in a Large Gas Fluidized Bed," *Can. J. of Chem. Eng.*, **51**, 401 (1973).

George, S. E., and J. R. Grace, "Entrainment of Particles from Aggregative Fluidized Beds," *AIChE Symp. Ser.*, **74**, No. 176, 67 (1978).

Horio, M., A. Taki, Y. S. Hsieh, and I. Muchi, "Elutriation and Particle Transport Through the Freeboard of a Gas-Solid Fluidized Bed," *Fluidization*, eds., J. R. Grace and J. M. Matsen, Plenum Press, New York and London, 509 (1980).

Langmuir, I. J., "The Velocity of Reaction in Gases Moving Through Heated Vessels and the Effects of Convection and Diffusion," Amer. Chem. Soc., **30**, 1742 (1908).

de Lasa, H. I., and J. R. Grace, "The Influence of the Freeboard Region in a Fluidized Bed Catalytic Cracking Regenerator," *AIChE J.*, **25**, No. 6, 984 (1979).

Matsen, J. M., "Entrainment Research: Achievements and Opportunities," Proceedings of NSF Workshop on Fluidization, H. Litman, p. 452 (1979).

Miyauchi, T., and S. Furusaki, "Relative Contribution of Variables Affecting the Reaction in Fluid Bed Contractors," *AIChE J.*, **20**, No. 6, 1087 (1974).

Rajan, R. R., and C. Y. Wen, "A Comprehensive Model for Fluidized Bed Coal Combustors," *AIChE J.*, **26**, No. 4, 642 (1980).

Rowe, P. N., K. T. Claxton, and J. B. Lewis, "Heat and Mass Transfer from a Single Sphere in an Extensive Flowing Fluid," *Trans. I. Chem. E.*, **43**, T14 (1965).

Wen, C. Y., *Dilute and Dense Phase Pneumatic Transport*, Chapter in "Bulk Materials Handling," **1**, ed., M. C. Hawk, University of Pittsburgh, 258 (1971).

Wen, C. Y., and L. H. Chen, "A Fluidized Bed Combustor Freeboard Model," The Proceedings of the 6th International Conference on Fluidized Bed Combustion, **III**, 1115 (1980).

Wen, C. Y., and L. H. Chen, "Fluidized Bed Freeboard Phenomena—Entrainment and Elutriation," *AIChE J.* (Jan., 1982).

Wen, C. Y., and L. T. Fan, "Model for Flow Systems and Chemical Reactors," Marcel Dekker, Inc., New York (1975).

Wen, C. Y., and R. F. Hashinger, "Elutriation of Solid Particles from a Dense Phase Fluidized Bed," *AIChE J.*, **6**, No. 2, 220 (1960).

Wen, C. Y., and W. S. O'Brien, *Pneumatic Conveying and Transporting*, Chapter 3 in "Gas-Solids Handling in the Process Industries," eds., J. M. Marchello and A. Gomezplata, Marcel Dekker, Inc., 89 (1976).

Yates, J. G., and P. N. Rowe, "A Model for Chemical Reaction in the Freeboard Region Above a Fluidized Bed," *Trans. Instn. Chem. Engrs.*, **55**, 137 (1977).

Zenz, F. A., and N. A. Weil, "A Theoretical-Empirical Approach to the Mechanism of Particle Entrainment from Fluidized Beds," *AIChE J.*, **4**, No. 4, 472 (1958).

Manuscript received June 16, 1981; revision received February 4, and accepted February 22, 1982

R & D NOTES

Polarographic Technique for the Determination of Effective Surface Area of Electrodes

R. J. LUTZ, ARUN MENAWAT,
and J. I. PETERSON

Biomedical Engineering and Instrumentation Branch
Division of Research Services
National Institutes of Health
Bethesda, MD 20205

INTRODUCTION

This paper describes a voltage-sweep polarographic method for determining the effective surface area of metal electrodes *in situ*. Sawyer and Roberts (1974) discuss the notion that the real or true surface area of a solid electrode can differ from its projected or geometric area because of surface roughness. This is particularly true for platinized platinum electrodes. Situations may arise where the surface of an electrode has an irregular geometry which makes micrometer or optical measurements difficult. In our own recent work, platinum electrodes involved in an experiment are not easily accessible for visual area measurements. The polarographic technique that we have utilized is a simple and reliable method which overcomes these difficulties. It has potential application in microelectrode studies where surface area is a required parameter.

