Hydrodynamics and mass-transfer-limited current distribution for a submerged stationary hemispherical electrode under jet impingement

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Abstract

The stationary hemispherical electrode under a submerged impinging jet is suggested as an experimental system that is amenable to in situ observation and has a uniform current distribution below the mass-transfer-limited value. The present work provides solutions for the steady-state boundary-layer hydrodynamics and convective diffusion. The observation of a boundary layer separation in the present work suggests that the model for convective diffusion impedance for this system must account for both the circulation region which follows the point of boundary layer separation and the boundary layer region itself. The present work is intended to provide a foundation for the design of stationary hemispherical electrode systems and for development of models for the corresponding impedance response.

Keywords: Mass transfer; Fluid mechanics; Current distribution; Impedance spectroscopy; Electrochemical kinetics; Experimental techniques

1. Introduction

Interpretation of electrochemical measurements is facilitated when experiments are conducted under well-defined and easily characterized flow conditions. Such experimental systems as the rotating disk electrode (RDE) [1] and the stationary disk electrode under a submerged impinging jet [2,3] have been used extensively in electrochemical investigations. The rotating and impinging jet disk electrode geometries are attractive because an accurate solution is available for convective diffusion, and the current distribution is uniform under mass-transfer-limited conditions.

Experimental investigations of electrochemical reaction mechanisms, however, are not generally conducted under mass-transfer limitation. The current and potential distribution on a disk electrode below the mass transfer limited current is not uniform, [4–6] and it has been shown that neglect of the nonuniform current distribution introduces error in estimation of kinetic parameters from steady state (dc) measurements. [7–9]

Even the most complete expressions available for convective diffusion impedance on a rotating disk electrode [10,11] or on a disk electrode under a submerged impinging jet [12] assume that the system may be treated as having a uniform current distribution. Numerical calculations presented by Appel and Newman [13] and Durbha et al. [14] demonstrated the influence of a non-uniform current distribution on the impedance response. Orazem et al. [15] suggested that the discrepancy between experimental measurements and a detailed mathematical model was due at least partially to the influence of the non-uniform current distribution seen below the mass transfer limit. This claim was discussed further by Orazem and Tribollet [11]. Matos et al. [16] have shown experimentally that the impedance response on a disk electrode was substantially different than that on a rotating hemisphere electrode (RHSE), for which the primary current and potential distributions are uniform.

As the mathematical models developed to date for the impedance response of a disk electrode with a non-uniform current distribution [13,14] are not in a form suitable for regression analysis of experimental data, the preferred ap-
approach for experimental investigation of electrode kinetics is to use geometries for which mass-transfer is well-defined and the primary current distribution is uniform. The rotating hemispherical electrode, introduced by Chin [17], has a uniform primary current distribution and would therefore be a suitable configuration for experiments conducted under conditions such that the current distribution is not influenced by the non-uniform accessibility to mass transfer. Nisançioğlu and Newman [18] showed that current distribution in the RHSE is uniform so long as the average current density has a value smaller than 68% of the average mass-transfer-limited value. A refined mathematical model for the convective diffusion impedance of a RHSE, developed by Barcia et al. [19], provided an excellent match to experimental impedance measurements conducted under these conditions.

Systems that employ a stationary electrode facilitate use of in situ observation or surface analysis techniques. Orazem et al. [12], for example, used images of a submerged impinging jet disk electrode obtained by in situ video microscopy to facilitate interpretation of impedance measurements in terms of viscoelastic properties of corrosion product films [12]. Such experiments using scanning ellipsometry on a submerged impinging jet disk electrode were used to distinguish between the influence of convective diffusion and hydrodynamic shear [20]. Flow channel experiments have been employed by Alkire and Cangellari [21] to show the role of current distribution on formation of salt films. To date, no experimental system has been described in the literature which has a uniform primary distribution, a stationary electrode amenable to in situ observation, and well-defined flow characteristics allowing control of convective diffusion. The objective of the present work was to develop the hydrodynamic and convective diffusion calculations for a stationary hemispherical electrode subjected to a submerged impinging jet. The use of a stationary electrode is intended to ensure that the primary and secondary current distributions would be uniform [22]. The present work provides a foundation for the design of electrode systems and for development of models for the impedance response.

