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Relation between the Size of the Electrode and Rotation Velocity at Rotating Ring Disk Electrode

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In electrolysis it is very difficult to detect and determine quantitatively intermediates produced at the electrode surface, especially in the cases of unstable materials. The rotating-ring-disk electrode method, developed by Frumkin and Nekrasov[1], has been recently regarded as one of the most useful means for the investigation of the intermediates of electrode reactions. Intermediates produced at the disk electrode would be transported by convective-diffusion to the ring electrode, where the electrochemical properties of the intermediates can be identified. When the rotation velocity is changed between 100 and 8000 rpm, a wide range of first-order rate constants of the intermediate reactions can be studied from 4×10^{-2} to 10^{3} sec^{-1}.[2] The higher the rotation velocity becomes, the faster the chemical intermediate reaction that can be measured.

When the species produced electrochemically on the disk electrode are stable, the ratio of the ring-limiting current to the disk-electrode current has been defined as the collection efficiency, N,[3] which is a function of the radii of the disk and ring electrodes. It has been shown that the collection efficiency, N, which is a very important factor in quantitative investigations, is independent of the angular velocity of rotation, the kinematic viscosity of the solution, the diffusion coefficient, and the concentrations of the species involved. The collection efficiency, N, can be calculated from the table which Albery and Bruckenstein[3] reported only when the flow in the vicinity of the electrode surface is laminar. On the contraty, at a high rotation velocity, which is often required in order to investigate fast intermediate chemical reactions, the Reynolds number increases and the flow in the vicinity of the electrode surface may become turbulent. Therefore, it is considered that each ring-disk electrode has a limit of maximum rotation rates, the limit depending on the total radius of the electrode involving the shroud part.

In this paper, as a basic study for the rotating-ring-disk electrode, the collection efficiency, N, was measured with various rotation velocities using an electrode in which the sizes of the disk and ring electrodes were constant, but in which the total radius of the electrode involving the shroud part was changed by setting arbitrary covers. It is shown that there is a maximum value of rotation velocity for each total radius of ring-disk electrodes. Moreover when the rates of the fast intermediate chemical reactions are to be measured, it may be pointed out that both the rotation velocity and the size of the electrode should be taken into consideration.

Experimental

Electrodes. The structure of the rotating-ring-disk electrode is shown in Fig. 1. A platinum disk electrode and a platinum ring electrode with platinum lead wires were fixed into a Teflon rod treated with a lathe. The disk radius was 5.00 mm, while the inner ring radius and outer ring radius were 5.50 and 6.50 mm respectively. The radius of the Teflon rod was

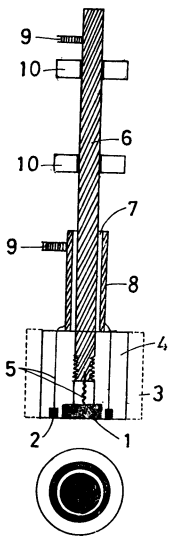

Fig. 1. Ring disk electrode.
1: Pt disk electrode, 2: Pt ring electrode, 3: Tube of acrylic resin, 4: Teflon, 5: Pt lead wire, 6: Shaft of steel, 7: Tube of acrylic resin, 8: Tube of brass, 9: Brushes of silver-carbon, 10: Bearings.

1) A. N. Frumkin and L. N. Nekrasov, *Dokl. Akad. Nauk SSSR*, **126**, 115 (1959).
2) W. J. Albery and S. Bruckenstein, *Trans. Faraday Soc.*, **62**, 1946 (1966).
3) W. J. Albery and S. Bruckenstein, *ibid.*, **62**, 1920 (1966).

8.00 mm, and by covering the tubes made with acrylic resin, the total radius of the electrode could be change to 12.5, 15.0, 20.0, or 30.0 mm. The Teflon and the steel shaft were connected by screwing down the shaft into the Teflon; the rotation showed little eccentricity. The shaft was supported by bearings at two points and was rotated by means of the rotation system. The external electrical contact of the shaft was made with silver-carbon brushes. As pretreatment, the electrode was polished to a mirror finish with sandpaper and and alumina powder and then electrolyzed both anodically and cathodically. Such electrode had a satisfactory reproducibility. The immersion depth of the electrode into the electrolyte solution was about 5 mm.

