

SHORT COMMUNICATION

AN EXPERIMENTAL STUDY OF IONIC MASS TRANSFER AT HORIZONTAL RING-DISC ELECTRODE UNDER LONGITUDINAL VIBRATION

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Ring-disc electrode devices under either rotation[1, 2] or stationary flowing solutions[3, 4] offer the possibility of detection of intermediate species[5-8] in electrochemical kinetics studies and the determination of micromolar levels of electroactive substances[9, 10].

The design of these electrodes can be optimized by solving simultaneously the corresponding hydrodynamic and diffusion boundary layer problem. In this case, the collection efficiency of the rotating ring-disc electrode for different ratios of ring-disc radii could be established[11, 12]. Conversely, when the mass transport problem cannot be solved, then the suitable radius values of the pair of electrodes can be approached on the basis of the rotating ring-disc electrode parameters.

The present paper reports a new ring-disc electrode device resulting from a previous study of ionic mass transfer at horizontal disc electrodes under longitudinal vibration[13]. The efficiency of the platinum ring-disc electrode device is established in comparison to that of the rotating ring-disc electrode in a conventional electrochemical system[8].

The electrolysis cell was similar to that described for the vibrating disc electrode[13]. The ring-disc working electrode consisted of a bright platinum disc of 0.55 cm dia. and a bright platinum ring of 0.58 cm and 0.64 cm internal and external dia. respectively (Fig. 1). The ring-disc electrode was mounted at the end of an inverted, hollow, truncated cone made of a light insulating material which was attached to the diaphragm of a commercial 7 in. dia. loudspeaker. The electric contacts of the ring and disc platinum electrodes were made with flexible leads through the interior of the cone. The counter electrode was a conventional platinum mesh symmetrically placed around the vibrating electrode. A saturated calomel electrode (*sce*) with a Luggin-Haber capillary tip was used as reference.

The vibration of the loudspeaker-working electrode system was excited with a variable reductor transformer-filament transformer directly connected to the 50 Hz main. The vibration amplitude was measured with an optical transducer mounted in the interior of the cone previously calibrated in air.

A 10^{-3} M CuCl_2 solution in 0.5 M KCl as supporting electrolyte was used free of oxygen by purified N_2

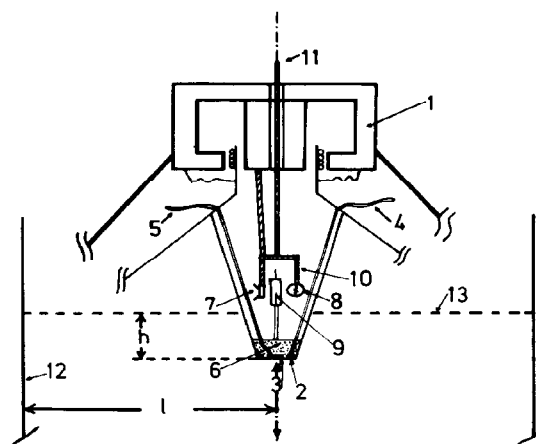


Fig. 1. Scheme of the ring-disc horizontal vibrating electrode device. 1, Loudspeaker; 2, ring electrode; 3, disc electrode; 4, ring contact; 5, disc contact; 6, epoxy resin; 7, detector; 8, emitter; 9, linear optical attenuator; 10, metallic support; 11, emitter-detector contact; 12, wall cell; 13, solution level; $h = 0.5$ cm; $L = 6.0$ cm.

bubbling. Triple distilled water was used in the preparation of the solutions. Runs were made under N_2 at $25^\circ\text{C} \pm 0.1$.

The current-potential curve at the disc was run in the usual way under a linear potential sweep at 0.0125 V s^{-1} from $+0.350 \text{ V}$ to -0.430 V vs sce . The potential at the ring was held constant at $+0.400 \text{ V vs sce}$. Runs were made at different vibration amplitudes $(\Delta X)_0$ in the 2.58×10^{-2} – 9.37×10^{-2} cm range.

