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An experimental study of mass transfer to ring - disc jet electrode

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Mass transfer when a jet of solution impinges at 90° to a stationary ring disc electrode has been investigated using an electrochemical method. The influence of various parameters such as the fluid velocity, the distance between the nozzle and the electrode surface as well as the concentration of the reacting species on the disc and the ring current was examined experimentally using the cathodic reduction of $CuCl_2$ and of $K_3Fe(CN)_6$ in KCl. It has been found that the stationary ring can be used for detection of intermediate species formed at the disc. An application of this system for the study of the anodic dissolution of a metal is given.

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1. Introduction

In an industrial electrochemical process, high mass transfer is frequently required. This can be achieved by stirring the solution, rotating the electrode or using a flow cell.

The most practical form of electrode for which a completely rigorous hydrodynamic treatment can be given is the rotating disc electrode. The mass transport equation for this electrode was developed by Levich [1].

Numerous techniques in which the stationary disc electrode is immersed in either a flowing or a rotating solution have also been described [2–16]. Only a few papers have dealt with simultaneous use of the ring and disc electrodes [12–15]. These investigations showed that the stationary ring can be used for detection of intermediate species formed at the disc.

The purpose of the present work is to examine the mass transfer to a stationary disc and ring electrode under a jet flow of solution. The influence of different parameters such as flow rate, distance between the jet and the electrode surface and concentration of reacting species on the limiting current, is studied. It is believed that the system can be applied in continuous electrochemical processes, electro-analytical or corrosion studies. Any variation of concentration of products formed on the disc will be immediately detected by the ring. This system is relatively simple and the electrical contact with a rotated electrode is thus avoided.

2. Experimental

The electrolytic cell (0.4 l) is shown in Fig. 1. It consists of a cylindrical part and two covers in plexiglas. The working and reference electrode were fixed to the upper cover while the inlet tube was introduced by the lower cover. For the fluid circulation system we used a Teflon pump working at constant speed. The flow rate, ranging from 0.33 to 50 $cm^3\ s^{-1}$, was adjusted by means of a by-pass and valves and it was measured with a flowmeter. The total volume (2 l) of electrolyte solution was placed in a large reservoir. Three types of nozzles were used as shown in Fig. 2.

All elements of the system were constructed from plexiglas, Teflon, polyethylene or glass without any metallic part so that corrosion is avoided.

The platinum ring–platinum disc electrode was prepared as described elsewhere [17]. The disc, internal ring and external ring radii were 0.375, 0.396 and 0.526 cm, respectively. The calculated collection efficiency [18] is equal to 0.42. This electrode can be fitted on an axis of a turbine so that it can be used as a rotating ring disc electrode. The Pt counter electrode was placed on the lower cover of the cell. All the potentials quoted in this work are referred to a normal calomel electrode.

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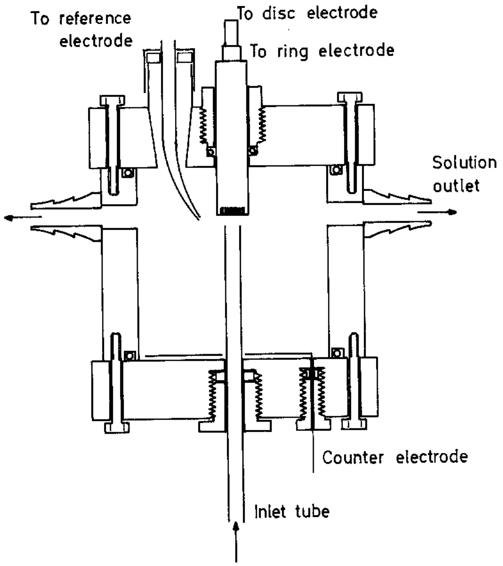

Fig. 1. Schematic representation of electrolytic cell.

Two types of solutions have been employed: (a) 10^{-3} M $CuCl_2$ in 0.5 M KCl and (b) equimolar solution of 10^{-3}, 5×10^{-3} and 10^{-2} M $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$ in 1 M KCl. All salts are obtained from Merck of p.a. quality. The disc potential was controlled with a potentiostat Amel Mod 549 in conjunction with a function generator Amel Mod 566 while the ring potential was maintained constant by a potentiostat Amel Mod 551. The disc and ring current were recorded simultaneously on a double pen recorder Sefram Servorac BPD.

