

In order to study electrochemical reactions on solid electrodes theoretically, it is necessary to accurately determine the transport phenomena of electrolytically active substances onto electrodes. The phenomena are discussed in detail in the general theory of Yoshizawa et al. [1], but, at any rate, the rotating disk electrode (RDE) is one of the schemes which satisfy the necessary conditions. Its theoretical formula was presented by Levich [2], and this was also confirmed experimentally. At present, the scheme is widely used in research on electrochemical reactions taking place on solid electrodes.

The rotating ring-disk electrode (RRDE) is a more advanced version of the RDE. Since the RRDE is also mentioned in the general theory of Yoshizawa et al., there might be some redundancies, but the writers would nevertheless like to discuss, to the extent of their knowledge, the fundamentals of the RRDE.

The origin of the rotating ring-disk electrode method goes back to 1959, when Frumkin, Levich et al. [3, 4] attempted to detect the unstable intermediate products in electrode reactions by constructing an electrode which combined a disk electrode with a ring electrode, that is, a disk electrode surrounded by a concentric ring electrode with insulating material between them. The

* Numbers in the margin indicate pagination in the foreign text.

products formed in electrochemical reactions on the disk electrode are transported to the ring electrode by convection-diffusion. The method involves the determination of the products on the disk electrode from the electrochemical reactants on the ring electrode, which are measured by the current/voltage relationship on the ring electrode.

The main items among the findings from the application of the RRDE to the study of the electrode reaction mechanisms are as follows [5, 6]:

- 1) rapid detection of electrolytic products
- 2) detection of the intermediate products
- 3) characterization of the final products and the intermediate products by such means as half-wave potential
- 4) measurement of the subsequent chemical reaction rates of the intermediate products
- 5) characterization of the pH dependency of this rate
- 6) measurement of the ratio between the various products formed at the electrode.

There are various RRDE-related books [2, 5, 6] and general theories [7, 8], but, as far as theoretical content is concerned, the book by Albery et al. [5] is probably most suitable for reference.

2. Theory

Fig. 1 shows the flux on the surface of a rotating electrode in fluid-dynamics terms. Due to the rotation of the electrode,

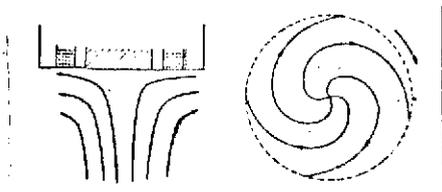


Fig. 1. Lines of solution flow near rotating electrode surface.

the products on the disk electrode reach the ring electrode immediately. Needless to say, an increase in the number of rotations is accompanied by an increase in the transport velocity.

Let us present the main theories which can be applied to the study of the electrode reaction mechanism in the subsequent sections.

2.1. Rate of Capture

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In order to utilize an RRDE as a means of quantitative determination, one must be able to express the transport of a chemical species from the disk electrode to the ring electrode theoretically. When



occurs on the disk electrode and its reverse reaction



occurs on the ring electrode, the ratio between the electric current at the disk electrode i_D and the current at the ring electrode i_R is the rate of capture N . That is,

$$N = -i_R / i_D \quad (1)$$

Ivanov and Levich [9] demonstrated that the rate of flux of an electrochemically active species from the disk electrode to the ring electrode was independent of the angular velocity of rotation and the kinetic viscosity, and the diffusion coefficient

and the concentration of the solution, and presented the following equation

$$N = 0.8 \left(1 - \frac{3}{4} \frac{r_1^3}{r_2^3} \right)^{1/3} \int_{r_1}^{r_2} \frac{x^2 dx}{(x^2 - 1) \left(x^2 - \frac{3}{4} \frac{r_1^3}{r_2^3} \right)} \quad (2)$$

where r_1 , r_2 and r_3 represent the disk diameter, inner ring diameter and outer ring diameter, respectively.

Albery and Bruckenstein [5, 10, 11] conducted a theoretical study of the rate of capture by solving the differential equation of transport very precisely.

The equation relating to the transport of chemical species B forming on the disk electrode surface is given by the following formula.

$$v_r \frac{\partial b}{\partial r} + v_x \frac{\partial b}{\partial x} = D \left(\frac{\partial^2 b}{\partial x^2} + \frac{\partial^2 b}{\partial r^2} + \frac{1}{r} \frac{\partial b}{\partial r} \right) \quad (3)$$

At distances of more than 10 Å from the electrode surface, the term for diffusion in the radial direction can be ignored, since diffusion in the radial direction is considerably smaller than convective flow in the same direction. On the basis of fluid dynamics, the following relational equations are also used.

$$v_r = Crx, \quad v_x = -Cx^2$$

where the convection constant $C = 0.510\omega^{3/2} \nu^{-1/2}$,

On the basis of these relationships, equation (3) becomes:

$$r \frac{\partial b}{\partial r} - x^2 \frac{\partial b}{\partial x} = \frac{D}{C} \frac{1}{x} \frac{\partial^2 b}{\partial x^2} \quad (4)$$

The boundary conditions for this differential equation are given as follows:

- 1) all domains: $x \rightarrow \infty, b \rightarrow 0$
- 2) disk ($r < r_1$): $x = 0, \partial b / \partial x = i_D / \pi r_1^2 n F D$
- 3) gap ($r_1 \leq r < r_2$): $x = 0, \partial b / \partial x = 0$
- 4) ring ($r_2 < r < r_3$): $x = 0, b = 0.$

The ring electric current may be expressed as follows.

$$i_R = n F D \int_{r_2}^{r_3} 2\pi r \left(\frac{\partial c}{\partial x} \right)_{x=0} r dr \quad (5)$$

