특별 강연

THE POSSIBILITY OF MEASUREMENT OF FLUCTUATING CONCENTRATION ON A ROTATING DISK*

(I)

SUNG MOO LEE**

ABSTRACT

In the measurement of fluctuating concentration and velocity of turbulence in the concentration polarized system, electrolysis on the fully developed rotating disk electrode, as a cathode, is not able to determine accurately those values, as the width of the disk electrode is too larger compared to the scales of turbulence to provide an uniformly linear accessibility.

In order to obtain the uniformly or linearly accessible surface and determine the correlation coefficient of turbulence, the typical RING ELECTRODE is considered. Different thin platinum wires are arranged with different distances in the direction of the streamlines on the disk and the other areas of the surface are artificially insulated.

Under the necessary assumptions, herein, a theoretical analysis is consistant with the experimental data obtained by other investigators. The edge effect in the arrangement of the uncoated sections and at the edge of the disk is adjustable with the typical geometry for being compensated with turbulent properties but it must be unavoidably negligible for the theoretical analysis on the rotating disk. Gas evolution, non-uniform current density and overpotentials are also controllable, more or less, with the typical structure of the system. Further investigations of the flow near corner, corrosion, and contamination of the ring electrode surface should be studied.

I. INTRODUCTION

It was already reported that the Hot-Wire Anemometer was much less suitable for measurement of turbulence in liquid (4) and the measurement of concentration in an electrolyte by means of the typical Hot-Film Anemometer gave unfortunately to errorenous results. (6) Furthermore, the recent work have developed that the concentration in turbulent motion was determined by the mass flux on the vicinity of the surface of the rotating disk, as a cathode, (2, 6, 12) under the assumption of uniform accessibility on the disk surface.

Unfortunately, the length of the disk may be so larger than the lengths of scales in turbulence that the decay of large scale eddies to smaller eddies progressively differ from point to point near the viscous sublayer. In the case of non-uniform accessibility, the deviation of the chemical and concentration overpotential and time variance will play seriously an important role for the measurements of the mass flux or current density on the surface of the disk. Therefore, the alternative geometry may be considered; in the presence of excess of an indifferent electrolyte, the ring electrode as a cathode on the surface of the rotating disk, on which thin electrodes are arranged on the surface with different distances in the direction of flow and the opposite surface

* 이 원고는 1965년도 본학회 임시총회에서 특별강연한 것이다.

** 연세대학교 이공대학 화학공학과

of the disk is insulated (coated) electrically with a resinous material.

When the electrolyte passes through the surface of the disk rotated, in the outward direction, the concentration boundary layer thickness is so smaller than the velocity boundary layer thickness that the Gradual Damping Hypothesis of Turbulnce of L. D. Landau and V. G. Levich is adopted well enough to measure the concentration profile on the surface of the ring electrodes. (3, 5, 6, 8, 9, 12) Since the constant concentration overpotential on the surface of the ring cathode can be maintained, under the assumption of uniform accessibility on the surface, in the presence of excess of a foreign electrolyte, the limiting current density to the surface is then proportional to the mass flux of A ions to the surface of the electrodes.

$$A^{z+}+Ze^{-}=A \tag{1}$$

$$I_{LIM}=Z\cdot F\cdot N_{A^{z+}} \tag{2}$$

$$N_{A^{z+}}=D_{A^{z+}}\left(\frac{\partial C_A}{\partial y}\right)_{y=0}=K_{A^{z+}}(C_{BA}-C_{0A}) \tag{3}$$

Hence, the limiting current density may be defined as,

$$I_{LIM}=Z\cdot F\cdot K_{A^{z+}}(C_{BA}-C_{0A}) \tag{4}$$

$$=Z\cdot F\cdot K_{A^{z+}}C_{BA} \tag{5}$$

Since the electrochemical reaction is very rapid on the surface, the concentration on the surface of the electrodes, C_{0A}, is of course zero (plating out). On the other hand, the rate of reaction on the artificially insulated portions is also zero ($N_{A^{z+}}=0$) and then no current flow exist on these portions. There are apparently two different regions, diffusion and chemical process region (2), on a ring electrode from the experiment of R. R. Dogonadge and V. G. Levich and then the deviation of the current density will resulted on the surface of the electrode by edge effect and gas evolution. Therefore, the changes of the concentration overpotential, the mass flux, and other complex effects bring an errorenous result in volt-ampere characteristic.

It is suggested that the gradually smaller widths of the ring electrodes and progressively smaller distances between the electrodes in the direction of flow for change of the geometric structure on the disk will be compensated, more or less, with the previous effects including the edge effect but it is not always certain. Furthermore, gas evolution will hinder the migration and the molecular diffusion of A ions to the vicinity of the surface to decrease the limiting current. (6) In order to avoid the effect, the insulated surfaces will be able to replaced a resinous material used with a very impure metal to react with the gas, (2) or a reducing or an oxidizing agent will be used in the electrolyte, and according to Levich, the protecting shield can be also used to compensate with the effect of gas evolution. (2) Such predictions, however, are uncertain because these are not able to classify precisely, since the proposed geometry of the electrodes on the disk is much complex for elimination of such undesirable effects.

