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The Approach to Limiting Current
in a Stagnant Diffusion Cell

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December, 1969

Abstract

The transient behavior of surface concentration and current density in a stagnant diffusion cell have been worked out with consideration of surface and concentration overpotentials and the ohmic resistance of the solution. Both theoretically and experimentally, the current density is found to overshoot the limiting current density during part of the transient.

Introduction

A stagnant diffusion cell is a capillary cell with an electrode at one end of a capillary filled with solution and open at the other end into a container with solution and containing the counter electrode. Such a cell is commonly used for diffusivity measurements^{1,2} because of its simple experimental setup and the easy measurement of current and time.

Early analyses^{3,4} showed that, for a constant concentration at the electrode surface, the current decreases in inverse proportion to the square root of time in an unsteady, one-dimensional diffusion, or $i\sqrt{t}$ is a constant for a given concentration of solution. Accordingly, the current would be infinite at zero time. Actually, for a constant applied potential, the current is finite and remains more or less constant until the reactant concentration at the electrode surface approaches a value of zero. The time required for this depends on the potential difference applied across the two electrodes and the properties of the solution itself. It may range from less than one hundred seconds in a well supported solution to several tens of thousands of seconds in a solution of a single electrolyte.

Davis, Horvath, and Tobias² have included the surface overpotential for linear electrochemical kinetics in their treatment. In the present work, the analysis is extended to include the ohmic resistance of the solution, as well as nonlinear electrochemical kinetics.

This work was motivated not so much by the ohmic and kinetic limitation at short times but more by the shape of the logarithmic current-time curves obtained in the measurement of integral diffusion coefficients,⁵

the study of the effect of ionic migration on limiting currents,⁶ and attempts to obtain limiting currents in cupric sulfate solutions in the absence of sulfuric acid.⁷ Under certain conditions, the current overshoots the limiting current. A similar phenomenon was predicted in the analysis of the current distribution on a rotating disk electrode^{8,9,10} and on plane electrodes in the walls of a flow channel.^{11,12} Experimental confirmation obtained in the present work may thus lend support to those analyses. The similarity to polarography in a binary salt solution¹³ should also be noted. No overshoot was predicted in that work, but a recalculation for that system shows that there can be an overshoot for large applied potentials.

Analysis

With the assumption of constant physical properties, the equation for unsteady diffusion in a stagnant diffusion cell for a solution without supporting electrolyte or with an excess of supporting electrolyte reduces to

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial y^2} \quad , \quad (1)$$

where $c = c_+/\nu_+ = c_-/\nu_-$ and

$$D = \frac{z_+ u_+ D_- - z_- u_- D_+}{z_+ u_+ - z_- u_-}$$

for a solution of a single electrolyte, and where c and D represent the concentration and effective diffusion coefficient of the reactant for a solution with an excess of supporting electrolyte.

Equation 1 should be solved with the initial condition that the concentration is uniform, $c = c_{\infty}$, throughout the capillary at $t = 0$. The concentration at the electrode surface can be taken, for the moment, to be an unknown function of time, $c = c_o(t)$ at $y = 0$. By taking the Laplace transform of equation 1 with respect to time and solving the resulting ordinary differential equation, one obtains for the transform of the concentration

$$\bar{c} = \frac{c_{\infty}}{s} + [\bar{c}_o(s) - \frac{c_{\infty}}{s}] e^{-y \sqrt{s/D}} \quad , \quad (2)$$

where s is the Laplace transform variable. Differentiation of equation 2 with respect to y , setting y equal to zero, and inversion by means of the convolution integral produce an equation relating the concentration gradient at the surface to the variation of the surface concentration

$$\left. \frac{\partial c}{\partial y} \right|_{y=0} = \frac{-1}{\sqrt{\pi D}} \int_0^t \frac{dc_o(t')}{dt'} \frac{1}{\sqrt{t-t'}} dt' \quad . \quad (3)$$

This equation is useful because the current density is also related to the concentration gradient at the surface

$$i = \frac{nFD}{1-t_R} \left. \frac{\partial c}{\partial y} \right|_{y=0} \quad , \quad (4)$$

where t_R is the transference number of the reactant ($t_R=0$ with an excess of supporting electrolyte). The current density is further related to the surface overpotential η_s by

$$i = i_o \left(\frac{c_o}{c_\infty} \right)^\gamma \left[\exp \left\{ \frac{\alpha Z F}{RT} \eta_s \right\} - \exp \left\{ - \frac{\beta Z F}{RT} \eta_s \right\} \right], \quad (5)$$

where i_o is the exchange current density, αZ and βZ are the transfer coefficients, and γ expresses the concentration dependence of the exchange current density.

