CONTROLLED POTENTIAL COULOMETRY EMPLOYING

A ROTATING DISK ELECTRODE

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ABSTRACT:

The application of a rotating disk working electrode to controlled potential coulometry and the electroreduction of copper (II) at a copper disk electrode are described. The electrode has the advantages of reproducible and calculable mass transfer conditions and electrolysis currents which are relatively free of stirring noise. The evaluation of the diffusion coefficient of the electroactive species from the coulometric current-time curve and the fabrication of the electrolysis cell and electrode are also described.

INTRODUCTION

Controlled potential coulometry is frequently employed for analysis and for obtaining information about the rates and mechanisms of electrode reactions.[1] The current-time (i-t) equation governing the reduction of a substance, O, at a mass transfer controlled rate, which was first derived by Lingane,[2] is

$$i = i_o \exp(-p_o t) \qquad (1)$$

$$p_o = m_o A/V \qquad (2)$$

where A is the working electrode area, V is the solution volume and i_o the initial current. The mass transfer parameter, m_o, is a proportionality constant between the limiting current and the concentration, C_o,

$$i = nFAm_oC_o \qquad (3)$$

The parameter, m_o, is a function of the diffusion coefficient, D_o, the stirring rate, the electrode dimensions, and other solution properties. The hydrodynamic conditions in most coulometry cells are not sufficiently well-defined, however, to allow m_o, and hence p_o, to be calculated a priori.

The rotating disk electrode (RDE) has been used for numerous voltammetric studies because it has the advantage of having particularly well-defined and reproducible mass transfer conditions attending its behavior and because a theoretical formulation of its limiting current, in terms of the Levich equation,[3] can be given:

$$i = 0.62 \ nFAC_oD_o^{2/3}\nu^{-1/6}\omega^{1/2} \qquad (4)$$

where ν is the kinematic viscosity and ω is the angular velocity of rotation. Hence for a RDE employed as an electrode for coulometry,

$$p_o = 0.62 \ D_o^{2/3}\nu^{-1/6}\omega^{1/2}AV^{-1} \qquad (5)$$

This communication describes the application of the RDE to bulk electrolysis and coulometric studies and demonstrates that the i-t behavior is indeed described by equations (1) and (5). Other advantages that arise from the use of the RDE for coulometry are efficient electrolysis conditions (i.e., short electrolysis times or large p_o-values) and electrolysis currents which are largely free from stirring noise.

EXPERIMENTAL

Reagents. The potassium sulfate and cupric sulfate were both of analytical grade. Metallic copper (assay 99.9%) was used as the primary standard in the volumetric determination of cupric sulfate solutions and in the fabrication of the RDE. The copper sulfate solution was standardized iodometrically with sodium thiosulfate.