According to the result of the theoretical analysis, the data of diffusion coefficient, Prantdl criterion, angular velocity, and radius-current density relationship were certainly approached to many experimental data investigated, at high Schmidt number. Analytical calculation and measurement of turbulence are followed by Reiss' method. (8, 9)

The investigation of electrical networks with the ring electrode assembly is considered to be out of this area. In turbulent motion, $Re>10^4$ and $y^+>5$ must be held for the desired experimentation.

II. THEORETICAL ANALYSIS AND STRUCTURE OF THE ROTATING DISK.

In the measurement of the current density, the mass transfer to the surface of the electrodes can be related to the fluctuating velocity on the vicinity of the surface of the rotating disk if the following assumptions are valid:

(1). The measurement of turbulence is excuted at high Schmidt number, $Re>10^4$, and isothermal condition.

(2). The fluid properties such as ρ, μ, ν, and D on the surface are constant.

(3). The scale of turbulence is relatively large with respect to the width of the electrodes. When the surface of every ring electrode along the disk in the direction of the streamline can be maintained a linear accessibility, this assumption is valid.

(4). No electrode reaction takes place except the dissolution and plating out of the active ions.

(5). Bounyancy, radiation, frictional heat are neglected.

(6). The edge effect and gas evolution are negligibly small.

(7). The assumptions of incompressible fluid and no slip or no thermal diffusion on the vicinity of the surface are available.

(8). Only the gradual damping theory of turbulence can be applied to the typical system.

Let us consider the continuity, momentum, and mass transfer equations in vector notation. (1, 6, 8, 10)

(a). Navier-Stokes equation for momentum balance;

$$\rho \frac{D\vec{v_i}}{D\theta} = -\nabla P + \mu \nabla^2 \vec{v_i} + \vec{\rho g_i} \tag{6}$$

(b). Mass transfer equation;

$$\frac{DC_i}{D\theta} = D_i \nabla^2 C_i + R_i \tag{7}$$

(c). The continuity equation;

$$\frac{D\rho}{D\theta} = -\rho(\triangle \cdot \vec{v_i}) \tag{8}$$

In order that a fluid may be continuously supplied to the disk surface, an uniform axial flow must be maintained. The mass transfer equation in cylinderical coordinate can be expanded as follows;

$$\frac{\partial C_i}{\partial \theta} + u\frac{\partial C_i}{\partial r} + \frac{v}{r}\frac{\partial C_i}{\partial \phi} + w\frac{\partial C_i}{\partial y} = D_i\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C_i}{\partial r}\right) + \frac{1}{r^2}\frac{\partial^2 C_i}{\partial \phi^2} + \frac{\partial^2 C_i}{\partial y^2}\right]$$

for symmetrical axial flow,

$$\frac{\partial C_i}{\partial \phi} = 0 \tag{9}$$

Since the thickness of the diffusion boundary layer is about one tenth of the Prandtl layer (viscous sublayer), the boundary layer theory can be applied to eliminate the minor terms from the previous equation. Considering the streamlines on the vicinity of the surface of the ring electrodes, the molecular diffusion to the surface of the electrodes in the axial direction is naturally predominant over that in the outward direction along the disk. Hence,

$$\frac{\partial C_A}{\partial \theta} + u\frac{\partial C_A}{\partial r} = D_A\frac{\partial^2 C_A}{\partial y^2} \tag{10}$$

Therefore, in the presence of the coated portions on the rotating disk, the concentration distribution is a function of the radius of the ring electrode and the distance from the surface in the axial direction.

For the time-smoothed equation of turbulence,

$$\frac{\partial \vec{C_A}}{\partial \theta} + \triangle \cdot (\overline{\vec{v_A} C_A} + \overline{\vec{v_A}' C_A'}) = D_A \nabla^2 \vec{C_A} \tag{11}$$

$$C_{OA} = \vec{C}_{BA} + C_A' = 0 \tag{12}$$

at the surface of the electrodes.

By the theory of Landau and Levich in the viscous sublayer,

$$\frac{d\bar{u}}{dy} = \bar{\Phi}_r \tag{13}$$

$$\bar{u} = \bar{\Phi}_r y \tag{14}$$

$$u = \bar{u} + u' \tag{15}$$

$$\Phi_r = \bar{\Phi}_r + \Phi_r' \tag{16}$$

$$\bar{\Phi}_r = v^{*2}/\nu \tag{17}$$

and similarly, for the fluctuating components,

$$u_r' = \Phi_r' y \tag{18}$$

$$w' = \Phi_y' y \tag{19}$$

$$v' = 0 \tag{20}$$

$$\Phi_r = \{(\bar{\Phi}_r + \Phi_r')^2 + (r\Phi'_y)^2\}^{1/2} \tag{21}$$

substituting the equations (14) and (18) into the equation (15),

$$u = \Phi_r y \tag{22}$$

The equation (10), therefore, can be rewitten as

Boundary condition are;

