Rotating Disk Flow in Electrochemical Cells: A Coupled Solution for Hydrodynamic and Mass Equations

O. E. Barcia,[a,c] N. Mangiavacchi,[b] O. R. Mattos,[a,*,z] J. Pontes,[b] and B. Tribollet[d,*]

[a]*Metallurgical and Materials Engineering Department, Escola Politécnica - Instituto Alberto Luis Coimbra de Pós-Graduação e Pesquisa, Federal University of Rio de Janeiro, Rio de Janeiro, Brazil*
[b]*Mechanical Engineering Department/GESAR Group, State University of Rio de Janeiro, Rio de Janeiro, Brazil*
[c]*Departamento de Físico-Química - Instituto de Química/Federal University of Rio de Janeiro, Brazil*
[d]*Laboratoire Interfaces et Systemes Electrochimiques, UPR15 du CNRS, Université Pierre et Marie Curie, 75252 Paris Cedex 05, France*

This work deals with the steady-state solution of a rotating disk flow, coupled, through the fluid viscosity, to the mass-concentration field of chemical species. The configuration refers to electrochemical cells where the working electrode consists of an iron rotating rod which is dissolved into the electrolyte, a 1 M sulfuric acid solution. Dissolution of the electrode gives rise to a thin concentration boundary layer, which, together with the potential applied to the electrode, results in an increase in the fluid viscosity and a decrease in the diffusion coefficient close to the electrode surface, both affecting the current. A phenomenological law is assumed, relating the fluid viscosity to the concentration of relevant chemical species. Parameters appearing in this law are evaluated based on experimental electrochemical data. The steady-state solution is obtained by solving the coupled hydrodynamic and mass-concentration equations.
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The rotating disk electrode (RDE) has been widely used in electrochemistry. Indeed, the theory for this kind of electrode is well established in the literature.[1-4]

The dissolution of the iron RDE in a 1 M sulfuric acid solution leads to the establishment of a thin mass-concentration boundary layer. This layer reduces the diffusion coefficient and increases the fluid viscosity, coupling the hydrodynamic and the mass-concentration fields. Despite this coupling, the stationary solution for both fields has traditionally been obtained separately.

Indeed, the concentration gradient in the diffusion layer at the steady state, when the migration is negligible and the diffusion coefficient is assumed to be concentration-independent, is described by

$$v_z \frac{\partial c}{\partial z} = D \frac{\partial^2 c}{\partial z^2}$$

In this equation, v_z is obtained by solving the Navier–Stokes and continuity equations using the von Karmán and Cochran approach.[5,6] The classical solution assumes both the density (ρ) and the viscosity (ν) of the solution as constants through the diffusion layer.[1-4] Newman et al.[7,8] have discussed the dependence of fluid physical parameters (ρ, ν) on the concentration.

Barcia et al.[9] studied the anodic dissolution of iron in acid sulfate solutions under mass-transport control. These authors propose an empirical law relating the fluid viscosity to the axial coordinate and not to the concentration of the chemical species resulting from the dissolution of the electrode itself. According to this approach, the hydrodynamic and mass-concentration fields remain uncoupled. Calabrese Barton and West[10] were the first to use an empirical law coupling both fields and solving the hydrodynamic and mass problem simultaneously to fit the experimental data for the steady-state limiting current and the electrohydrodynamic impedance of the zinc–KOH system. In this work,[10] the authors introduce the following equation

$$\frac{\nu(z)}{\nu_\infty} = 1 + [\nu(0)/\nu_\infty - 1]\theta^\alpha \qquad [1]$$

where θ is the dimensionless concentration, $\theta = c(z) - c_\infty/c(0) - c_\infty$, and α is an empirical parameter. For the nonuniform viscosity $[\nu(0)/\nu_\infty \neq 1]$, the value of α used was 1 and 3, and the viscosity ratio obtained was 5.5 and 2.1, respectively. According to the authors, although the model using nonuniform viscosity and $\alpha = 3$ had a strong experimental basis, it did not satisfy the experimental results. This fact led the authors to consider that some other assumptions must be reevaluated, such as the use of the Stokes–Einstein relationship or the simple power law dependence of viscosity on concentration. It is important that Eq. 1 involves two unknown parameters $\nu(0)/\nu_\infty$ and α.

In the present paper, the validity of the Stokes–Einstein relationship was maintained and another approach to study the dependence of the viscosity on the concentration was adopted. With this objective, the von Karmán equations for rotating disk flow coupled, through the viscosity, with the mass-transport equation of representative chemical species were solved. In the present paper, only the steady-state problem was analyzed.

