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Article

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Analysis Method for Rotating Disk Voltammograms of Electrocatalytic Reaction —Oxygen Reduction Reaction—

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ABSTRACT

Rotating disk voltammograms of electrocatalytic reactions were often analyzed on a model of the totally irreversible reaction. The problem with the conventional method is pointed out, and the validity of an analysis method on a model of the electrocatalytic reaction is demonstrated for oxygen-reduction reaction (ORR) as an example. Rotating disk voltammograms of ORRs sometimes show gradual change in the limiting current region called residual slope. The phenomenon has been explained on a random distribution model in which the catalytic sites communicate in long-range electron transfer with the electronic conductors that locate at distances (*z*), and are uniformly distributed with respect to *z*. Observed data of an ORR were well reproduced by non-linear least squares analysis on the random distribution model. The result of the analysis is briefly discussed.



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Keywords : Rotating Disk Electrode, Steady-state Current, Residual Slope, Long-range Electron Transfer

1. Introduction

The reciprocal sum relationship of the rate-determining step kinetics in sequential multi-step steady-state reactions has been generalized (see Appendix I) and its importance has also been emphasized for example in analysis of steady-state voltammograms at rotating disk electrodes (RDEs) and ultramicroelectrodes as well as steady-state enzyme kinetics in a previous paper.¹ Our group has also emphasized that it is not preferable to analyze electrocatalytic reactions on an irreversible reaction model. We will re-explain the latter point here in a little more detail. Rotating disk voltammetry is frequently used to analyze oxygen-reduction reactions (ORRs)

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which are usually typical electrocatalytic reactions.² Steady-state voltammograms of ORRs are often analyzed on a model of the totally irreversible reaction: $O + ne^- \rightarrow R$ (O: oxidant, R: reductant, *n*: total number of the electron for the reductions) with a reciprocal sum formula:²

$$\frac{1}{i_{\rm s(O)}} = \frac{1}{i_{\rm e(O)}} + \frac{1}{i_{\rm d(O)}},\tag{1}$$

where $i_{s(O)}$, $i_{e(O)}$, and $i_{d(O)}$ are, respectively, the steady-state current, the electrode kinetic-controlled steady-state current, and diffusion-controlled limiting steady-state current for the reduction of O. $i_{d(O)}$ is given by Levich equation at RDE:³

$$i_{\rm d(O)} = -0.620nFAD_{\rm O}^{2/3}\omega^{1/2}v^{-1/6}c_{\rm O} = -L_{\rm O}\omega^{1/2}c_{\rm O} = -M_{\rm O}c_{\rm O},$$

(with $L_{\rm O} \equiv 0.620nFAD_{\rm O}^{2/3}v^{-1/6}, M_{\rm O} \equiv L_{\rm O}\omega^{1/2}$) (2)

where $D_{\rm O}$ and $c_{\rm O}$ are the diffusion coefficient and the bulk concentration of O, respectively; ω is the rotating speed in radian of RDE; ν is the kinetic viscosity of the solution; *F* is the Faraday constant; and *A* is the surface area of the electrode. On the other hand, $i_{\rm e(O)}$ is given by



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$$i_{e(O)} = -nFAk_{e(O)}c_O \tag{3}$$

with

$$k_{\rm e(O)} = k^{\circ} \exp\left[\frac{-\alpha F(E - E^{\circ'} {\rm rds})}{RT}\right],\tag{4}$$

where $E^{\circ'}_{rds}$ and α are, respectively, the formal potential and the transfer coefficient of the rate-determining single electron transfer process of the redox couple O/R. E, R, and T are, respectively, the electrode potential, the gas constant, and the absolute temperature. $k_{e(O)}$ and k° are, respectively, the interfacial electron transfer rate constant of the rate-determining step (rds) in the reduction of O (at E) and the standard one (at $E^{\circ'}_{rds}$) of the redox couple O/R. Combination of Eqs. 1-3 secures linear relationship between 1/ $i_{s(\Omega)}(E)$ vs. $1/\omega^{1/2}$ to evaluate the electron transfer kinetic parameters (k° , α , and $E^{\circ'}_{rds}$) involved in $k_{e(O)}(E)$. The reciprocal sum formula is sometimes called Koutecký-Levich equation^{4,5} but the term seems to be inappropriate, since Koutecký and Levich focused (not on the steady-state current-potential curve in the totally irreversible system but) on the limiting current in the electrocatalytic system in solution in their original papers.^{3,6} Equation 1 does not reflect any catalytic properties, and then $1/i_{s(O)}(E)$ vs. $1/\omega^{1/2}$ plots are not suitable for analysis of rotating disk voltammograms of ORRs.