i). $C_A = C_{BA}$ at $r_i = 0$, and $y > 0$

ii). $C_A = C_{0A} = 0$ at $R_i > r_i > 0$, and $y = 0$

iii). $C_A = C_{BA}$ at $R_i + \Delta R_i > r_i > R_i$ and $y \to \infty$

For the first approximation, the concentration profile on the vicinity of the surface of the electrode,

$$\Phi_r y \frac{\partial C_A}{\partial r} = D_A \frac{\partial^2 C_A}{\partial y^2} \tag{23}$$

$$\frac{C_A - C_{0A}}{C_{BA} - C_{0A}} = \frac{3}{\Gamma\left(\frac{1}{3}\right)} \int_o^{\mu} e^{-\mu^3} d\mu \tag{24}$$

$$\mu = \frac{y}{\left(1 - \frac{R_i^3}{r_i^3}\right)^{1/3}} \left(\frac{\omega}{\nu}\right)^{1/2} \left(\frac{\nu \Phi_r}{6 D_A}\right)^{1/3} \tag{25}$$

$$= \frac{y}{r^{1/3}} \left(\frac{\omega}{\nu}\right)^{1/2} \left(\frac{\nu \Phi_r}{6 D_A}\right)^{1/3} \tag{26}$$

Hereon, the assumption that the fluctuation in circumferential direction is smaller than the radial fluctuation, because of centrifugal force and symmetrical vorticity, becomes apparently true in addition to that previousaly described. Considering the over-all concentration profile with the time variance,

$$\int_{Ri}^{Ri+\Delta Ri} dr \int_0^{\infty} \frac{\partial C_A}{\partial \theta} dy + \int_{Ri}^{Ri+\Delta Ri} dr \int_0^{\infty} \Phi_r y \frac{\partial C_A}{\partial r} dy = \int_{Ri}^{Ri+\Delta Ri} dr \int_0^{\infty} D_A \frac{\partial^2 C_A}{\partial y^2} dy \tag{27}$$

$$\frac{\partial}{\partial \theta} \int_{Ri}^{Ri+\Delta Ri} dr \int_0^{\infty} C_A dy + \int_{Ri}^{Ri+\Delta Ri} d\left[\int_0^{\infty} \Phi_r y C_A dy\right] = \Delta R_i \int_0^{\infty} D_A d\left[\frac{\partial C_A}{\partial y}\right] \tag{28}$$

$$\frac{1}{\Delta R_i} \frac{\partial}{\partial \theta} \int_{Ri}^{Ri+\Delta Ri} dr \int_0^{\infty} \left(\frac{C_A - C_{0A}}{C_{BA} - C_{0A}}\right) dy + \frac{1}{\Delta R_i} \int_{Ri}^{Ri+\Delta Ri} d\left[\int_0^{\infty} \left(\frac{C_A - C_{0A}}{C_{BA} - C_{0A}}\right) \Phi_r y dy\right]$$

$$= \int_0^{\infty} D_A d\left\{\frac{\partial}{\partial y}\left(\frac{C_A - C_{0A}}{C_{BA} - C_{0A}}\right)\right\} = \frac{N_{A^{2+}}}{C_{BA} - C_{0A}} \tag{29}$$

$$6^{1/3} \phi \left(\frac{\omega}{\nu}\right)^{-1/3} \left(\frac{D_A}{\nu}\right)^{1/3} R_i^{1/3} \frac{\partial \Phi_r^{-1/4}}{\partial \theta} + \frac{6^{1/3}}{3} \left[\frac{1}{\Gamma\left(\frac{1}{3}\right)}\right] \left(\frac{\omega}{\nu}\right)^{-1} \left(\frac{D_A}{\nu}\right)^{2/3} R_i^{-1/3} \Phi_r^{1/3}$$

$$= K_{A,\,LOC} \tag{30}$$

where,

$$\phi = \int_0^{\infty} \left(\frac{C_A - C_{0A}}{C_{BA} - C_{0A}}\right) d\mu \tag{31}$$

