



Current at a Rotating Disk Electrode under Electrosorption and Surface Diffusion Limitation

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Following a model for the current limited by adsorption and surface diffusion at a rotating disk electrode (rde), the case is analyzed when surface diffusion is preceded by adsorption with charge transfer. The electrode surface consists of a distribution of reaction sites embedded in a supporting phase where electrosorption and surface diffusion take place. Electrosorption is described by five parameters, an equilibrium potential (E_{ad}^0), a microscopic partial charge transfer (z_{ad}), a charge transfer coefficient (β_{ad}), and the rate constants for desorption and adsorption (k_1 and k_2 , respectively). Analytical expressions for the current – overpotential (j vs η_{ad}) and the Koutecký – Levich (KL) relation ($1/j$ vs $1/\omega^{1/2}$) are provided as a function of electrosorption parameters and surface diffusivity (D_s). The KL relation is linear, with the same slope as for a classical rde, whereas the intercept ($1/j_K$) depends on electrosorption parameters and D_s . Tafel relations for the intercept current ($\log j_K$ vs. η) are provided for the general and limiting cases. Effects of the radial convective transport in the electrolyte over reaction sites, and of the overlapping of surface diffusion areas are included in the model. The analytical expressions can be used to determine surface diffusion kinetics parameters from rde results.

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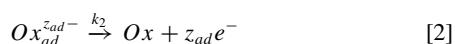
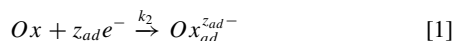
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Reactivity at electrode surfaces is in most cases localized on active sites. On single crystalline surfaces, active sites favor the interaction with electrolyte species,^{1–4} or expose appropriate electronic orbitals that enhance reactivity.^{5,6} Localized reactivity is more remarkable on composite material surfaces, like supported catalysts and partially blocked surfaces, and when the reactions are mediated by an interaction with the electrode surface, like electrocatalyzed reactions,^{1,3} electroadsorption,⁷ and electrodeposition.^{4,8} Unlocalized reactivity is less usual and requires the participation of non-interacting reactants.⁹

Areas surrounding active sites, called supporting or inactive areas, may participate in the electrochemical reaction in different ways. If adsorption is favored, the inactive areas concentrate reactants and become a parallel path for the supply of species to active sites. Predominance of the adsorption path over the direct electrolyte path is very probable in this case, even at low adsorbabilities, by a pure concentration effect.¹⁰ After adsorption, the species diffuse toward the active sites leading to adsorption-surface diffusion mediated mechanisms, like the spillover,^{11–18} and the bifunctional mechanisms.^{19,20} Surface diffusion mediated reactions require an optimal degree of interaction of the adsorbed species with inactive areas, which should lead to a ‘volcano’ dependence of reaction rate with the adsorption energy like the encountered for many catalytic reactions.²¹

The rotating disk electrode (rde) technique is very appropriate for the study of surface kinetics in electrochemical reactions because it provides controlled and well defined hydrodynamics in the electrolyte. A model was presented in previous works for the current limited by surface diffusion at an rde, assuming an adsorption/desorption equilibrium of dissolved species on inactive areas followed by diffusion toward embedded, disk shape, reaction centers.^{22,23} Analytical equations for transport limited current as a function of adsorption and surface diffusivity of the species were obtained, together with examples of the application to experimental results.^{22,24,25}

In this work, an extension of the surface diffusion model is presented by assuming the possibility of adsorption with charge transfer (*electrosorption*). With this aim, the following scheme will be considered for the reduction of a dissolved species (Ox):



Reactions 1 and 2 describe the adsorption/desorption equilibrium over the support, whereas 3 is the reaction at the edge of active sites after surface diffusion from the adsorption point. The complete process involves the exchange of z electrons, being z_{ad} transferred at the adsorption site and $z - z_{ad}$ at the active site. Parameter z_{ad} is a *microscopic partial charge transfer*, as introduced by Lorentz and Salié,²⁶ that may have integer or fractional value, and always $z_{ad} \leq z$. This concept is different from the *electrosorption valency*, which is a macroscopic structural parameter characteristic of double layers with specific adsorption.²⁷

For modelling purposes, the electrode surface will be a random distribution of reaction disk centers embedded in an rde, following the same reaction scheme provided in previous works.^{22,23} Analytical solutions are obtained for current limited by electrosorption and surface diffusion. The overlapping of surface diffusion areas around active centers is accounted for by an approximation.²³ The effect of the radial convective transport, which is always present with reaction centers on an rde, is also included in the model.

Model

Mass balance equation.—A reduction process with reductive adsorption and oxidative desorption will be considered, like in Eqs. 1–3. In the steady-state, mass balance of the adsorbed species (c_s) on the surface surrounding active centers is given by:

$$D_s \frac{\partial^2 c_s}{\partial r^2} + \frac{D_s}{r} \frac{\partial c_s}{\partial r} = k_1 c_s \exp \left[\beta_{ad} \frac{z_{ad} F}{RT} \eta_{ad} \right] - k_2 c_{y=0} \exp \left[-(1 - \beta_{ad}) \frac{z_{ad} F}{RT} \eta_{ad} \right] \quad [4]$$

Where positive signs are assigned to oxidative currents and to overpotentials favoring oxidation, as usual. Eq. 4 assumes a first order adsorption/desorption following Butler-Volmer kinetics, and relates the adsorbed concentration with surface diffusivity, D_s , the electrosorption charge, z_{ad} , rate constants for desorption and adsorption, k_1 and k_2 , and the (modified) symmetry factor for the electrosorption, β_{ad} . The symmetry factor is close to 0.5 for single step electrochemical processes with dissolved reactants and products,²⁸ but, for electrosorption, given the intrinsic asymmetry of the process, the parameter may depart considerably from this value.⁹ The overpotential (η_{ad}) in Eq. 4 can be referred to the potential under equilibrium between the electrosorbed

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surface concentration far from any reaction site ($c_s(\infty)$) and the electrolyte concentration in front of the surface ($c_{y=0}$):

$$\eta_{ad} = E - E_{ad}^0 = \frac{RT}{z_{ad}F} \ln \left[\frac{k_1 c_s(\infty)}{k_2 c_{y=0}} \right] \quad [5]$$

E_{ad}^0 is a property of the reactant and the inactive surface, favouring high positive values the reductive adsorption. A surface diffusion length for reductively adsorbed species can be defined:

$$\lambda_s = \sqrt{\frac{D_s}{k_1}} \exp \left[-\beta_{ad} \frac{z_{ad}F}{2RT} \eta_{ad} \right] \quad [6]$$

Where λ_s is the average distance travelled by ad-species between an adsorption and a desorption event. It depends exponentially on electrode potential, as a difference from the pure chemical adsorption analyzed in previous works.²² An additional potential dependence of λ_s could be implicit in parameter D_s , when the double-layer electric field interacts with the adsorbate dipole moment changing the activation energy for surface diffusion.^{4,9} Such dependence will not be considered here.