The following dimensionless variables are used to solve equation (4):

$$\omega = \frac{(C - C^*)}{C^*} x \quad (6)$$

$$u = \frac{r - r_1}{r_1} \quad (7)$$

Using ω and u , equation (4) becomes:

$$r \omega \frac{\partial u}{\partial r} - \omega^2 \frac{\partial^2 u}{\partial \omega^2} = \frac{\partial^2 u}{\partial \omega^2} \quad (8)$$

At this point, the rate of capture N can be expressed as:

$$N = - \frac{i_R}{i_D} = \frac{2}{r_1^2} \int_{r_2}^{r_3} r \left(\frac{\partial u}{\partial \omega} \right)_{\omega=0} r dr \quad (9)$$

Equation (8) has been solved by a new method using the Laplace transform and the Airy function, so that the following equation has been presented for the rate of capture in equation (8):

$$N = 1 - F\left(\frac{\alpha}{\beta}\right) + \beta^{1/3} [1 - F(\alpha)] - (1 + \alpha + \beta)^{1/3} \left\{ 1 - F\left[\frac{\alpha}{\beta} (1 + \alpha + \beta)\right] \right\} \quad (10)$$

where $\alpha = (r_2/r_1)^3 - 1$, $\beta = (r_3/r_1)^3 - (r_2/r_1)^3$ and $F(\theta) =$

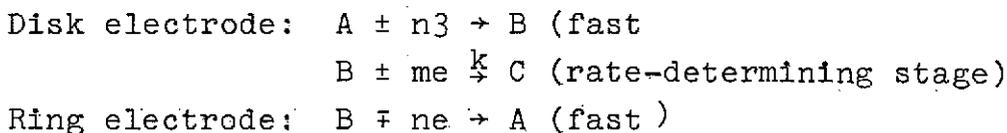
$\frac{\sqrt{3}}{2\pi} \int_0^\theta \frac{d\lambda}{\lambda^{1/3}(1+\lambda)}$. In addition, this $F(\theta)$ may be integrated to give:

$$F(\theta) = \frac{\sqrt{3}}{4\pi} \ln \frac{(1+\theta^{1/3})^{1/3}}{1+\theta} + \frac{3}{2\pi} \arctan \left(\frac{2\theta^{1/3}-1}{3^{1/3}} \right) + \frac{1}{4}$$

From these theoretical calculations, Albery et al. express N as a function of r_2/r_1 and r_3/r_2 . In addition, they used electrodes of various sizes to obtain the rates of capture for the $\text{Cu}^{2+}/\text{Cu}^+$ system, the Br_2/Br^- system, and the Ag/Ag^+ system and others, thereby establishing the validity of their theoretical equations.

2.2. Explanation of Complex Electrode Reaction Mechanism

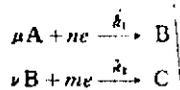
The electrochemically active species A undergoes an electrochemical reaction at the disk electrode to form substance B which, in turn, reacts electrochemically with C at a certain rate. Meanwhile, the portion of B which did not react electrochemically at the disk electrode is transported to the ring electrode, where it is detected. A theoretical equation for obtaining the constant k for this reaction rate was presented by Ivanov and Levich [2, 12]. This was followed by another theoretical equation for the same system, which was established by Albery et al. [11].



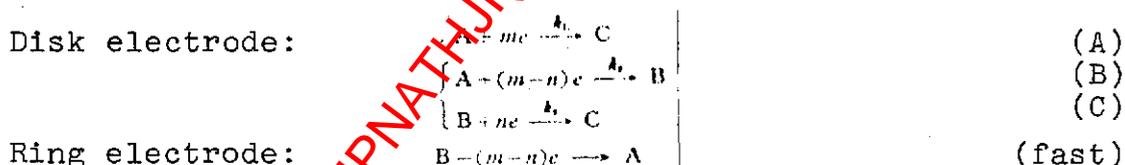
$$i_a/i_D = \frac{-N}{1 + 3^{1/2} \Gamma(4/3) k D^{2/3} \nu^{1/6} / 0.510^{1/3} \omega^{1/2}} \quad (11)$$

Constant k may be obtained by measuring the rates of capture while varying the number of rotations.

Filinovskii [13] has submitted theoretical equations for determining the reaction rate constant and the degree of reaction in the following two-stage electrochemical reaction.



Bockris et al. [14] considered the following reaction system, which is a slightly more complex version of the above system, and presented a theoretical equation which makes it possible to determine which reaction proceeded at what rate.



Assuming that the electric current from reaction (A) is x times as much as the electric current from reaction (B), the relational equation expressed by the following formula would become valid.

$$\frac{i_D}{i_R} = \frac{x+1}{N} + \frac{(x+2)k'}{N\omega^{1/2}} \quad (12)$$

where $k' = 1.6 D^{-2/3} \nu^{1/6} k_3$. D is the diffusion coefficient of B. It is possible to obtain x and k_3 by plotting the relationship of i_D/i_R to $\omega^{-1/2}$, while varying the number of rotations of the electrode. Representative relational graphs are shown in Fig. 2.

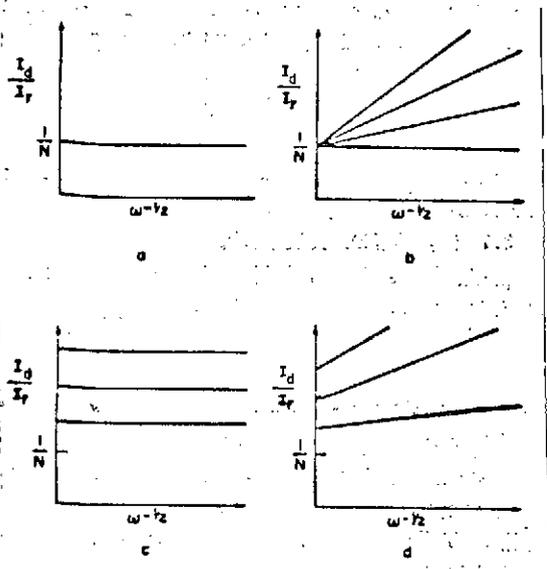


Fig. 2. Relational graphs of i_D/i_R to $\omega^{-1/2}$. The reaction mechanism is explained by plotting the relationship with set potential as parameter, and then determining which one of relations a to d above is applicable.

through either primary or secondary chemical reactions.

