

IONIC MASS TRANSFER AT ROTATING ELECTRODES FORMED BY SOLIDS OF REVOLUTION. ROTATING ONE-BASE SPHERICAL SEGMENT ELECTRODES*

O. A. COBO† S. L. MARCHIANO and A. J. ARVÍA
Instituto Superior de Investigaciones, División Electroquímica,
Facultad de Ciencias Exactas, Universidad Nacional de La Plata,
La Plata, Argentina

Abstract—The ionic mass transfer at rotating electrodes formed by a one-base spherical segment has been experimentally studied by the usual electrochemical methods.

For electrodes which involve an electrochemical active area having angle up to 40 deg, the mass-transfer rate equation is

$$i_L = (0.62 \pm 0.06) zFc_1^0 D_1^{2/3} \nu^{-1/6} \omega^{1/2}.$$

Résumé—Le transport ionique de matière sur des électrodes tournantes consistant en un segment sphérique à une base a été étudié expérimentalement par les méthodes habituelles électrochimiques.

Pour des électrodes comprenant une surface électrochimique active avec un angle jusqu'à 40 degrés, l'équation de transport de matière est

$$i_L = (0,62 \pm 0,06) zFc_1^0 D_1^{2/3} \nu^{1/6} \omega^{1/2}.$$

Zusammenfassung—Es wurde der ionische Stofftransport an rotierenden Kugelsegmentelektroden mittels gebräuchlicher elektrochemischer Methoden experimentell untersucht.

Für Elektroden, deren aktive Fläche einen Winkel von 40° aufweist, gehorcht die Stofftransportgeschwindigkeit folgender Gleichung:

$$i_L = (0,62 \pm 0,06) zFc_1^0 D_1^{2/3} \nu^{1/6} \omega^{1/2}.$$

INTRODUCTION

THE SOLUTION of the boundary-layer partial differential equations in spherical polar co-ordinates, r , θ and ϕ , for the flow associated with a rotating sphere was given some time ago.¹⁻⁴ The solution on either hemisphere was thought to be valid up to the immediate vicinity of the equator, where interaction with the flow from the other hemisphere occurs, and the solution is invalidated. The approximate solution derived for the hemisphere indicates that the velocity components in spherical co-ordinates along θ and ϕ retain the same form as the velocity components along r and ϕ for the rotating disk in cylindrical co-ordinates, and for small θ the solution should agree with the solution for the rotating disk, the numerical coefficients of the velocity-component equation being approximately the same.⁵ Therefore, the similarity of the equations for the velocity components of the rotating sphere and the rotating disk suggest that, from the standpoint of mass transport processes, rotating electrodes formed by a solid of revolution, such as a one-base spherical segment, may fit a maximum mass transport rate equation similar to that already developed by Levich⁶ and further improved by other authors⁶⁻⁹ for the rotating disk electrode.

This means that the condition of a uniformly accessible surface, implied for the rotating disk, can be extended to rotating solids of revolution when the electrochemically active part is restricted to small angles. Matsuda has demonstrated that for an electrode formed by a solid of revolution under stagnation flow the above idea is

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† On leave of absence from the Chemistry Department of the Universidad del Sur, Bahía Blanca, Argentina.

valid, that is, the diffusional boundary layer in the neighbourhood of the stagnation point can be taken as constant.^{10,11}

The present paper refers to the experimental study of the ionic mass transport on rotating electrodes whose electrochemically active part is an axially placed one-base spherical segment. One of the aims in studying this type of electrodes was to have a better design for rotating electrodes particularly suitable for the kinetics of electrode reactions where gases are evolved. If the viscosity of the electrolytes is relatively high, as is the case to a large extent with ionic melts, gas bubbles sticking to the electrode surface provoke a significant distortion of the hydrodynamics of the system, also modify appreciably the working electrode area, and are the cause of an additional variable resistance, particularly at low rotation speeds. This drawback can be minimized by the present electrode geometry which from this viewpoint is more promising than the rotating disk electrode.

EXPERIMENTAL TECHNIQUE

Schemes of the working electrodes are shown in Fig. 1.