BACKGROUND

The area measurement method is particularly relevant to work in our laboratory that has involved the measurement of wall shear stress and mass transfer coefficients in plastic models of arterial geometries with the goal of understanding the interrelationship of fluid flow and the initiation of atherosclerosis (Lutz et al., 1977). Wall shear stress and mass transfer coefficients were measured using an electrochemical technique described by Hanratty and co-worker for turbulence measurements in pipes (Fortuna and

---

0001-1541-82-6540-1027-$2.00. © The American Institute of Chemical Engineers, 1982.

Hanratty, 1971; Mizushina, 1971). This technique has potential for continued biomedical applications. A considerable body of literature exists, for example, regarding shear measurements in arterial branching flow systems (e.g., Bergel et al., 1976; Nerem and Cornhill, 1980), and around prosthetic heart valves (e.g., Yoganathan et al., 1978). The electrochemical shear technique which requires a knowledge of the surface area of the electrodes may find increased utility in these systems. Briefly, this shear technique utilizes a small inert electrode, usually of nickel or platinum wire, imbedded flush with the wall of the flow conduit. The test solution consists of a redox couple (commonly, potassium ferricyanide and potassium ferrocyanide) which flows through the model. A diffusion limited reduction reaction occurs at the small platinum cathode which is positioned in the model at the desired location for shear rate or mass transfer measurement. A large platinum anode downstream provides the reverse reaction maintaining constant electrolyte composition. The diffusion current to the cathode is coupled to the convective motion (velocity gradient) across the electrode surface. Solution of the boundary layer equations give the following result for shear rate, s, vs. electrode current, i: (Lutz et al., 1977)

$$s = Bi^3 \tag{1}$$

where the constant B is, among other things, a function of the electrode area. For circular electrodes, the constant is inversely proportional to the electrode diameter to the fifth power, D^5. In the mass transfer measurements the diffusion current, given by Faraday's equation, is equated to the flux of ferricyanide ions, represented by a mass transfer coefficient to give

$$k = \frac{i}{AFC_o} \tag{2}$$

where k = mass transfer coefficient
F = Faraday's constant
C_o = bulk concentration of ferricyanide
and A = electrode surface area.

In either case, accurate determinations of the effective electrode diameter are essential for calculating shear rate from Eq. 1, or mass transfer coefficient from Eq. 2.

METHODS

Consider a stationary electrode (cathode) whose circular cross sectional surface is exposed in a quiescent redox solution (in our case, 0.01 M potassium ferricyanide and 0.01 M potassium ferrocyanide in 1.0 X NaOH). If the initial potential is zero, ferricyanide is not reduced at the electrode. As the potential of the cathode is made continuously more negative, a charging current develops which eventually plateaus. Then the reduction current in the system increases as ferricyanide diffuses to and reacts at the cathode surface. At higher negative potentials, the system becomes concentration diffusion limited as reduction at the electrode surface is relatively fast compared with the rate of transport of ions to the surface. The bulk diffusion rate of the ferricyanide ions toward the electrode is not dependent on the electrode potential because the electric field is saturated by a high concentration of non-reducible ions (the basis of the polarographic principle). In time, a zone of depletion of ferricyanide concentration extends further and further from the electrode surface and the current decreases. The current thus passes through a maximum value, called the peak current, i_p. Mathematical analysis of the diffusion equations for this configuration has been presented by Randles (1948) and the solution is also given by Meites (1965, p. 414) as

$$i_p = (Kn^{3/2}D_o^{1/2}C_o)Av^{1/2} \tag{3}$$

where

A = the cross sectional area of the electrode
D_o = the diffusivity of the electroactive substance
C_o = the bulk concentration of the electroactive substance