Model Development

From the literature[11,12] it is reasonable to assume the viscosity of an electrolytic solution to be concentration-dependent. An exponential law relating viscosity and concentration was deduced in Ref. 12. Equation 2 is a simplified version based on Ref. 12 and was previously used in our recent paper[13]

$$\frac{\nu(z)}{\nu(\infty)} = \exp\left[m \frac{c(z) - c(\infty)}{c(0) - c(\infty)} \right] \qquad [2]$$

Here, $\nu(z)/\nu(\infty)$ is the ratio between the local and bulk viscosities, $c(z)$ being the concentration at a distance z away from the electrode surface and $c(0)$ and $c(\infty)$ the interface and bulk concentrations, respectively. In this equation, m is a parameter equal to $\ln[\nu(0)/\nu(\infty)]$ that varies only with the interfacial concentrations. Consequently, Eq. 2 has only one unknown parameter, while Eq. 1 has two unknowns. Equation 2 can be rewritten in a dimensionless form as

$$\nu^*(\xi) = \exp(m\theta) \qquad [3]$$

where

$$\nu^*(\xi) = \nu(z)/\nu(\infty) \qquad [4]$$

$$\theta(\xi) = \frac{c(z) - c(\infty)}{c(0) - c(\infty)} \qquad [5]$$

and ξ is the classical dimensionless distance defined by $\xi = [\Omega/\nu(\infty)]^{1/2}z$. Equation 3 introduces a dependence between the viscosity and the concentration. Therefore, the continuity, Navier–Stokes, and mass-transport equations are coupled and can no longer be solved independently.

* Electrochemical Society Active Member.
[z] E-mail: omattos@metalmat.ufrj.br

Table I. $\nu(0)/\nu(\infty)$ for $Sc = 1500$ considering $c(0) = 1.8$, 2.0, and 2.2 M.

$c(0)$	1.8	2.0	2.2
$\nu(0)/\nu(\infty)$	1.8	2.2	2.5

Table II. $\nu(0)/\nu(\infty)$ for $Sc = 2200$ considering $c(0) = 1.8$, 2.0, and 2.2 M.

$c(0)$	1.8	2.0	2.2
$\nu(0)/\nu(\infty)$	1.2	1.4	1.7

For an RDE, the classical continuity, Navier–Stokes, and mass-transport equations for a fluid with the viscosity varying along the axial coordinate can be written as[4]

$$\frac{\partial v_r}{\partial r} + \frac{v_r}{r} + \frac{\partial v_z}{\partial z} = 0 \qquad [6]$$

$$v_r\frac{\partial v_r}{\partial r} - \frac{v_\theta^2}{r} + v_z\frac{\partial v_r}{\partial z} = \nu\left[\frac{2}{r}\frac{\partial}{\partial r}\left(r\frac{\partial v_r}{\partial r}\right) - \frac{2v_r}{r^2}\right] + \frac{\partial}{\partial z}\left(\nu\frac{\partial v_r}{\partial z}\right) \qquad [7]$$

$$v_r\frac{\partial v_\theta}{\partial r} + \frac{v_r v_\theta}{r} + v_z\frac{\partial v_\theta}{\partial z} = \frac{\nu}{r^2}\frac{\partial}{\partial r}\left[r^3\frac{\partial}{\partial r}\left(\frac{v_\theta}{r}\right)\right] + \frac{\partial}{\partial z}\left(\nu\frac{\partial v_\theta}{\partial z}\right) \qquad [8]$$

$$v_z\frac{\partial c}{\partial z} = \frac{\partial D}{\partial z}\frac{\partial c}{\partial z} + D\frac{\partial^2 c}{\partial z^2} \qquad [9]$$

where z, r, v_r, v_θ, and v_z stand for their classical meaning. The von Karmán[5] similarity solution reads

$$v_r = r\Omega F(\xi) \qquad [10]$$

$$v_\theta = r\Omega G(\xi) \qquad [11]$$

$$v_z = [\nu(\infty)\Omega]^{1/2}H(\xi) \qquad [12]$$

where $F(\xi)$, $G(\xi)$, and $H(\xi)$ are dimensionless functions and Ω is the rotating speed. Assuming the Stokes–Einstein equation, νD = constant

$$D(z)\nu(z) = D(\infty)\nu(\infty) \qquad [13]$$

where $D(\infty)$ is the bulk diffusion coefficient. In analogy with Eq. 4, a dimensionless diffusion coefficient is defined