3. Results

3.1. *Current voltage curves*

Typical current voltage curves obtained in 10^{-3} M $CuCl_2$ solution with a stationary ring disc electrode are shown in Fig. 3. The disc potential was swept at 0.01 V s^{-1} from 0.35 V toward more negative values while the ring was held constant at 0.4 V. The nozzle was placed 0.01 cm under the surface of the electrode. These curves vary with the fluid velocity and are quite similar to those obtained by previous workers with a rotating ring disc electrode [19]. The first plateau observed on the disc electrode corresponds to the reduction of Cu^{2+}:

$$Cu^{2+} + e \rightarrow Cu^{+}.$$

The ring current increases simultaneously due to the re-oxidation of Cu^{+} produced on the disc. At more negative potentials, Cu^{+} ions are deposited on the surface of the disc and the ring current falls.

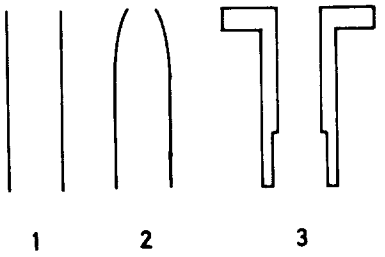

Fig. 2. Schematic of various types of inlet tube.

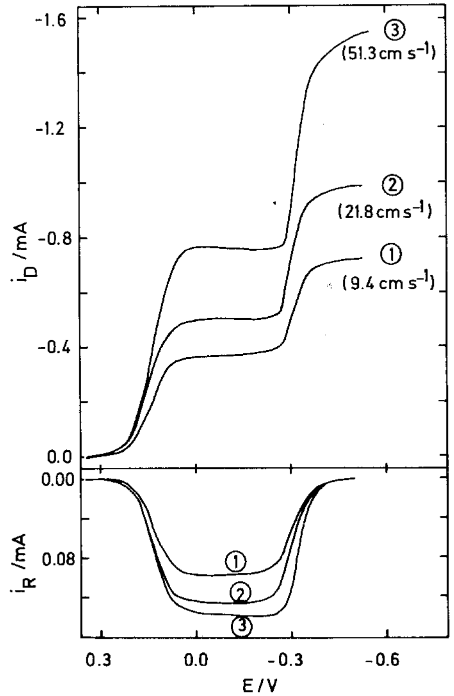

Fig. 3. Disc and ring response in 10^{-3} M $CuCl_2$ + 0.5 M KCl. $dE_D/dt = 0.01$ V s^{-1}, $E_R = 0.4$ V. Inlet tube 1, nozzle–electrode distance 0.01 cm.

3.2. *Influence of the distance between the nozzle and the electrode surface*

In Fig. 4 the disc limiting current i_D is plotted as a function of the square root of the flow velocity u. A linear relationship is observed. The Reynolds number ranges from about 70 to 10^4. For the sake of clarity the corresponding ring current has been omitted and will be discussed subsequently. It is evident from Fig. 4 that the distance between the

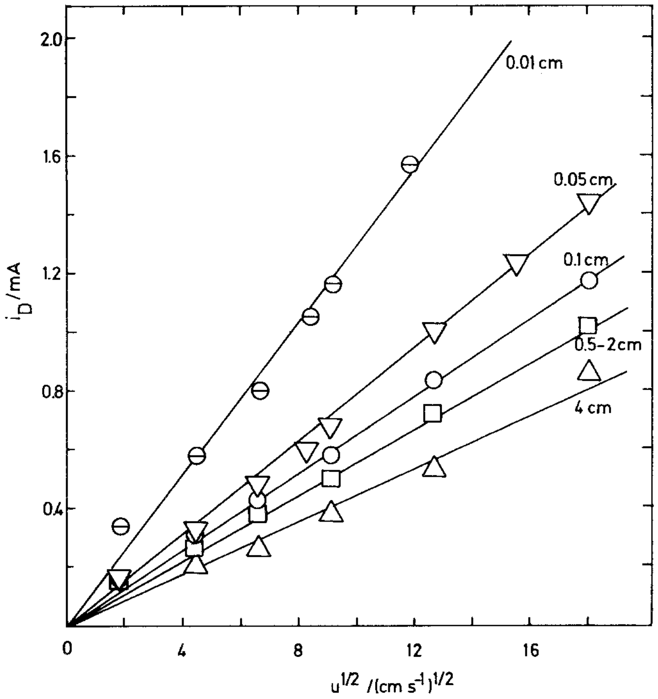

Fig. 4. Influence of the square root of flow velocity on limiting current for various nozzle–electrode distances. Inlet tube 2.