Since the term of Φ_r' only in the equation (21) is predominantly a function of time,

$$\frac{\partial \Phi_r^{-1/3}}{\partial \theta} = -\frac{1}{3} \Phi_r^{-4/3} \cdot \frac{\partial \Phi_r}{\partial \theta} = -\frac{1}{3} \Phi_r^{-4/3} \frac{\partial \Phi_r'}{\partial \theta} \tag{32}$$

$$= -\frac{1}{3} \bar{\Phi}_r^{-1/3} \frac{\partial}{\partial \theta}\left(\frac{\Phi_r'}{\bar{\Phi}_r}\right) \tag{33}$$

and expanding $\Phi_r^{1/3}$ in the equation (30) by Tayler's series for approximate calculation,

$$\Phi_r^{1/3} = \bar{\Phi}_r^{1/3} + \frac{1}{3} \bar{\Phi}_r^{-1/3} \Phi_r' + \cdots\cdots \tag{34}$$

hence,

$$K_{A,\,LOC}=\frac{2}{\Gamma\left(\frac{1}{3}\right)6^{1/3}}\left(\frac{D_A}{R_i}\right)^{1/3}\left(\frac{D_A}{\nu}\right)^{1/3}\left(\frac{\omega}{\nu}\right)^{-1}\left(\frac{\bar{\Phi}_r}{\nu}\right)^{1/3}+\frac{2}{3}\left[\frac{1}{\Gamma\left(\frac{1}{3}\right)6^{1/3}}\right]\left(\frac{D_A}{R_i}\right)^{1/3}\left(\frac{D_A}{\nu}\right)^{1/3}\times$$
$$\left(\frac{\omega}{\nu}\right)^{-1}\left(\frac{\bar{\Phi}_r}{\nu}\right)\left(\frac{\Phi_r'}{\bar{\Phi}_r}\right)-\frac{2}{6^{2/3}}\left(\frac{\omega}{\nu}\right)^{-1/2}\left(\frac{D_A}{\nu}\right)^{1/3}\left(\frac{R_i}{\bar{\Phi}_r}\right)^{1/3}\phi\frac{\partial}{\partial\theta}\left(\frac{\Phi_r'}{\bar{\Phi}_r}\right) \tag{35}$$

If a local mass transfer coefficient and a local current density will be defined in terms of an average and fluctuating components as follow (10);

$$K_{A,\,LOC}=\overline{K}_A+k'_{A,\,LOC} \tag{36}$$

$$I_{A,\,LIM}=\overline{I}_A+i'_{A,\,LOC} \tag{37}$$

When those equations (35) and (36) are compared to regard as the selection of time variables,

$$\overline{K}_A=\frac{2}{\Gamma\left(\frac{1}{3}\right)6^{1/3}}\left(\frac{D_A}{R_i}\right)^{1/3}\left(\frac{D_A}{\nu}\right)^{1/3}\left(\frac{\omega}{\nu}\right)^{-1}\left(\frac{\bar{\Phi}}{\nu}\right)^{1/3} \tag{38}$$

$$k'_{A,\,LOC}=\frac{2}{3\Gamma(1/3)6^{1/3}}\left(\frac{D_A}{R_i}\right)^{1/3}\left(\frac{D_A}{\nu}\right)^{1/3}\left(\frac{\omega}{\nu}\right)^{-1}\left(\frac{\bar{\Phi}_r}{\nu}\right)^{1/3}\left(\frac{\Phi_r'}{\bar{\Phi}_r}\right)$$
$$-\frac{2}{6^{2/3}}\left(\frac{\omega}{\nu}\right)^{-1/2}\left(\frac{D_A}{\nu}\right)^{1/3}\left(\frac{R_i}{\bar{\Phi}_r}\right)^{1/3}\phi\frac{\partial}{\partial\theta}\left(\frac{\Phi_r'}{\bar{\Phi}_r}\right) \tag{39}$$

hence,

$$k'_{A,\,LOC}=\frac{1}{3}\overline{K}_A\left(\frac{\Phi_r'}{\bar{\Phi}_r}\right)-\frac{2}{6^{2/3}}\left(\frac{\omega}{\nu}\right)^{-1/2}\left(\frac{D_A}{\nu}\right)^{1/3}\left(\frac{R_i}{\bar{\Phi}_r}\right)^{\frac{1}{3}}\phi\frac{\partial}{\partial\theta}\left(\frac{\Phi_r'}{\bar{\Phi}_r}\right) \tag{40}$$

$$3(k'_{A,\,LOC}/\overline{K}_A)=\frac{\Phi_r'}{\bar{\Phi}_r}-\left(\frac{6^{1/3}\phi}{\overline{K}_A}\right)\left(\frac{\omega}{\nu}\right)^{-1/2}\left(\frac{D_A}{\nu}\right)^{1/3}\left(\frac{R_i}{\bar{\Phi}_r}\right)^{1/3}\frac{\partial}{\partial\theta}\left(\frac{\Phi_r'}{\bar{\Phi}_r}\right) \tag{41}$$

$$3\frac{k'_{A,\,LOC}}{\overline{K}_A}=\frac{\Phi_r'}{\bar{\Phi}_r}-\tau\cdot\frac{d}{d\theta}\left(\frac{\Phi_r'}{\bar{\Phi}_r}\right) \tag{42}$$

where τ is defined as time constant,

$$\tau=\left(\frac{6^{1/3}\phi}{\overline{K}_A}\right)\left(\frac{\omega}{\nu}\right)^{-1/2}\left(\frac{D_A}{\nu}\right)^{1/3}\left(\frac{R_i}{\bar{\Phi}_r}\right)^{1/3} \tag{43}$$