Against such backgrounds, our group proposed a model of the electrocatalytic system including a bi-directional electron transfer reaction as follows:¹

We may reasonably consider that there exist the electrocatalytic sites (C) for the reduction of O on the electrode surface in the electrocatalytic system, and C binds O to form a CO complex that is electrochemically reduced to CR and regenerates C by releasing R. $k_{c,r(C)}$ is the rate constant of the reductive catalytic process (O-binding process) of C and not potential dependent, while $k_{e(CO)}$ and $k_{e(CR)}$ are, respectively, the rate constants of the rds in the electrochemical reduction of CO and oxidation of CR on the electrode surface. When the reductive electrocatalytic reaction-controlled steady-state current is expressed by $i_{ec,r(C)}$, the overall steady-state electrocatalytic reduction of C is given by the following reciprocal formula as a function of E:¹

$$\frac{1}{i_{s(O)}} = \frac{1}{i_{d(O)}} + \frac{1}{i_{ec,r(C)}} = \frac{1}{i_{d(O)}} + \frac{1}{i_{c,r(C)}} \left(1 + K_{N(C)} + \frac{k_{c,r(C)}}{k_{e(CO)}} \right)$$

$$\left(\text{with } i_{ec,r(C)} = \frac{i_{c,r(C)}}{1 + K_{N(C)} + \frac{k_{c,r(C)}}{k_{e(CO)}}} \right)$$
(6)

with

$$i_{\rm c,r(C)} \equiv -nFAk_{\rm c,r(C)}\Gamma_{\rm C},\tag{7}$$

$$K_{\rm N(C)} \equiv \frac{k_{\rm e(CR)}}{k_{\rm e(CO)}} = \exp\left[\frac{F(E - E^{\circ\prime} r_{\rm ds(C)})}{RT}\right],\tag{8}$$

$$k_{\rm e(CR)} = k^{\circ}{}_{\rm C} K_{\rm N(C)}{}^{1-\alpha_{\rm C}}, \qquad (9)$$

$$k_{\rm e(CO)} = k^{\circ}_{\rm C} K_{\rm N(C)}^{-\alpha_{\rm C}},\tag{10}$$

where $i_{c,r(C)}$ is the reductive catalytic reaction-controlled steady-state limiting current and Γ_C is the total surface concentration of C; $E^{\circ'}_{rds(C)}$ and α_C are, respectively, the formal potential and the transfer coefficient of the single electron interfacial transfer rds of the redox couple CO/CR; $K_{N(C)}$ is the Nernstian equilibrium constant of the rds in the CO/CR redox; $k_{e(CO)}$, $k_{e(CR)}$, and k°_{C} are, respectively, the rate constants for the reduction of CO and the oxidation of CR, and the standard one of the rds of the redox couple CO/CR.

In Eq. 6, $i_{d(O)}$ is proportional to $\omega^{1/2}$, and $i_{ec,r(C)}$ is constant at a given *E*. Therefore, $1/i_{s(O)}(E)$ vs. $1/\omega^{1/2}$ plot will be linear on this model. However, since $i_{ec,r(C)}$ is a complex function of the parameters characterizing the electrode kinetics and the catalytic process, $1/i_{s(O)}(E)$ vs. $1/\omega^{1/2}$ plot analysis does not yield fruitful information. In contrast, at $E \ll E^{\circ'}_{rds(C)}$, $K_{N(C)}$ and $k_{c,r(C)}/k_{e(CO)}$ become zero and $i_{ec,r(C)}$ becomes identical with $i_{c,r(C)}$ to yield the limiting value $i_{s(O)}^{lm}$ given by

$$\frac{1}{i_{\rm s(O)}^{\rm lim}} = \frac{1}{i_{\rm d(O)}} + \frac{1}{i_{\rm c,r(C)}} = -\frac{1}{L_{\rm O}\omega^{1/2}c_{\rm O}} - \frac{1}{nFAk_{\rm c,r(C)}\Gamma_{\rm C}}.$$
 (11)

Since $i_{c,r(C)}$ is independent of *E*, $1/i_{s(O)}^{lim}$ vs. $1/\omega^{1/2}$ plot clearly gives the catalytic property of C as well as the diffusion property of O. This is exactly Koutecký–Levich analysis.