nozzle and the electrode surface is an important factor determining the current at the disc electrode and therefore the current at the ring electrode. The closer the gap between the nozzle and electrode surface, the higher is the current. The most important variation is found at 10^{-1}–10^{-2} cm. These observations hold for all types of nozzle used in this work and are in contradiction with previous results [4] where the authors stated that no dependence of the limiting current density on the distance between the working electrode and the inner outlet tube was detected. However, the dependence of the limiting diffusion current on the distance between the electrode surface and the

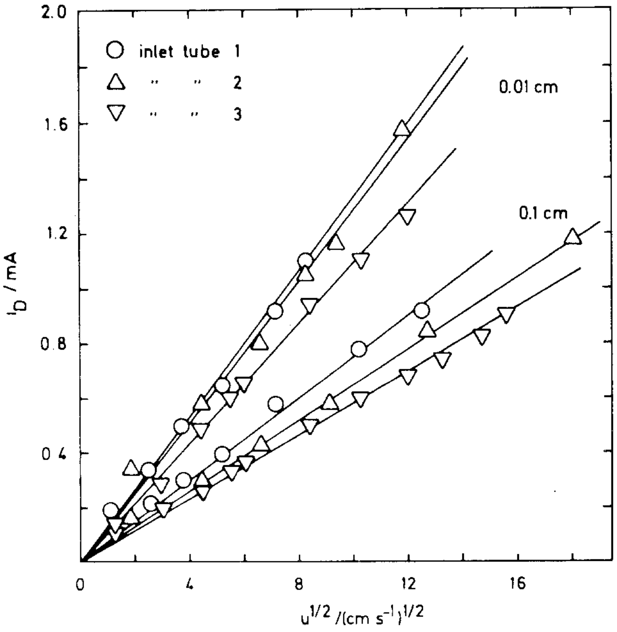

Fig. 5. Plot of limiting current versus square root of flow velocity for different types of inlet tube.

nozzle has also been observed by Yamada *et al.* [11] and Coeuret [16].

3.3. *Influence of the diameter and the form of the nozzle*

The internal diameters of the three nozzles were 0.60, 0.34 and 0.51 cm, respectively (Fig. 2). No appreciable effect caused by this diameter or the form of the nozzle was observed. This finding is illustrated by plotting the disc current versus the square root of the flow velocity in Fig. 5. Each straight line corresponds to a constant gap between the nozzle and the electrode surface.

3.4. *Influence of concentration*

The influence of concentration is confirmed by using an equimolar solution of ferricyanide and ferrocyanide in 1 M KCl as the supporting electrolyte. The disc was held at − 0.1 V for reduction of ferricyanide ion while the ring was held at + 0.5 V for oxidation of ferrocyanide ion. As the latter is already present in the solution, the ring current was therefore subtracted from the initial current which is not due to the species produced on the disc.

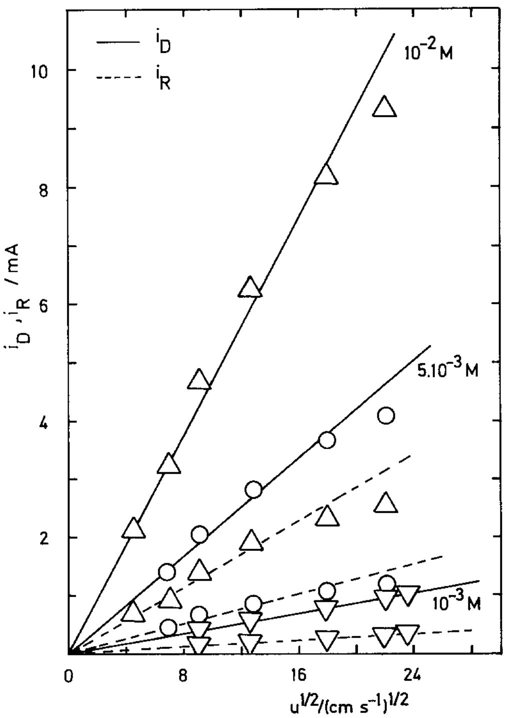

Fig. 6. Influence of the square root of flow velocity on the limiting current for various concentrations of reacting species. Inlet tube 2; nozzle–electrode distance, 0.5 cm.

Results are reported in Fig. 6 where the disc and ring currents at different concentration (10^{-3}, 5×10^{-3} and 10^{-2} M) are plotted. The straight line obtained was found to pass through the origin for each concentration.