Current-voltage curves (Fig. 2) vary with the vibration amplitude $(\Delta X)_0$. The disc current exhibits a first cathodic current plateau in the 0 to -0.2 V range which corresponds to the first level electroreduction of Cu^{2+} to Cu^+ and a second one at potential more negative than -0.3 V which is associated with the second level electroreduction of Cu^+ to Cu . The height-ratio of these cathodic current plateaux is practically equal to 2. The first current plateau at the disc is associated with the appearance of a simultaneous

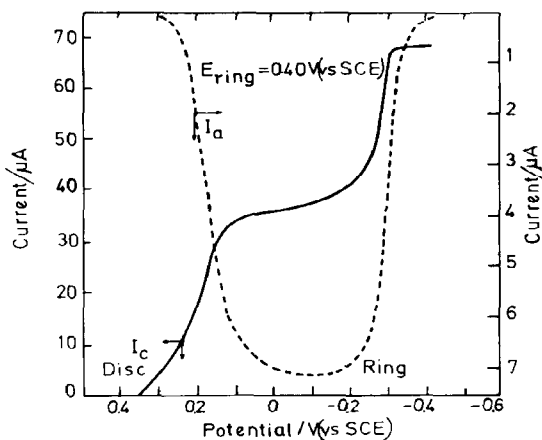


Fig. 2. Disc and ring response in 10^{-3} M $\text{CuCl}_2 + 0.5$ M KCl aqueous solution. $(dE/dt)_{\text{disc}} = 0.0125$ V s $^{-1}$; $(E)_{\text{ring}} = 0.4$ V vs sce, $(\Delta X)_0 = 6.8 \times 10^{-2}$ cm, 25°C.

anodic current at the ring held at +0.4 V due to the reoxidation of Cu^+ produced on the disc. No soluble species are detected at the ring for the second electroreduction level at the disc.

From the curves obtained at different vibration amplitudes the ratio of the ring and disc currents (I_r/I_d) were obtained. Figure 3 shows the relationship between the current ratio with the vibration amplitudes in the 2.58×10^{-2} cm $\leq (\Delta X)_0 \leq 9.37 \times 10^{-2}$ cm range for the particular electrode geometry described in this work.

The reproducible electrochemical response of the horizontal ring-disc vibrating electrode under modulated pulsed mass transport is very similar to that found for the same electrochemical reaction in the rotating ring-disc electrode under steady state conditions[8]. The new device is useful in the 4×10^{-2} cm $\leq (\Delta X)_0 \leq 6.8 \times 10^{-2}$ cm range, where the I_r/I_d ratio becomes practically independent of $(\Delta X)_0$. The collection efficiency calculated from the current ratio is 0.189, a value which is slightly lower than that of the rotating ring-disc electrode under a comparable geometrical design ($N = 0.243$)[11].

The correlation previously established for ionic

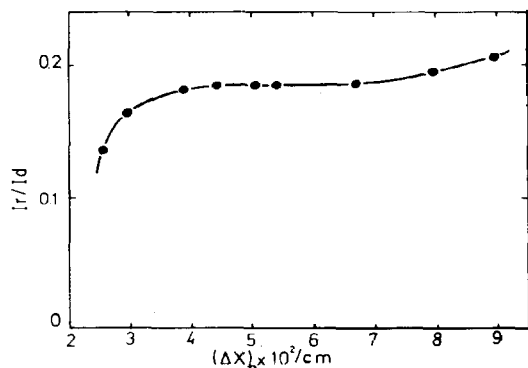


Fig. 3. Plot of I_r/I_d vs $(\Delta X)_0$ for the experimental condition indicated in Fig. 2.

mass transfer at a vibrating disc[13] is valid in the 6.35×10^{-3} cm $< (\Delta X)_0 < 5.5 \times 10^{-2}$ cm range which is larger than the $(\Delta X)_0$ range where the collection efficiency behaves constant. The deviation for linearity at $(\Delta X)_0 < 4 \times 10^{-2}$ cm is easily understood in terms of the hydrodynamic flow pattern produced by the vibrating electrode[14, 15]. The latter can be associated with an average symmetric axial back and forth flow in a cylindrical box where the extent of the box in the case of the ring-disc device is twice the sum of the disc radius plus the thickness of the inert gap plus the thickness of the ring. Therefore, for having a flow of solution over the whole area determined by the extent of the box, $(\Delta X)_0$ should be, in principle, sufficiently large to pump reaction products from the disc to the ring electrode surface. Obviously, when this situation is not fulfilled, then the collection efficiency should approach zero.

On the other hand, the upper useful value of $(\Delta X)_0$ in the ring-disc vibrating device is very close to that corresponding to the validity of the ionic mass transfer correlation at the vibrating disc. This coincidence suggests that in both cases there is an increasing influence of a turbulent component when $(\Delta X)_0$ is greater than 6.8×10^{-2} cm, so that the conditions for a constant I_r/I_d ratio are no longer obeyed.

These results encourage the use of ring-disc vibrating devices under a certain range of $(\Delta X)_0$ in the study of electrochemical reactions where the cell design makes use of mobile electrical contacts, and the centering of the electrode is rather difficult.

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