The theoretical equation for the case in which the electrolytic products at the disk electrode undergo a primary reaction was presented by Aldery and Bruckenstein [16].

$$\frac{N}{N_k} = 1 + 1.28 \left(\frac{\nu}{D} \right)^{1/3} \frac{k}{\omega} \quad (13)$$

where N is the rate of capture characteristic of geometric electrodes and N_k is the rate of capture produced when a primary reaction is taking place in the solution. By using an electrode with a thin gap and a thin ring, it is possible to determine the primary reaction rate constant from about 3×10^{-2} to 10^3 sec^{-1} .

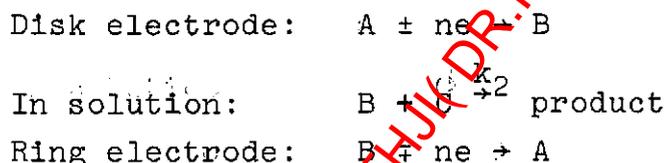
The electric current \times voltage curve on the ring electrode, while a reversible electrochemical reaction is in progress at the disk electrode, was studied theoretically and then validated for the Ag/Ag^+ system [15].

2.3. Subsequent Chemical Reaction Rate of Electrode Reaction Products

Theoretical equations have been submitted for the determination of reaction rate constants during the transformation of the intermediate products, which were formed electrochemically, into other compounds

Furthermore, Albery [17, 18] submitted a theoretical equation which seeks the primary reaction rate from the transient behavior of the ring current, when the disk electric current is varied from zero to the stationary value, and demonstrated that it could be determined up to 10^4 sec^{-1} . In practice, the validity of this theoretical equation has been confirmed by means of reaction systems with known rate constants, such as the bromination reaction of anisole [19].

Theoretical equations have also been submitted for the case in which the electrochemical reaction products at the disk electrode undergo a secondary reaction with chemical species in the solution [20, 21]. A fairly complex procedure is required in order to obtain the rate constant k_2 for such a case, but its general outline would be as follows:



The following formulas are given as the differential equations of this case.

$$v_r \frac{\partial b}{\partial r} + v_x \frac{\partial b}{\partial x} = D \frac{\partial^2 b}{\partial x^2} - k_1 bc \quad (14)$$

$$v_r \frac{\partial c}{\partial r} + v_x \frac{\partial c}{\partial x} = D \frac{\partial^2 c}{\partial x^2} - k_1 bc \quad (15)$$

These equations are solved using the same procedure as the one used to obtain the rate of capture. Employing the ring electric current $i_{R,k}$, produced when the concentrations of B and C on the electrode surface become equal at the inner perimeter of the ring, and the rate of capture N_k for that case, the following relational equations are given:

$$i_{R,k} = 0.21 \pi r_1^2 n F D \omega^{1/2} \nu^{-1/2} k_2^{-1} \quad (16)$$

$$N_k = \frac{0.339 r_1^2 D^{1/2} (1 - F(\alpha)) \omega}{r_1^2 \nu^{1/2} k_2} c_\infty \quad (17)$$

Here, $F(\alpha)$ is the value fixed by the form of the electrode at the place where the rate of capture is sought, and c_∞ is the concentration of the chemical species in the solution which takes part in the secondary reaction. The validity of these theoretical equations has been confirmed in the reaction between allyl alcohol and bromine [22] and in the reaction between As (III) and iodine [23]. The analysis of faster reactions is possible by increasing the number of rotations. For instance, it is possible to seek the rate constant of up to $k_2 \approx 10^9 \text{ M}^{-1}\text{s}^{-1}$ at 3000 rpm.

In addition, theoretical equations have also been conceived for the reaction mechanisms of the case in which intermediate products formed at the disk electrode are converted rapidly, as well as reversibly, into electrochemically inactive species [24]. These reaction systems, studied by Albery et al., can be organized as in Table 1 [24].

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TABLE 1. THEORETICAL EQUATIONS SUBMITTED FOR VARIOUS REACTION SYSTEMS

Disc electrode	Solution	Ring electrode	Ref.
A → B	nothing	B → A l.c.	11
rev. A ⇌ B	nothing	B ⇌ A rev.	15
A → B → P	nothing	B → Q l.c.	11
O → B	B + A → P	B → Q l.c.	20
O → B	B + A → P	B → Q l.c.	21
O → B	B → P	B → Q l.c.	16
rev. G ⇌ B	B ⇌ A	B ⇌ G rev.	24
A ⇌ B	nothing	B ⇌ A	24

l.c. = limited current
 rev. = reversible system

2.4. Digital Simulation Method of Bard et al.

Prater and Bard [25] devised a digital simulation model of the rotating ring-disk electrode, which is shown in Fig. 3. By

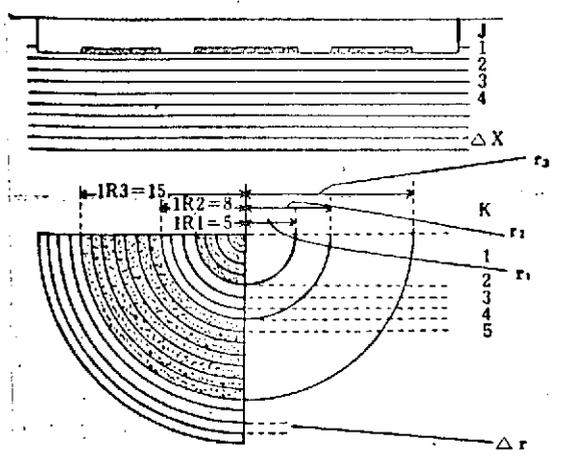


Fig. 3. Digital simulation model.

studying the various theoretical equations solved by Albery, Bruckenstein and others, using numerical value calculations conducted by means of an electronic computer they confirmed that the results obtained by Albery and others were in good agreement with the results from the simulation method. They first sought the rates of capture in simple systems, which did not include chemical reactions, and then studied the transient behavior of the disk and ring electrodes [25]. They then submitted the method for obtaining the chemical reaction rate constant for the case in which the electrolytic products of the disk electrode are converted into electrolytically inactive species through primary or secondary chemical reactions [26]. They also demonstrated that the ECE mechanism or the catalytic mechanism could be studied fairly easily by means of this method [27].