3.5. *Ratio of ring to disc current*

A plot of the ratio of ring to disc current as a function of flow rate is shown in Fig. 7. It can be seen that this ratio is small when the nozzle is very close to the electrode and the flow rate is an important factor as well. As the nozzle–electrode distance increases i_R/i_D remains relatively constant. This observation is true for the three types of nozzle used. The concentration of electro-active species has little influence on the ratio i_R/i_D (Fig. 6).

4. Discussion

It is clear from the present study that the ring disc jet electrode behaves qualitatively in a similar way to the rotating ring–disc electrode. The fluid flow for the rotating ring disc electrode can be described by three velocity components: u_z the fluid velocity in the direction normal to electrode surface, u_x the radial velocity and u_y the tangential velocity. This latter component u_y does not exist for the ring disc jet electrode. As a matter of fact, the fluid impinging the disc electrode is ejected radially towards the ring without any tangential velocity due to the rotation of the electrode.

The flow characteristics of the wall jet electrode have been described by previous workers [9, 11, 16]. For the case of a disc or conical electrode axially placed in laminar flow, the mass transfer equation given in terms of dimensionless quantities is [2–4]:

$$(Sh)_x = 0.78\,(Re)_x^{1/2}\,(Sc)^{1/3}$$

where $(Sh)_x$, $(Re)_x$ and (Sc) are the Sherwood, Reynolds and Schmidt numbers, respectively. For an electrochemical system the maximum diffusional current density i_{diff} becomes:

$$i_{diff} = 0.78\,nFDC^0\,(u/\nu r)^{1/2}\,(Sc)^{1/3}$$

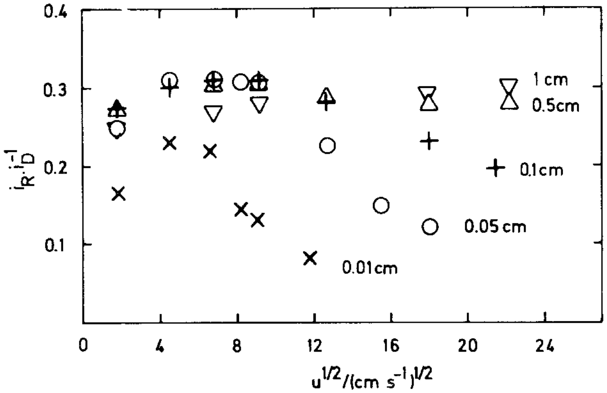

Fig. 7. Plot of ratio i_R/i_D versus square root of flow velocity for different nozzle–electrode distances. Inlet tube 2.

where n is the number of electrons, F the Faraday constant, D the diffusion coefficient, C^0 the bulk concentration, u the flow velocity, ν the kinematic viscosity and r the radius of the disc.

This equation predicts that the limiting current density increases linearly with the concentration of the reacting ion and with the square root of the fluid velocity. According to Yamada *et al.* [11], the limiting diffusion current is found to depend on the 3/4 power of the volume flow rate in contrast to the 1/2 or 1/3 power of the flow rate in usual flow conditions of hydrodynamic voltammetry. The data obtained in this work fit quite well to a straight line when the limiting current is plotted as a function of the square root of fluid velocity. Certainly, the log–log plot of these data gave a slope approaching 1/2 but not 3/4. These results are in good agreement with the equation given above. However there is a dependence of the limiting current on the nozzle–electrode distance. As the nozzle is moved far from the electrode the disc current decreases. This can be explained by a lower flow velocity near the electrode surface and by some dispersion of the jet. For a large nozzle–electrode distance, the straight line i_D versus $u^{1/2}$ tends to intercept the i-axis, due probably to the intervention of the natural convection. The latter is more pronounced at very low fluid velocity.