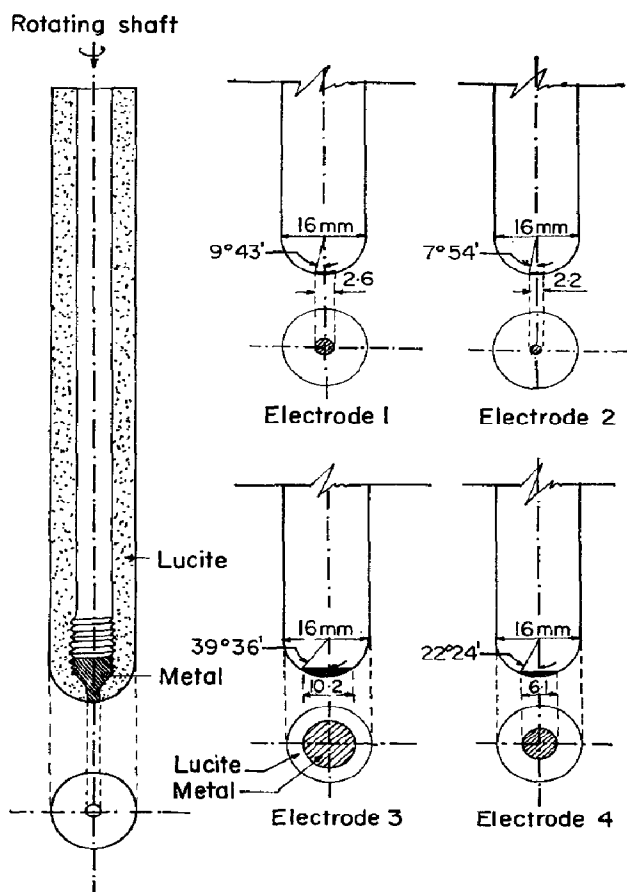


FIG. 1. Scheme of the working electrodes.

The electrochemically active part of the electrode was made either of nickel or copper rods of different diameters embedded in Lucite rods of 1.60 cm dia., keeping the axial symmetry of the system. The entire pieces were shaped on the lathe

so that the electrochemically active part of the pieces was formed by one-base spherical segments of various angles as illustrated in Fig. 1. The radius R was kept constant while the angle θ was changed from about 7 to 40°. These electrodes were used either as polished nickel-plated copper electrodes or as copper electrodes, according to the electrode reaction selected to study the convective-diffusion processes.

The limiting conditions established for the hydrodynamic boundary layer on a rotating sphere¹⁻⁴ were taken into account in the working electrode design.

The rotating electrodes were symmetrically placed into a thermostated cylindrical glass electrolysis cell of 10 cm dia., facing the counter-electrode. This was a large concave surface piece made of the same metal as the working electrode and located at the bottom of the electrolysis cell, to attain the best uniformity of the macroscopic distribution at the working electrode.

The same drive and electronic arrangement for control recently described in detail for rotating disk electrodes¹² was also employed in these experiments. The rotating electrodes were driven at constant speed in the range from about 100–1200 rev/min.

To study the rate of ionic mass transport three conventional reactions were employed, the oxidation of ferrocyanide ion, the reduction of ferricyanide ion and the electrodeposition of copper ion. The two first reactions were studied with equimolar aqueous solutions of $K_4[Fe(CN)_6]$ and $K_3[Fe(CN)_6]$ in 2.0 M NaOH as supporting electrolyte. The concentration of the reacting ions were 0.002, 0.005 and 0.01 M and either activated nickel electrodes or activated nickel-plated electrodes were employed. The third reaction was studied on copper electrodes employing 0.005 M $CuSO_4$ aqueous solutions in 1.5 M H_2SO_4 .

The viscosities of the solutions were measured in the conventional way and the diffusion coefficients were calculated through the $D\eta/T$ ratio^{13,14} or determined with the rotating disk electrode.

Parallel experiments were performed with the same electrochemical systems on rotating disk electrodes of the same material as those forming the one-base spherical segment electrodes. These experiments were considered as a sound way of establishing the actual magnitude of the dispersion of results on the new electrodes as compared to that obtained on the rotating disk electrode, which has been repeatedly used very successfully and of which the theory has been extensively developed.

Steady potentiostatic current/potential curves were recorded at 25 and 30°C employing the usual circuitry.

RESULTS AND INTERPRETATION

The current/potential curves, as shown in Figs. 2–4, exhibit well-defined limiting currents, and depend on the reaction occurring at the electrochemical interface. Thus, for the anodic as well as the cathodic reactions taking place with the $K_4[Fe(CN)_6]/K_3[Fe(CN)_6]$ system, the whole E/I curve can be practically fitted to a concentration polarization equation at any overpotential. For the electrodeposition of copper, however, in the region preceding the convective-diffusion plateau, the reaction is under intermediate control, because of its electrochemical kinetic behaviour.¹⁵ For the three reactions studied the shapes of the current/potential curves resemble those found for the rotating disk electrode⁶ as well as for some electrodes formed by solids of revolution placed into an axially symmetrical flow.¹¹ The stability and