$$D^*(\xi) = D(z)/D(\infty) \qquad [14]$$

Upon introducing Eq. 3, 4, and 10-14 in Eq. 6-9, the following system is obtained for the dimensionless profiles F, G, H, and θ

$$2F + H' = 0 \qquad [15]$$

$$F^2 - G^2 + HF' - \nu^* F'' - \nu^{*\prime} F' = 0 \qquad [16]$$

$$2FG + HG' - \nu^* G'' - \nu^{*\prime} G' = 0 \qquad [17]$$

$$Sc H\theta' - \frac{\theta''}{\nu^*} + \frac{\nu'}{\nu^2}\theta' = 0 \qquad [18]$$

where the prime designates differentiation with respect to ξ and Sc is the Schmidt number, defined by $Sc = \nu(\infty)/D(\infty)$. The boundary conditions are $F = H = 0$ and $G = \theta = 1$ at $\xi = 0$ and $F = G = \theta = 0$ at $\xi = \infty$. When $\nu(\xi)/\nu(\infty) = 1$, the above equations are reduced to the usual form,[1-4] and the resolution of the hydrodynamic equations and of mass transport is done in the classic way: the hydrodynamic problem is solved first and the resulting hydrodynamic field is used to solve the mass-concentration-transport equation. To keep this solution general in Eq. 18, the migration is neglected. To take into account the migration, it is necessary to solve the mass-transport problem for all species present in solution and then to define completely the electrochemical system as Calabrese Barton and West did in Ref. 10. Equations 15-18 are numerically solved in a staggered grid of uniformly spaced points, using second-order finite-difference approximations for the derivatives.

Results and Discussion

As mentioned above, the purpose of this paper is to improve the previous analysis conducted by Barcia et al.,[9] working with iron in sulfuric acid medium. Considering the case of anodic dissolution of iron in a 1 M H_2SO_4 solution in the potential range where the polarization curves show a current plateau, the limit current density is given by Ref. 9

$$i = nF\frac{1}{Sc}\frac{1}{\nu(0)/\nu(\infty)}[c(\infty) - c(0)]\sqrt{\nu(\infty)\Omega}\left(\frac{d\theta}{d\xi}\right)_{\xi=0} \qquad [19]$$

This system was experimentally studied by Barcia et al.,[9] Ferreira et al.,[14] and Geraldo et al.[15] For a rotation rate of 900 rpm, Barcia et al.[9] obtained an experimental current density of 1.1 A/cm². By using the electrohydrodynamic impedance technique, a Schmidt number (Sc) close to 8000 was found at the electrode surface, whereas the bulk value is around 2000. Consequently, a concentration profile was proposed considering the existence of a highly concentrated Fe++ solution at the electrode surface.[9,14,15] Barcia et al.[9] determined the saturated Fe++ concentration, $c(0)$ = 1.8 M, corresponding to the current plateau of 1.1 A/cm².

Solving Eq. 15-18 requires specification of the bulk Schmidt number and the m parameter, appearing in Eq. 2. This parameter ultimately defines the ratio $\nu(0)/\nu(\infty)$. The Schmidt number in the bulk solution is estimated to be between 1500 and 2200; thus, these two extreme values are considered to develop the derivation, and the ratio $\nu(0)/\nu(\infty)$ was evaluated using Eq. 2 and the following procedure:

1. A set of values is assumed for the angular velocity, the Schmidt number, the bulk viscosity, and the interface concentration, through the m parameter.

2. The nondimensional profiles F, G, H, and θ are obtained by numerically solving Eq. 15-18. The results lead to a value of $\nu(0)/\nu(\infty)$ and to the slope $\theta'(0)$ at the interface.

3. The above results and the assumed values are inserted in Eq. 19, leading to an estimation of the current density at the interface. This current is compared to the one obtained by Barcia et al.[9]

4. The ratio $\nu(0)/\nu(\infty)$ is changed, keeping all other parameters constant, and steps 1–3 are iterated until convergence to the experimental value of the current density is achieved. This process is accelerated by employing the Newton–Raphson method. This iterative procedure could be implemented because Eq. 2 involves only one unknown.

The viscosity gradient value $[\nu(0)/\nu(\infty)]$ changes with the Sc and $c(0)$. In the problem considered in this work, the anodic dissolution of Fe in acid sulfate,[9] there are two limiting values of Sc, 1500 and 2200. The interfacial concentration $[c(0)]$ of Fe++ is estimated to be between 1.8 and 2.2 M; thus, the viscosity gradient is derived for both cases. Tables I and II present these results.