2. Mathematical development

A schematic illustration of a stationary hemispherical electrode under a submerged impinging jet is presented in Fig. 1. Following the development made for the planar electrode under a submerged impinging jet (see, for example [23]), the nozzle was assumed to be sufficiently large and distant that the flow toward the electrode surface can be described as being a potential flow with uniform axial velocity. The walls of the enclosure were assumed to be sufficiently distant that they do not influence the flow patterns near the electrode surface. The mathematical development progressed in two stages. In the first, a boundary layer approach were used to obtain the flow velocity near the electrode surface. This flow velocity was then used in the solution of the corresponding form of the convective diffusion equation. This development follows closely the development presented by Barcia et al. [19] for the rotating hemispherical electrode.

2.1. Fluid flow

Following the usual boundary layer development for forced flow [24], a solution was obtained for the potential flow. The potential flow solution provided the pressure distribution over the electrode surface and far-field boundary conditions needed for solution of the boundary layer equations.

2.1.1. Potential flow calculation

The velocity potential \( \phi \) satisfies Laplace’s equation, which can be written in spherical polar coordinates as

\[
\frac{\partial}{\partial r} \left( r^2 \frac{\partial \phi}{\partial r} \right) + \frac{1}{\sin(\theta)} \frac{\partial}{\partial \theta} \left( \sin(\theta) \frac{\partial \phi}{\partial \theta} \right) = 0
\]

where the radial component of the fluid velocity is given by

\[
v_r = -\frac{\partial \phi}{\partial r}
\]

the angular or colatitude component of the fluid velocity is given by

\[
v_\theta = -\frac{1}{r} \frac{\partial \phi}{\partial \theta}
\]

and \( r \) and \( \theta \) are the radial and angular components, respectively.

The no-penetration boundary conditions can be expressed as

\[
\frac{\partial \phi}{\partial r} \bigg|_{r=r_{\text{inlet}}} = 0
\]

for the insulating plane and as

\[
\frac{\partial \phi}{\partial \theta} \bigg|_{\theta=\pi/2} = 0
\]

for the insulated plane.
for the electrode surface. A symmetry condition for the centerline can be expressed as

$$\frac{\partial \phi}{\partial \theta} \bigg|_{r=0} = 0$$

(6)

Under the assumption that the flow can be considered to emanate from a point source located infinitely far from the insulating plane, the flow potential should approach an asymptotic behavior far from the electrode expressed as

$$\phi \bigg|_{r \to \infty}, \theta = \frac{c \phi r^2}{2} \left(3 \cos^2(\theta) - 1\right)$$

(7)

where \(c\) is a hydrodynamic constant. Eq. (7) was previously applied in the development of the potential flow solution for a submerged jet impingement onto a flat disk.

[25] Thus, use of Eq. (7) constitutes a statement that, far from the electrode, the influence of the shape of the hemispherical electrode should diminish.

The solution of Eq. (1) subjected to boundary conditions (Eqs. (4)-(7)) is given by

$$\phi = -c \phi r^2 \left(\frac{1}{2} + \frac{1}{3} \cos^2(\theta) - 1\right)$$

(8)

with the corresponding stream function \(\psi\) given by

$$\psi = -c \phi r^2 \left(r^3 - \frac{r^2}{2}\right) \sin^2(\theta) \cos(\theta)$$

(9)

Computed values for flow trajectories, given as \(-\psi c \phi r^2\), are presented in Fig. 2 as a function of dimensionless position scaled by the hemisphere radius \(r_0\).

where the velocity is given by the potential flow solution. Thus, given that \(v_{r|0} = 0\) and, from Eqs. (8) and (3), that \(\psi_{r|0} = \frac{1}{2} c r_0 (\sin(2\theta))\)

the pressure gradient at the electrode surface can be expressed as

$$\frac{1}{\rho c^2 r_0^2} \frac{\partial p}{\partial \theta} = \frac{25}{4} \sin(4\theta)$$

(12)

The dimensionless pressure gradient along the electrode surface is given in Fig. 3 as a function of colatitude angle \(\theta\). The dimensionless pressure gradient changes sign at a position of \(\theta = \pi/4\). As is shown in the subsequent section, the reversal of the pressure driving force for flow induces separation of the velocity boundary layer.