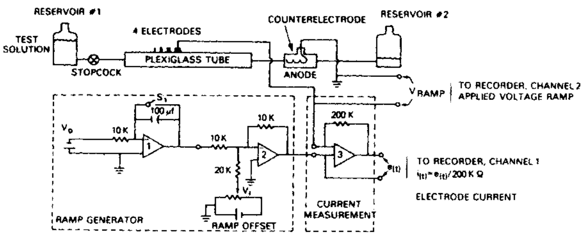

Figure 1. Schematic diagram of test system. Upper portion represents electrodes of known area imbedded in plexiglass tube. Lower portion is schematic of the ramp voltage generator and current measurement circuit.

v = the voltage ramp rate
n = the number of electrons exchanged per molecule
K = a numerical constant.

The original solution to the equation was derived for one dimensional diffusion to a recessed electrode surface through a stagnant column of fluid which does not precisely describe our experimental system. Therefore, for our system, the equation constant was determined empirically, and the technique was tested by checking the functional dependence of peak current on two parameters, electrode area, A, and ramp rate, v.

EXPERIMENTAL

The experimental system for testing the applicability of this technique to our shear stress and mass transfer system is shown in Figure 1. It consisted of a two foot long straight section of plexiglass tubing 1/4 in. (6.4 mm) in diameter with three platinum wire electrodes imbedded in the wall and polished flush with the lumenal surface. Three different sized electrodes were used each having a known diameter, 0.016, 0.020 and 0.032 in. (0.41, 0.51 and 0.81 mm). Each end of the plexiglass tube was connected to a 100 ml reservoir containing the test electrolyte (0.01M potassium ferricyanide, 0.01M potassium ferrocyanide in 1.0N NaOH). The tube was purged between each run using fluid from the reservoirs. A counter electrode (anode) of large surface area was made by coiling a 4 in. (102 mm) length of 0.032 in. (0.81 mm) platinum wire and it was positioned at one end of the plexiglass tube

A ramp voltage was applied to each of the three cathodes at several ramp speeds between 0.021 and 0.083 V/s, and the peak current was measured. The usual initial interelectrode voltage was +0.4 V. Figure 1 also shows a schematic of the circuit used to vary the ramp speed and the initial voltage. A simple integration circuit was used to generate the ramp voltage. The ramp or sweep rate was controlled by adjusting the variable DC supply, V_o (usually between 0.1 and 0.4 V). The initial DC voltage for the start of the ramp was determined by voltage source V_i, a constant input voltage into the negative input of the second operational amplifier for summing. The ramp was started and stopped by opening or closing switch S1. The potential applied to each electrode, V_{ramp}, was recorded with time on a chart recorder simultaneously with the output of amplifier 3, $e(t)$, which was a measure of the diffusion current $i(t)$ from which the peak current i_P could be determined. The peak current, i_p, was correlated with electrode area and voltage ramp speed in accordance with Eq. 3.

An independent check of the effective electrode surface area was made for each electrode in the system and compared to the area calculated from the measured wire diameter. This was accomplished by inserting the straight plexiglass tube which contained the electrodes into a flow system made up of the same redox solution and by establishing a condition of laminar, Poiseulle flow through the tube. Knowing the diameter of the tube and the steady flow rate, a theoretical calculation of shear rate, s, was possible. By measuring the current cubed, i^3, Eq. 1 was used to calculate B for each electrode. The constant B contains diameter as the unknown parameter (Lutz et al., 1977), so that the effective diameter can be estimated for each electrode by a method that is independent of the voltage sweep polarographic technique. In each case, the estimated effective electrode diameter fell within 10% to 13% of the nominal wire diameter as measured by a micrometer. The estimated diameter in each case was consistently greater than the micrometer measurement which could reflect a systematic error in calculating the effective electrode surface using the shear rate calculations of Eq. 1. For example, an error in the flow meter calibration would give an error in the theoretical value of shear in the tube and thus an error in the calculated effective area from Eq. 1. It could also indicate an effective surface area greater than that calculated from measured