Recently, Puglisi and Bard submitted a simulation method for examining the reaction mechanism of the dimerization of disk electrode products [28]. This method is used for explaining complex organic electrode reactions. In addition, Bard et al. apply this method to the explanation of the mechanism of electrochemical luminescence, as well as to the research on the

electric current distribution of the ring-disk electrode (see Sections 3.4 and 3.5).

A general theory of the digital simulation method was also published by Prater [29]. For example, it gives the computer program used for obtaining the primary reaction rate.

Albery et al. [30] have also recently conducted a comparison between the simulation method, which uses a computer, and the analysis method, based on the resolution of differential equations for the rate of capture, primary and secondary chemical reactions and the transient current behavior.

2.5. Other Theories

The time required for the transport of the disk electrode products to the ring electrode, that is, the transition time, has been calculated theoretically by Bruckenstein and Feldman [31]. The transition time is expressed by the following formula relating to the physical size of the electrodes, the diffusion coefficient of the chemical species formed at the disk electrode and the viscosity of the solution.

$$\omega T = 43.1 \left(\frac{\nu}{D} \right)^{1/2} \left[\log \frac{r_2}{r_1} \right]^{1/2} \quad (18)$$

In addition, the theory of the transient method [32] and an RRDE theory using the alternating current method [33] have been submitted by Albery et al.

3. Applications of Rotating Ring-Disk Electrodes

The rotating ring-disk electrode is not easy to construct because of the complexity of the electrode components. Furthermore, it is necessary that there should be no eccentricity when

it is rotated and that the number of rotations can be varied. For these reasons, it has not been an easily operable method for researchers in electrochemistry, among others. But, since the device also recently became available on the market in our country, it is expected to be widely applied to the explanation of electrode reaction mechanisms in the futur.

Below, we list some of the items which have been studied thus far using the method in question.

3.1. Reaction Mechanism of Reduction of Dissolved Oxygen

The reduction of dissolved oxygen manifests a complex reaction behavior, which is affected, among other things, by the electrode material or the pH of the solution. The reaction mechanism has been discussed in the past on the basis of the detection of hydrogen peroxide, an electrochemically active compound, which is sometimes present as an intermediate product.

The reduction reaction at a gold amalgam electrode was studied in alkali solution by Frumkin et al. [3, 4]. Also, Nekrasov et al. [34] recently studied the reaction in the presence of a boundary activator. The reaction mechanism on a gold electrode has been studied by Yeager et al. [35].

With a platinum electrode, the reduction reaction mechanism is quite complex, due to the formation of an oxidation film on the electrode surface. Its behavior in alkali solution was first studied by Müller et al. [36, 37] (Fig. 4). Bockris et al. [38] then used the diagnostic equations of the electrode reaction mechanism submitted by Müller et al. [14] to explain the behavior. Bockris et al. [39] also demonstrated that the reduction reaction taking place on a platinum electrode, which has been subjected to oxidation treatment in an acidic aqueous solution of sulfuric

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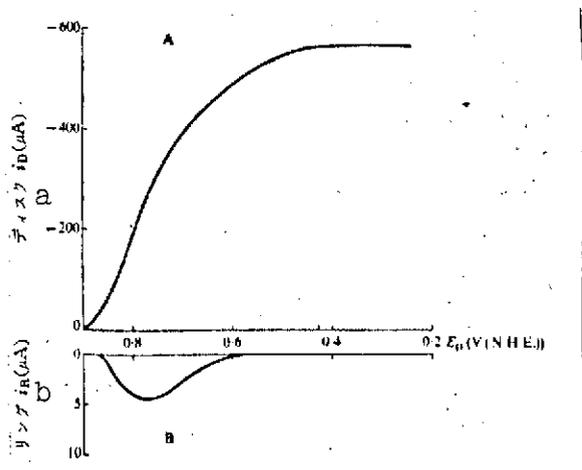


Fig. 4. Reduction of oxygen on ring-disk electrode: A. reduction of oxygen on flat Pt disk electrode; B. limit oxidation current for H_2O_2 on ring electrode. (KOH: 0.125 M, $\omega = 5$ Hz).

Key: a. Disk; b. Ring

acid, was considerably affected by minute quantities of impurities in the solution.

A study of the case of a silver electrode in an alkali solution [40] was conducted using a three-section rotating electrode (Ag disk, Ag small disk, Pt large disk).

3.2. Reactions Involving Inorganic Compounds

The electrode reaction mechanisms of halogens have been studied frequently by Bruckenstein, Johnson and others. The subjects covered include a study of the adsorption and oxidation of Br^- ions on a Pt electrode [14], and a detailed discussion concerning iodine, namely, the electrode reaction mechanisms of I^+ , I_2 , I^- and IO_3^- in salt solutions of hydrochloric acid or perchloric acid [42]. The adsorption and desorption behaviors between I^- and I_2 at a Pt electrode in 1 M sulfuric acid have also come under study recently [43], resulting in, among other things, the presentation of the relational diagram shown in Fig. 5, which indicates the variation in I_2 adsorption from the reversible state to the irreversible state.