Apparatus. A Model 170 Electrochemistry System (Princeton Applied Research Corporation, Princeton, N. J.) was employed throughout the study. The electrolysis cell (Fig. 1) was constructed from 45 mm glass tubing.
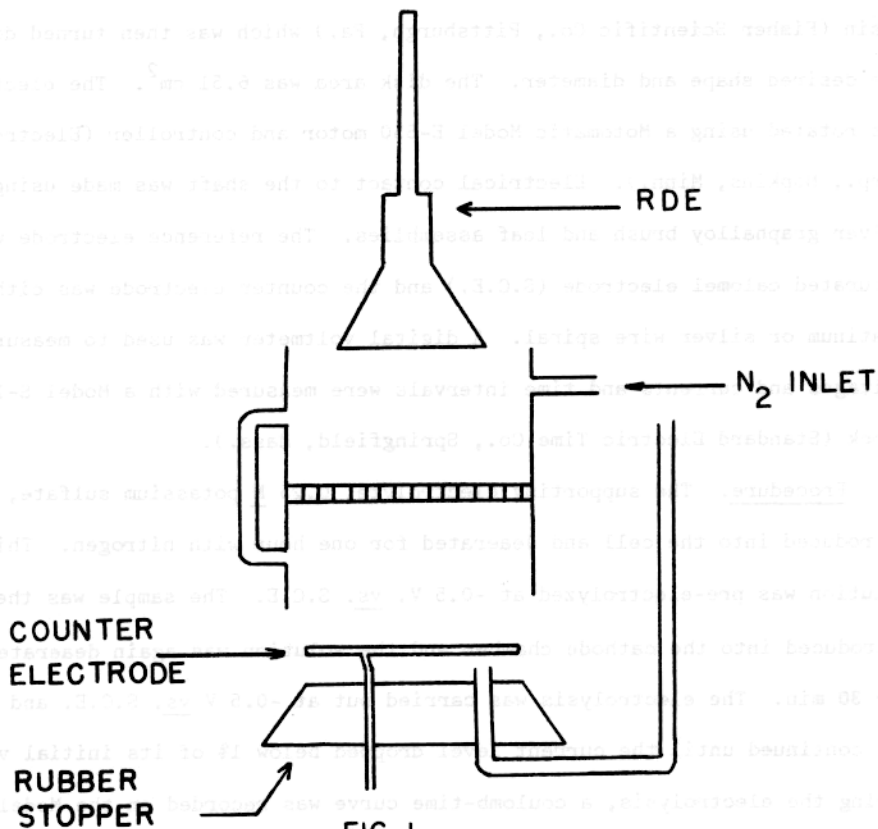

RDE

N$_2$ INLET

COUNTER
ELECTRODE

RUBBER
STOPPER

FIG. I

RDE and electrolysis cell.

A 40 mm medium fritted glass disk divided the 6 cm high cell approximately 2 cm from the bottom into cathode and anode compartments. The top of the cell was sealed with a Teflon cover with appropriate ports for a N$_2$ bubbler, the reference and the working electrode. The bottom was closed with a rubber stopper. A 4 mm side arm connecting cathode and anode compartment was used to equalize the pressure between the anode and cathode compartments when supporting electrolyte solution was introduced into the lower

compartment through the 5 mm glass tube which entered the lower compartment through the rubber stopper. The RDE working electrode was fabricated from a 5/16-inch thick copper disk of 2.88 cm diameter, which was soldered to a brass shaft 11 cm in length. This was mounted in Quickmount self-setting resin (Fisher Scientific Co., Pittsburgh, Pa.) which was then turned down to the desired shape and diameter. The disk area was 6.51 cm^2. The electrode was rotated using a Motomatic Model E-550 motor and controller (Electrocraft Corp., Hopkins, Minn.). Electrical contact to the shaft was made using two silver graphalloy brush and leaf assemblies. The reference electrode was a saturated calomel electrode (S.C.E.) and the counter electrode was either a platinum or silver wire spiral. A digital voltmeter was used to measure voltages and currents and time intervals were measured with a Model S-10 clock (Standard Electric Time Co., Springfield, Mass.).

Procedure. The supporting electrolyte, 0.25 M potassium sulfate, was introduced into the cell and deaerated for one hour with nitrogen. This solution was pre-electrolyzed at -0.5 V. vs. S.C.E. The sample was then introduced into the cathode chamber and the solution was again deaerated for 30 min. The electrolysis was carried out at -0.5 V vs. S.C.E. and was continued until the current level dropped below 1% of its initial value. During the electrolysis, a coulomb-time curve was recorded on the Model 170 recorder, and current values were obtained manually by monitoring the output of the Model 170 d.c. current amplifier.

