Numerical solutions to the equation that governs steady-state mass transport to a hexagonal array of small redox-active disks embedded in an otherwise inert rotating disk electrode, RDE, under both diffusion-limited and mixed, first order kinetic control were obtained using COMSOL. Analytical expressions were found, which accurately reproduced the simulations, yielding, for limiting cases, a behavior in agreement with that reported in the literature. This formalism was applied to the analysis of thin films of nanoparticles dispersed in inert high area supports attached to the surface of an inactive RDE. The results obtained made it possible to verify that, at loadings within the range of relevance to electrocatalytic materials for low temperature fuel cells, the use of a modified Koutecky-Levich-like equation for determining rate constants of first order redox processes is indeed warranted.

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Theoretical Analysis of Microelectrode Arrays under Forced Convection

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Technical electrodes for low-temperature fuel cells and a few other applications are composed of electrocatalytic particles of nm in size dispersed in an otherwise inert matrix, most commonly high-area carbon, a tactic that makes it possible to optimize utilization of often expensive and scarce materials. Over the last two to three decades, strategies have been developed and implemented to reduce and hopefully replace such materials by more abundant and cheaper elements. Some schemes involve the use of submonolayer amounts of noble metals adsorbed on suitable inert core substrates, whereas others seek to modify carbon with functional groups, including common transition metals, e.g. iron and cobalt, yielding discrete microscopic active sites, the structure of which continues to be the subject of heated debate. Among the most common techniques for assessing the potency of these types of electrocatalysts is the rotating disk electrode, RDE, whereby a very thin layer of the material is spread on the surface of an inert disk made of an inactive substrate, such as glassy carbon, using a binder, commonly Nafion, to impart the layer mechanical integrity. It has become common practice among researchers in the area to analyze the results obtained from such measurements by using the Koutecky-Levich, KL, formalism, i.e. plots of the reciprocal of the observed current flowing through the RDE vs the reciprocal of the square root of the rotation rates for various values of the applied potential. This approach often yields straight lines from which kinetic parameters can be extracted, based on the values of the slope and intercepts, provided the system fulfills the strict requirements upon which the aforementioned formalism is based. Considerable care must be exercised, however, to properly account for mass transport effects toward such an ensemble of individual active sites. In particular, as the density of nanoparticles or active sites is decreased, each site behaves as an independent ultramicroelectrode, a factor that is not considered in the KL formalism. Although significant progress has been made toward gaining a theoretical understanding of arrays of electrodes incorporating active materials in the form of spheres or disks either attached onto or embedded into otherwise inert flat substrates, a strict and explicit analysis of data collected for these systems under forced convection has not, as of yet, been reported in the literature.

This contribution presents a rigorous analysis of data collected with a RDE incorporating arrays of disks embedded in a hexagonally close-packed arrangement on its surface under steady-state conditions based on numerical simulations using COMSOL. This arrangement affords an accurate representation of ensembles of spherical particles of the same diameter. Also to be discussed are analytical expressions which, provided certain conditions are met, closely reproduce the results of the simulations.

Theoretical Aspects

Of concern here is to find solutions of the steady state convective-diffusion equation that governs mass transport for a rotating disk electrode (RDE) of radius \( r_2 \) consisting of an array of a number, \( N_1 \), of hexagonally packed, electrochemically active disk electrodes of radius \( r_1 \), individually surrounded by a concentric insulating ring, of radius, \( r_3 \), as depicted schematically in the Left Panel, Figure 1. The approach to be employed regards the response of the system to be given by the sum of contributions due to identical individual disk-ring electrodes assuming the axial fluid velocity to be given by the leading term in the Cochran expansion for a RDE, and a total neglect of radial convection (see “Governing Equation”, Table I). This tactic reduces the problem to solving the governing equation for a single cylinder or, equivalently, within the axisymmetric domain specified in the Right Panel, Figure 1, subject to the appropriate boundary conditions (see Table I). The latter include no flux across the insulating segments, i.e. the curved wall and the ring, and constant concentration of reactant at the flat surface opposite to that of the ring disk. This specific strategy, introduced by Amatore et al. more than three decades ago, allows

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Figure 1. Left Panel: Top-down view of a section of the surface of a RDE consisting of a hexagonal, closed-packed arrangement of disk microelectrodes of radius \( r_1 \) embedded in concentric inactive disks of radius \( r_2 \). Right Panel: Domain employed in the theoretical simulations (see shaded area), where \( R_1 \) and \( R_2 \) are the corresponding dimensionless radii and \( H \) the dimensionless height of an individual cylinder in the array (see Table I).
a rather general analysis of the problem, whereby issues regarding the degree of diffusion layers overlap is implicitly accounted for (see also Davies et al. Ref. 14). In this analysis, the redox reaction responsible for the current was assumed to be first order in the reactant. Also defined in Table I are the dimensionless variables and dimensionless parameters expressed in terms of their dimensioned counterparts.