As already stated in Section 2.3, studies have also been conducted on the reaction rates of electrolytically formed I_2 [23] or Br_2 [20] with As (III), which is present in the solution.

The reduction reaction mechanisms of permanganates in alkali solutions have been studied by Heusler et al. [44].

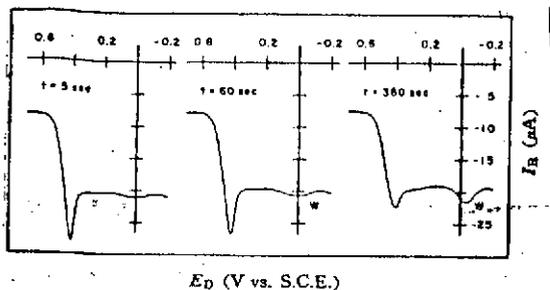
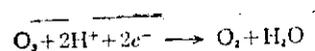


Fig. 5. $I_R - E_D$ curve showing the change in I_2 adsorption state. 2.0×10^{-4} M NaI, 1.0 M H_2SO_4 , 2500 rpm.

It has also been explained that the reduction reaction of ozone in an acidic solution [45] is



and that the initial stage of the oxidation reaction of carbon monoxide in an alkali solution [46] is



Another recent study concerns the reactions of hydrogen peroxide at an Ag electrode in alkali solutions, particularly its electrolytic reduction and oxidation, as well as its catalytic decomposition rates [47]. The question of to what extent the oxygen produced by the electrolysis of water can become super-saturated on the anode surface in a strong KOH solution has also been studied using an Ni disk electrode and a Cd ring electrode [48]. Other studies include a study of gas-producing reactions using two-ring electrodes [49, 50], and a study of the dissolution reaction mechanism of TiO electrodes [51].

3.3. Dissolution and Electrodeposition Reactions of Metals and Alloys

There has been an energetic study of the subject by a group including Bruckenstein, Miller and Johnson. Let us first summarize their findings.

They conducted various experiments using the $Cu-Cu^+-Cu^{2+}$ system. In an aqueous solution of potassium chloride, for instance, Cu^{2+} demonstrates a two-stage reduction wave, with Cu^+ being formed in the first wave. By means of the measurement of the rate of capture after setting a ring electrode to the electric

potential level for the oxidation of this Cu^+ (Fig. 6), they investigated the design, the shielding effect and other aspects of a potentiostat, which enables independent fixed potential settings for the two electrochemical systems of the disk electrode and the ring electrode in the same solution [52].

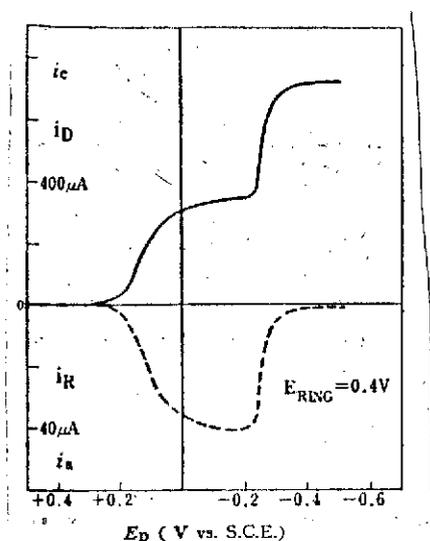
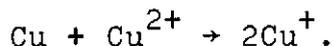


Fig. 6. Current-voltage curves in solution of 10^{-3} M CuCl_2 - 0.5 M KCl. —: disk electrode; ---: ring current

0.5 M hydrochloric acid solution [55]. Cu and Cu^{2+} undergo a homogenization reaction to form Cu^+ , that is,



The rotating ring-disk electrode was used to determine the equilibrium constant in this system, and it was found to be 5.6×10^{-7} for the case of a 0.2 M sulfuric acid solution [56]. The electrodeposition and stripping of copper on platinum surfaces were also studied [57]. The analysis of the simultaneous stripping of Cu^{2+} and Ag^+ was also studied, and it was discovered that

with mixed Cu-Ag electrodeposition, it was possible to determine the two elements simultaneously, regardless of whether the deposit was greater or less than a monoatomic layer [58]. Regarding the anode behavior of Cu in alkali solution, a study was conducted using an RRDE and a split ring-disk electrode in which the ring electrode is in two separate horseshow-shaped parts (see Fig. 7), and Cu (III), which is soluble for the anode domain of the oxygen generation, was detected and identified [59]. In addition, this electrode system was used to elaborate on a research method

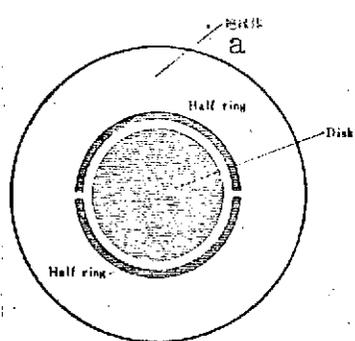


Fig. 7. Split ring-disk electrode.

Key: a. Insulator

for the corrosion of alloys and its application to the anode behavior of Cu-Zn alloy in aqueous solutions of ammonia [60]. More recently, Miller et al. studied the corrosion of copper and the Cu 30 Zn alloy in a 0.1 M HCl and 1 M NaCl solution containing oxygen, and obtained the open circuit corrosion rate as a function of the number of rotations and temperature from the amount of Cu^+ detected from the ring electrode [61].