Electrolysis Vessel. The electrolysis vessel, the inner radius of which was 40.0 mm, has an upward capillary in the center and two platinum counter electrodes at the bottom of the vessel. Using a vessel the inner radius of which was 70.0 mm, the effect of the size of the vessel on the relation between the collection efficiency and the rotation velocity was tested.

Reagents, Solutions and Atmosphere. The water was distilled once, after it was treated with an ion-exchange resin. All the chemicals were of reagent-grade quality. The electrolyte solution was a $CuCl_2$ (10^{-3} mol/l) aqueous solution, with KCl (0.2 mol/l) used as a supporting electrolyte. The electrode rotation assembly was set in a large, dry box made of acrylic resin and vekulite sheets. In this box liquid nitrogen was placed in a jar in order to introduce a nitrogen atmosphere; furthermore, by passing purified nitrogen gas through during all the experiments, the electrolyte solution was deoxygenated. The temperature of the electrolyte solution was 17°C.

Measurements. Two potentiostats, Hokuto Denko PS-1000 A, were used to control the potentials of the ring and disk electrodes independently. The reference electrode was a saturated calomel electrode. The ring current was measured with a Toa Recorder, EPR-2T, and the disk current, with a Keithley Electrometer, 610B. The electrode rotation assembly was made so that its rotation velocity could be changed from zero to 7000 rpm, and the rotation velocity was measured by a revolution-indicator.

Results and Discussion

In this investigation, the oxidation-reduction reaction;

$$Cu^{2+} + e^- \rightleftarrows Cu^+ \qquad (1)$$

was taken as a model reaction. The potential of the disk electrode was set to form Cu^+ at -0.15 V, which is the cathodic limiting-current region of Reaction (1), and the ring electrode, at 0.60 V, the anodic limiting-current region. The collection efficiency of the electrode used here was 0.309 (on the base of the table of Albery and Bruckenstein's paper)[3]. The whole outer radii involving the shroud of the ring-disk electrode were changed in the manner described before. The collection efficiencies were measured and plotted against the rotation velocities, as is shown in Fig. 2. The collection efficiencies obtained agreed with the

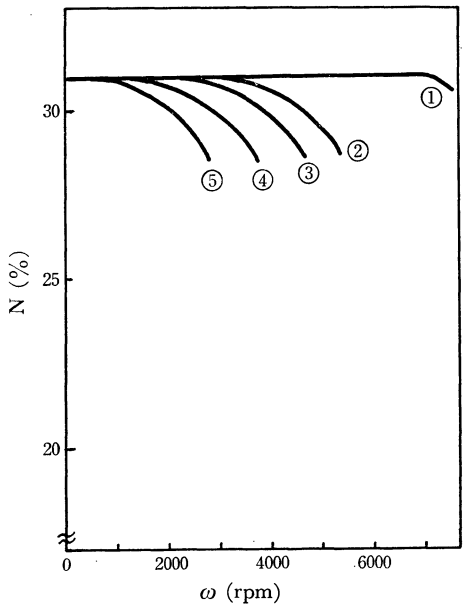

Fig. 2. Relation between rotation velocity and collection efficiency. Total radius of rotating ring disk electrode (cm), ①: 0.80, ②: 1.25, ③: 1.50, ④: 2.00, ⑤: 3.00.