The values presented in Tables I and II diminish with Sc and are significantly lower than those previously obtained.[9,14-16] Indeed, when the mass and hydrodynamic equations are solved independently, the values obtained for $\nu(0)/\nu(\infty)$ are equal to 4, whereas when the coupling problem is considered, the value of $\nu(0)/\nu(\infty)$ is equal to 2.6. As it can be seen in Tables I and II, independently of the Sc value, the larger the concentration at the electrode surface $[c(0)]$, the higher the value of $\nu(0)/\nu(\infty)$. However, a value of $\nu(0)/\nu(\infty) = 4$ is never obtained.
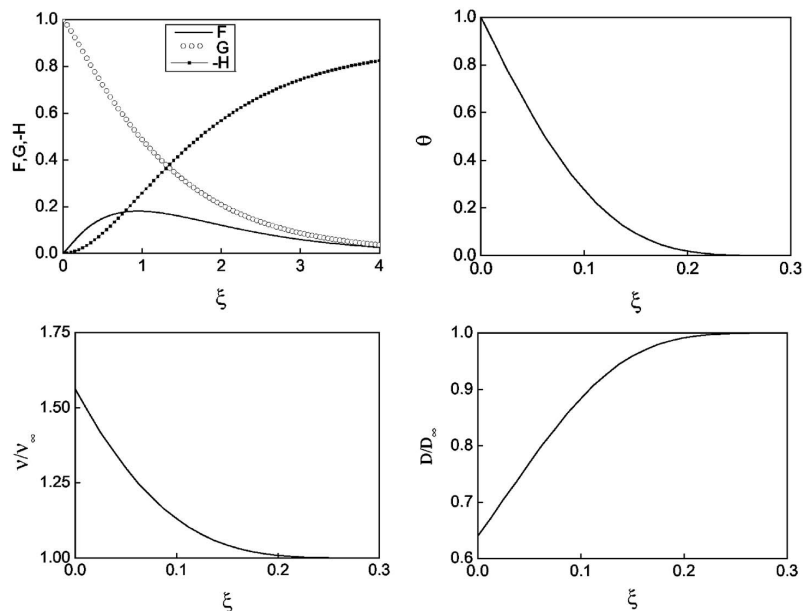
Figure 1. Stationary profiles for F, G, H, $\theta v^*(0)$, and D^* obtained for $v(0)/v(\infty)$ = 1.6 and Sc = 2000, after data from Barcia et al.[9]
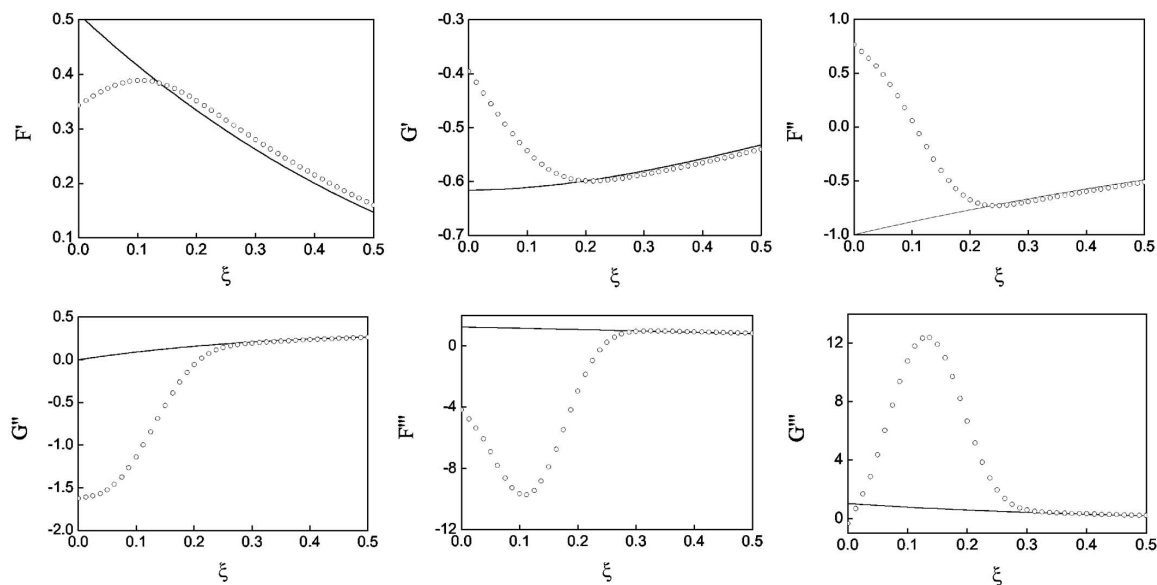

Figure 2. The first three derivatives of the nondimensional velocity profiles, F and G, for the constant and variable viscosity cases, with $v(0)/v(\infty)$ = 1.6 and Sc = 2000, after data from Barcial et al.[9] The continuous curve represents the constant viscosity and the discontinuous curve represents the variable viscosity.