In connection with the stripping analysis method, Johnson et al. improved on the conventional single electrode by adopting the RRDE, and succeeded in reducing the duration of electrodeposition prior to the stripping, as well as in lowering the minimum detection level (see Fig. 8). For instance, they succeeded in detecting 10^{-10} M of Ag^+ in a solution of 0.1 M H_2SO_4 by using glassy carbon for the disk and platinum for the ring [62]. The detection of Hg (II) was also conducted using the same method [63]. Satisfactory results were obtained in a state in which a thin gold film was electrodeposited on the glassy carbon disk electrode, so that they could measure 0.1-0.4 ppm of Hg (II). The mean relative deviation in the measurement of the 0.1 ppm

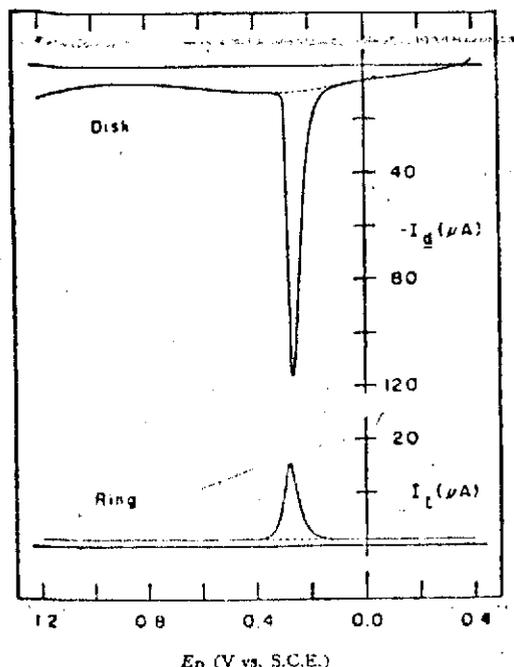


Fig. 8. I_D - E_D and I_R - E_D curves in voltametry accompanied by collection. 1.00×10^4 M Ag^+ , $t_{dep} = 5$ min
 $E_D: -0.40$ V, $E_R: 0.00$ V,
 $\omega^{1/2} = 6.47$ (rad sec) $^{1/2}$
 Induced voltage: $E_D = 5.0$ V/min

level was 7.5%, thus indicating that the limit of detection with this method was approximately 0.01 ppm.

The oxidation-reduction reaction of a platinum electrode itself in a 1 M H_2SO_4 solution and a 0.1 M $HClO_4$ solution was studied [64]. It was determined that Pt (II) was formed when the oxidized platinum electrode was reduced, and that unidentified chemical species were formed during the oxidation reaction. The behavior of a silver electrode in alkali solution has also been studied [65]. Soluble products from the oxidation and reduction reactions of the silver disk electrode were measured with the ring electrode, and, in addition,

the formation of surface oxide was examined. Also, the electro-deposition of Ag under potential has been studied [66].

Another finding from research was that when an anodic dissolution reaction of In is taking place in a 0.07 M perchloric acid solution with a current density greater than 10 mA/cm^2 , the In is dissolved in the form of In^+ [67].

The oxidation-reduction reactions and the electrode absorption behaviors, as well as electrodeposition reactions of various metallic ions, have been studied in recent times. In a study of the electrochemical reaction mechanism of Sn (II) on a gold electrode in a 4 M hydrochloric acid solution, the various

processes from the easily-achieved adsorption of Sn (II) by the electrode, its oxidation into Sn (IV) and its reduction to metallic Sn were examined in detail [68]. The electrochemical behaviors of Bi have also been studied using a platinum electrode [69] or a gold electrode [70] in the form of an RRDE. Another detailed investigation of the adsorption of Pb onto a gold electrode in a 0.5 M potassium chloride solution was conducted [71], in which the electrodeposition under potential and anodic stripping was studied, among other things.

A dissertation by Kiss and Farkas entitled "A study of the dissolution of metals and electrodeposition of metallic ions using the RRDE" has been submitted in a series of nine reports so far [72-78]. The dissertation, together with its related studies [79-81], attests to the fact that the application of the RRDE is being carried out widely in Hungary as well. Kiss et al. derived theoretical relational equations independently, and, at the same time, conducted experiments using the Cu system.

The anodic behaviors of iron, particularly dissolution reactions in which Fe^{2+} or Fe^{3+} ions are formed on the surface of iron in the passive state, have been studied on the basis of ring electrode behaviors [82]. The growth of passive-state oxidation film and the dissolution mechanism were examined on the basis of experimental results. In addition, a study concerning the inhomogeneous dissolution of an iron anode during the transition from the active domain of iron to the passive domain has been carried out by Gabrielli et al. [83].

As far as cadmium is concerned, the electrochemical oxidation-reduction reaction mechanisms of $\text{Cd}/\text{Cd}(\text{OH})_2$ electrodes in concentrated alkali solution was studied by Okinaka [84]. Also, Armstrong et al. [85] investigated, among other things, the relationship between the formation of oxidation film and active dissolution. /219

The dissolution and precipitation reaction mechanisms of zinc, the important material in batteries, have been studied in alkali solutions by Hull et al. [86] and by Yamashita et al. [87]. It is noted that Yamashita et al. used the procedure submitted by Bockris et al. [14] for the analysis of the reaction mechanisms.

As far as the dissolution reactions of binary alloys are concerned, the dissolution of alloys containing noble metals such as an Au-Cu alloy has been studied [88], apart from the study by Miller et al., mentioned earlier.

3.4. Research on Organic Electrode Reactions

As we stated in Section 2.4, Bard et al. have submitted theoretical equations based on the simulation method. Recently, they published many studies regarding the applications of these equations to organic electrode reactions. When anthracene derivatives are oxidized and reduced in nonaqueous solvents, anion and cation radicals are produced, and the collision of these radicals is sometimes luminescent. This phenomenon is called electrochemical luminescence. Bard et al. produced anion and cation radicals at the disk electrode and the ring electrode of an RRDE and observed electrochemical luminescence [89]. They went further by examining the luminescent mechanism by means of the simulation method [90], and even obtained efficiency values in the cases of 9,10-diphenylanthracene, rubrene and the pyrenes [91].