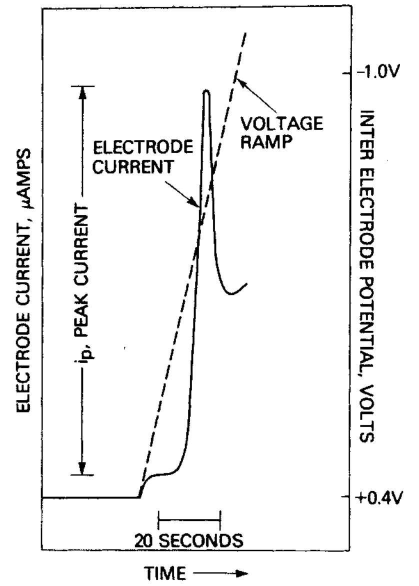

Figure 2. Typical chart recording of current from 0.032 in. (0.81 mm) platinum electrode (solid line) showing the changing applied potential (dashed line).

electrode diameter due to surface roughness or to slight curvature of the electrode surface which results from mounting it flush with the tube wall.

RESULTS

Figure 2 represents the data of a typical test showing electrode current and applied potential as a function of time for the 0.032 in. (0.81 mm) diameter electrode at a ramp rate of 0.042 V/s. The peak height, i_p, measured from the plateau in the current to its maximum, is 15.62 μamp. As the applied voltage proceeds from an initial value of +0.4 v toward more negative voltages, the current rises and falls, reaching a peak value, i_p in about 20 seconds. The peak current is plotted in Figure 3 for the three electrodes [0.016, 0.020, 0.032 in. (0.41, 0.51, 0.81 mm)] at three different voltage ramp speeds. For each ramp speed, a good linear correlation ($r^2 = 0.99$) existed between peak current, i_p, and electrode area. The lines extrapolate to zero peak current at zero area. If the data are replotted as peak current, i_p, vs. ramp speed, $(v)^{1/2}$, for each of three electrodes a similarly good linear correlation is achieved as shown in Figure 4. In the later case, the lines extrapolate to a small current value (less than 1 μamp) at zero ramp speed which reflects a small steady state current for the initial *DC* applied voltage. The results plotted in Figures 3 and 4 substantiate the functional dependence of peak current on electrode area and voltage ramp speed as given by Eq. 3. The reproducibility of repeat runs at a given electrode and a given ramp rate had a standard deviation of approximately 2%. For a fluid with an electroactive substance of known concentration and known diffusivity, the constant, K, in Eq. 3 can be determined empirically by taking the slopes of the lines in Figure 3. The percentage error associated with calculating surface area of this method using the empirical constant determined by our trial runs is approximately 3%.

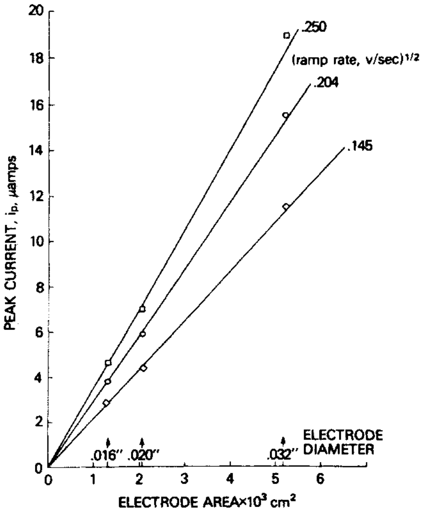

Figure 3. Test data plotted as peak current, i_p, versus electrode area for 3 electrodes 0.016, 0.020 and 0.032 in. (0.41, 0.51 and 0.81 mm) and at 3 different voltage ramp rates, 0.145 (◇), 0.204 (○), and 0.250 (□), $(V/S)^{1/2}$.