Substitution of Eq. 6 into Eq. 4 gives rise to:

$$\frac{\partial^2 c_s}{\partial r^2} + \frac{1}{r} \frac{\partial c_s}{\partial r} = \frac{1}{\lambda_s^2} \left(c_s - c_{y=0} \frac{k_2}{k_1} \exp \left[-\frac{z_{ad}F}{RT} \eta_{ad} \right] \right) \quad [7]$$

Equation 7 can be solved by a standard procedure using the appropriate boundary conditions at the edge of a reaction center and far enough, which for a surface diffusion limited reaction are:

$$\begin{aligned} c_s(r_p) &= 0 \\ c_s(\infty) &= \frac{k_2}{k_1} c_{y=0} \exp \left[-\frac{z_{ad}F}{RT} \eta_{ad} \right] \end{aligned} \quad [8]$$

The resulting adsorbed surface concentration is (Appendix A):

$$c_s(r) = \frac{k_2}{k_1} c_{y=0} \exp \left[-\frac{z_{ad}F}{RT} \eta_{ad} \right] \left(1 - \frac{K_0 \left(\frac{r}{\lambda_s} \right)}{K_0 \left(\frac{r_p}{\lambda_s} \right)} \right) \quad [9]$$

Eq. 9 is for a reduction preceded by reductive electrosorption. If reduction is preceded by oxidative adsorption, the same expression is valid but with surface diffusion length given by $\lambda_s = (D_s/k_1)^{1/2} \exp[(1-\beta_{ad})z_{ad}F\eta_{ad}/(2RT)]$ (cf. Eq. 6). Analogous equations can be written for oxidation reactions with due account for the signs of current and overpotential. In the next section, analytical equations for the current as a function of electrosorption and surface diffusion parameters will be obtained. Overlapping of surface diffusion areas and the effect of radial transport in the electrolyte over the rde surface will be included in the treatment.

Current limited by electrosorption and surface diffusion.—In the steady state, three parallel contributions to the faradaic current can be considered at an rde with surface covered by a distribution of reaction centers, the surface diffusion current, the electrosorption current, and the electrolyte current. The three paths differ in the place where charge transfer occurs, the edge of active centers, the surrounding areas, and the surface of active centers, respectively. In addition, the radial convection generated by the rde on top of active centers will be treated as an additional current contribution on the surface of active centers.

Surface diffusion current.—Species adsorbed on inactive areas may diffuse and discharge at the edges of reaction centers. The resulting current (j_{edges}) can be obtained from Eq. 9 after application of Fick's first law and Faraday law at the edge of embedded disk centers with radius r_p :

$$j_{edges}(\eta) = -(z - z_{ad})FN_p2\pi r_p D_s \left(\frac{\partial c_s}{\partial r} \right)_{r=r_p} \quad [10]$$

Where the charge transferred at the edges after the preceding electrosorption is $z-z_{ad}$. The factor $N_p2\pi r_p$ accounts for the length of

edges available for reaction in a distribution of active centers. After substitution of Eq. 9, the surface diffusion current is:

$$j_{edges}(\eta_{ads}) = -\frac{(z - z_{ad})}{z} B_{sp} \frac{\theta_p}{r_p} c_{y=0} \exp \left(-\left(1 - \frac{\beta_{ad}}{2} \right) \frac{z_{ad}F}{RT} \eta_{ad} \right) \quad [11]$$

Where the following identities have been used:

$$B_{sp} = 2zFk_2 \sqrt{\frac{D_s}{k_1}} \frac{K_1 \left(\frac{r_p}{\lambda_s} \right)}{K_0 \left(\frac{r_p}{\lambda_s} \right)} \quad [12]$$

$$\theta_p = N_p \pi r_p^2 \quad [13]$$

Notice that j_{edges} in Eq. 11 shows a multiple dependence on the overpotential, which is explicit in the exponential factor and implicit in B_{sp} through λ_s (Eq. 6).

Electrosorption current.—Reductive adsorption and oxidative desorption on inactive areas may give rise to a faradaic current given by:

$$\begin{aligned} j_{ad} &= (1 - \theta_p)Fz_{ad} \left(k_1 \bar{c}_s \exp \left[\beta_{ad} \frac{z_{ad}F}{RT} \eta_{ad} \right] \right. \\ &\quad \left. - k_2 c_{y=0} \exp \left[-(1 - \beta_{ad}) \frac{z_{ad}F}{RT} \eta_{ad} \right] \right) \end{aligned} \quad [14]$$

To obtain an analytical expression, it is necessary to calculate the concentrations of dissolved and adsorbed species on the electrode surface, i.e. $c_{y=0}$ and \bar{c}_s , respectively. $c_{y=0}$ will be obtained from the solution of the hydrodynamic equations for an rde, as shown in the next section. For \bar{c}_s , an average value will be calculated by considering a distribution of active centers where each center is surrounded by a 'cloud' of centers at a half average distance $d_{1/2}$. For a square array distribution, for example, the average half distance is given by $d_{1/2} = 1/2(1/N_p^{1/2} - 2r_p)$. The average adsorbed concentration (\bar{c}_s) can be obtained from the integration of the surface concentration over the surrounding area, using Eq. 9:

$$\begin{aligned} \bar{c}_s &= \frac{1}{\pi(d_{1/2}^2 - r_p^2)} \int_{r_p}^{d_{1/2}} 2\pi r c_s dr \\ &= \frac{c_{y=0} k_2 \exp \left[-\frac{z_{ad}F}{RT} \eta_{ad} \right]}{k_1} \\ &\quad \times \left(1 + \frac{2\lambda_s}{(d_{1/2}^2 - r_p^2)} \frac{d_{1/2} K_1 \left(\frac{d_{1/2}}{\lambda_s} \right) - r_p K_1 \left(\frac{r_p}{\lambda_s} \right)}{K_0 \left(\frac{r_p}{\lambda_s} \right)} \right) \end{aligned} \quad [15]$$

The current due to the electrosorption process results after substitution of Eq. 15 into Eq. 14:

$$j_{ad} = -(1 - \theta_p) \frac{z_{ad}}{z} c_{y=0} B_{sp} B_{ad} \exp \left[-\left(1 - \frac{\beta_{ad}}{2} \right) \frac{z_{ad}F}{RT} \eta_{ad} \right] \quad [16]$$

Where the parameter B_{ad} is given by:

$$B_{ad} = \frac{r_p K_1 \left(\frac{r_p}{\lambda_s} \right) - d_{1/2} K_1 \left(\frac{d_{1/2}}{\lambda_s} \right)}{(d_{1/2}^2 - r_p^2) K_1 \left(\frac{r_p}{\lambda_s} \right)} \quad [17]$$

B_{ad} is always a positive quantity, irrespective of the values of the three distances involved (r_p , λ_s and $d_{1/2}$), so only cathodic j_{ad} may result, which is consistent with the reductive adsorption-reduction scheme adopted: a single adsorption event gives rise to net current only if the adsorbed species is able to arrive and discharge at the edge of a reaction center; otherwise current will cancelled out by oxidative desorption.

Electrolyte current.—Dissolved species may react on the front surface of the reaction centers. The current generated by a distribution of centers covering partially the surface of an rde is given by:

$$j_{front} = -\theta_p (c^* - c_{y=0}) B_L \omega^{1/2} \quad [18]$$

Where B_L is the Levich parameter:

$$B_L = 0.62zFD^{2/3}v^{-1/6} \quad [19]$$

Surface electrolyte concentration ($c_{y=0}$).—A condition necessary for application of the model to a distribution of centers is that the surface concentration must be laterally uniform in front of the electrode surface, which is accomplished under sufficiently high rotation rates:^{22,23}

$$\omega \geq \frac{D^{2/3}v^{1/3}r_p}{\delta_h^2 r_D} \quad [20]$$

Where r_D is the electrode radius, and δ_h is the minimum distance above the electrode surface with uniform concentration. The concentration at the surface is given by the solution of hydrodynamics Equations:²⁹

$$c_{y=0} = c^* - 0.8934 \left(\frac{3D\omega^{-3/2}v^{1/2}}{0.51} \right)^{1/3} \frac{j}{zFD} \quad [21]$$

Radial transport in the electrolyte.—The radial transport over reaction centers is responsible for the homogeneous surface concentration profile in front of the rde, necessary for model conditions, but in addition, it may contribute to additional current generation. The radial flow by diffusional and convective forces has been already treated in the literature. With respect to diffusional radial transport, Levart studied the effect on an idealized partially blocked rde by using a numerical method,³⁰ and concluded that the radial diffusion is negligible for electrodes diameters $2r_D > 1$ mm and rotation rates $\omega > 1$ s⁻¹ (>10 rpm). Similar conclusions were attained by Filinovsky,³¹ and Moldoveanu and Anderson³² studying current response of an array inside a convective flow-through rectangular channel. In such system, the diffusion parallel to the array plane contributes minimally compared with the perpendicular diffusion. We may assume, therefore, that the contribution by diffusive radial transport is minimal provided conditions implicit in Eq. 20 are more restrictive than Levart condition.