2.1.2. Boundary layer flow calculation

Under assumption of uniform fluid properties, the equations governing a thin boundary layer on an axisymmetric surface

$$p + \frac{1}{\rho c^2} \frac{\partial p}{\partial \theta} = \text{constant}$$

(10)
body of rotation [24,26] can be written in terms of conservation of momentum in the colatitude direction
\[ \frac{\partial v_\theta}{\partial \theta} + \frac{\partial v_\xi}{\partial \xi} = -\frac{1}{\rho_0} \frac{\partial p}{\partial \theta} + \nu \frac{\partial^2 v_\theta}{\partial \theta^2} \] (13)
and conservation of mass
\[ \frac{\partial v_\theta}{\partial \theta} + \frac{\partial v_\xi}{\partial \xi} + \frac{\nu}{\rho_0} \cot (\theta) = 0 \] (14)
Eqs. (13) and (14) can be expressed conveniently in dimensionless form as
\[ \frac{1}{4} \frac{\partial F(\theta, \xi)}{\partial \theta} \frac{\partial F(\theta, \xi)}{\partial \theta} - H(\theta, \xi) \frac{\partial F(\theta, \xi)}{\partial \xi} = \sin (4\theta) + \frac{1}{2} \frac{\partial^2 F(\theta, \xi)}{\partial \xi^2} \] (15)
and
\[ \frac{1}{2} \frac{\partial F(\theta, \xi)}{\partial \theta} - 2 \frac{\partial F(\theta, \xi)}{\partial \xi} + \frac{1}{2} F(\theta, \xi) \cot (\theta) = 0 \] (16)
respectively, where the pressure gradient was introduced from Eq. (12), \( \xi \) is the dimensionless radial position given in terms of the hydrodynamic constant \( a \) as
\[ \xi = \sqrt{\frac{\theta}{v}} \] (17)
\( H(\theta, \xi) \) is the dimensionless radial velocity, such that
\[ v_\theta = -2 \sqrt{\nu H(\theta, \xi)} \] (18)
and \( F(\theta, \xi) \) is the dimensionless colatitude velocity, such that
\[ v_\xi = \frac{1}{2} \nu \partial F(\theta, \xi) \] (19)
The no-slip boundary conditions at the electrode surface for the colatitude and radial velocity components can be expressed as
\[ F(\theta, \xi)|_{\xi=\infty} = 0 \] (20)
and
\[ H(\theta, \xi)|_{\xi=\infty} = 0 \] (21)
respectively. The condition that the flow must approach the potential flow solution far from the surface is expressed by
\[ F(\theta, \xi)|_{\xi=0} = \sin (2\theta) \] (22)
Comparison between Eqs. (22) and (11) reveals that \( a = 5c_0 \), which provides that the boundary layer equations corresponding to a jet impinging upon a planar surface are recovered for \( \theta = 0 \).
Following Howarth [26], \( H(\theta, \xi) \) and \( F(\theta, \xi) \) can be expanded in terms of \( \theta \) and \( \xi \) as
\[ H(\theta, \xi) = \sum_{i=3}^n \frac{\partial^n}{\partial \theta^i} H_{2i-1}(\xi) \] (23)
and
\[ F(\theta, \xi) = \sum_{i=0}^n \frac{\partial^{2i-1}}{\partial \theta^{2i-1}} F_{2i-1}(\xi) \] (24)
respectively. The \( \sin (4\theta) \) term arising in Eq. (15) from the colatitude pressure gradient can be expanded as
\[ \sin (4\theta) = 4\theta - \frac{\theta^3}{3!} + \frac{\theta^5}{5!} - \frac{\theta^7}{7!} + \cdots \]
\[ + \frac{(\theta)^{2i+1} (4\theta)^{2i-1}}{(2i-1)!} \] (25)
and the \( \cot (\theta) \) term appearing in Eq. (16) can be expanded as
\[ \cot (\theta) = \frac{1}{\theta} - \frac{\theta}{3!} + \frac{\theta^3}{5!} - \frac{2\theta^5}{9!} + \cdots \] (26)
Introduction of Eqs. (23)–(26) into Eqs. (15) and (16) yields a series of coupled ordinary differential equations in \( \xi \) corresponding to a given order of \( \theta \). The number of terms in the series \( n \) can be arbitrarily selected to achieve a desired level of accuracy.
In the present work, the number of terms in the expansions (Eqs. (23)–(26)) was limited to \( n = 14 \) because terms of higher-order in the expansion (Eq. (25)) for the colatitude pressure gradient were negligibly small as compared to the largest terms in Eq. (15). The resulting set of ordinary differential equations were solved using the Band algorithm introduced by Newman.[27] The boundary condition (Eq. (22)) for the colatitude velocity was applied at \( \xi = 40 \). The gradient expressions \( F_{2i-1}(0) \) and \( H_{2i-1}(0) \) were obtained by substituting the no-slip boundary conditions in Eqs. (15) and (16).