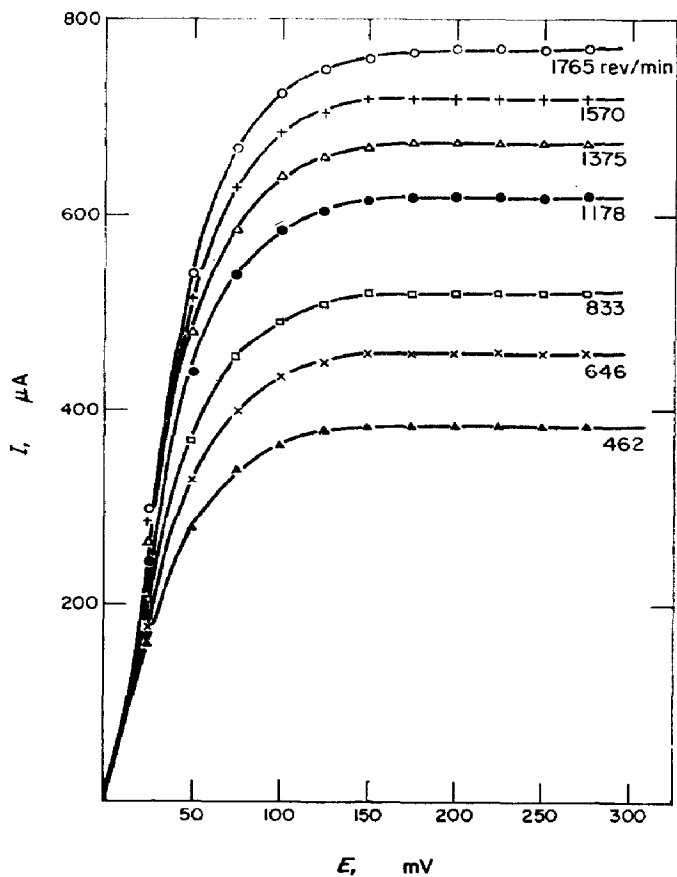


FIG. 2. Current/potential curves for the reduction of ferricyanide ion. $C_{[\text{Fe}(\text{CN})_6]^{3-}}^{\circ} = C_{[\text{Fe}(\text{CN})_6]^{4-}}^{\circ}, 5 \times 10^{-3} \text{ M}$; $C_{\text{NaOH}}^{\circ} = 2.0 \text{ M}$; 25°C , Electrode 1.

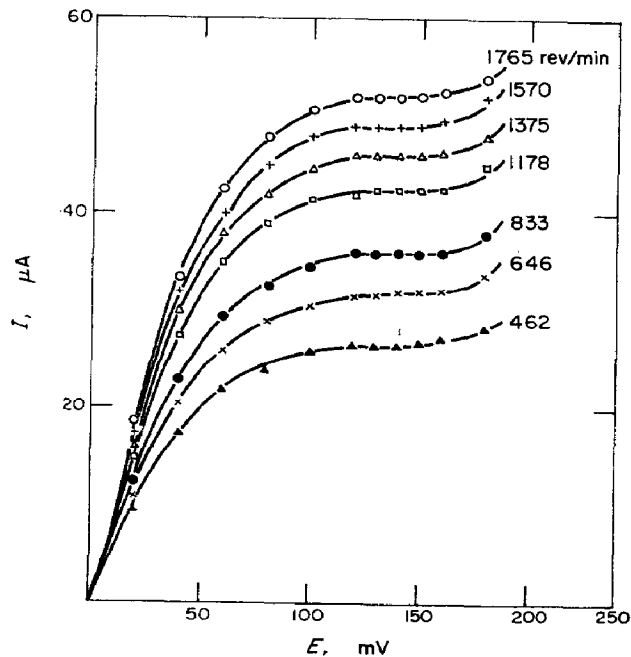


FIG. 3. Current/potential curves for the oxidation of ferrocyanide ion. $C_{[\text{Fe}(\text{CN})_6]^{4-}}^{\circ} = C_{[\text{Fe}(\text{CN})_6]^{3-}}^{\circ}, 2 \times 10^{-3} \text{ M}$; $C_{\text{NaOH}}^{\circ} = 2.0 \text{ M}$; 25°C ; Electrode 3.

