

THE DIFFUSION BOUNDARY LAYER OF A ROTATING DISK ELECTRODE AS A THIN LAYER SPECTROELECTROCHEMICAL CELL

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INTRODUCTION

Interest in our laboratory has focused on the development and implementation of techniques that combine well-defined convective diffusion systems with spectroscopic techniques, and thereby impart molecular specificity to the highly sensitive information derived from purely electrical measurements. The present contribution exploits the well-defined diffusion boundary layer generated by the RDE to create the equivalent of a spectroscopic cell bearing characteristics closely resembling those of optically transparent thin layer spectroelectrochemical cells (OTTLE) introduced by Kuwana and Heineman¹ for the detection and characterization of electrochemically generated species. One of the major advantages of this proposed strategy is the possibility of reducing the large IR drop of the OTTLE enabling transient measurements to be performed in a much shorter time scale. In addition, the ability to work under steady state with continuous replenishment of fresh solution might prove beneficial for the study of systems for which decomposition of electrogenerated species may impair reliable quantitative analysis. Although some preliminary aspects of this technique were presented in previous communication, the coupling of the RDE to a state of the art OLIS rapid scan spectrophotometer led to great improvements in detection sensitivity over a wide UV-visible spectral region.

EXPERIMENTAL

Measurements were performed with a commercial Au rotating disk electrode (Pine Instruments) using a rather conventional, three-electrode cell, equipped with a quartz window. Light emerging from an OLIS rapid scan spectrophotometer is directed at near normal incidence through the window toward the electrode. Once reflected, the beam exits the cell and is deflected via a mirror/lens assembly, placed at ca. 90° with respect to the axis of rotation of the disk, toward the flat end of a liquid filled optical fiber with its other end facing a photomultiplier. Experiments were performed in 10mM K₄Fe(CN)₆ in 0.25 M K₂SO₄ aqueous solutions prepared with ultrapure water (Barnstead) for which the oxidized product, Fe(CN)₆³⁻ displays an absorption peak centered at 420 nm. Both the diffusion coefficients and molar absorptivities of these species are known with accuracy thereby providing ideal conditions for assessing in a rather rigorous fashion quantitative aspects of this spectroelectrochemical technique. For these measurements, single beam spectra were first collected at a potential negative to the onset of Fe(CN)₆⁴⁻ oxidation (E_{ref}), and then at a series of potentials sufficiently positive for partial or total oxidation of the species to ensue, E_{sam}, at a fixed rotation rate ω within 300 – 2500 rpm.

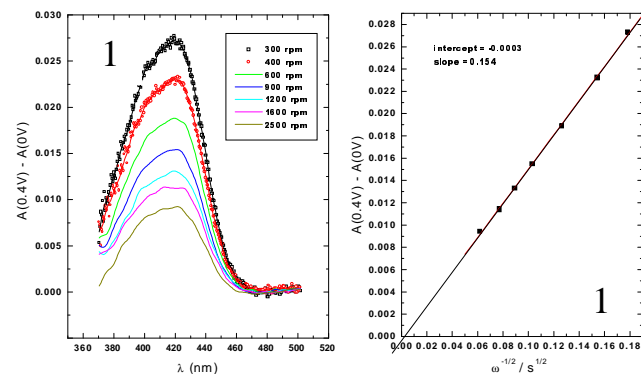
RESULTS AND DISCUSSION

According to theory, the change in absorbance observed for the electrode polarized at a potential positive enough to achieve limiting current conditions, i_{lim}, i.e. 0.4 V, compared to that recorded at a potential at which no reaction ensues, 0.0 V, A(0.4V) – A(0.0 V) is given by:

$$A(0.4V) - A(0.0 V) = 3.22B\epsilon_0 D_0^{1/3} \nu^{1/6} \omega^{-1/2} c_R^0 \quad (1)$$

where D₀ is the diffusion coefficient of Fe(CN)₆⁴⁻ in cm²/s, ν is the kinematic viscosity of the solution in cm²/s, and ω is the rotation rate of the disk in radian/s, ε₀ is the

molar absorptivity of Fe(CN)₆⁴⁻ in mol⁻¹cm², and B = 0.5055. The left panel, Fig. 1 shows plots of A(0.4V) – A(0V) versus λ (nm) for seven values of ω for the oxidation of 10mM Fe(CN)₆⁴⁻ in 0.25 M K₂SO₄ aqueous solution in the region 370 to 500 nm where only absorption of Fe(CN)₆³⁻ is significant. A plot of A(0.4V) – A(0V) at 420 nm, i.e. versus ω^{-1/2} was found to be linear in agreement with Eq.(1) (see right panel, Fig. 1).

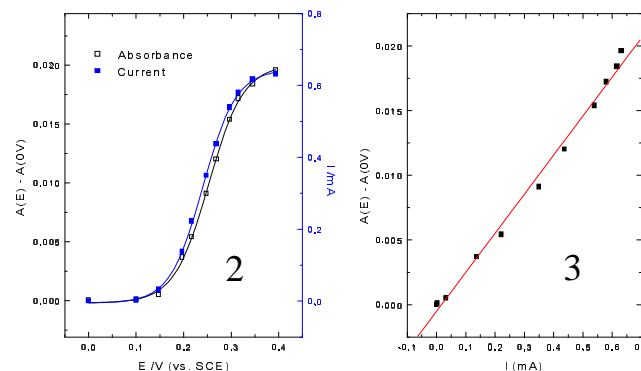


Theory also predicts a direct proportionality between the absorbance and current at any arbitrary potential at which oxidation occurs. As is well known,

$$I = nFA(D_R/\delta_R)[c_R^0 - c_R^s(E)] \quad (2)$$

Hence, dividing Eq.(1) by this latter expression one obtains for values of the various parameters involved

$$[A(E) - A(E_0)]/I = (3.655 \times 10^{-5})(D_0/D_R)^{1/3}(\epsilon_0/D_R)^{1/3}\omega^{-1} \quad (3)$$



On this basis, at any particular rotation rate, [A(E) – A(E₀)] is proportional to I; hence, a plot of [A(E) – A(0V)] versus E should have the same shape as the current curve as shown by experimental curves in Fig. 2. According to this figure, the plot of [A(E)–A(0V)] versus I can be obtained in Fig 3, which shows a proportionality between the absorbance and current value. If we take literature data of (D₀/D_R) = 1.15,⁴ and our experimental data of D_R = 6.8 × 10⁻⁶ cm²/s and ε₀ = 1.04 × 10⁶ mol⁻¹cm², as well as rotation rate 600 rpm (i.e. 0.0159 radian/s), plug into equation (3), the conversion factor between current and absorbance difference scales, [A(E) – A(E₀)]/I is 32.1 A⁻¹, which is close to the slope found experimentally, 30.6 A⁻¹.

ACKNOWLEDGMENTS

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