Calculations were performed using COMSOL Multiphysics v5.2, by selecting the height of the domain in terms of dimensionless variables, \( H \), (see right panel, Figure 1) to be three times the dimensionless thickness of the diffusion boundary layer, \( \Delta = 1.612S^{-1/3} \), where \( S = \nu/D \), the Schmidt number, \( \nu \) is the kinematic viscosity of the solution and \( D \), the diffusion coefficient of the redox active species. No changes in the results were observed by increasing \( H \) beyond this value. Furthermore, the dimensionless radius of the domain, \( R_3 \), in terms of the corresponding radius of the microelectrode, \( R_1 \), is given by \( R_2 = R_1/\sqrt{1-\theta} \), where 1 - \( \theta \) is the coverage of the active area. Lastly, the results will be expressed in terms of a dimensionless current, \( \rho \), defined in Eq. 1 as the ratio of the actual current normalized by the limiting current for a fully active disk surface, as predicted by the Levich classical formalism, a quantity referred to in the literature as the attenuation.\(^{12,15} \) As indicated in Eq. 1, the integral in the numerator is over the surface of the active disk, \( R_1 \), whereas the normalizing factor, \( \pi R_2^2 \), represents the dimensionless area of the disk-ring.

\[
\rho = \left( \frac{1}{\pi R_2^2} \right) \frac{\int_0^{R_1} 2\pi R \psi_n|_{Z=0} dR}{\left( \frac{1}{\Delta \cdot Sc} \right)} \quad [1]
\]

and \( \psi_n|_{Z=0} = \frac{\psi}{\pi R_2^2} \int_0^{R_1} \frac{dR}{Z} \) represents the total (convective and diffusive), normal outward flux across the boundary at \( Z = 0 \), as implemented in COMSOL. The domain was meshed with a free-triangular mesh of size \( M = (10/\Delta + 1/R_1)^{-1} \), with an electrode boundary 100 times smaller than \( M \), and a mesh surrounding \( Z = 0 \), \( R = R_1 \) 200 times smaller than the mesh of the domain. Lastly, the Codina crosswind stabilization was used,\(^{16} \) but it correctly predicted the behavior of a macroscopic fully homogeneous electrode.

For the type of applications of interest herein, \( r_1 \) ranges from 2 to 40 nm, and the rotation rates \( \omega \) can vary from 100 to 2500 rpm (the maximum \( \omega \) achievable with a popular commercial RDE brand), hence, \( 2 \times 10^{-5} \leq R_1 \leq 5 \times 10^{-3} \). Furthermore, \( \nu = 0.01 \text{ cm}^2/\text{s} \), and \( D \), for common redox species, is in the range \( 10^{-6} \leq D < 5 \times 10^{-3} \text{ cm}^2/\text{s} \). On this basis, \( \Delta \), would fall in the range 0.075 to 0.276. Without loss of generality, and unless otherwise noted, all the calculations presented herein will assume \( D = 10^{-5} \text{ cm}^2/\text{s} \), i.e. \( \Delta = 0.16 \), and \( Sc = 1000 \), which represent values commonly found in actual experiments.