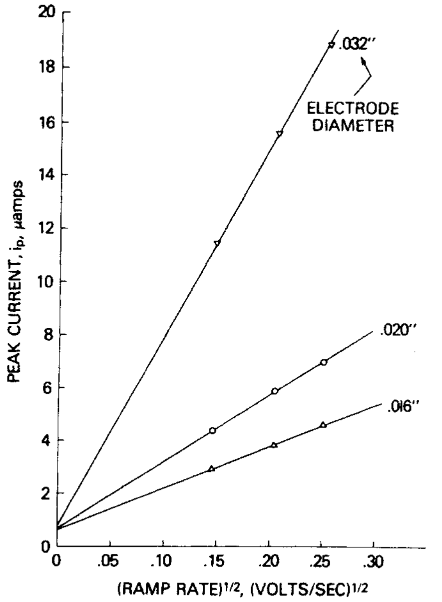

Figure 4. Test data replotted as peak current, i_p, versus voltage ramp rate to the one half power for 3 electrodes.

DISCUSSION

The results of our tests using the voltage sweep polarographic technique on electrodes of known surface area showed good agreement with Eq. (3) in terms of the functional dependence of peak current on area and ramp speed, even though our experimental arrangement deviated from the assumptions of one dimensional linear diffusion used to derive the equations. This is consistent with the findings of Lingane (1964) and Bard (1961) who used unshielded planar electrodes to study chronopotentiometry and chronoamperometry. They reported that the equations derived for these latter two methods using linear diffusion theory agreed well with experiments using unshielded electrodes possessing a hemispherical diffusion domain as long as the transition times were short. This is equivalent to using an appropriately fast ramp rate so that the peak current is achieved in a short time interval.

For a known diffusivity and electrolyte concentration, the constant K can be calculated from the slope of any line in Figure 3. For comparison, the K calculated from our experiments was 6.05×10^5 compared to a value of 2.69×10^5 given in Meites (1965, p. 414). The deviation probably results from a difference between the geometric configuration of our test system and that of the theoretical solution. For a fixed electrolyte composition and concentration at constant temperature the terms preceeding A and $v^{1/2}$ can be combined into a single, empirical calibration constant for the system and used to determine unknown electrode surface areas in systems with similar configurations as the test system. To this end, the technique was used to determine the unknown areas of numerous plantinum wire electrodes which were part of an arterial flow model being used for shear rate and mass transfer studies. The electrodes in the flow model were inaccessible to any convenient optical method for area measurement, and in some instances machining had altered the circular shape and smoothness of the electrode's surface. Optical methods would not reveal possible contaminants or films that could build up on the surfaces with time, thus changing their conductance properties. Impedance measurements seemed impractical since the numerous electrodes were distributed in several branch sites in the flow model each with a different location relative to the counter electrode which would alter the impedance readings.

This polarographic technique is a quick, convenient method for electrode area measurements involving simple circuitry. Area measurements are independent of the geometry of the fluid test system for sufficiently fast ramp rates so that the peak current is achieved before the zone of concentration depletion reaches toward the opposite walls of the test channel. For our system, it had the added advantage that the unknown area measurements could be made *in situ* with the identical test solution being used for the shear rate or mass transfer studies. Randles (1948) lists numerous other electrolyte systems for which the voltage sweep polarographic method is applicable. The method was originally intended as a means of measuring the concentration of electroactive species by polarography, but lends itself easily to electrode area calculations.