Figure 1 shows the typical examples of the $i_{s(O)}$ as well as $i_{d(O)}$ and $i_{ec,r(C)}$ as functions of *E*. When $|i_{d(O)}| \approx |i_{c,r(C)}|$ (Fig. 1a), $|i_{s(O)}^{lim}|$ is lower than $|i_{d(O)}|$, and $i_{s(O)}$ value becomes close to $i_{ec,r(C)}$ and predominantly reflects electrocatalytic properties characterized by the parameters $(k_{c,r(C)}\Gamma_c, \frac{k_{c,r(C)}}{k_{c,r(C)}}, E^{\circ'}_{rds(C)}, and \alpha_C)$. On the other hand,



Figure 1. Typical examples of the $i_{s(0)}$, $i_{d(0)}$ and $i_{ec,r(C)}$, under the conditions of $E^{\circ'}{}_{rds(C)} = 0.75$ V, $\alpha_{C} = 0.5$, and $k_{c,r(C)}/k^{\circ}{}_{C} = 1$. (a) $i_{d(O)}/A$ was set to -3 mA cm^{-2} , and $i_{c,r(C)}/A$ to -1 mA cm^{-2} . (b) $i_{d(O)}/A$ was set to -1 mA cm^{-2} , and $i_{c,r(C)}/A$ to -3 mA cm^{-2} , conversely.

when $|i_{d(O)}| \ll |i_{c,r(C)}|$ (Fig. 1b), $i_{s(O)}^{lim} \cong i_{d(O)}$ and the $i_{s(O)}$ value is predominantly characterized by the diffusion property of O (M_O) and the electrode kinetic property of the reduction of CO as well as $E^{\circ'}_{rds(C)}$ in the onset region (see Appendix II). Therefore, it is very important to measure $i_{s(O)}$ under the conditions of $|i_{d(O)}| \gg |i_{c,r(C)}|$, that is at low values of $k_{c,r(C)}\Gamma_C$ and/or at high values of $\omega^{1/2}c_O$, in the characterization of the electrocatalytic properties.

On the model described in Eq. 5, $i_{s(O)}$ should reach $i_{s(O)}^{lim}$ at $E \ll E^{\circ'}_{rds(C)}$. However, $|i_{s(O)}|$ values often increase with a decrease in *E* in the limiting current region, especially under the condition of that $|i_{d(O)}| \approx |i_{c,r(C)}|$. Such a gradual (sometimes linear) change of $i_{s(O)}$ in the limiting current region is called residual slope.⁷ The phenomena cannot be explained by the above simple electrocatalytic model (which may be called homogeneous catalyst model). In this paper, we attempt to describe the phenomena on an electrocatalytic reaction model involving homogeneous catalytic cites that locate at different distances from conductive electrode materials and undergo long-range electron transfer with the conductive materials. The derived equation was fitted to the real data using zirconium-oxynitride as an ORR catalyst,^{8,9} and the result of non-linear least squares analysis was discussed.

2. Modeling

As judged from Eq. 10, $k_{e(CO)}$ increases exponentially with a change of E in the negative potential direction. Therefore, $k_{c,r(C)}$ / $k_{e(CO)}$ as well as $K_{N(C)}$ becomes zero at $E \ll E^{\circ'}{}_{rds(C)}$, and $i_{ec,r(C)}$ becomes identical with $i_{c,r(C)}$ (that is the reductive catalytic reactioncontrolled current) as can be seen from Eq. 6. Here we assume that there exist heterogeneous catalysts with different k°_{C} . Some of the catalysts with low values of k°_{C} give the limiting value of the electrocatalytic reaction-controlled current at more negative potentials compared with catalysts with high values of k°_{C} ; low k°_{C} values can be compensated by negative shift in E to satisfy the condition that $k_{\rm c,r(C)}/k_{\rm e(CO)} \approx 0$. Under such conditions, overall $|i_{\rm ec,r(C)}|$ increases gradually with a negative shift in E in the limiting current region, because the observed catalytic current is the sum of the contribution from all catalysts. Especially, the long-range electron transfer property can be well compensated by exponentially increasing property of $k_{e(CO)}$ with a negative shift in E, when it exponentially decreases k°_{C} with an increase in the distance (z) between the catalytic center and electronic conductor:^{10,11}