Radial convection, on the other hand, may have more significant

reaction of species flowing parallel over reaction centers at a velocity (v_r) within a certain distance δ_r (Fig. 1).

The current originated in this way can be obtained from the following double integration:

$$j_{radial} = -\frac{zFc_{y=0}}{\pi r_D^2} \int_0^{r_D} \sqrt{N_p} dr \int_0^{2\pi r} v_r 2r_p \delta_r \sqrt{N_p} dr \quad [22]$$

Where δ_r is estimated from adimensional mass transport numbers in Appendix C. The use of surface concentration ($c_{y=0}$) in Eq. 22 assumes that δ_r is much shorter than the electrolyte Nernst diffusion length. The radial velocity at δ_r (v_r) is taken from the linear approximation of the solution of von Karman and Cochran under steady-state conditions:²⁹

$$v_r = 0.51 v^{-1/2} \omega^{3/2} \delta_r r \quad [23]$$

Substitution of Eq. 23 into 22 and integrations gives for the radial convective current:

$$j_{radial} = -2.272\theta_p c_{y=0} B_L \omega^{1/2} \quad [24]$$

Where substitution of parameter δ_r determined in Appendix C has been carried out:

$$\delta_r = 2.088 r_p^{1/2} r^{-1/2} \omega^{-1/2} D^{1/3} v^{1/6} \quad [25]$$

Eq. 24 has a formal similarity with the electrolyte current (Eq. 18), as expected, and must be considered a qualitative description of the contribution of radial convection to the current. Its quantitative validity should be tested experimentally, a possible way is described below, and a correction factor may be applied if necessary.

Total current.—This parameter is obtained by adding all the contributions calculated, including the radial transport:

$$j = j_{edges} + j_{ad} + j_{front} + j_{radial} \quad [26]$$

Solving the system of Equations 11, 16, 18, 21, 24, 26, yields the expressions for the electrolyte concentration at the surface, four current contributions, and the total current.

$$c_{y=0} = c^* \frac{B_L \omega^{1/2}}{B_{sp} \exp \left[- \left(1 - \frac{\beta_{ad}}{2} \right) \frac{z_{ad} F}{RT} \eta_{ad} \right] \left(\frac{z - z_{ad}}{z} \frac{\theta_p}{1 - \theta_p} r_p^{-1} + \frac{z_{ad}}{z} B_{ad} \right) + \left(\frac{2.272\theta_p}{1 - \theta_p} + 1 \right) B_L \omega^{1/2}} \quad [27]$$

$$j_{edges} = -c^* \frac{\left(\frac{z - z_{ad}}{z} \right) B_{sp} \theta_p r_p^{-1} \exp \left(- \left(1 - \frac{\beta_{ad}}{2} \right) \frac{z_{ad} F}{RT} \eta_{ad} \right) B_L \omega^{1/2}}{B_{sp} \exp \left[- \left(1 - \frac{\beta_{ad}}{2} \right) \frac{z_{ad} F}{RT} \eta_{ad} \right] \left(\frac{z - z_{ad}}{z} \frac{\theta_p}{1 - \theta_p} r_p^{-1} + \frac{z_{ad}}{z} B_{ad} \right) + \left(\frac{2.272\theta_p}{1 - \theta_p} + 1 \right) B_L \omega^{1/2}} \quad [28]$$

$$j_{ad} = -c^* \frac{\frac{z_{ad}(1 - \theta_p)}{z} B_{sp} B_{ad} \exp \left[- \left(1 - \frac{\beta_{ad}}{2} \right) \frac{z_{ad} F}{RT} \eta_{ad} \right] B_L \omega^{1/2}}{B_{sp} \exp \left[- \left(1 - \frac{\beta_{ad}}{2} \right) \frac{z_{ad} F}{RT} \eta_{ad} \right] \left(\frac{z - z_{ad}}{z} \frac{\theta_p}{1 - \theta_p} r_p^{-1} + \frac{z_{ad}}{z} B_{ad} \right) + \left(\frac{2.272\theta_p}{1 - \theta_p} + 1 \right) B_L \omega^{1/2}} \quad [29]$$

$$j_{front} = -c^* \frac{\theta_p \left(\left(\frac{2.272\theta_p}{1 - \theta_p} \right) B_L \omega^{1/2} + B_{sp} \exp \left[- \left(1 - \frac{\beta_{ad}}{2} \right) \frac{z_{ad} F}{RT} \eta_{ad} \right] \left(\frac{z - z_{ad}}{z} r_p^{-1} \frac{\theta_p}{1 - \theta_p} + \frac{z_{ad}}{z} B_{ad} \right) \right) B_L \omega^{1/2}}{B_{sp} \exp \left[- \left(1 - \frac{\beta_{ad}}{2} \right) \frac{z_{ad} F}{RT} \eta_{ad} \right] \left(\frac{z - z_{ad}}{z} \frac{\theta_p}{1 - \theta_p} r_p^{-1} + \frac{z_{ad}}{z} B_{ad} \right) + \left(\frac{2.272\theta_p}{1 - \theta_p} + 1 \right) B_L \omega^{1/2}} \quad [30]$$

$$j_{radial} = -c^* \frac{2.272\theta_p B_L^2 \omega}{B_{sp} \exp \left[- \left(1 - \frac{\beta_{ad}}{2} \right) \frac{z_{ad} F}{RT} \eta_{ad} \right] \left(\frac{z - z_{ad}}{z} \frac{\theta_p}{1 - \theta_p} r_p^{-1} + \frac{z_{ad}}{z} B_{ad} \right) + \left(\frac{2.272\theta_p}{1 - \theta_p} + 1 \right) B_L \omega^{1/2}} \quad [31]$$

$$j = -c^* \frac{\left(B_{sp} \exp \left[- \left(1 - \frac{\beta_{ad}}{2} \right) \frac{z_{ad} F}{RT} \eta_{ad} \right] \left(\frac{z - z_{ad}}{z} \frac{\theta_p}{1 - \theta_p} r_p^{-1} + \frac{z_{ad}}{z} B_{ad} \right) + \left(\frac{2.272\theta_p}{1 - \theta_p} \right) B_L \omega^{1/2} \right) B_L \omega^{1/2}}{B_{sp} \exp \left[- \left(1 - \frac{\beta_{ad}}{2} \right) \frac{z_{ad} F}{RT} \eta_{ad} \right] \left(\frac{z - z_{ad}}{z} \frac{\theta_p}{1 - \theta_p} r_p^{-1} + \frac{z_{ad}}{z} B_{ad} \right) + \left(\frac{2.272\theta_p}{1 - \theta_p} + 1 \right) B_L \omega^{1/2}} \quad [32]$$

contribution to the steady-state current.³³ It is possible to estimate an additional contribution to the current, j_{radial} , by considering the

Equations 27–32 assume no overlapping of surface diffusion areas, which is a restrictive condition, only valid with very low surface site

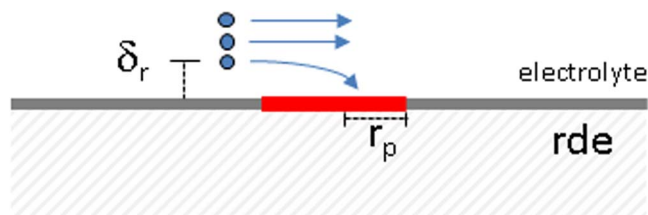


Figure 1. Generation of radial convective current.

densities, low surface diffusivities, and/or low overpotentials. Most general treatment should include the possibility of the overlapping of surface diffusion areas.