NOTATION

A = electrode surface area
B = constant in electrochemical shear rate equation (Lutz, 1977, Eq. 12)
C_o = bulk concentration of electroactive species
D = diameter of circular electrode
D_o = diffusivity of electroactive species
F = Faraday's constant
i = current in shear rate or mass transfer Eq. 1 or 2
i_p = peak current in voltage sweep polaragraphic method
k = mass transfer coefficient
K = constant in Eq. 3 (Meites, 1965)
n = number of electrons exchange per molecule
s = shear rate
v = voltage sweep rate

LITERATURE CITED

Bard, A. J., "Effect of Electrode Configuration and Transition Time in Solid Electrode Chronopotentiometry," *Anal. Chem.*, **33**, 11 (1961).

Bergel, D. H., R. M. Nerem, and C. J. Schwartz, "Fluid Dynamic Aspects of Arterial Disease," *Atherosclerosis*, **23**, 253 (1976).

Fortuna, G., and T. J. Hanratty, "Frequency Response of the Boundary Layer on Wall Transfer Probes," *Int. J. Heat and Mass Transfer*, **14**, 1499 (1971).

Lingane, P. J., "Chronopotentiometry and Chronoamperometry with Unshielded Planar Electrodes," *Anal. Chem.*, **36**, 1723 (1964).

Lutz, R. J., J. N. Cannon, K. B. Bischoff, R. L. Dedrick, R. K. Stiles, and D. L. Fry, "Wall Shear Stress Distribution in a Model Canine Artery During Steady Flow," *Circulation Research*, **41**, 391 (1977).

Meites, L., *Polarographic Techniques*, 2nd ed., John Wiley and Sons, New York (1965).

Mizushina, T., "The electrochemical method in transport phenomena," *Advances in Heat Transfer*, T. F. Irvin and J. P. Hartnett, eds., New York, Academy Press, p. 87 (1971).

Nerem, R. M., and J. F. Cornhill, "The Role of Fluid Mechanics in Atherogenesis, "*J. Biomech. Eng.*, **102**, 181 (1980).

Randles, J. E. B., "A Cathode Ray Polarograph, Part II: The Current-Voltage Curves," *Trans. Faraday Soc.*, **44**, 327 (1948).

Sawyer, D. T., and J. L. Roberts, *Experimental Electrochemistry for Chemists*, John Wiley and Son, New York (1974).

Yoganathan, A. P., W. H. Corcoran, and E. C. Harrison, "Wall Shear Stress Measurements in the Near Vicinity of Prosthetic Aortic Heart Valves," *J. of Bioeng.*, **2**, 369 (1978).

Manuscript received May 18, 1981; revision received September 14, and accepted October 9, 1981.

Numerical Calculation of Effectiveness Factors for the Michaelis-Menten Type Kinetics with High Thiele Moduli

HO NAM CHANG

Department of Chemical Engineering
Korea Advanced Institute of Science and Technology
Seoul 131, Korea

It is common chemical engineering practice to employ effectiveness factors in determining whether the chemical or biochemical reactions in solid-supported catalysts are limited by pore and/or film diffusion. The results of calculated effectiveness factors for various chemical reactions and the asymptotic expressions thereof are well documented by Aris (1975).

Recently, there have been extensive investigations on immobilized enzymes and microbial cells, which permit the reuse of a number of expensive enzymes and thus reduce the production cost of several biochemical processes (Mosbach, 1976). In order to understand the efficacies of these immobilized enzymes and cells compared with those of free ones, there have been growing interests among chemical and biochemical engineers in evaluating effectiveness factors for immobilized enzymes and cells in solid supports (Moo-Young and Kobayashi, 1972; Lee and Tsao, 1974; Ramachandran, 1975).

Unlike most of chemical reactions, enzymic reaction is an isothermal one and is represented mostly by the Michaelis-Menten equation. This simple looking boundary value problem has not been solved analytically yet. Therefore, generally we resort to numerical methods for the solution of the problem. However, in the case of high Thiele moduli it is not uncommon to experience numerical

0001-1541-82-6082-1030-$2.00. © The American Institute of Chemical Engineers, 1982.