$$k^{\circ}_{\rm C}(z) = k^{\circ}_{\rm C}^{\rm max} \exp(-\beta z), \qquad (12)$$

where $k_{\rm C}^{\circ \max}$ is the maximum value of $k_{\rm C}^{\circ}$ at z = 0, and β is the decay constant. Combination of Eqs. 10 and 12 yields the rate constant of the rds in the reductive interfacial electron transfer of CO that locates at a distance of z ($k_{\rm e(CO)}(z)$):

$$k_{\rm e(CO)}(z) = k_{\rm C}^{\circ \max} \exp(-\beta z) (K_{\rm N(C)})^{-\alpha_{\rm C}}.$$
(13)

The reductive electrocatalytic reaction-controlled current due to the catalysts at a distance z ($i_{ec,r(C)}(z)$) is given by

$$i_{ec,r(C)}(z) = -\frac{nFAk_{c,r(C)}\Gamma_{C}(z)}{1 + K_{N(C)} + \frac{k_{c,r(C)}}{k_{e(CO)}(z)}}$$
$$= \frac{i_{c,r(C)}(z)}{1 + K_{N(C)} + \frac{k_{c,r(C)}}{k_{e(CO)}(z)}}.$$
(14)

Figure 2a shows calculated values of $i_{ec,r(C)}(z)$ at $\beta z = 0, 3, 6$, and 9 as well as the sum of those $i_{ec,r(C)}(z)$ as functions of E to show the appearance of the residual slope. Figure 2b shows the model of electron transfer reaction at different distances of the catalytic center from the electron conductor. We assumed here that the surface concentrations of the catalysts with 4 different values of $z(\Gamma_{C}(z))$ are identical with each other ($\Gamma_{\rm C}(z) = \Gamma_{\rm C}/4$). Therefore, the expected total value of $i_{ec,r(C)}$ is identical with the sum of the 4 values of $i_{ec,r(C)}(z)$. It can be well recognized that sigmoidal $i_{ec,r(C)}(z)$ vs. E curve shifts to the direction of the negative potential with an increase in z and that $i_{ec,r(C)}(z)$ reaches $i_{c,r(C)}(z)$ at $E \ll E^{\circ'}_{rds(C)}$. This means that an exponentially decreased value of k°_{C} with an increase in z is well compensated by a shift in E to the negative potential direction to satisfy $k_{c,r(C)}/k_{e(CO)}(z) \approx 0$. The sum of the 4 $i_{ec,r(C)}(z)$ values yield an almost straightly decreasing line against E. This is so-called residual slope.⁷

Here we propose a model in which all catalytic sites are homogeneous in nature, but the catalytic sites with $k^{\circ}_{C}(z)$ are uniformly distributed with respect to z ($0 \le z \le d_0$; d_0 being the maximum value of z). $\Gamma_{C}(z)$ becomes independent of z as given by

$$\int_0^{d_0} \Gamma_{\rm C}(z) \mathrm{d}z = \Gamma_{\rm C}, \quad \Gamma_{\rm C}(z) = \Gamma_{\rm C}/d_0. \tag{15}$$

The proposed model to be considered here may be called "random distribution model". On this model, $i_{ec,r(C)}(z)$ is given as follows:



Figure 2. (a) $i_{ec,r(C)}(z)$ values at $\beta z = 0, 3, 6$, and 9 as well as the sum of those $i_{ec,r(C)}(z)$ as functions of *E*. $i_{ec,r(C)}(z)$ values were calculated by Eq. 14 with $k_{e(CO)}(z)$ given in Eq. 13 at $i_{c,r(C)}(z)/A = -1 \text{ mA cm}^{-2}$, $E^{\circ'}_{rds(C)} = 0.75 \text{ V}$, $\alpha_C = 0.5$, $k_{c,r(C)}/k_C^{\circ max} = 1$ and $\Gamma_C(z) = \Gamma_C/4$. (b) Schematic view of the catalytic centers locating at the 4 different distances from the electronic conductor.