The local average current density, $\overline{I_A}$, is defined as, (6)

$$\overline{I}_A=\frac{2\pi\int_{Ri}^{Ri+\Delta Ri}I_{A,\,LIM}r\,dr}{S_i} \tag{44}$$

where,

$$S_i=\pi[(R_i+\triangle R_i)^2-R_i^2] \tag{45}$$

therefore,

$$\overline{I}_{A,\,LIM}=\frac{3}{\Gamma\left(\frac{1}{3}\right)}\frac{\left(\frac{\omega}{\nu}\right)^{1/3}\left(\frac{\nu\bar{\Phi}_r}{6D_A}\right)^{1/3}}{\left(1-\frac{R_i^3}{r^3}\right)^{1/3}}\overline{C}_{BA}Z\cdot FD_A \tag{46}$$

$$=\frac{2\pi ZFD_A\overline{C}_{BA}}{\pi[(R_i+\Delta R_i)^2-R_i^2]}\cdot\frac{3\left(\frac{\omega}{\nu}\right)^{1/2}\left(\frac{\nu\bar{\Phi}_r}{6D_A}\right)^{1/3}}{\Gamma\left(\frac{1}{3}\right)}\int_{Ri}^{Ri+\Delta Ri}\frac{r^2dr}{(r^3-R_i^3)^{1/3}} \tag{47}$$

$$=\frac{6D_AZF\left(\frac{\omega}{\nu}\right)^{1/2}\left(\frac{\nu\bar{\Phi}_r}{6D_A}\right)^{1/3}}{\Gamma\left(\frac{1}{3}\right)[(R_i+\Delta R_i)^2-R_i^2]}\cdot\overline{C}_{BA}\left\{\frac{1}{2}(r^3-R_i^3)^{2/3}\right\}_{Ri}^{Ri+\Delta Ri} \tag{48}$$

$$=\frac{3\left(\frac{\omega}{\nu}\right)^{1/2}\left(\frac{\nu\bar{\Phi}_r}{6D_A}\right)^{1/3}\overline{C}_{BA}}{2\,\Gamma\left(\frac{1}{3}\right)R_i\Delta R_i}\cdot ZFD_A[3\,R_i^2\Delta R_i]^{2/3} \tag{49}$$

$$=\frac{9\,ZFD_A\left(\frac{\omega}{\nu}\right)^{1/2}\left(\frac{\nu\bar{\phi}_r}{6D_A}\right)^{1/3}}{2\,\Gamma\left(\frac{1}{3}\right)\quad 3^{1/3}}\cdot R_i^{1/3}\Delta R_i^{-1/3}\overline{C}_{BA} \tag{50}$$

$$=\frac{9}{2\cdot 3^{1/3}\Gamma(1/3)}\cdot\left(\frac{\omega}{\nu}\right)^{1/2}\left(\frac{\nu\bar{\phi}_r}{6D_A}\right)^{1/3}\left(\frac{R_i}{\Delta R_i}\right)^{1/3}ZFD_A\overline{C}_{BA} \tag{51}$$

$$=\frac{9}{2(3^{1/3})6^{1/3}\Gamma\left(\frac{1}{3}\right)}\cdot\left(\frac{\omega}{\nu}\right)^{1/2}\left(\frac{R_i}{\Delta R_i}\right)^{1/3}\left(\frac{D_A}{\nu}\right)^{1/3}(\bar{\phi}_r D_A\nu^2)^{1/3}ZF\overline{C}_{BA} \tag{52}$$

$$=\frac{9}{2^2 3^{1/3}}ZF\omega^2R_i^{2/3}(\Delta R_i)^{-1/3}\overline{K}_A\frac{\omega}{\nu}^{1/2}\overline{C}_{BA} \tag{53}$$