**Results**

**Diffusion limited current for arrays of active disk-insulating ring electrodes.**—Shown in Panel A, Figure 2, are plots of \( \rho_{lim} \), the value of \( \rho \) under diffusion limited conditions, i.e. \( \psi_{n|Z=0} > 0 \) (see Table I), obtained from the simulations, as a function of 1 - \( \theta \), i.e. the coverage of the active area of the entire electrode. As indicated in the figure, in the limit as 1 - \( \theta \) \( \rightarrow 1 \), \( \rho_{lim} \rightarrow 1 \), i.e. the current approaches that corresponding to a fully active surface, and, as 1 - \( \theta \) \( \rightarrow 0 \), \( \rho_{lim} \rightarrow 0 \), i.e. the electrode becomes fully blocked. A more detailed presentation of these data for small values of 1 - \( \theta \) is given in log-log form in Panel B, Figure 2. In this region, the micro-electrodes in the array become separated by distances large enough so that their diffusion boundary layers are not expected to overlap significantly, and \( r_1 \) (or \( R_1 \)) is much smaller than the thickness of the diffusion boundary layer of the RDE, \( \delta \) (or \( \Delta \)). Under such conditions, each disk behaves as a regular disk microelectrode, \( \mu_{disk} \), for which the steady state diffusion limited current is indeed well-known,\(^{18} \) i.e. \( i_{lim}^{disk} = 4nFAC_{bulk} D/\pi r_0 \), where \( r_0 \) is the radius of the \( \mu_{disk} \). On this basis, the diffusion limited current for the entire array can be expressed in terms of the dimensionless quantities defined herein as follows:

\[
\rho_{lim, R_1 < 1, \theta -> 0} = (1 - \theta) \left( \frac{4 \Delta}{\pi R_1} \right) \quad [2]
\]

i.e. \( \rho_{lim, R_1 < 1, \theta -> 0} \) for a fixed value of \( \Delta/R_1 \), becomes proportional to 1 - \( \theta \), the total active area of the array, which correctly predicts the diminishing role of convection when the disks are small and well separated. In related work, Amatore et al.\(^{17} \) derived a theoretical expression for the limiting current flowing through an active disk embedded in the flat end of a cylinder under quiescent conditions, assuming the flux of the reactive species was constant over the entire opposing wall. In fact, equating Eqs. (8a) and (9) in Amatore et al.\(^{11} \) and substituting the result into Eq. (54) in Treimer et al.,\(^{10} \) yields exactly Eq. 2 above.

An empirical equation that fits the data across all values of 1 - \( \theta \) and \( R_1 \) may be shown to be given by:

\[
\rho_{lim} = \left( 1 - (1 - \theta) \left( \frac{4 \Delta}{\pi R_1} \right) \right) + \left( \frac{\pi R_1 \Delta}{4} \right) \left( \frac{1}{\sqrt{1+\theta}} \right) + \frac{1}{1+\theta} \quad [3]
\]

where for Sc ranging from 800 to 1400, \( \lambda \approx 1.60(R_1 + 1) \). Shown in Figure 3 are plots of the % error = 100 \times (\rho_{lim} - \rho_{lim}^3)/\rho_{lim}^3 as a function of 1 - \( \theta \) for various values of \( R_1 \) (see legend), where the symbol \( \rho_{lim}^3 \) represents the values of \( \rho_{lim} \) as determined from Eq. 3. As clearly evidenced from these data, Eq. 3

**Table I. Governing Equations and Boundary Conditions Both in Dimensioned and Dimensionless Forms (see text for details).**

| Governing Equation | Dimensionless Form |
|--------------------|--------------------|
| \( D \left( \frac{\partial^2 \psi}{\partial r^2} + \frac{\partial \psi}{r \partial r} \right) = -a \left( \frac{\partial \psi}{\partial r} \right) \right)^2 + \frac{\partial^2 \psi}{\partial z^2} \right) \] | \( \frac{1}{\pi R_2^2} \int_0^{R_1} \frac{2\pi R \psi_n|_{Z=0} dR}{\left( \frac{1}{\Delta \cdot Sc} \right)} \) |
| Geometric Parameters | \( r_2 = r_1/\sqrt{1-\theta} \) |
| \( h = 38 \) | \( H = 3\Delta \) |
| \( \Delta = 1.612S^{-1/3} \) | \( \Delta = 1.612S^{-1/3} \) |
| \( \psi_n|_{Z=0} = \psi_{n|Z=0} \) | \( \psi_n|_{Z=0} = KC \) |
| \( k_o = D/\delta \) | \( k_o = 1/(Sc \cdot \Delta) \) |
| Limiting Current | \( \psi_n|_{Z=0} = KC \) |
| \( C_{Z=0, R \leq R_1} = 0 \) | \( C_{Z=0, R \leq R_1} = 0 \) |
| \( \rho_{lim}^3 \) | \( \rho_{lim}^3 \) |

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reproduces within less than 1% the results obtained from our simulations.