Overlapping of surface diffusion areas.—Surface diffusion overlapping will be included by using the same approximation as in previous work to a partially blocked surface.²³ Analogous equations are formulated and solved following an identical procedure for a reduction process preceded by reductive adsorption (Appendix B). The resulting expressions are:

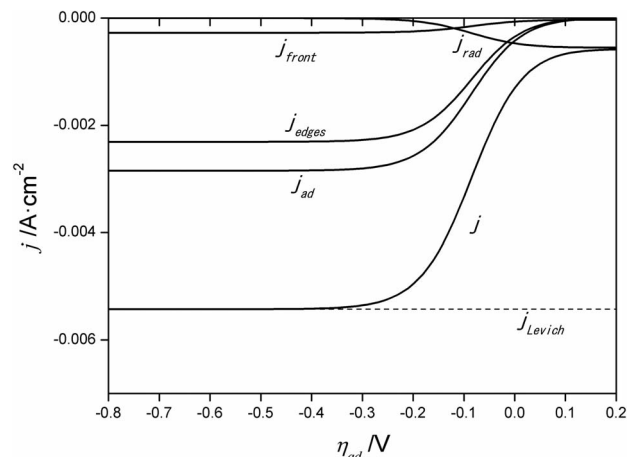


Figure 2. Components of the current as a function of overpotential, calculated with surface diffusion overlapping correction (Eqs. 34–38). Parameters: $\omega = 210 \text{ s}^{-1}$, $z = 4$, $z_{ad} = 1$, $D = 1.7 \cdot 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$, $D_s = 10^{-8} \text{ cm}^2 \cdot \text{s}^{-1}$, $\nu = 0.01 \text{ cm}^2 \cdot \text{s}^{-1}$, $c^* = 1.1 \cdot 10^{-6} \text{ mol cm}^{-3}$, $r_p = 10^{-7} \text{ cm}$, $\theta_p = 0.05$, $k_1 = 28000 \text{ s}^{-1}$, $k_2 = 0.006 \text{ cm} \cdot \text{s}^{-1}$, $\beta_{ad} = 0.5$.

lapping, for three values of β_{ad} parameter. High β_{ad} gives rise to intense surface overlapping, and the correction is more notorious.

$$c_{y=0} = c^* \frac{B_L \omega^{1/2}}{\frac{z-z_{ad}}{2z(1-\theta_p)} B_s^* N_p \exp\left[-\left(1 - \frac{\beta_{ad}}{2}\right) \frac{Fz_{ad}}{RT} \eta_{ad}\right] + B_{ad}^* \exp\left[-(1 - \beta_{ad}) \frac{Fz_{ad}}{RT} \eta_{ad}\right] + \left(\frac{2.272\theta_p}{1-\theta_p} + 1\right) B_L \omega^{1/2}} \quad [33]$$

$$j_{edges} = -c^* \frac{\frac{z-z_{ad}}{2z} B_L B_s^* N_p \exp\left[-\left(1 - \frac{\beta_{ad}}{2}\right) \frac{Fz_{ad}}{RT} \eta_{ad}\right] \omega^{1/2}}{\frac{z-z_{ad}}{2z(1-\theta_p)} B_s^* N_p \exp\left[-\left(1 - \frac{\beta_{ad}}{2}\right) \frac{Fz_{ad}}{RT} \eta_{ad}\right] + B_{ad}^* \exp\left[-(1 - \beta_{ad}) \frac{Fz_{ad}}{RT} \eta_{ad}\right] + \left(\frac{2.272\theta_p}{1-\theta_p} + 1\right) B_L \omega^{1/2}} \quad [34]$$

$$j_{ad} = -c^* \frac{B_L B_{ad}^* (1 - \theta_p) \exp\left[-(1 - \beta_{ad}) \frac{Fz_{ad}}{RT} \eta_{ad}\right] \omega^{1/2}}{\frac{z-z_{ad}}{2z(1-\theta_p)} B_s^* N_p \exp\left[-\left(1 - \frac{\beta_{ad}}{2}\right) \frac{Fz_{ad}}{RT} \eta_{ad}\right] + B_{ad}^* \exp\left[-(1 - \beta_{ad}) \frac{Fz_{ad}}{RT} \eta_{ad}\right] + \left(\frac{2.272\theta_p}{1-\theta_p} + 1\right) B_L \omega^{1/2}} \quad [35]$$

$$j_{front} = -c^* B_L \theta_p \omega^{1/2} \left(1 - \frac{B_L \omega^{1/2}}{\frac{z-z_{ad}}{2z(1-\theta_p)} B_s^* N_p \exp\left[-\left(1 - \frac{\beta_{ad}}{2}\right) \frac{Fz_{ad}}{RT} \eta_{ad}\right] + B_{ad}^* \exp\left[-(1 - \beta_{ad}) \frac{Fz_{ad}}{RT} \eta_{ad}\right] + \left(\frac{2.272\theta_p}{1-\theta_p} + 1\right) B_L \omega^{1/2}} \right) \quad [36]$$

$$j_{radial} = -c^* \frac{2.272\theta_p B_L^2 \omega}{\frac{z-z_{ad}}{2z(1-\theta_p)} B_s^* N_p \exp\left[-\left(1 - \frac{\beta_{ad}}{2}\right) \frac{Fz_{ad}}{RT} \eta_{ad}\right] + B_{ad}^* \exp\left[-(1 - \beta_{ad}) \frac{Fz_{ad}}{RT} \eta_{ad}\right] + \left(\frac{2.272\theta_p}{1-\theta_p} + 1\right) B_L \omega^{1/2}} \quad [37]$$

$$j = -c^* B_L \omega^{1/2} \left(1 - \frac{B_L \omega^{1/2}}{\frac{z-z_{ad}}{2z(1-\theta_p)} B_s^* N_p \exp\left[-\left(1 - \frac{\beta_{ad}}{2}\right) \frac{Fz_{ad}}{RT} \eta_{ad}\right] + B_{ad}^* \exp\left[-(1 - \beta_{ad}) \frac{Fz_{ad}}{RT} \eta_{ad}\right] + \left(\frac{2.272\theta_p}{1-\theta_p} + 1\right) B_L \omega^{1/2}} \right) \quad [38]$$

Where B_s^* and B_{ad}^* are given by Eqs. B8 and B12, respectively. Fig. 2 shows a plot of the different current contributions. Fig. 3 compares current - overpotential curves with and without surface diffusion over-

Koutecký-Levich (KL) analysis.—The plot $1/j$ vs $1/\omega^{1/2}$ is used for the analysis of rde results to obtain kinetics parameters of the electrochemical reaction.²⁹ The expression for a continuous disk electrode

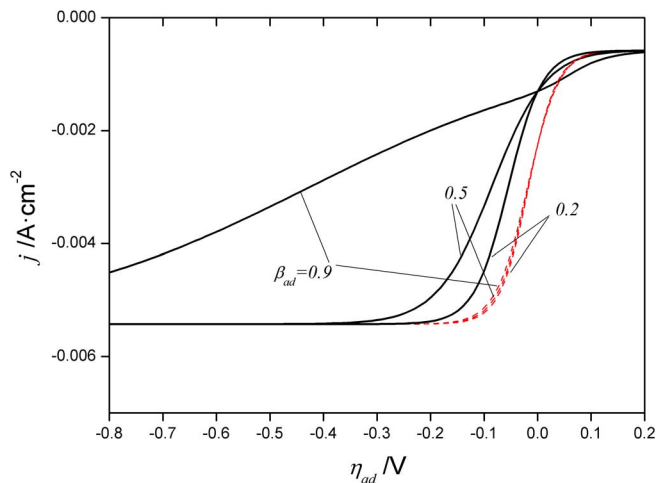


Figure 3. Current as a function of overpotential, calculated with (Eq. 38, continuous black line) and without (Eq. 32, red dashed line) surface diffusion overlapping correction, for three values of β_{ad} . Other parameters as in Fig. 2.