The ohmic drop in a capillary of length L is

$$\Delta\Phi_{ohm} = iL/\kappa_\infty, \quad (6)$$

and the concentration overpotential is

$$\eta_c = \frac{RT}{ZF} \left[\ln \left(\frac{c_o}{c_\infty} \right) + t_R \left(1 - \frac{c_o}{c_\infty} \right) \right], \quad (7)$$

where $Z = -z_+ z_- / (z_+ - z_-)$ for reaction of a cation from a solution of a single electrolyte, and $Z = -n$ for a solution with an excess of supporting electrolyte. For the case of metal deposition from a solution of a single electrolyte, the concentration overpotential expressed by equation 7 includes an ohmic contribution due to the variation of the conductivity in the diffusion layer.¹⁴ Hence, it is appropriate to use the conductivity of the bulk solution in equation 6. The total potential difference V_* applied between the electrode and the solution outside the capillary (as measured by a reference electrode of the same kind as the working electrode) is the sum of the concentration overpotential, the surface overpotential, and the ohmic potential drop

$$V_* = \eta_c + \eta_s + \Delta\phi_{ohm} \quad (8)$$

It seems appropriate to define a dimensionless current density I and a dimensionless exchange current density J as

$$I = \frac{ZFL}{RT\kappa_\infty} i \quad , \quad J = \frac{ZFL}{RT\kappa_\infty} i_o \quad , \quad (9)$$

to define a dimensionless applied potential V and total overpotential η as

$$V = \frac{ZF}{RT} V_* \quad , \quad \eta = \frac{ZF}{RT} (\eta_c + \eta_s) \quad , \quad (10)$$

and a dimensionless surface concentration θ as

$$\theta = c_o/c_\infty \quad . \quad (11)$$

Then equations 5 through 8 can be rewritten as

$$I = V - \eta = J[\theta^{\gamma-\alpha} e^{\alpha E} - \theta^{\gamma+\beta} e^{-\beta E}] \quad (12)$$

where

$$E = \eta - t_R(1-\theta) \quad , \quad (13)$$

and equations 3 and 4 can be combined to read

$$I = \frac{NL}{\sqrt{\pi D}} \int_0^t \frac{d\theta(t')}{dt'} \frac{1}{\sqrt{t-t'}} dt' \quad , \quad (14)$$

where

$$N = - \frac{nZF^2 Dc_{\infty}}{(1-t_R)RT\kappa_{\infty}} \quad (15)$$

is a dimensionless parameter related to the relative importance of concentration overpotential and ohmic drop in balancing the applied potential. If we now define a dimensionless time τ by

$$\tau = t/t_c, \quad (16)$$

where

$$t_c = N^2 L^2 / \pi D, \quad (17)$$

then equation 14 can be written as

$$I = \int_0^{\tau} \frac{d\theta(\tau')}{d\tau'} \frac{1}{\sqrt{\tau-\tau'}} d\tau'. \quad (18)$$

Equations 12, 13, and 18 constitute four equations for the determination of the time dependence of I , θ , and η , as well as E . They can be solved numerically when the six parameters, α , β , γ , J , V , and t_R are known for a given system. One more parameter, V , could be eliminated, but this might obscure the physical significance of the results.

Numerical Calculation Method

The integral in equation 18 was approximated by a sum by an adaptation of the method of Acrivos and Chambré.¹⁵ Since equation 18 involves an indefinite integral, it is only necessary to solve a

nonlinear set of equations at each time step. By the nature of the problem, $\theta = 1$ at $\tau = 0$. For the details of the calculation method, one may refer to reference 16.

Theoretical Results

The dimensionless current density I is plotted against the dimensionless time τ in figure 1 with V as a parameter. The values of α , β , γ , J , and t_R are all taken to be equal to 0.5. The higher the total applied potential V , the shorter the flat part of the curve. For high values of V , the current density overshoots the limiting current, a phenomenon that has been observed experimentally in many of our curves of log current versus log time. For a given value of V , the flat part of the curve persists longer for larger values of the characteristic time t_c . A high value of t_c results from a high transference number of the reactant and a low conductivity of the solution. For a solution without supporting electrolyte, t_c might easily be 5×10^5 sec.

The decrease of surface concentration θ with time is plotted in figure 2 with identical parameters. The higher the applied potential, the faster the surface concentration drops to zero. The time required for the surface concentration to drop to 10 percent and 1 percent of the bulk value is plotted in figure 3.

Experimental Results

Figure 4 shows the transient behavior of the current density with various amounts of supporting electrolyte. These curves have qualitatively the same shape as the theoretical curves in figure 1, particularly with regard to the transient overshooting of the limiting current.

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Figure 1. Decrease of current density in a stagnant diffusion cell.

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Figure 2. Decrease of surface concentration in a stagnant diffusion cell.

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Figure 3. Transient time in a stagnant diffusion cell, showing the dimensionless time required for the surface concentration to drop to 10 and 1 percent of the bulk value.

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Figure 4. Observed transient behavior in a stagnant diffusion cell (5 cm long), showing the effect of concentration of supporting electrolyte.