$$i_{ec,r(C)}(z) = \frac{i_{c,r(C)}/d_0}{1 + K_{N(C)} + \frac{k_{c,r(C)}}{k_{e(CO)}(z)}} = \frac{i_{c,r(C)}/d_0}{1 + K_{N(C)} + P_C \exp(\beta z)}.$$
(with $P_C \equiv k_{c,r(C)} (K_{N(C)})^{\alpha_C} / k_C^{\circ \max}$) (16)

The total current of the reductive electrocatalytic reaction-controlled current $(i_{ec,r(C)})$ is given by

$$i_{\text{ec,r(C)}} = \int_{0}^{d_0} i_{\text{ec,r(C)}}(z) dz$$

= $\frac{i_{\text{c,r(C)}}}{d_0} \int_{0}^{d_0} \frac{1}{1 + K_{\text{N(C)}} + P_{\text{C}} \exp(\beta z)} dz.$ (17)

Now, if we have $1 + K_{N(C)} + P_C \exp(\beta z) \equiv u$, $du/dz = \beta(u - 1 - K_{N(C)})$ and then we get

$$i_{ec,r(C)} = \frac{i_{c,r(C)}}{\beta d_0} \int_{1+K_{N(C)}+P_C}^{1+K_{N(C)}+P_C} \frac{u}{u} \frac{du}{(u-1-K_{N(C)})}$$

$$= -\frac{i_{c,r(C)}}{\beta d_0(1+K_{N(C)})} \left[\ln u - \ln(u-1-K_{N(C)}) \right]_{1+K_{N(C)}+P_C}^{1+K_{N(C)}+P_C} \exp(\beta d_0)$$

$$= -\frac{i_{c,r(C)}}{\beta d_0(1+K_{N(C)})} \left[\ln \left(\frac{1+K_{N(C)}+P_C}{1+K_{N(C)}+P_C} \right) - \beta d_0 \right]$$

$$= \frac{i_{c,r(C)}}{1+K_{N(C)}} \left[\frac{1}{\beta d_0} \ln \left(\frac{1+K_{N(C)}+P_C}{1+K_{N(C)}+P_C} \exp(\beta d_0) \right) + 1 \right].$$
(18)

Therefore, the total current of the reductive electrocatalytic reaction of O is given by

$$\frac{1}{i_{s(0)}} = \frac{1}{i_{d(0)}} + \frac{1}{i_{ec,r(C)}}$$

$$= -\frac{1}{M_{0}c_{0}} - \frac{1}{nFAk_{c,r(C)}\Gamma_{C}} \left\{ \frac{1 + K_{N(C)}}{1 + \frac{1}{\beta d_{0}}\ln\left(\frac{1 + K_{N(C)} + P_{C}}{1 + K_{N(C)} + P_{C}\exp(\beta d_{0})}\right)} \right\}.$$
(19)

Similar equation has been proposed for a random enzyme orientation model in enzyme-based bioelectrocatalytic reactions,^{7,12} although the derivation is somewhat different from the present one. Since $K_{\rm N(C)}$ and $P_{\rm C}$ become zero at $E \ll E^{\circ'}_{\rm rds(C)}$, $i_{\rm ec,r(C)}$ reaches the limiting current that is identical with $i_{\rm c,r(C)}$ at sufficiently negative potentials, and $i_{\rm s(O)}$ also reaches the limiting current ($i_{\rm s(O)}^{\rm im}$);

$$\frac{1}{i_{\rm s(O)}^{\rm im}} = \frac{1}{i_{\rm d(O)}} + \frac{1}{i_{\rm c,r(C)}} = -\frac{1}{M_{\rm O}c_{\rm O}} - \frac{1}{nFAk_{\rm c,r(C)}\Gamma_{\rm C}}.$$
 (20)

However, it is often difficult to observe $i_{s(O)}^{\lim}$ within the measuring potential window because the residual slope property drastically increases the overpotential (see also Fig. 2), especially under the condition of $|i_{d(O)}| \approx |i_{c,r(C)}|$.