is:

$$\frac{1}{j} = \frac{1}{c^*} \left(\frac{1}{j_K} + \frac{1}{B_L \omega^{1/2}} \right) \quad [39]$$

Where j_K corresponds to the current in the absence of electrolyte mass-transfer limitation ($c_{y=0} = c^*$), limited by any other kinetics type (physical, chemical or electrochemical).^{29,34,35} When the limiting kinetics is surface diffusion and electroadsorption, the corresponding KL expression can be obtained from Eq. 38, accounting for diffusion area overlapping:

$$\frac{1}{j} = -\frac{1}{c^*} \left(\frac{1}{\frac{z-z_{ad}}{2z(1-\theta_p)} B_s^* N_p \exp[-(1-\frac{\beta_{ad}}{2}) \frac{Fz_{ad}}{RT} \eta_{ad}] + B_{ad}^* \exp[-(1-\beta_{ad}) \frac{Fz_{ad}}{RT} \eta_{ad}] + \left(\frac{2.272\theta_p}{1-\theta_p}\right) B_L \omega^{1/2}} + \frac{1}{B_L \omega^{1/2}} \right) \quad [40]$$

Notice that the first term in Eq. 40, corresponding to the KL intercept ($1/j_K$), includes a rotation rate dependent term ($\left(\frac{2.272\theta_p}{1-\theta_p}\right) B_L \omega^{1/2}$) accounting for radial convection. KL plots for different overpotentials are shown in Fig. 4. High overpotential and low rotation rates allows for current limitation by adsorption and surface diffusion. In this case, KL slope is the same as for the continuous rde (Eq. 39), and the intercept current (j_K), obtained by extrapolation, is determined by active sites distribution parameters (r_p , θ_p) and surface diffusion kinetics (B_s^* , B_{ad}^* , β_{ad} , z_{ad} , η_{ad}). The equation predicts a linear logarithmic dependence of j_K with overpotential with a change in the slope due to a change from $\beta_{ad}/2$ at low overpotential to β_{ad} at high overpotential (Fig. 5). Tafel slope doubling is a common effect of mass transport^{28,36-39}. Here, the slope change indicates the passing from growing surface diffusion areas at low overpotential to overlapped surface diffusion areas at high overpotential.

Radial convection predominance is attained at high enough rotation rates and/or low overpotentials. Predominance at high rotation rates is reflected by the increase in KL slope, approaching the value $m = -\frac{1}{c^* B_L} \left(\frac{\theta_p^{-1} + 1.272}{2.272} \right)$, while the intercept goes to zero (Fig. 4). Predominance at low overpotential leads to constant j_K (Fig. 5). In this way, the conditions when radial convection is predominant can be characterized experimentally if the rotation rates are accessible and there is no other kinetics limiting apart from surface diffusion kinetics (like charge transfer, or chemical reaction).

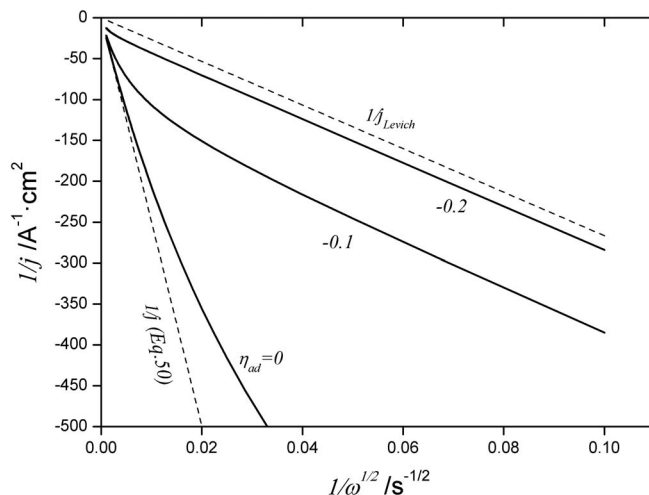


Figure 4. K-L plot (Eq. 40) for three values of η_{ad} , together with theoretical plot for a continuous rde (Eq. 39, $1/j_{Levich}$) and an array rde with predominant radial convection (Eq. 50). Other parameters as in Fig. 2.

Limiting cases.—There are some cases of practical relevance that give rise to simplification of the expressions.

Adsorption without charge transfer ($z_{ad} = 0$).—Total current (Eqs. 32 and 38, without and with surface diffusion overlapping, respectively) reduce to those obtained in previous work for physicochemical adsorption, ie Eqs. 24d and 28d in Ref. 23 (notice that expressions in Ref. 23 do not include the effect of radial convection). The KL

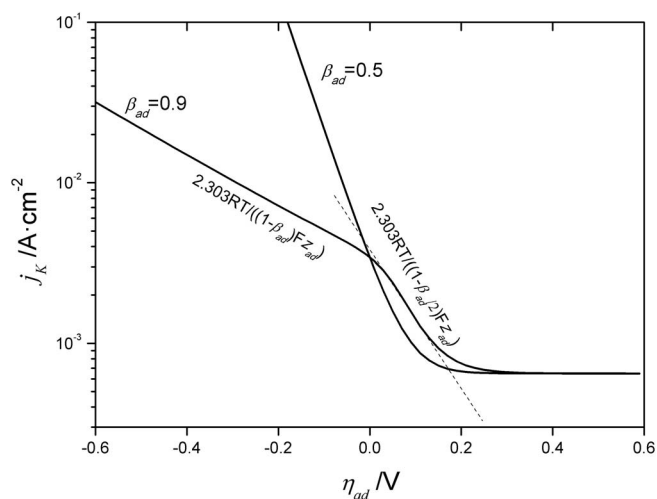


Figure 5. Plot of j_K as a function of overpotential for current limited by electroadsorption and surface diffusion (Eq. 40), for two values of β_{ad} . Expressions for Tafel slopes are indicated. Other parameters as in Fig. 2.

equations are (without and with surface diffusion overlapping):

$$\frac{1}{j} = -\frac{1}{c^*} \left(\frac{1 - \theta_p}{\pi r_p B_{sp} N_p + 2.272 \theta_p B_L \omega^{1/2}} + \frac{1}{B_L \omega^{1/2}} \right) \quad [41]$$

$$\frac{1}{j} = -\frac{1}{c^*} \left(\frac{1 - \theta_p}{0.5 B_s^* N_p + 2.272 \theta_p B_L \omega^{1/2}} + \frac{1}{B_L \omega^{1/2}} \right) \quad [42]$$

The KL slope is the same as for the continuous disk electrode, whereas the intercept is dependent on surface coverage and diffusion rate but is independent on overpotential.

Adsorption without charge transfer mechanism should give rise to well defined limiting currents in rde voltammetric experiments, below or at the Levich value ($j_L = -c^* B_L \omega^{1/2}$) depending on the surface centers density and surface diffusion length.^{22,23} In contrast, the electroadsorption mechanism is characterized by apparently increasing limiting currents with overpotential up to the Levich limiting current. Both types of behavior can be seen in many rde results of the recent literature of the oxygen reduction reaction on electrocatalytic surfaces.