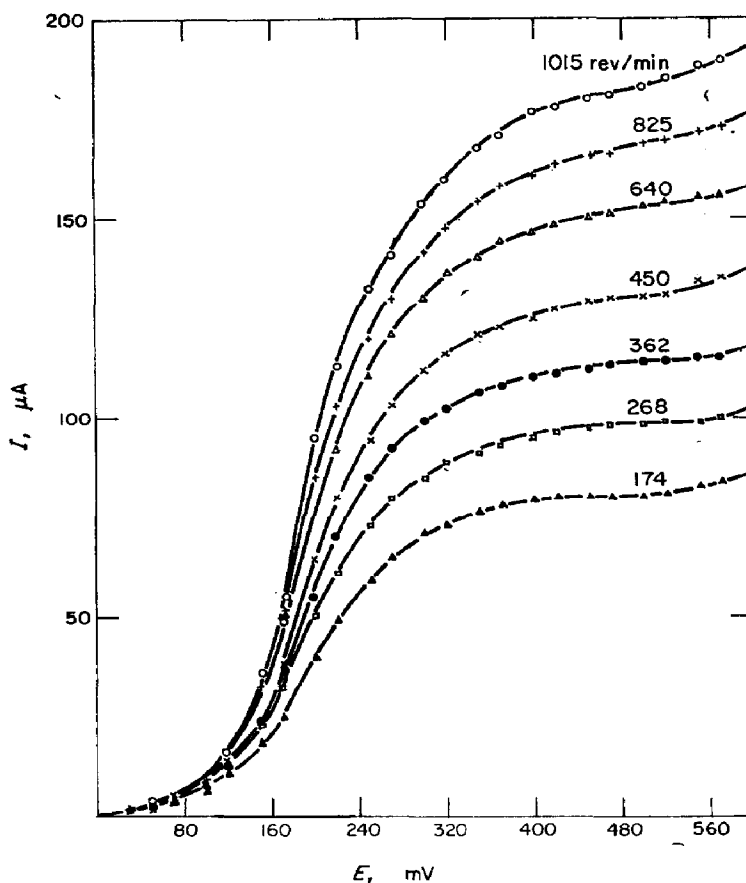


FIG. 4. Current/potential curves for the electrodeposition of copper ion. $C_{\text{Cu}^{2+}}^{\circ}, 5 \times 10^{-3} \text{ M}$; $C_{\text{H}_2\text{SO}_4}^{\circ}, 1.5 \text{ M}$; 25°C ; Electrode 2.

reproducibility of results is promising and comparable to the results obtained with the rotating disk electrode.

The limiting current changes linearly with the concentration of the reacting species (Fig. 5). As shown in Figs. 6 and 7, the limiting current increases linearly with the square root of the angular velocity of the working electrodes, ω , and follows the equation

$$i_L = (0.62 \pm 0.06)zFC_1^{\circ}D_1^{2/3}\nu^{-1/6}\omega^{1/2}, \quad (1)$$

where i_L is the limiting cd (A/cm^2), C_1° the concentration of the reacting ion in the bulk of the solution (mol/cm^3), D_1 the diffusion coefficient (cm^2/s), ν the kinematic viscosity of the solution (cm^2/s) and ω the angular velocity of the rotating electrode (rad/s). Equation (1) resembles Levich's equation for the rotating disk electrode.

The dispersion of results shown in the Figs. 6 and 7 is within ± 10 per cent. This error is acceptable as far as the present measurements are concerned. As illustrated by that figure, the effect of the angle associated with the one-base spherical segment is practically negligible for the range of angles covered at present.

These results are therefore quite reasonable and will be further developed with the corresponding theory for this type of electrodes.

The rate equation established above resembles the form of the general equation

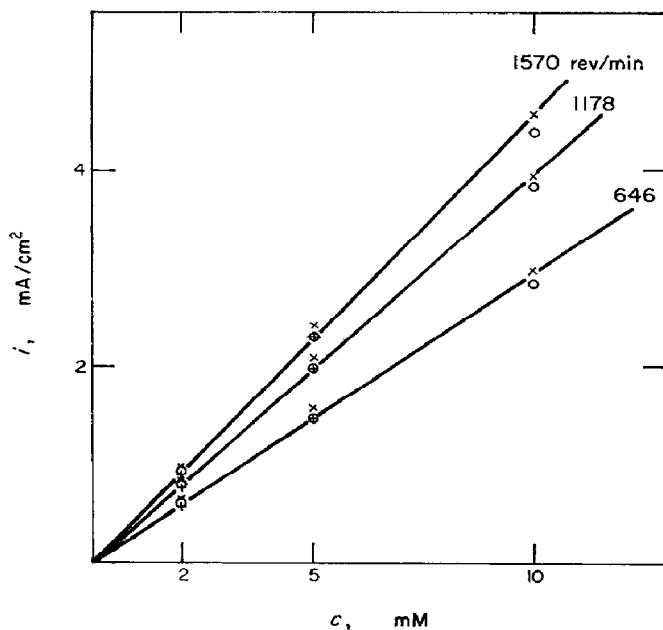


FIG. 5. Concentration dependence of the limiting i_l at constant rotation speeds. Reduction of ferricyanide ion. 25°C.
 O, Electrode 0; X, Electrode 1; +, Electrode 2; Δ , Electrode 3.