On the other hand, when the nozzle–electrode distance is very small, a high mass transfer rate is obtained. In this case the effect of turbulence is more rapidly reached. The diffusion layer becomes thinner as the fluid is forced through a very small gap. The most important effect occurs in the region ranging from 10^{-1} to 10^{-2} cm. For intermediate separations there is no dependence between the limiting current and the nozzle–electrode distance (Fig. 4). It is of interest to note that the diameter as well as the form of the nozzle has little influence on the limiting current. Indeed, for each inlet tube used, the plot of current versus square root of fluid velocity (on the basis of the section of each inlet tube) shows a series of straight lines (Fig. 5) with almost identical slope. As mentioned above, the current is controlled by the fluid velocity at the electrode surface which is a function of the nozzle–electrode distance. The ratio of the ring to disc current depends also on the location of the nozzle (Fig. 7). The smaller the gap, the higher the disc current and the lower the ring current. In other words, the ratio i_R/i_D is very low when the nozzle is very close to the electrode particularly at high fluid velocity. As a matter of fact, part of the fluid which impinges on the electrode surface goes back to the bulk of the solution without passing radially to be detected at the ring electrode. This occurs easily with a small gap. There is some critical distance where the ratio i_R/i_D remains relatively constant around 0.3. In all cases the values i_R/i_D are lower than those obtained with the same electrode at different rotation rates. For the latter the experimental collection efficiency was 0.4 which is very close to the calculated one. In the wall jet region [9] the flow can be divided into two sublayers: the inner layer where the flow is influenced by the wall and the outer layer where the flow is influenced by the surrounding fluid. The velocity is inversely proportional to the radial distance from the disc surface. Then the radius of the disc and ring electrode are important factors determining the limiting diffusion current and hence the ratio i_R/i_D.

The theory is also obeyed at different concentrations of the electro-active species ranging from 10^{-2} to 10^{-3} M. The ratio i_R/i_D is constant over this range of concentration. This would suggest that the system can be suitable for electroanalytical purposes and for electrochemical studies if the supporting electrolyte is in large excess.

5. Application to anodic dissolution studies

For this purpose we used a Sn ring–Sn disc electrode in a 0.2 M Na_3PO_4 solution. Typical curves are shown in Fig. 8. The general aspect of these curves is quite similar to the one obtained previously with a rotating ring disc electrode [20]. The disc potential was swept at 0.01 V s^{-1} from − 1.2 V to the anodic region and the ring potential was held at − 1.3 V. The current–voltage curve on the disc showed two anodic peaks. The first and the second peak correspond to the formation of stannous and stannic species, respectively. The cathodic ring current (lower curve) rises simultaneously with the disc current due to the reduction of the soluble species provided from the disc. The ratio between the ring and the disc current taken at the first peak is equal to 0.15 compared with 0.39 obtained for a rotating ring disc electrode [20].

This example illustrates that the system can be used for study of anodic dissolution and corrosion of metals under fluid flow. The ring electrode provides additional information on the mechanism of the reactions. However it should be noted that as material is removed from the electrode by dissolution, irregularities on the surface of the disc become more and more important. They will contribute to create eddy turbulences and therefore a low ratio i_R/i_D.

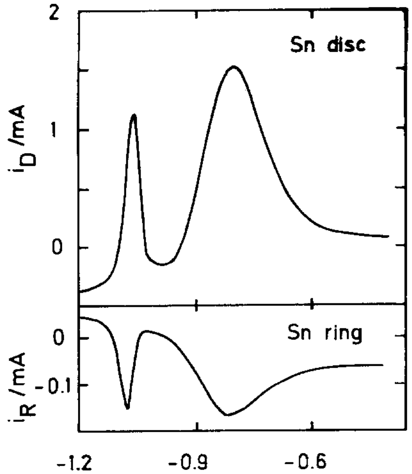

Fig. 8. Disc and ring response in 0.2 M Na_3PO_4. dE_D/dt = 0.01 V s^{-1}, E_R = − 1.3 V. Inlet tube 2, nozzle–electrode distance 1 cm, u = 83.6 cm s^{-1}.

6. Conclusions

From the results obtained in this work, the ring–disc jet electrode appears to be a promising technique for electrochemical, electroanalytical or corrosion studies in a continuous flow of solution. This system can also provide information concerning the mechanism of the reaction. A compromise exists between a high mass transfer rate and a high i_R/i_D ratio by choosing an intermediate nozzle–electrode distance as well as a suitable radius for the disc and ring electrode.

However this system presents some disadvantages. In fact the inlet tube and the electrode surface must be centered symmetrically in order to eliminate any non-uniform flow of the electrolyte. One further difficulty comes from the fact that the distance between the nozzle and the electrode surface has to be controlled and measured precisely. This is particularly important when the distance is very small.

One advantage of the ring–disc jet electrode is its simplicity because the double electrical connection with a rotating electrode is avoided. It can be used advantageously in a continuous process.

Much work remains to be done on the best design of ring–disc jet electrode systems for particular application and for greater precision in limiting current measurements.

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