The velocity distribution near the electrode surface can be approximated by Taylor’s series expansions for \( F(\theta, \xi) \) and \( H(\theta, \xi) \) as
\[ F(\theta, \xi) = \left[ \sum_{i=3}^{14} \frac{\partial^{2i-1}}{\partial \theta^{2i-1}} F_{2i-1}(0) \right] \xi \]
\[ + \frac{1}{8} \sum_{i=3}^{14} \frac{\partial^{2i-1}}{\partial \theta^{2i-1}} F_{2i-1}(0) \xi^2 \] (27)
and
\[ H(\theta, \xi) = \left[ \sum_{i=3}^{14} \frac{\partial^{2i-1}}{\partial \theta^{2i-1}} H_{2i-1}(0) \right] \xi^2 \]
\[ + \frac{1}{8} \sum_{i=3}^{14} \frac{\partial^{2i-1}}{\partial \theta^{2i-1}} H_{2i-1}(0) \xi^3 \] (28)
respectively. Calculated values for coefficients \( F_{2i-1}, F_{2i-1}^*, H_{2i-1}, H_{2i-1}^* \) are given in Table 1.
In order to minimize the influence of finite-difference errors on evaluation of $F_{2i-1}$ and $H_{2i-1}$, the differential equations were approximated to the order of the square of the mesh-size, and the numerical values were obtained by extrapolation to zero mesh size. The number of digits given in Table 1 are consistent with the standard deviation obtained through the regression procedure. The expansions (Eqs. (27) and (28)) for $B(\theta, \xi)$ and $F(\theta, \xi)$ were used in the development of the convective diffusion boundary layer equations presented in a subsequent section.

2.1.3. Boundary layer separation

Boundary layer separation takes place at the location where the normal derivative of the colatitude velocity, i.e., $(\partial \theta v / \partial \theta)|_{r=\infty, \theta=\theta_0}$, has a value equal to zero. Thus, boundary layer separation is observed at the value of $\theta$ where the dimensionless shear stress,

$$ B(\theta) = \sum_{i=1}^{n} \theta^{2i-1} F_{2i-1} (0) $$

has a value equal to zero. The value of $\theta$ at which separation was calculated depended slightly on the number of terms retained in the series expansion. The point of separation reached a value of 54.79° for $n = 14$. A plot of $B(\theta)$ is presented in Fig. 4 as a function of $\theta$, showing clearly the point of boundary layer separation. The corresponding result obtained by Barcia et al. [19], and reproduced in the present work, for the rotating hemisphere is presented in Fig. 4 to provide comparison. No separation was observed in the boundary layer calculations for the rotating hemisphere, although a small region of separation is observed near the singularity where the electrode contacts the insulating plane.

2.2. Steady-state mass transfer

Under the assumptions that the Peclet number is large and that the concentration of the reactant $c_R$ is small with respect to the supporting electrolyte, the steady-state convective diffusion equation can be written as

$$ v_r \frac{\partial c_R}{\partial r} + v_\theta \frac{\partial c_R}{\partial \theta} = D \frac{\partial^2 c_R}{\partial \theta^2} $$

(30)

where the velocity is obtained from the development presented in the previous sections. The interest in the present work is the calculation of the mass-transfer-limited current distribution; thus, the boundary conditions for Eq (30) are given as

$$ c_R|_{r=\infty, \theta=\theta_0} = c_i $$

(31)

$$ c_R|_{r=\infty, \theta=\theta_0} = c_\infty $$

(32)

and

$$ c_R|_{r=0, \theta=\theta_0} = c_\infty $$

(33)

Fig. 4. Distribution of dimensionless surface shear stress calculated for $\psi = 14$. Solid lines represent the result for the stationary hemisphere, and dashed lines represent the result for the rotating hemisphere [19].