The local fluctuating current density, $i'_{A,\,LOC}$ is defined as,

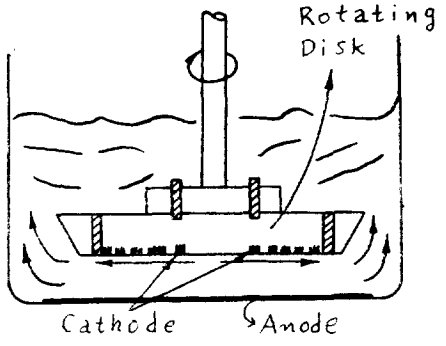

Fig. Ⅰ. Side View of the Rotating Disk

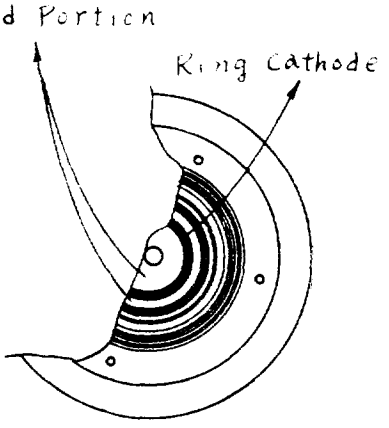

Fig. Ⅱ. The Plane View of the Rotating Disk

$$i'_{A,\,LOC}=k'_{A,\,LOC}\,\nu\cdot ZFC'_{BA} \tag{54}$$

Into a container of about 5 to 10 cm diameter, add a sufficient amount of the electrolyte solution containing 0.01 molal A ion with excess of an indifferent electrolyte of a common anion. 3 to 5 cm disk electrode is made of silver and the upper surface and the axis of the rotating disk are coated with a resinous material. The opposite surface of the disk plate (Fig. 1) roles as a cathode. Relatively wide portion around the center of the disk is coated by the same material and the other vacant areas between electrodes are also coated as same manner. These are, however, better to take smaller distances close to the opposite edge of the disk in the outward direction.

The widths of the test ring electrodes are also gradually smaller along the surface of the disk in the direction of the flow as in Fig. 2. In the experiment, Reynolds Number must be beyond 10^4.

According to Reiss (10), the time average term of the local mass transfer coefficient, $\overline{K}_A$, is similar to the reciprocal of the electrical resistance in the concentration boundary layer and the fluctuating of mass transfer coefficient, $k'_{A,\,LOC}$, is also similar to the difference between the electrical capacitance and the time constant of turbulent eddies. Since the fluctuation in current reflects well enough to the velocity fluctuation in the viscous layer, the root-mean square of $k'_{A,\,LOC}$ can be measured with Random Signal Voltmeter at different values of Reynolds number. (10) The spectra of longitudinal turbulent intensity at several distances from the center of the disk is obtained by use of Harmonic Wave Analyzer for $Re>10^4$. (11) The fluctuation of velocity $F_\mu(n)$ was defined as,

$$F_\mu(n)=\frac{d(\overline{u'^2}_n)}{\overline{u'^2}dn} \tag{55}$$

where $d(\overline{u'^2})$ is the contribution to $\overline{u'^2}$ from frquencies $n\text{-}dn/2$ and dn of the effective band width of the measuring analyzer. (11)

III. DISCUSSION

If the Hot-Film anemometer will be used in the measurement of concentration in turbulent flow it must take some limitations or it may be not able to obtain so relatively accurate data in the experiment that it is substantially impractical or useless for the measurement (2, 4, 6, 7).

Most of all investigators, in recent works, have worked on the turbulent transport on the fully developed rotating disk surface and the measurements of the concentration distribution as a function of distance from the surface in the direction parallel to the axis of the disk. If the one side of the surface of the rotating disk would be employed as a cathode, the surface should be not uniformly accessible to the turbulent motion of the fluid, because the length of the disk is larger than the lengths of scales in turbulence and then the decay of large scale eddies to eddies progressively smaller in scale differs in point to point near the viscous sublayer. At the same time, concentration overpotential is deviated on the surface of the electrodes and it is, therefore, difficult to measure the constant current density without linear accessibility on the surface. Furthermore, it is impossible to classify the lengths between two points in order to measure the correlation coefficient R.

In the presence of a foreign electrolyte, the electrical conductivity of the solution increases significantly and thereby decreases the ohmic potential drop. Particularly, the addition of excess of the foreign electrolyte (negligible the effect of ratio of the concentration of ions migrated to that of the foreign electrolyte) is able to give the solution to be electrically neutrial during the electrolysis and compensate the undesired ohmic potential drop with the additional ohmic potential resulted by the migration of the foreign electrolyte. The limiting current density may be defined as,

for the active A ions;

$$-I_{A,\,LIM}=-Z^{+}D_{A}F\frac{\partial C_{A}}{\partial y}-\gamma_{A}Z^{+2}F\left(\frac{\partial \Psi}{\partial y}\right)C_{A} \tag{56}$$

for a constant potential;

$$\frac{\partial \Psi_{j}}{\partial y}=0 \tag{57}$$

for the inert anions;

$$-I_{j}=-Z^{-}D_{j}F\frac{\partial C_{j}}{\partial y}-\gamma_{j}Z^{-2}F\left(\frac{\partial \Psi}{\partial y}\right)C_{j}=0 \tag{58}$$

As the result, the rate of change of the concentration in the solution changes linearly with the distance from the surface of the disk in the direction parallel to the axis of the disk. Nevertheless, the fluctuation of the current will occur, when the surfaces of the electrodes are consquently not uniformly accessible.

Considering the mass transport to the vicinity of the surface of the disk electrodes, the mechanism of convective and molecular diffusion can be examined by two hypotheses of turbulence damping; (1) the Prandtl-Taylor hypothesis of complete cessation of turbulence in the viscous sublayer (2) the hypothesis of L. D. Landau and V. G. Levich on the gradual damping of turbulence. (3, 6, 12) In the case of the Prandtl-Taylor model at high Schmidt number, as a matter of fact, the thickness of the sublayer becomes too larger to give a correct velocity distribution, because the fluctuation velocity varies abruptly near the sublayer. Therefore, it will be very reasonable to choose the model of Levich which is four-layered structure in the addition to Von Karmen's. Herein, a different expression for the mass flux to the vicinity of the surface, of course, will result in which depends upon the selection of any one of the models concerning on the turbulence damping.