Figure 1 presents the nondimensional velocity, concentration, viscosity, and diffusion-coefficient profiles, F, G, H, θ, v^*, and D^*, obtained for $v(0)/v(\infty)$ = 1.6 and Sc = 2000.

Estimation of the ratio between the thicknesses of the hydrodynamic δ_h and the concentration δ_c boundary layers can be made by employing the following relation proposed by Levich[1]

$$\delta_c/\delta_h \approx 2 \, Sc^{1/3} \qquad [20]$$

Outside the concentration boundary layer[17] the viscosity gradient no longer exists and the velocity profiles are close to those obtained for the constant viscosity case. In particular, the value of H = −0.88559 obtained far from the disk for the variable viscosity case is only slightly different from H = −0.8844, the asymptotic value for the constant viscosity case. Assuming a thickness of δ_h = 6 for the hydrodynamic boundary layer, by using Eq. 20 a thickness of δ_c = 0.24 was estimated for the concentration boundary layer. The profiles obtained numerically ($\delta_c \approx$ 0.24) agree with this value. Nevertheless, the derivatives of the velocity profiles are strongly affected by the concentration boundary layer, as shown in Fig. 2.
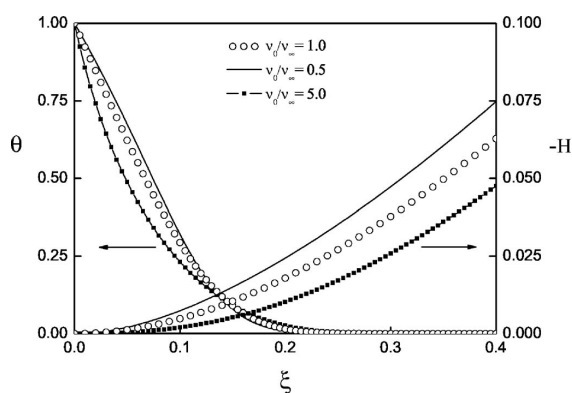
Figure 3. Profiles of the dimensionless axial velocity and dimensionless concentration vs dimensionless coordinate ξ for $Sc = 2000$ and three values of $\nu(0)/\nu(\infty)$.

These results show that by coupling the RDE equations, a less-important steady gradient profile and lower values of $\nu(0)/\nu(\infty)$ than those assumed in previous works[9,16] can be found. However, as can be seen in Fig. 3, whose results agree with those obtained by Calabrese Barton et al.,[10] the velocity is influenced strongly by the presence of a viscosity gradient. These low values of the viscosity gradient are sufficient to destabilize the coupled hydrodynamic and chemical species fields, in the range of parameters actually found in typical electrochemical cells, and to explain the oscillations observed in the plateau of iron dissolution.[13-16,18] The existence of such gradient was evidenced by the high Schmidt number at the electrode surface (8000) compared with the bulk electrolyte value (around 2000). This gradient profile could be justified by the presence of a gel-like layer at the electrode surface.[9] An exponential coupling between mass and viscosity destabilizes the hydrodynamic system and are now, in the present paper, giving rise to values of $\nu(0)/\nu(\infty)$ lower than the previous values used to account for the electrohydrodynamic impedance. The question now opened is whether, by using this low gradient profile, the experimental results of hydrodynamic impedance can be simulated as previously reported.[9] A new formalism is necessary, and this work is already in progress in our laboratory.

Conclusions

The results obtained in this work show that solving the hydrodynamic equations coupled to the equation of convective diffusion is imperative whenever the physical solution properties vary from the electrode surface to the bulk solution. The dependence between the viscosity gradient and the concentration used in this work involved only one unknown. This made it possible to use an iterative methodology to obtain the experimental value of the current density. Based on this result, a new solution for hydrodynamic impedance in the presence of a gradient profile must be proposed. This work is already in progress in our laboratory. Indeed, the relationship considered in this work would allow further development concerning electrohydrodynamic impedance, in which this profile would be used to solve the coupled equations concerning the nonsteady-state problem.

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