Full charge transfer at adsorption ($z_{ad} = z$).—If the whole charge transfer occurs at the adsorption site, then the process occurring at the reaction site after surface diffusion is of physico-chemical nature. The expression for the total current with surface diffusion overlapping correction and accounting for radial convection from Eq. 38 is now:

$$j = -c^* \frac{\left(2z F k_2 \sqrt{\frac{D_s}{k_1}} (1 - (1 - \frac{\beta_{ad}}{2}) \frac{z_{ad} F}{RT} \eta_{ad}) \left(\frac{z - z_{ad}}{z} r_p^{-1} \frac{\theta_p}{1 - \theta_p} \right) + \left(\frac{2.272 \theta_p}{1 - \theta_p} \right) B_L \omega^{1/2} \right) B_L \omega^{1/2}}{2z F k_2 \sqrt{\frac{D_s}{k_1}} (1 - (1 - \frac{\beta_{ad}}{2}) \frac{z_{ad} F}{RT} \eta_{ad}) \left(\frac{z - z_{ad}}{z} r_p^{-1} \frac{\theta_p}{1 - \theta_p} \right) + \left(\frac{2.272 \theta_p}{1 - \theta_p} + 1 \right) B_L \omega^{1/2}} \quad [47]$$

$$\frac{1}{j} = -\frac{1}{c^*} \left(\frac{1}{\left(\left(\frac{2.272 \theta_p}{1 - \theta_p} \right) B_L \omega^{1/2} + 2z F k_2 \sqrt{\frac{D_s}{k_1}} (1 - (1 - \frac{\beta_{ad}}{2}) \frac{z_{ad} F}{RT} \eta_{ad}) \left(\frac{z - z_{ad}}{z} r_p^{-1} \frac{\theta_p}{1 - \theta_p} \right) \right)} + \frac{1}{B_L \omega^{1/2}} \right) \quad [48]$$

$$j = -c^* B_L \omega^{1/2} \times \left(1 - \frac{B_L \omega^{1/2}}{B_{ad}^* \exp \left[-(1 - \beta_{ad}) \frac{Fz}{RT} \eta_{ad} \right] + \left(\frac{2.272 \theta_p}{1 - \theta_p} + 1 \right) B_L \omega^{1/2}} \right) \quad [43]$$

Under high reductive overpotentials ($\eta_{ad} \ll 0$) the current reduces to the Levich equation ($j = -c^* B_L \omega^{1/2}$). The KL analysis results:

$$\frac{1}{j} = -\frac{1}{c^*} \times \left(\frac{1}{B_{ad}^* \exp \left[-(1 - \beta_{ad}) \frac{Fz}{RT} \eta_{ad} \right] + \left(\frac{2.272 \theta_p}{1 - \theta_p} \right) B_L \omega^{1/2}} + \frac{1}{B_L \omega^{1/2}} \right) \quad [44]$$

The intercept current shows an exponential dependence on overpotential that, together with the implicit dependence in B_{ad}^* (Eq. B12), give rise to a change in Tafel slope from $(1 - \beta_{ad}/2)$ to $(1 - \beta_{ad})$ when going from low to large (negative) overpotential. Experimentally, this process can be differentiated from the general case by lower Tafel slope values because they involve the adsorption charge corresponds with the full charge transferred. Full charge transfer at the adsorption step followed by surface diffusion can be the case of electrodeposition when adatoms are electrochemically generated and diffuse toward the growth sites.⁸

Large surface diffusion length ($\lambda_s \gg d_{1/2}$).—A third simplifying limiting case is under strong overlapping of surface diffusion areas, when the surface diffusion length is much larger than the distance between particles. The situation is probable at high coverage or high overpotential. The total current and KL expression obtained from Eq. 38:

$$j = -c^* \frac{z_{ad} F k_2 B_L \omega^{1/2}}{z_{ad} F k_2 + \exp \left[(1 - \beta_{ad}) \frac{z_{ad} F}{RT} \eta_{ad} \right] \left(\frac{2.272 \theta_p}{1 - \theta_p} + 1 \right) B_L \omega^{1/2}} \quad [45]$$

$$\frac{1}{j} = -\frac{1}{c^*} \times \left(\frac{1}{z_{ad} F k_2 \exp \left[-(1 - \beta_{ad}) \frac{Fz_{ad}}{RT} \eta_{ad} \right] + \left(\frac{2.272 \theta_p}{1 - \theta_p} \right) B_L \omega^{1/2}} + \frac{1}{B_L \omega^{1/2}} \right) \quad [46]$$

The KL plot keeps the same linear slope, whereas j_K shows a soft dependence with overpotential (if $z_{ad} \ll z$) and a single value of the Tafel slope.

Very short surface diffusion length ($\lambda_s \rightarrow 0$).—Under negligible surface diffusion, the total current can be obtained from Eq. 32 (no account of overlapping):

The intercept current shows now single linear dependence with overpotential. KL slope is the same as for the continuous electrode (except when radial convection term predominates). Short surface diffusion can be ascribed to the case of an electrochemical reaction preceded by electroadsorption on the reaction site. This situation was studied for continuous rde by Laviron, who shows the prevalence of the adsorbed reaction path over direct reaction by dissolved species.¹⁰ Vargas et al. assume a reaction limited by a Langmuir-Hinshelwood adsorption mechanism and arrive to a non-linear KL plot with decreasing slope when approaching the intercept,⁴⁰ which is different from the linear KL obtained here with Henry isotherm. Non-linearity of KL is also expected with electrodes covered by a film.²⁹

Negligible adsorbability.—If adsorption on inactive areas is low and the concentration of adsorbed species negligible, the reaction takes place predominantly by dissolved species on the front surface of reaction centers, and the current is given by:

$$j = -c^* \frac{2.272 B_L \omega^{1/2}}{1.272 + \theta_p^{-1}} \quad [49]$$

The KL relation is characterized by higher slope than the continuous disk value, and zero intercept (Fig. 4):

$$\frac{1}{j} = -\frac{1}{2.272 c^* B_L \omega^{1/2}} \left(1.272 + \frac{1}{\theta_p} \right) \quad [50]$$

Increasing KL slope is normally attributed in rde experiments to a decrease in the charge transfer number (z), for instances when

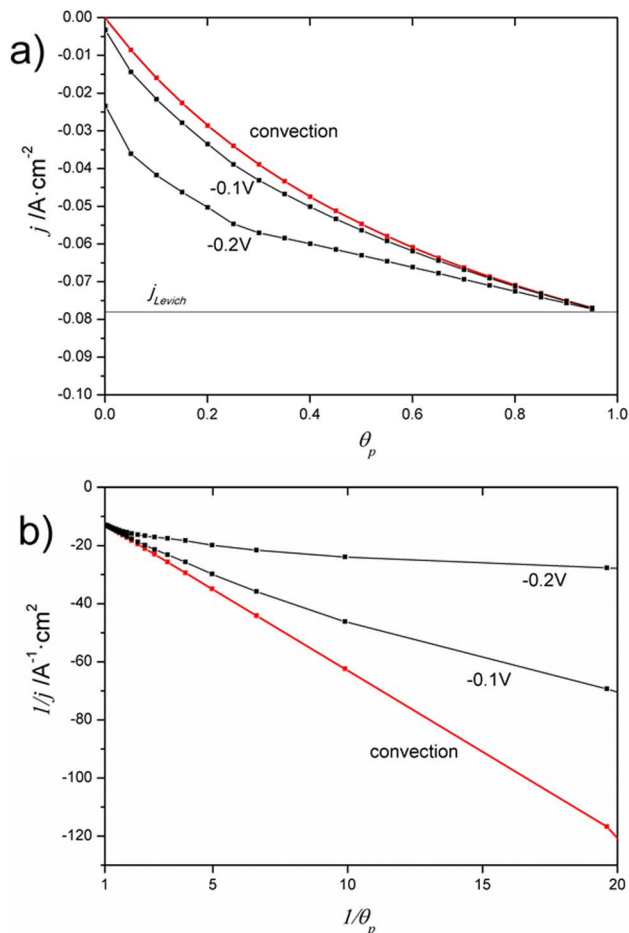


Figure 6. a) j vs. θ_p and b) $1/j$ vs. $1/\theta_p$ plots, without (Eqs. 49 and 50, red line), and with (Eqs. 38 and 40, black line) surface diffusion-electrosorption at two overpotentials. Other parameters as in Fig. 2.

hydrogen peroxide is produced in oxygen reduction experiments. Here it is shown that the same effect can be attributed to the radial convection over reaction sites. Fig. 6 shows the dependence of current on centers coverage and the inverse $1/j$ vs. $1/\theta_p$ relation for current limited by pure convection (radial and axial), according to Eqs. 49 and 50, compared with the case with surface diffusion and electroadsorption contribution (Eq. 40). Eq. 50 can be used to test experimentally the validity of the radial convection current (Eq. 24).