RESULTS AND DISCUSSION

A typical ln i vs. time plot is shown in Fig. 2. The average value of m_o for four electrolyses of 0.4 milliequivalent-amounts of copper (II) contained in 15 ml. solution calculated from the slope of these curves was found to be $4.44 \pm 0.08 \times 10^{-3}$ cm/sec for an ω of 98.6 sec^{-1} (rotation rate of 15.6 rev/sec). This m_o-value, and a ν-value of 0.01 cm^2/sec yields a value of $6.16 \pm 0.16 \times 10^{-6}$ cm^2/sec for D_o for copper (II) ion in this
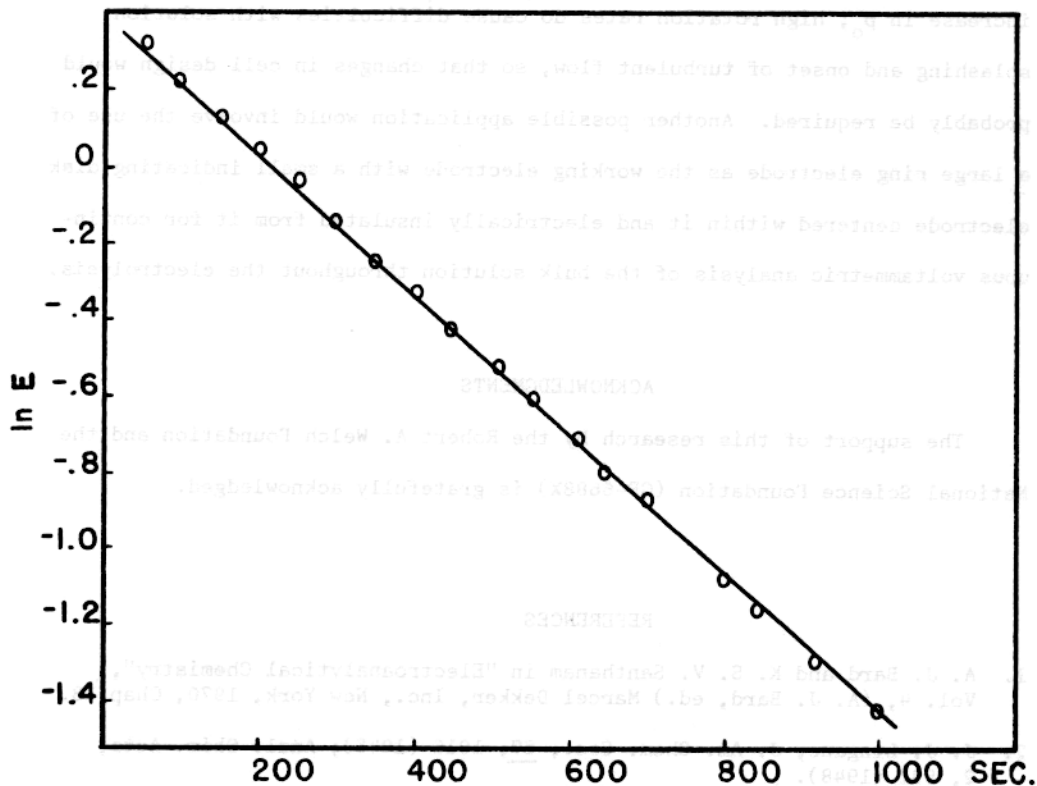
FIG. 2

Controlled potential coulometry current-time decay plot

medium. An independent calculation of D_o by RDE voltammetric determination of the limiting current and equation (4) yields a value of 5.95×10^{-6} cm^2/sec, in good agreement with the coulometric value. The error of the coulometric determinations of copper (II) at the RDE was less than 1%.

The results indicate that the RDE is a useful working electrode for coulometry with low stirring noise and the advantage of a p_o value that can be computed before the experiment from known electrode and solution parameters. The p_o-value could be increased, with a consequent decrease in the electrolysis time, by increasing ω. For example, a nine-fold increase in rotation rate, to about 8500 rev/min, would cause a three-fold

increase in p_o; high rotation rates do cause difficulties with solution splashing and onset of turbulent flow, so that changes in cell design would probably be required. Another possible application would involve the use of a large ring electrode as the working electrode with a small indicating disk electrode centered within it and electrically insulated from it for continuous voltammetric analysis of the bulk solution throughout the electrolysis.

ACKNOWLEDGMENTS

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