Table 1

<table>
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<tr>
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The concentration $c_R$ can be expanded as a series function of $\hat{\theta}, \hat{\xi}$, and $\xi$ as

$$c_R - c_\infty = \sum_{i=1}^{n} \phi^{(2i-2)}_{1,2i-1}(\xi)$$

$$+ \xi Sc^{1/3} \sum_{i=1}^{n} \phi^{(2i-3)}_{2,2i}(\xi)$$

such that the first term of the expansion provides the solution under the assumption that the Schmidt number $Sc$ is infinitely large and the second term provides a correction for a finite value of $Sc$.

The characteristic dimensionless distance for mass transfer can be defined as

$$Z = \xi Sc^{1/3}$$

which accounts for the difference in scale between the convection and mass transfer boundary layer thicknesses. For $n = 14$, Eqs. (30), (34) and (35) yield 14 coupled ordinary differential equations for $\phi^{(2i-2)}_{1,2i-1}$ and $\phi^{(2i-3)}_{2,2i}$, which were solved numerically.

The flux at the electrode surface is given by

$$N_f = -D_R \frac{dc_R}{d\theta}vert_{\theta=0}$$

which can be evaluated in the form of a mass-transfer-limited current density in terms of the dimensionless variables introduced above as

$$i_{lim}(\theta) = \frac{nF(c(c_\infty - c_\infty)D_R S_{c}^{-1/3} Re^{1/2}}{r_0} \times \left[ \sum_{i=1}^{n} \phi^{(2i-2)}_{1,2i-1}(0) + \xi Sc^{-1/3} \right]$$

$$\times \left[ \sum_{i=1}^{n} \phi^{(2i-3)}_{2,2i}(0) \right]$$

where the Reynolds number $Re$ is defined to be

$$Re = \frac{\sigma^2 a^2}{\nu}$$

Eq. (39) can be expressed in terms of a characteristic number

$$N^* = \frac{nF(c(c_\infty - c_\infty)D_R S_{c}^{-1/3} Re^{1/2}}{r_0}$$

as

$$\frac{i_{lim}(\theta)}{N^*} = \Psi(\theta) + \xi Sc^{-1/3} A(\theta)$$

where $\Psi(\theta)$ is the mass-transfer-limited current density for an infinite Schmidt number, and $A(\theta)$ is the correction to account for the finite value of the Schmidt number. Thus,

$$\Psi(\theta) = -\sum_{i=1}^{n} \phi^{(2i-2)}_{1,2i-1}(0)$$

and

$$A(\theta) = -\sum_{i=1}^{n} \phi^{(2i-3)}_{2,2i}(0)$$

Calculated values for $\phi^{1,2i-1}_{1,2i-1}(0)$ and $\phi^{2,2i}_{1,2i-1}(0)$ are provided in Table 2. In order to minimize the influence of finite-difference errors, the differential equations were approximated to the order of the square of the mesh-size, and the numerical values were obtained by extrapolation to zero mesh size.

The calculated values for $\Psi(\theta)$ and $A(\theta)$ are presented in Fig. 5(a) and (b), respectively, as functions of colatitude angle $\theta$. The boundary layer solution is valid only up to the point of boundary layer separation. The result obtained for the stationary hemispherical electrode is in stark contrast to that obtained by Barcia et al. [19] for the rotating hemispherical electrode, also shown in Fig. 5, which does not show such a boundary layer separation. For the stationary

![Fig. 5. Calculated mass-transfer limited current density for a hemispherical electrode subjected to a submerged impinging jet. Solid lines represent results for the stationary electrode, and the dashed lines represent results for the rotating hemispherical electrode [19]. Contribution to Eq. (40) (a) for an infinite Schmidt number; (b) providing correction for a finite Schmidt number.](image-url)
for this system will be approximate and will require a level of empiricism, in the form of an adjustable parameter, in order to treat the circulation region which follows the point of boundary layer separation.

More work is needed to develop the stationary hemispherical electrode under a submerged impinging jet. The location of cell walls and modifications to the geometry insulating plane may influence the location of the point of boundary layer separation. If, as suggested by the literature,[28] mass transfer will be significantly enhanced within the region of circulation following the point of separation, a more quantitative treatment of mass transfer suitable for identification of Schmidt number may yet be possible. Nevertheless, from the context of kinetic studies, the advantages of having facilitated in situ observation and a uniform current distribution can be more significant than the disadvantage posed by the need for empirical treatment of mass transfer.

Table 2

<table>
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References