Table I summarizes the KL intercept values for the general and limiting cases studied.

Table I. KL intercept current (j_K), for a reduction process limited by reductive adsorption and surface diffusion, and under different limiting cases. The expressions are presented without and with surface diffusion overlapping correction. The term accounting for radial convection has been omitted.

Case	No overlapping correction	λ_s overlapping correction
General	$-c^* B_{sp} \exp[-(1 - \frac{\beta_{ad}}{2}) \frac{z_{ad} F}{RT} \eta_{ad}] (\frac{z-z_{ad}}{z} \frac{\theta_p}{1-\theta_p} r_p^{-1} + \frac{z_{ad}}{z} B_{ad})$	$-c^* (\frac{z-z_{ad}}{2z(1-\theta_p)}) B_s^* N_p \exp[-(1 - \frac{\beta_{ad}}{2}) \frac{F z_{ad}}{RT} \eta_{ad}]$
$z_{ad} = 0$	$-c^* \frac{\pi r_p B_{sp} N_p}{1-\theta_p}$	$+B_{ad}^* \exp[-(1 - \beta_{ad}) \frac{F z_{ad}}{RT} \eta_{ad}]$
$z_{ad} = z$	$-c^* B_{sp} B_{ad} \exp[-(1 - \frac{\beta}{2}) \frac{z F}{RT} \eta_{ad}]$	$-c^* \frac{0.5 B_s^* N_p}{1-\theta_p}$
$\lambda_s \gg d_{1/2}$	-	$-c^* B_{ad}^* \exp[-(1 - \beta) \frac{z F}{RT} \eta_{ad}]$
$\lambda_s \rightarrow 0$	$-c^* 2z F k_2 \sqrt{\frac{D_s}{k_1}} r_p^{-1} (\frac{z-z_{ad}}{z} \frac{\theta_p}{1-\theta_p}) (1 - (1 - \frac{\beta_{ad}}{2}) \frac{z_{ad} F}{RT} \eta_{ad})$	$-c^* z_{ad} F k_2 \exp[-(1 - \beta_{ad}) \frac{z_{ad} F}{RT} \eta_{ad}]$
Very low adsorption	0	0

Conclusions

An analytical model is presented for a reaction limited by adsorption with charge transfer and surface diffusion. The equations for the current are provided as a function of electroadsorption kinetics and surface diffusion, including the effects of surface diffusion overlapping and radial convection. Radial convective transport predominates at low overvoltage and high rotation rates, and gives rise to a simple linear relation between the inverse current and the inverse coverage of reaction sites ($1/j$ vs. $1/\theta_p$). The KL analysis for the general and some limiting cases are described.

Acknowledgment

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Appendix A

Eq. 7 can be solved by means of a change of variable to transform it into the homogeneous Bessel equation:

$$u = c_s - \frac{k_2}{k_1} c_{y=0} \exp\left[-\frac{z_{ad} F}{RT} \eta_{ad}\right] \quad [A1]$$

$$\frac{\partial^2 u}{\partial r^2} + \frac{1}{r} \frac{\partial u}{\partial r} - \frac{u}{\lambda_s^2} = 0 \quad [A2]$$

Boundary conditions for an array of centers under surface diffusion limitation are (Eq. 8):

$$c_s(r_p) = 0 \Rightarrow u(r_p) = -\frac{k_2}{k_1} c_{y=0} \exp\left[-\frac{z_{ad} F}{RT} \eta_{ad}\right] \quad [A3]$$

$$c_s(\infty) = \frac{k_2}{k_1} c_{y=0} \exp\left[-\frac{z_{ad} F}{RT} \eta_{ad}\right] \Rightarrow u(\infty) = 0 \quad [A4]$$

The first boundary implies surface diffusion limited reaction at active edges. The second boundary assumes equilibrium of the adsorbed concentration far from a reaction center; such boundary introduces the constraint of no surface diffusion overlapping so the inter-centers distance must be larger than the surface diffusion length. An approximate treatment for the case with overlapping surface diffusion will be given below using the geometrical approximation of an array of center to a partially blocked surface, as in previous work [Appendix B].

The general solution of Eq. A2 is:

$$u(r) = C_1 I_0\left(\frac{r}{\lambda_s}\right) + C_2 K_0\left(\frac{r}{\lambda_s}\right) \quad [A5]$$

The integration constants can be determined from the boundary conditions. By reverting the change of variables, the surface concentration results:

$$c_s(r) = \frac{k_2}{k_1} c_{y=0} \exp\left[-\frac{z_{ad} F}{RT} \eta_{ad}\right] \left(1 - \frac{K_0\left(\frac{r}{\lambda_s}\right)}{K_0\left(\frac{r_p}{\lambda_s}\right)}\right) \quad [A6]$$

Appendix B

The case for an array with overlapping surface diffusion areas will be treated by means of a geometrical approximation of an array of active centers to a partially blocked

surface, as in previous work.²³ The solution of Eq. 7 is now carried out with boundary conditions for a partially blocked surface:

$$c_s(r_s) = 0 \Rightarrow u(r_s) = -\frac{k_2^*}{k_1^*} c_{y=0} \exp\left[-\frac{z_{ad} F}{RT} \eta_{ad}\right]$$

$$\left(\frac{dc_s}{dr}\right)_{r=0} = 0 \Rightarrow \left(\frac{du}{dr}\right)_{r=0} = 0 \quad [B1]$$

The second boundary condition fixes the surface concentration gradient at the center of the blocked surface (Newmann boundary). Applying the boundaries to the solution of Eq. 7 (Eq. A5) results:

$$c_s(r) = \frac{k_2^*}{k_1^*} c_{y=0} \exp\left[-\frac{z_{ad} F}{RT} \eta_{ad}\right] \left(1 - \frac{I_0\left(\frac{r}{\lambda_s}\right)}{I_0\left(\frac{r_s}{\lambda_s}\right)}\right) \quad [B2]$$

The current at the edges of blocking areas (j_{edges}) of radius r_s , limited by surface diffusion with charge transfer adsorption is obtained from application of Fick's first law and Faraday law at the edges:

$$j_{edges}(\eta) = -(z - z_{ad}) F N_p 2\pi r_s D_s \left(\frac{\partial c_s}{\partial r}\right)_{r=r_s} \quad [B3]$$

The resulting expression is:

$$j_{edges}(\eta) = -\frac{(z - z_{ad})}{z} N_p \pi r_s c_{y=0} B_s \exp\left[-z_{ad} F \frac{\eta_{ad}}{RT} \left(1 - \frac{\beta}{2}\right)\right] \quad [B4]$$

$$B_s = 2z F k_2 \sqrt{\frac{D_s}{k_1}} \frac{I_1\left(\frac{r_s}{\lambda_s}\right)}{I_0\left(\frac{r_s}{\lambda_s}\right)} \quad [B5]$$