Figure 3 shows a typical example of $i_{s(O)}$ and $i_{ec,r(C)}$ as functions of *E* in the random distribution model (at $\beta d_0 = 10$) as well as those in the homogeneous catalyst model (at $\beta d_0 = 0$) under the condition of $i_{c,r(C)}/i_{d(O)} = 3$. The limiting value of $i_{ec,r(C)}$ is identical with $i_{c,r(C)}$, as recognized from Eq. 20 ($K_{N(C)} \approx 0$, $P_C \approx 0$ at $E \ll E^{\circ'}_{rds(C)}$). The sigmoidally rising property of $i_{ec,r(C)}$ vs. *E* curve becomes gentle



Figure 3. $i_{s(O)}$ and $i_{ec,r(C)}$ as functions of *E* in the random distribution model (at $\beta d_0 = 10$) and in the homogeneous catalyst model (at $\beta d_0 = 0$) at $i_{d,r}/A = -1 \text{ mA cm}^{-2}$, $i_{c,r(C)}/A = -3 \text{ mA cm}^{-2}$, $E^{\circ'}_{rds} = 0.75 \text{ V}$, $\alpha_C = 0.5$, $k_{c,r(C)}/k_C^{\circ max} = 1$.

with an increase in βd_0 . It is noteworthy that $|i_{s(O)}^{\text{lim}}| = 0.75 |i_{d(O)}|$ under the present condition of $i_{c,r(C)}/i_{d(O)} = 3$ (see Eq. 20).

3. Data Analysis of ORR on Random Distribution Model

 ZrO_xN_y -multi-walled carbon nanotube (MWCNT) catalystmodified glassy carbon (GC) electrode was chosen as a random distribution model electrode. Because zirconium oxide has a large bandgap of approximately 5.0 eV, the bandgap decreases to only 2.6 eV even when zirconium oxide is nitrided to be Zr_2ON_2 .¹³ Therefore, the electronic conductivity of ZrO_xN_y particles with a diameter of approximately 10 nm seems to be insufficient to function effectively for some catalytic sites in the particle. In other words, the catalytic sites become effective when an electronic conductor is located near the surface. It can be assumed that k°_{C} exponentially decreases with an increase in the distance between the catalytic sites and the electronic conductor.

 ZrO_xN_y particles with a diameter of approximately 10 nm were highly dispersed on the MWCNTs in the ZrO_xN_y-MWCNT catalyst made from zirconium phthalocyanine as a precursor.⁸ The surface of the particles was partially covered with deposited carbon derived from the phthalocyanine by thermal decomposition. Thus, the electrons must be supplied from the electronic conductors such as the MWCNTs and the deposited carbon, and the ORR would proceed on the catalytic sites on the surface. The catalytic sites can be considered to uniformly distribute on the surface because the catalyst was prepared homogeneously. Hence, ZrO_vN_v-MWCNT catalyst had homogeneous catalytic sites that located at different distances from the electronic conductors and underwent the long-range electron transfer with the conductive materials. This was the reason why we focused on the ZrOxNv-MWCNT-modified electrode catalyst as a random distribution model electrode. In addition, the dependence of the kinetic parameters on the catalyst loading on the GC disc electrode might be useful to discuss the homogeneity of the catalytic sites and the ratio of the utilization of the loaded catalyst. Therefore, we performed the RDE measurements at three different catalyst loadings.

Figure 4a shows rotating disk voltammograms of ORR at ZrO_xN_y -MWCNT-modified electrodes at $\omega = 2500 \text{ rpm} = 2500/(60 \times 2\pi) \text{ s}^{-1}$ and at several loading amounts (($A\Gamma_C$)_{exp}) of the catalyst. The detailed experimental procedures have been reported in a previous study,⁸ and are omitted here. Equation 19 was fitted to



Figure 4. (a) Rotating disk voltammograms of ORR at ZrO_xN_y –MWCNT-modified electrodes and non-linear least-squares curve fitting with Eq. 19. A reversible hydrogen electrode (RHE) was used as the reference electrode. (b) Schematic view of the interpretation of the data analysis.

Table 1. The refined values of the fitting parameters.