Active Disk Electrode Below Limiting Current.—Additional calculations were performed, wherein the total normal flux of reactant to the disk electrode was assumed to be controlled by the kinetics of a first-order reaction in the reactant, i.e. \( \Psi' = K C_x \), for a range of dimensionless rate constants, \( K = k/\nu \), where \( k \) is the dimensioned potential-dependent rate constant of a redox process. The results obtained could be represented to a very good degree of accuracy by the following analytical expression:

\[
\frac{1}{\rho_{im}^{lim}} = \frac{1}{(1 - \theta) K/K_o} + \frac{1}{\rho_{im}^{lim}}
\]

(4)

In fact, for \( 0.01 < 1 - \theta < 0.99 \), \( 0.0005 < R_1 < 0.002 \), and \( 10^{-4} < K/K_o < 10^{5} \), where \( K_o \) is defined as the rate of mass transport to a fully-active electrode surface under diffusion limited conditions (see Table I), the agreement was better than 2% at a value of \( R_1 = 0.002 \) (see Figure 4), and even smaller for decreasing values of \( R_1 \) (data not shown).

For very small values of \( K/K_o \), the first term in the right hand side of Eq. 4 will be larger than the second term, and, as expected, the system will be under kinetic control. Furthermore, for \( R_1 \) much smaller than the thickness of the diffusion layer of the RDE (as would be the case within the range of parameters of interest herein), \( 4 \Delta / \pi R_1 >> 1 \), and, therefore, Eq. 3 simplifies to

\[
\frac{1}{\rho_{im,R_1<\Delta}} = \frac{\pi R_1}{4 \Delta (1 - 0)} + 1
\]

(5)

This expression can then be substituted into Eq. 4 to yield

\[
\frac{1}{\rho_k} = \frac{K_o}{(1 - \theta) K} + \frac{\pi R_1}{4 \Delta (1 - 0)} + 1
\]

(6)

which, as shown in Figure 4, reproduces the numerical simulations to within 5% even up to a value of \( R_1 \) as large as 0.002 and a 1-\( \theta \) as low as 0.05. Rather unexpectedly, Eq. 6 is identical to that proposed by Zoski et al.8 (cf. Eq. 10 in this reference) once the dimensionless quantities are expressed in terms of their dimensioned counterparts, i.e.

\[
\frac{1}{I_{array}} = \frac{1}{nF A_{disk} (1 - 0) c_{bulk}} \left\{ \frac{\pi r_1}{4D} + \frac{\delta}{D} (1 - 0) + \frac{1}{k} \right\}
\]

(7)

where \( I_{array} \) is the current of the whole array and \( A_{disk} \) is the cross-sectional area of the entire disk electrode. As noted by these authors, the first two terms in parenthesis are attributed to mass transport to the individual nanoparticles under quiescent conditions and to convection, respectively, and the last term accounts for the kinetics. Moreover, in the absence of convection, Eq. 7 reduces to that proposed recently by Kim and Bard19 (See Eqs. 2 and 3 in that reference) in their analysis of Koutecky-Levich plots for microelectrodes. On the other hand, when the transport due to convection becomes much larger than diffusion toward the small particles, or equivalently, \( \frac{\delta}{r_1} (1 - 0) \gg 1 \), Eq. 7 yields:

\[
\frac{1}{I_{array}} = \frac{1}{nF A_{disk} c_{bulk}} \left\{ \frac{\delta}{D} + \frac{1}{k (1 - 0)} \right\}
\]

(8)

Eq. 8 is a Koutecky-Levich expression, where the kinetic term becomes proportional to the active area of the electrode, \( 1 - \theta \), and the
convective contribution to the cross-sectional area of the electrode, $A_{\text{disk}}$. Since the range of rotation rates of RDE measurements involving dispersed electrocatalysts rarely exceeds 2500 rpm and $r_1 < 30$ nm, even for a 1% coverage, the first term in parenthesis in the right hand of Eq. 7 would represent a contribution of 3% of the mass transport limitation. In fact, for four surveyed papers$^{4,20–22}$ the ratio $4\delta(1 - \theta)/\pi r_1$ was on the order of $10^2$. A similar criterion has been suggested by Masa et al.$^7$ and Davies et al.$^{14}$ who use the relationship between the diffusion boundary layer thickness and the separation between the particles, i.e. $\delta/2r_2$, or equivalently, $\delta\sqrt{1 - \bar{\theta}/2r_1} \gg 1$. Hence, contributions to mass transport to the nanoparticles other than those derived from convection are indeed negligible, and, therefore, Eq. 8 can be used with confidence.