	CuSO ₄	H ₂ SO ₄	Applied potential	t_c/V^2
	<u>M</u>	<u>M</u>	volt	sec
1	0.1003	0.175	0.355	28.5
2	0.0998	0.100	0.355	71.2
3	0.0999	0.050	0.355	198
4	0.1001	0.020	0.350	553

The surface concentration was also measured optically for an unsupported, 0.0385 M cupric sulfate solution at 25°C; the results are shown in figure 5 for two values of the applied potential, 0.80 and 0.60 volt. The measured variations of the surface concentration are compared with the theoretical predictions in the same figure. The following data were used for the calculations:

		source
conductivity κ_{∞}	4.13×10^{-3} mho/cm	17
diffusivity D	6.07×10^{-6} cm ² /sec	18
transference number t_R	0.383	19
kinetic parameters, α, β, γ	0.5	
Z	1	

The length of the cell L was 15 cm, the area of the electrode was 0.178 cm², and the calculated characteristic time t_c was 5.60×10^6 sec. There are no exchange current density data available in the literature for an unsupported CuSO₄ solution, a reasonable estimate being that it lies between 0.1 and 1.0 mA/cm². The solid lines are theoretical calculations at an exchange current density of 0.1 mA/cm², and the dashed lines are calculated at 1.0 mA/cm². The solid lines represent a satisfactory fit to the experimental results.

An unexplained observation should be recorded here. For a solution 0.1 M in CuSO₄ and 1.375 M in H₂SO₄, the current time curves in figure 6 were obtained. The current drops suddenly at about 0.3 sec. This phenomenon was fairly reproducible in a well supported electrolyte. No such step change was observed for solutions with little or no supporting electrolyte.

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Figure 5. Transient behavior of surface concentration of copper sulfate (0.0385M) in a stagnant diffusion cell (● 0.60 volt; ○ 0.80 volt; dashed lines, $i_0 = 1.0 \text{ mA/cm}^2$, solid lines, $i_0 = 0.1 \text{ mA/cm}^2$).

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Figure 6. Theoretical and observed transient behavior at very short time.
Total applied voltage 0.225 V, ● Run 82, ○ Run 83; ▲ Run 84; △ Run 85.

Before the runs, the electrode was predeposited with copper at 0.1 volt for one to three minutes. Values of the parameters for the theoretical calculations are $\alpha = 0.75$, $\beta = 0.25$, $\gamma = 0.5$, $t_R = 0$, $\kappa_\infty = 0.493$ mho/cm, $Z = 2$, $D = 5.09 \times 10^{-6}$ cm²/sec, $t_c = 740$ sec, $V_* = 0.225$ volt, and the exchange current density is estimated to lie between 1 and 10 mA/cm² for a cathode surface prepared by electrodeposition.²⁰

Before the step change of current density, the horizontal part of the curve was found to fall between the curves for theoretical predictions of exchange current of 1 and 10 mA/cm². The charging of the electrode double layer should be complete in a time of about 0.5 millisecond.

Conclusion

In this work, the transient behavior has been worked out for a stagnant diffusion cell. The resulting time dependence of the surface concentration for an unsupported electrolyte agrees with the theoretical predictions within the uncertainty of the available electrochemical kinetic parameters. The current density is found, experimentally and theoretically, to overshoot the limiting current, in harmony with predictions for the current distribution on plane and disk electrodes.

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Nomenclature

c_i	concentration of species i , mole/cm ³
c_o	surface concentration of reactant, mole/cm ³
D	diffusion coefficient, cm ² /sec
F	Faraday's constant, 96,500 coul/equiv
i	current density, A/cm ²
i_o	exchange current density, A/cm ²
I	dimensionless current density
J	dimensionless exchange current density
L	length of diffusion cell, cm
n	number of electrons produced when one reactant ion or molecule reacts
N	dimensionless parameter
R	universal gas constant, joule/mole-deg
s	Laplace transform variable, sec ⁻¹
t	time, sec
t_c	characteristic time, sec
t_R	transference number of reactant
T	temperature, deg K
u_i	mobility of species i , cm ² -mole/joule-sec
V	dimensionless applied potential
V_*	applied potential, volt
y	distance from electrode, cm
z_i	charge number of species i
Z	$-z_+z_-/(z_+-z_-)$ for unsupported electrolyte - n with excess supporting electrolyte

α, β, γ	electrochemical kinetic parameters
η	dimensionless total overpotential
η_c	concentration overpotential, volt
η_s	surface overpotential, volt
θ	dimensionless surface concentration
κ_∞	conductivity of the bulk solution, mho/cm
ν_+, ν_-	numbers of cations and anions produced by dissociation of one molecule of electrolyte
τ	dimensionless time
$\Delta\Phi_{ohm}$	ohmic potential drop, volt

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