value of 30.9% when the rotation velocity was not so high. As is illustrated in Fig. 2. the value of N began to decrease with the increase in the rotation velocity. Moreover, this decrease appeared at a lower rotation velocity when the electrode radius was larger. When the rotation velocity was higher than a certain critical value, which was related to the radius of the electrode, the collection efficiency, N, came to decrease; at the same time, it was recognized that the electrolyte solution bacame turbulent and that the bubbles were engulfed at the electrode surface. This reason has also been studied at the rotating-disk elecctrode[4,5], as a result of the increase in the Reynolds number N_{Re}, the laminar flow becomes a turbulent flow as the rotation velocity increases. The Reynolds number is related to the kinematic viscosity ν (cm²/sec), the radius of the electrode r (cm), and the rotation angular velocity ω(rad/sec):

$$N_{Re} = \frac{r^2\omega}{\nu} \qquad (2)$$

When the electrode surfaces are smooth enough and there is no eccentricity of rotation, the critical point of the Reynolds number where the flow of the solution changes from laminar to turbulent may be unchanged with the same electrolyte solution even if the radii of the electrodes are different. From Eq. (2) it can be understood that the larger

4) V. G. Levich, "Physicochemical Hydrodynamics," Prentice-Hall (1962).

5) Z. Gaus and R. N. Adams, *J. Phys. Chem.*, **67**, 866 (1963).

the radius of the electrode, the lower is rotation velocity which is the critical point for the change from laminar flow to turbulent.

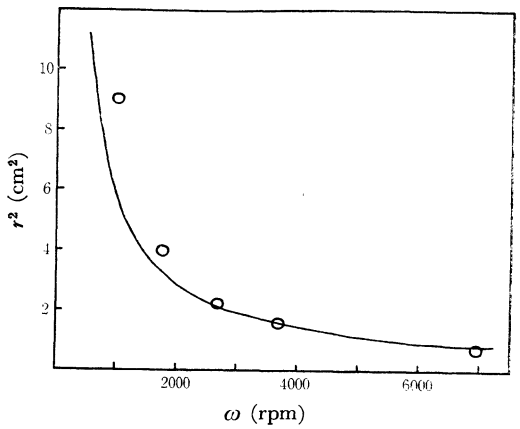

Fig. 3. Relation between r^2 and critical rotation velocity.
Solid line: $N_{Re}=6\times10^4$.

Figure 3 shows the $r^2-\omega$ relation. The solid line indicates the value calculated when $N_{Re}=6\times10^4$. In this case, the kinematic viscosity $\nu=0.01$ (cm^2/sec) is used. The measured points agreed quite well with the solid line. When the radius of the electrode is large, the critical points deviate slightly from the solid line. This may be explained by considering that, though, at the outer side of the shroud, the flow is turbulent, at the inner region, where the ring and disk electrode are locates, the flow may be laminar. In the study of the rotating-disk electrode, it was reported that the critical point is reached when N_{Re} is $10^4\sim10^5$. Therefore, $N_{Re}=6\times10^4$ is a reasonable value. Further, the same results were obtained when the electrolysis vessel with a radius of 70 mm was used instead of one with a 40 mm radius.

It may be concluded that there are limited regions of rotation velocity, depending on the electrode size. In cases where high rates of mass transport are desired, the total radius of the electrodes must be as small as possible for the rotating ring-disk electrode method. For example, when we study the intermediates with a rate constant of 10^3 sec^{-1}, the rotation velocity must be higher than 8000 rpm, but at the same time the total radius of the electrode must be smaller than 0.7 cm because of the laminar flow (probably also dependent on the eccentricity of the rotation). However, in such a high rotation velocity, special regard should be paid to the so-called edge effect, the mixing effect, etc.[6]

On the other hand, a turbulent flow is generally required for effective mixing and shorter reaction times in heterogeneous chemical reactions. Therefore, this method is interesting in connection with a quantitative investigation of the turbulent flow. As the critical point from laminar flow to turbulent can be simply and briefly measured by means of the rotating ring-disk electrode technique, using the relation between the collection efficiency and the rotation velocity, this method is considered to be a good tool for liquid turbulence studies.

The authors wish to thank Dr. M. Sukigara for his useful discussions.

6) R. N. Adams, "Electrochemistry at Solid Electrodes," Marcel Dekker, New York (1969).