RRDE's have also been used in research on the electrohydrodimerization ($2R + 2e^- + 2H^+ \rightarrow R_2H_2$) [92, 93]. In other words, they studied the reduction reactions of dimethylfumarate, cinnamic acid nitrile, and fumaronitrile at a platinum electrode in DMF solvent with TBAI as supporting salt, using an RRDE, as well as cyclic voltametry and coulombmetry [92]. They submitted the mechanism for the process in which these compounds become anion radicals

through single-electron reduction and are then dimerized, and determined that their dimerization rate constants were 110 (dimethylfumarate), 880 (cinnamic acid nitrile) and 7×10^5 (fluoronitrile) $\ell/\text{mole}\cdot\text{sec}$. In addition, they examined the reduction reaction mechanism of dimethylfumarate in the presence of cinnamic acid nitrile or acrylonitrile in detail [93].

The quinone imine hydrolysis rates of 3-methyl-p-aminophenol in 0.01 M sulfuric acid and p-aminophenol in 0.2 M sulfuric acid were measured by Adams et al. [94] using a ring-disk electrode of carbon paste electrodes. The rate constants of $0.58 \pm 0.03 \text{ sec}^{-1}$ and $0.52 \pm 0.006 \text{ sec}^{-1}$ were obtained respectively.

The reduction reaction mechanism of nitrobenzene in alkali solution was studied by means of a gold RRDE [5], and it was found that phenylhydroxylamine and nitrobenzene anion radicals were formed as intermediate products of reduction. Fig. 9 shows the i_D - i_R relationship in NaOH.

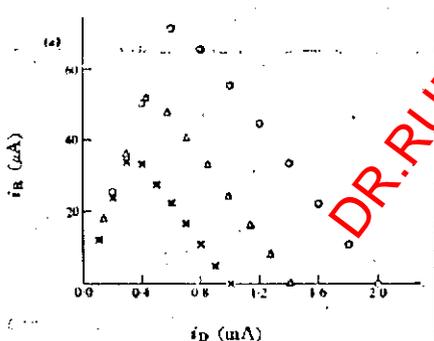


Fig. 9. Ring current as a function of disk current during nitrobenzene reduction. 3 M NaOH, E_R : -0.565 V
x: 5, Δ : 10, o: 20 (Hz/sec)

Oxidation reactions in non-aqueous solvents such as aniline, α -naphthylamine and α -aminoanthracene have also been studied [95]. It was found that, particularly in aniline, the oxidation reaction progressed via benzidine and p-aminophenylamine, which are dimerides.

Other studies include subjects such as the reduction reaction of p-nitroaniline [96], the electrolytic oxidation of N,N-dimethylaniline [97], the electrolytic reduction reactions of benzophenone and benzaldehyde [98, 99] and the oxidation reaction of anthracene and 9,10-diphenylanthracene [100].

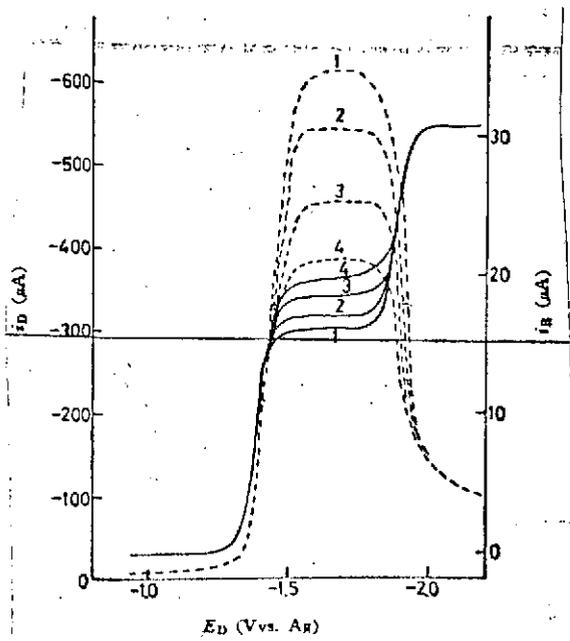


Fig. 10. Formation of anion radical and protonation by proton donor in single-electron reduction of benzalaniline.

1000 rpm, E_R : -0.20 V

Methyl alcohol concentration:

1. 0.0 M/l;
2. 1.0×10^{-2} M/l;
3. 1.5×10^{-2} M/l;
4. 2.0×10^{-2} M/l.

detection current shows a decrease at the ring electrode. Fujinaga et al. also produced an RRDE recently and analyzed the oxidation reaction mechanisms of anthracene derivatives [103].

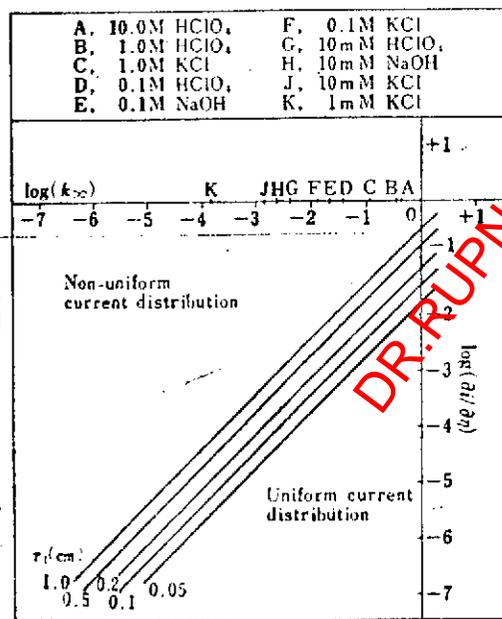
Johnson et al. [104] studied the products of the electrolytic reduction of benzyl in strong alkali solution using an amalgam ring-disk electrode. Cis and trans forms of stilbene-thiolate were detected as products, and their ketolization rate constants were determined by the digital simulation method.