Eq. B4 can be used for a square array of centers with overlapping of surface diffusion areas by using a geometrical approximation consisting of the substitution of $2\pi r_s$ for parameter g (edges length), and replacing r_s in terms of the density and size of active centers:²³

$$g = 2r_s \left(\pi - 4\arccos\left(\frac{1}{2r_s \sqrt{N_p}}\right)\right)$$

$$r_s = 0.7 \left(\frac{1}{\sqrt{N_p}} - r_p\right) \quad [B6]$$

The resulting Equation for edges current with overlapping surface diffusion areas:

$$j_{edges}(\eta) = -\frac{(z - z_{ad})}{z} \frac{N_p}{2} c_{y=0} B_s^* \exp\left[-\left(1 - \frac{\beta}{2}\right) \frac{z_{ad} F}{RT} \eta_{ad}\right] \quad [B7]$$

$$B_s^* = g B_s \quad [B8]$$

Adsorption/desorption currents

The adsorption/desorption process also leads to a faradaic current that can be calculated from the following expression:

$$j_{ad} = \theta_s F z_{ad} \left(k_1^* \bar{c}_s \exp\left[\beta_{ad} \frac{z_{ad} F}{RT} \eta_{ad}\right] - k_2^* c_{y=0} \exp\left[-(1 - \beta_{ad}) \frac{z_{ad} F}{RT} \eta_{ad}\right]\right) \quad [B9]$$

The average value of c_s (\bar{c}_s) can be calculated from:

$$\bar{c}_s = \frac{1}{\pi r_s^2} \int_0^{r_s} 2\pi r c_s dr = \frac{k_2^*}{k_1^*} c_{y=0} \exp\left[-\frac{z_{ad} F}{RT} \eta_{ad}\right] \left(\frac{I_2\left(\frac{r_s}{\lambda_s}\right)}{I_0\left(\frac{r_s}{\lambda_s}\right)}\right) \quad [B10]$$

Where the integration is carried out using Eq. B2 for surface concentration. The current due to electroadsorption results:

$$j_{ad} = -\theta_s c_{y=0} B_{ad}^* \exp\left[-\frac{z_{ad}(1 - \beta_{ad})F}{RT} \eta\right] \quad [B11]$$

Where B_{ad}^* is given by

$$B_{ad}^* = z_{ad} F k_2 \left(1 - \frac{I_2\left(\frac{r_s}{\lambda_s}\right)}{I_0\left(\frac{r_s}{\lambda_s}\right)}\right) \quad [B12]$$

Total diffusion limiting current

For the total current flowing through the electrode surface, three contributions must be considered for surface diffusion limitation and with charge transfer adsorption:

$$j = j_{front} + j_{radial} + j_{edges} + j_{ad} \quad [B13]$$

j_{front} is the current due to reaction of dissolved species on the front surface of reaction centers under diffusion limiting conditions, given by Eq. 18; j_{radial} is the current due to radial convection over reaction centers, given by Eq. 24. Using electrolyte concentration over front of the surface ($c_{y=0}$) from Eq. 21, and solving the system of equations (Eqs. 18, 21, 24, B7, B11, and B13), yields Eqs. 33–38.

Appendix C

The reaction distance over reaction centers (δ_r) (Eqs. 22–25) can be estimated from the mass transfer number under laminar flow over a flat surface:³⁶

$$Sh_{avg} = 0.6774 Re^{1/2} Sc^{1/3} = 0.6774 \left(\frac{v_{r,\infty} 2r_p}{\nu}\right)^{1/2} \left(\frac{\nu}{D}\right)^{1/3} \quad [C1]$$

Where $v_{r,\infty}$ is the average radial velocity far from the disk surface. Using $v_{r,\infty} = \omega r$ and the relation between the average Sherwood number (Sh_{avg}) and the reaction distance:

$$Sh_{avg} = \frac{2r_p}{\delta_r} \quad [C2]$$

The reaction distance is:

$$\delta_r = 2.088 r_p^{1/2} r^{-1/2} \omega^{-1/2} D^{1/3} \nu^{1/6} \quad [C3]$$

The value resulting for aqueous solution at 2500 rpm and $r_p = 10^{-7}$ nm is $\delta_r = 0.6$ nm.

List of Symbols

Symbol	Description	Units
B_{ad}	adsorption factor (Eq. 17)	cm^{-1}
B_{ad}^*	adsorption factor with surface diffusion overlapping (Eq. B12)	$\text{C} \cdot \text{cm} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$
B_L	Levich factor (Eq. 19)	$\text{C} \cdot \text{cm} \cdot \text{mol}^{-1} \cdot \text{s}^{-1/2}$
B_s	partially blocked factor (Eq. B5)	$\text{C} \cdot \text{cm}^2 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$
B_s^*	(= $B_s \cdot g$) surface diffusion factor with surface diffusion overlapping (Eq. B8)	$\text{C} \cdot \text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$
B_{sp}	surface diffusion factor (Eq. 12)	$\text{C} \cdot \text{cm}^2 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$
c^*	bulk electrolyte concentration	$\text{mol} \cdot \text{cm}^{-3}$
c_s	adsorbed concentration	$\text{mol} \cdot \text{cm}^{-2}$
\bar{c}_s	average adsorbed concentration	$\text{mol} \cdot \text{cm}^{-2}$
$c_s(\infty)$	adsorbed concentration far from a reaction site	$\text{mol} \cdot \text{cm}^{-2}$
$c_{y=0}$	surface electrolyte concentration	$\text{mol} \cdot \text{cm}^{-3}$
$d_{1/2}$	Half distance between centers	cm
d	lattice parameter of a surface square distribution of centers	cm
D	diffusion coefficient in the electrolyte	$\text{cm}^2 \cdot \text{s}^{-1}$
D_s	surface diffusion coefficient	$\text{cm}^2 \cdot \text{s}^{-1}$
F	Faraday constant (96485)	$\text{C} \cdot \text{mol}^{-1}$
g	active edges length of superposed blocked areas (Eq. B6)	cm
I_n	modified Bessel function of first kind and order n	-
J	total current	$\text{A} \cdot \text{cm}^{-2}$
j_{edges}	current component due to adsorbed species reaction at the edges of the centers	$\text{A} \cdot \text{cm}^{-2}$
j_{front}	current component due to reaction of dissolved species at the front surface of the centers	$\text{A} \cdot \text{cm}^{-2}$
j_K	current from the intercept of a Koutecky-Levich plot	$\text{A} \cdot \text{cm}^{-2}$
j_L	diffusion limited current from Levich equation	$\text{A} \cdot \text{cm}^{-2}$
j_{radial}	current component due to radial convection over the centers	$\text{A} \cdot \text{cm}^{-2}$
k_1	desorption rate constant	s^{-1}
k_2	adsorption rate constant	$\text{cm} \cdot \text{s}^{-1}$
K_n	modified Bessel function of second kind and order n	-
N_p	density of centers	cm^{-2}
r	radial coordinate	cm
r_D	radius of the rotating disk	cm
r_p	radius of a reaction center (disk shape)	cm
r_s	radius of a blocking area (disk shape)	cm
v_r	average radial velocity	$\text{cm} \cdot \text{s}^{-1}$
Z	total electrons exchanged	-
z_{ad}	electrons exchanged at adsorption	-

Greek

β_{ad}	charge transfer coefficient of electroadsorption	-
δ_h	homogeneous concentration distance	cm
δ_r	reaction distance	cm
η_{ad}	overpotential	V
λ_s	surface diffusion length of electroactive species (Eq. 6)	cm
ν	kinematic viscosity	$\text{cm}^2 \cdot \text{s}^{-1}$
θ_p	coverage	-
ω	angular rotation rate	s^{-1}

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