If the assumptions described previously, however, is valid for measurement, the equation (10) will be analogous to the equaton (28) derived by Reiss (9), and then the results of the equation (10) will be able to

compute with other experimental data obtained by a trial and error. If it is not valid, however, an another investigation should be examined.

According to the equation (51), the average current density at the vicinity of the surface of the electrodes will be proportional to 2/3 power of the diffusion coefficient, -1/3 power of the Schmidt number, 1/2 power of the angular velocity, -1/3 power of the widths of the electrodes, and 1/3 power of the distances between electrodes and the center of the disk. When those results compare with other experimental data, these can be visualized how the geometric properties are affected to the measurement: (1) for the terms of the angular velocity and the Schmidt number (or Prandtl criterion), the numbers of the powers were consistant with that being found by Riddiford and Gregory. (9) Fortunately, -1/3 power of the Schmidt number for laminar flow was well coincided with that from the theory of Landau and Levich. The power on the Schmidt number, however, will be given here that a deviation from the previous result is depended on a different model of the turbulent damping. (2) The power of the diffusion coefficient is also consistant well with that in laminar region at high Reynolds number. (3) 1/3 power of the distances between the electrodes and the center of the disk was approached to the experimental data of M. M. Nikiforova under the supervision of B. N. Kabnov (6) and it was followed that the current density is increases remarkably with the decrease in the widths of the electrodes. From this result, a theoretical prediction was verified that the smaller the width of the electrode, the larger is the working portion of the electrode surface. (2, 6)

Further investigation of the current density on the electrodes can be brought a new geometric structure such as gradually smaller widths of the ring electrodes and lengths between the electrodes along the surface of the disk in the outward direction for improvement of the experimental data.

Imagine a liquid streamline past and the active ions reacted or deposited rapidly on a given cathode($R_i + \triangle R_i > r_i > R_i$). The migration and deposite of A ions take place only on the portion of the ring electrodes, and on other surfaces, the reaction is artificially inhibited. In the upstream of the electrode ($r_i < R_i$), the rate of reaction is zero and the mass flux is also nothing ($N_A{}^{z+}=0$).

If the given ring electrodes will be arranged on the disk surface with different distances between the electrodes, the measurement of real turbulent motion will be possilble from point to point along the surface of the disk, when the surfaces are uniformly or linearly accessible except the coated portions. The widths of the ring electrodes, of course, are different each other.

It is, however, true that the edge effect is influenced to the experimental date on every edge of the electrode. At r_i very close to R_i, the diffusion flux will be noticeably higher than the maximum flux in the absence of the coated section. On the other words, two process regions will exist on each electrode; the diffusion process region at the front edge in the direction of flow and the chemical process region at the opposite edge, although these regions are not evidently distinguished. (2) Near the diffusion region, the diffusion current is much greater than the current corresponding to the rate of the electrode reaction.

On the other hand, the current density drops gradually across the electrode from the diffusion region. By this result, the concentration overpotential on the vicinity of the surface of the disk electrodes will lose not only the linearity for the current density but also constancy of the chemical overpotential. Furthermore, the effect of the concentration polarization is compelled to decrease by the change of chemical and concentration overpotentials. All these combined effects bring the errorenous results in the volt-amperec characteristic curve. In the presence of gas evolution, the change of the chemical overpotential is also remarkably increased and then affected significantly on the polarization curve. (6) Therefore, it is suggested that the edge effect is compensated; when the structure of gradually smaller widths of the ring electrodes and distances between the electrodes in the direction of flow toward the edge of the disk is provided in experiment.

The velocity of the streamline is faster approach to the outside edge of the rotating disk than thak near

the center because of the centrifugal force and then the decay of the turbulent eddies to smaller eddies is gradually increased. In order to maintain the linear accessibility on the electrodes, the time of scales has to be fixed uniform. Since the smaller widths of the electrodes are equivalent to the portions of larger working ability of the electrodes, it means that the diffusion region must be not only decreased to be maintained the accessibility on the surface but also increased the mass flux by turbulence. The magnitude of the error, as far as the effect is concerned, is so lesser order compared to the actual value that it can be negligible in the measurement under the assumptions described.

Gas evolution will hinder the migration and the molecular diffusion of the active ions to the vicinity of the surface to decrease the limiting current density. This effect, however, will inevitably bring other current flow to the anode. In the presence of the foreign electrolyte, as a matter of fact, the potential on the anode was maintained to be equal to zero but in the presence of gas evolution, the chemical overpotential exceeds relatively the magnitude of the concentration overpotential.