As part of the research on the physical properties of liquid crystal substances, the writers dissolved p-methoxybenzylidene-p-n-butylaniline (MBBA), a representative compound of the nematic liquid crystals, and benzalaniline, which comprises its skeletal structure in nonaqueous solvents, and conducted various electrochemical measurements of both compounds [101, 102]. Fig. 10 shows the formation of an anion radical by the single-electron reduction of benzalaniline in DMF, as detected in the form of an increase in the oxidation current at the ring electrode. This graph also shows that the anion radical undergoes protonation when a proton donor is added, so that the radial

3.5. Examination of Electric Current Distribution Uniformity on Disk Electrode

As is apparent from the general theory of Yoshizawa et al. [1], the electric current distribution on the disk electrode, as solved by Levich, is uniform. This condition was also a prerequisite for the derivation of the theoretical equations concerning the ring-disk electrode. However, Newman [105, 106], who undertook an intensive examination of the current distribution uniformity on the disk electrode, demonstrated that uniformity in the radial direction was not valid when taking the effect of the electric field into consideration. The conditions which are necessary for the uniformity of current distribution in considering the effects of the charge shift resistance and the polarization of concentration have been presented. Fig. 11 shows

these conditions, organized by Albery et al. into a practical form for experimental use [5].



One method for the determination of whether or not the current distribution is uniform is the copper plating of the disk and the measurement of its thickness [107]. But Albery et al. used a ring-disk electrode and examined the deviation from the theoretical value of the rate of capture [5, 108]. In other words, when they experimented with a thin gap-thin ring electrode, it was found that the current density was greater on the outer perimeter of the disk electrode than in the center.

Fig. 11. Conditions for uniformity of current distribution. A-K: values for representative supporting electrolytes, in 25°C aqueous solution.

More recently, a study of the current distribution has been conducted by Newman et al. [109], using a ring-disk electrode or a sectioned disk electrode. Among other things, this involved dividing the research into two parts, namely one with the limit current and another with currents below that level. Other intensive efforts in this area include a study of the potential distribution by Gabrielli et al. [110], an investigation using the digital simulation method by Prater et al. [111], and an argument by Miller et al. [112], which also incorporates other methods.

Needless to say, experiments with rotating electrodes are usually conducted for the state of laminar flow. But, if the flow on the electrode surface changes from laminar to turbulent flow, there should be a wide deviation of such values as the rate of capture from the theoretical values. There are also a few studies which discuss the relationship between the starting point of the turbulent flow and the Reynolds number or Prandtl number by examining the number of rotations which diminish the rate of capture for electrodes of various sizes [113, 114].

3.6. Study of Photoelectrode Reactions

The writers have been studying the behaviors of semiconductor electrodes under the irradiation of light, and have adopted the rotating disk-ring method as one of the means of analyzing reaction mechanisms. In other words, by constructing an electrode system consisting of a disk electrode of a single-crystal semiconductor such as TiO_2 , ZnO or CdS and a ring electrode of gold, platinum or amalgam, and by conducting the measurement in the manner shown in Fig. 12, characteristic reactions which occur on semiconductor electrodes specifically under the irradiation of light are being pursued [115-118].

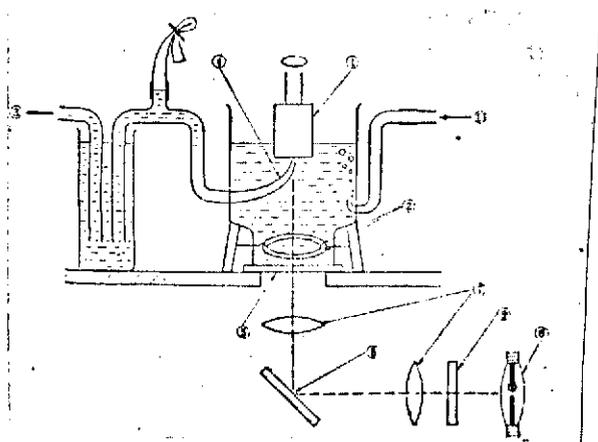


Fig. 12. Electrolytic cell and condition of light irradiation: 1. ring-disk electrode; Pt electrode pair; 3. to saturated calomel electrode; 4. rugin capillary; 5. quartz plate; 6. light source; 8. quartz lenses; 8. quartz mirror; 9. filters; 10. nitrogen gas.

adopted the rotating ring-disk electrode system for the study of photodissociation reaction mechanisms. With this system, the disk electrode section is replaced with quartz, and light is irradiated from the interior of the cylinder of the rotating electrode through the quartz disk. The system is designed to detect the products of photochemical reactions taking place on the quartz plate by electrochemical means at the ring disk, and it was applied to the photodissociation reactions of such substances as

benzophenone. The writers also constructed a similar device recently [120], and are currently engaged in the comparative study of the photoreduction reaction mechanism and the electrochemical reduction reaction mechanism of $K_3Fe(C_2O_4)_3$.

3.7. Others

In this general discussion, we did not include a separate section for experimental devices and so on, but an actual experiment would have to involve a fairly complex procedure, such as the construction of a ring-disk electrode. Research concerning experimentation methods, such as construction methods of simple electrodes [121, 122] and various control systems for the number of rotations [123, 124], is also being advanced.

4. Conclusion

The rotating ring-disk electrode system is one of the most suitable methods for analyzing the complex electrode reaction mechanisms which take place on solid electrode surfaces. In this report, the writers have attempted to list as many dissertations as they could collect, but, as is apparent from the sections above, the method is still only used by a limited number of researchers. This is probably because of the complexity of the electrode, as well as the cumbersome appearance of the operational procedure, but it would seem likely that its use will spread hereafter to such applications as the analyses of organic electrode reactions.

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