species $i$ (mol/m$^3$) |
| $C_b^i$ | Molar concentration of species $i$ in the solution bulk (mol/m$^3$) |
| $D_i$  | Diffusion coefficient of species $i$ (m$^2$/s) |
| $i$    | Current density (A/m$^2$) |
| $i_{lim}$ | Limiting current density (A/m$^2$) |
| $k_i$  | Reaction constant of species $i$ (s$^{-1}$) |
| $K$    | Equilibrium constant |
| $S_i$  | Schmidt number of species $i$ |

Greek

| Symbol | Description |
|--------|-------------|
| $\delta_D$ | Diffusion layer thickness (m) |
| $\delta_R$ | Reaction layer thickness (m) |
| $\Omega$ | RDE rotating speed (Hz) |
| $\nu$  | Kinematic viscosity (m$^2$/s) |

ORCID

P. H. M. Leal https://orcid.org/0000-0001-9414-1303
O. R. Mattos https://orcid.org/0000-0003-1551-0997

References

1. V. G. Levich, *Physicochemical hydrodynamics*, 1st ed., Prentice-Hall, Englewood Cliffs, (1962).
2. T. F. Kassner, *J. Electrochem. Soc.*, 114, 689 (1967).
3. S. E. Beacom, J. Robert, and N. Hollyer, *J. Electrochem. Soc.*, 109, 495 (1962).
4. W. H. Smyrl and J. Newman, *J. Electrochem. Soc.*, 118, 1079 (1971).
5. C. M. A. Brett and A. M. C. F. Oliveira-Brett, in *Comprehensive chemical kinetics*, C. H. Bamford and R. G. Compton, Editors, vol. 26, p. 355, Elsevier Science (1986).
6. F. Opek and P. Beran, *J. Electroanal. Chem. Interfacial Electrochem.*, 69, 1.
7. J. Koutecký and V. G. Levich, *Zhurnal Fiz. Khimii*, 32, 1965 (1958).
8. S. Rebouillat, M. E. G. Lyons, and T. Bannon, *J. Solid State Electrochem.*, 3, 215 (1999).
9. R. R. Dogonadze, *Zhurnal Fiz. Khimii*, 32, 2437 (1958).
10. Y. V. Tolmachev and D. A. Scherson, *J. Phys. Chem. A*, 103, 1572 (1999).
11. J. M. Hale, *J. Electroanal. Chem.*, 6(3), 187 (1963).
12. J. M. Hale, *J. Electroanal. Chem.*, 8(5), 332 (1964).
13. R. G. Compton, M. E. Laing, D. Mason, R. J. Northing, and P. R. Unwin, *Proc. R. Soc. A Math. Phys. Eng. Sci.*, 418, 113 (1988).
14. R. G. Compton and R. G. Harland, *J. Chem. Soc. Faraday Trans. 1 Phys. Chem. Condens. Phases*, 85, 761 (1989).
15. T. von Kármán, *Zeitschrift für Angew. Math. und Mech.*, 232 (1921).
16. W. G. Cochran and S. Goldstein, *Math. Proc. Cambridge Philos. Soc.*, 30, 365 (1934).
17. D. Britz and J. Strutwolf, *Digital simulation in electrochemistry*, 4th ed., p. 402, Springer, (2016).
18. R. P. Bell and W. J. Albery, in *Proceedings of the Chemical Society*, p. 169–170 (1963).
19. E. Kåtelhönn and R. G. Compton, *Analyst*, 140, 2592 (2015).