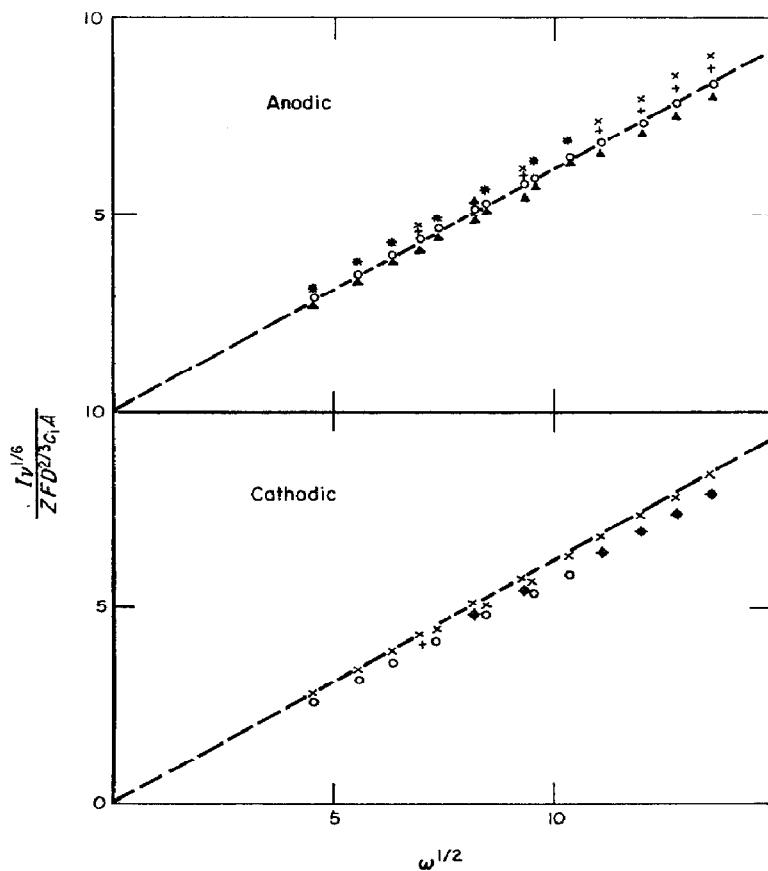


FIG. 6. Plots of the experimental equation (a) oxidation of ferrocyanide ion. (b) reduction of ferricyanide ion.
 O, Electrode 0; X, Electrode 1; +, Electrode 2; Δ , Electrode 3.

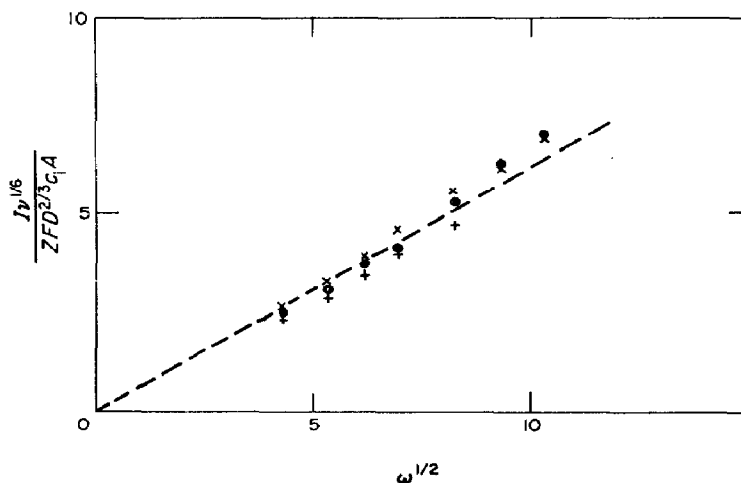


FIG. 7. Plot of the experimental equation; electrodeposition of copper ions. 25°C.
 ×, Electrode 1; +, Electrode 2; ●, Electrode 3.

derived for mass transport flux at electrodes formed by solids of revolution under stagnation flow,¹¹ which as a limiting case covers the flat disk electrode axially placed to the direction of the flux. A crude comparison of these equations suggests that the extension of the same generalization to electrodes formed by solids of revolution in stagnation flow is in principle possible, if these electrodes are rotated at a constant speed in the electrolyte solution.

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