Concluding Remarks

Analytical expressions have been herein proposed that reproduce rather accurately mass transport to an array of hexagonally-packed active disks embedded in an otherwise inert rotating disk electrode. Conditions were found under which one such expression reduces to that proposed earlier by Zoski et al., for a microelectrode array under linear convection. Moreover, in the absence of convection, this expression reduces to a Koutecky-Levich type equation recently proposed by Bard et al. for a first-order redox reaction on a microelectrode under stagnant conditions. It followed from the analysis presented in this work that, for particles of nm size and loadings most commonly used in the literature, a Koutecky-Levich analysis is indeed warranted.

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References

1. S. Listser and G. McLean, Journal of Power Sources, 130, 61 (2004).
2. R. R. Adric, J. Zhang, K. Sasaki, M. B. Vukmirovic, M. Shao, J. X. Wang, A. U. Nilekar, M. Mavrikakis, J. A. Valerio, and F. Uribe, Topics in Catalysis, 46, 249 (2007).
3. R. Ohnman, A. L. Dicks, and Z. Zha, International Journal of Hydrogen Energy, 37, 357 (2012).
4. T. J. Schmidt, H. A. Gasteiger, G. D. Stäb, P. M. Urban, D. M. Kolb, and R. J. Behm, Journal of The Electrochemical Society, 145, 2354 (1998).
5. T. J. Schmidt, H. A. Gasteiger, and R. J. Behm, Journal of The Electrochemical Society, 146, 1296 (1999).
6. K. J. J. Mayrhofer, B. B. Blizanac, M. Arenz, V. R. Stamenkovic, P. N. Ross, and N. M. Markovic, The Journal of Physical Chemistry B, 109, 14433 (2005).
7. J. Masa, C. Batchelor-McAuley, W. Schulmann, and R. G. Compton, Nano Research, 7, 71 (2014).
8. C. G. Zoski, J. L. Fernández, K. Imaduwage, D. Gunasekara, and R. Vudari, Journal of Electroanalytical Chemistry, 651, 80 (2011).
9. K. R. Ward, M. Gara, N. S. Lawrence, R. S. Hartshorne, and R. G. Compton, Journal of Electroanalytical Chemistry, 695, 1 (2013).
10. S. Treimer, A. Tang, and D. C. Johnson, Electroanalysis, 14, 165 (2002).
11. C. Amatore, J. M. Savelé, and D. Tessier, Journal of Electroanalytical Chemistry and Interfacial Electrochemistry, 147, 39 (1983).
12. E. Levart, J. Electroanal. Chem. Interfacial Electrochem., 187, 247 (1985).
13. J. Newman, The Journal of Physical Chemistry, 70, 1327 (1966).
14. T. J. Davies and R. G. Compton, Journal of Electroanalytical Chemistry, 585, 63 (2005).
15. A. J. J. Jeburan, N. S. Georgescu, and D. A. Scherson, The Journal of Physical Chemistry C (2016).
16. F. Schlegel, Understanding Stabilization Methods, in, COMSOL Blog, https://www.comsol.com/blogs/understanding-stabilization-methods/ (2014).
17. C. Bertet, R. Ferrigno, and H. H. Girault, Journal of Electroanalytical Chemistry, 486, 56 (2000).
18. K. Aoki and J. Osteryoung, Journal of Electroanalytical Chemistry and Interfacial Electrochemistry, 122, 19 (1981).
19. J. Kim and A. J. Bard, Analytical Chemistry, 88, 1742 (2016).
20. K. Ke, K. Hiroshima, Y. Kamitaka, T. Hatanaka, and Y. Morimoto, Electrochimica Acta, 72, 120 (2012).
21. V. S. Murthy, R. C. Urian, and S. Mukerjee, The Journal of Physical Chemistry B, 108, 11011 (2004).
22. T. Inasaki and S. Kobayashi, Electrochimica Acta, 54, 4893 (2009).