If the surfaces of the ring electrodes will be not uniformly accessible from the standpoint of diffusion by gas evolution and other turbulent properties, an another geometry shall be considered that the coated portion near the center of the disk is replaced the inert plastic material such as glyptal with a very impure metal which has a lower chemical overpotential. If the evolved gas will be reacted with the metal on the center portion, such an undesirable effect will be eliminated anyhow. (2, 6) It, however, is not evident. Reduction or oxidation of the evolved gas near the surface of the disk with a reducing or an oxidizing agent is brought up more complex situations, e., i., deviation of the balance of the ionic migration, concentration overpotential, and electrical double layer. According to the theory of electrochemical potential of R. R. Dogonadze and V. G. Levich, a gas protector as an anode on the center portion of the disk was used to eliminate the effect of gas evolution on the disk surfaces but it was also uncertain.

IV. CONCLUSION

If the circumferential fluctuation is very smaller than the radial fluctuation and the effective lengths of electrodes, in the addition to the assumptions described previously, the following conclusions can be stated;

(1). The average current density at the vicinity of the surfaces of the electrodes is proportional to -1/3 power of Schmidt number, 1/2 power of the angular velocity, 2/3 power of the diffusion coefficient, -1/3 power of the widths of the electrodes, and 1/3 power of the distances between electrodes and the center of the disk. When such assumptions are not valid, otherwise, another investigation must be predicted.

(2). It is suggested that the edge effect can be compensated somehow with the proposed ring electode as in the figures. Practically, the edge effect must be negligible in the actual measurement.

(3). In order to measure the concentration and the velocity in turbulence, the proposed RING ELECTRODE on the rotating disk may be practicable.

(4). The four-layered gradual damping theory of Landau-Levich must be applied to the system at $Re > 10^4$ and high Schmidt number.

V. NOMENCLATURE

C_{BA} ; Concentration of A ion in the bulk.

C_{OA} ; Concentration of A ion on the surface of the electrode.

$\overline{C}_{BA}$; Average concentration of A ion in the bulk.

D_A ; Molecular diffusion coefficient.

F ; Faraday constant.

K ; Mass transfer coefficient.

$\overline{K}_A$; Local average mass transfer coefficient.

$k'_{A,LIM}$; Local mass transfer coefficient of fluctuation.

$N_{A^{z+}}$; Mass flux of A ion to the surface of the electrodes.

P ; Pressure.

R_i ; Radial distance between i electrode and the center of the disk.

ΔR_i ; Width of i ring electrode on the disk.

r_i ; Radius of i electrode.

v_i ; velocity of i component.

y ; Distance from the surface of the disk in the direction parallel to the axis of the disk.

y^+ ; Dimensionless characteristic distance of y.

Z ; Number of atomic valance.

g ; Acceleration velocity.

μ ; Viscosity.

ρ ; Density.

ν ; Kimematic viscosity.

ω ; Angular velocity.

γ_A ; Mobility of A ion.

VI. REFERENCES

1. Bird, R.B., Stewart, W.E., & Lightfoot, E.N., Transport Phenomena, John Wiley & Sons, Inc., N.Y., 1962.
2. Dogonadze, R.R., Levich, V.G., & Chizmadzhev, Yu. A., (English Edition) Russ. J. Phys. Chem., 34, 1102, 1960.
3. Frank-Kameneskii, D.A., Diffusion and Heat Exchange in Chemical Kinetics, Princeton University Press, N.J., 1955.
4. Hinze, L.O., Turbulence, McGraw-Hill Book Co., Inc., N.Y., 1959.
5. Lamb, D.E., Manning, F.S., & Wilhelm, R.H., Measurement of Concentration Fluctuation with an Electrical Conductivity Probe, A.I. Ch. E. Journal, No. 4, Vol. 6, 682, 1960.
6. Levich, V.G., Physicochemical Hydrodynamics, (English Edition) Prentice-Hall, Inc., N.Y., 1962.
7. Ling, S.C., & Hubbard, P.G., The Hot-Film Anemometer, J. Aero. Sci., 23, 890, 1956.
8. Litt, M., & Serad, G., Chemical Reaction on a Rotating Disk, M.S. Thesis in Chemical Engineering, University of Pennsylvania, 1963.
9. Reiss, L.P., & Hanratty, T.H., An Experimental Study of the Unsteady Nature of the Viscous Sublayer, A.I. Ch. E., No. 2, Vol. 1, 159, 1963.
10. Reiss, L.P., & Hanratty, T.H., Measurement of Instantaneous Rates of Mass Transfer to a Small Sink on a Wall, A.I. Ch. E., Vol. 6, 682, 1960.
11. Sanaborn, V.A., Experimental Evaluation of Momentum Terms in Turbulent Pipe Flow, NACA, TN 3266, 1955.
12. Schlichting, Herman, Boundary Layer Theory, McGraw-Hill Book Co., Inc., N.Y., 1960.
13. Toor, H.L., A.I. Ch. E., Journal, Vol. 8, 1962.