$(A\Gamma_{\rm C})_{\rm exp}$	E°′ _{rds} / V	$k_{\rm c,r(C)}/k_{\rm C}^{\circ \max}$	$k_{\rm c,r(C)}\Gamma_{\rm C}$ / $10^{-4}{\rm s}^{-1}{\rm mol}{\rm m}^{-2}$	$eta d_0$
0.55 mg	0.7304 ± 0.0007	0.88 ± 0.02	3.870 ± 0.009	10.46 ± 0.04
0.98 mg	0.7300 ± 0.0003	1.04 ± 0.01	11.66 ± 0.01	12.9 ± 0.1
1.39 mg	0.734 ± 0.002	2.7 ± 0.2	29.5 ± 0.3	12.0 (fix)

those data using 4 fitting-parameters: $E^{\circ'}_{rds}$, $k_{c,r(C)}/k_{C}^{\text{max}}$, $k_{c,r(C)}/\Gamma_{C}$, and βd_0 by a non-linear squares method on Gnuplot[®] (Ver. 5.4) with the fixed values as $A = 0.283 \text{ cm}^2$, $D_0 = 1.80 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$, v = $8.01 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$, $c_0 = 1.1 \times 10^{-3} \text{ mol dm}^{-3}$, $\alpha_C = 0.5$, F = 96485 C mol^{-1} , $R = 8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$, and T = 303.15 K. The data with $(A\Gamma_C)_{exp} = 0.55$ and 0.98 mg were well reproduced by Eq. 19, as shown in Fig. 4a, while such a 4-parameter fitting was not successful for the data with $(A\Gamma_C)_{exp} = 1.39 \text{ mg}$, most probably because the $i_{s(O)}/A$ value is very close to $i_{d,r}/A$ (= -6.5 mA cm^{-2}). Therefore, for the data with $(A\Gamma_C)_{exp} = 1.39 \text{ mg}$, βd_0 value was fixed to be 12, and 3-parameter fitting was applied. The derived fitting parameters are listed in Table 1.

The refined values of $E^{\circ'}_{rds}$ are almost independent of $(A\Gamma_{C})_{exp}$. This indicates that the catalysts used are homogeneous. The $k_{c,f(C)}\Gamma_C$ values appear to increase with $(A\Gamma_{\rm C})_{\rm exp}$. Therefore, almost all catalysts locating at $z \le d_0$ seem to be working effectively, suggesting that the ratio of the utilization of the loaded catalyst was almost constant even at large amounts of the catalyst loading. The $k_{c,r(C)}/k_{C}^{\circ \max}$ values seem to slightly increase with an increase in $(A\Gamma_{\rm C})_{\rm exp}$, but when we assume that $k_{\rm c,r(C)}$ is independent of $(A\Gamma_{\rm C})_{\rm exp}$, the amount of the variation of $k_{C}^{\circ \max}$ corresponds at most to the change of $\beta d_0 \approx 1$ in the long-range electron transfer (Eq. 12). In addition, since the observed voltammograms do not show the limiting value within the potential recorded, some ambiguity arises in the fitting refinement of $k_{c,r(C)}/k_{C}^{\circ \max}$ as well as $k_{c,r(C)}\Gamma_{C}$. Therefore, the change in $k_{c,r(C)}/k_{C}^{\circ\max}$ does not seem to be worth discussing here. Since the refined values of βd_0 are about 10–12 and β may be around 10 nm⁻¹,¹⁴ the catalytic sites seem to locate within about 1 nm from the conductive material in the potential window recorded here. This interpretation may be illustrated as shown in Fig. 4b. There should exist other catalysts at z > 1 nm, but such catalysts could not work effectively because of too small $k^{\circ}_{C}(z)$ values within the present measuring potential window.

4. Conclusions

We have confirmed that rotating disk voltammograms of electrocatalytic reactions including ORRs must be analyzed not on a model of totally irreversible reactions but on a suitable model of electrocatalytic reactions. It should be noteworthy that observed steady-state current-potential curves of ORRs are predominantly characterized by the diffusion property of oxygen, when the limiting current becomes close to the diffusion-limiting current. Therefore, for the evaluation of the performance of the catalyst, it is very important to set the experimental conditions such that the limiting current is less than the diffusion-limiting current by increasing in the rotating speed and/or decreasing the amount of the catalysis on the electrode surface.

In rotating disk voltammetry of ORRs, we may sometimes observe gradual and almost linear change in the limiting current region called residual slope. The phenomenon has been explained on the random distribution model in which we consider that the catalytic sites locate at distances (z) from the electronic conductor and are uniformly distributed with respect to z, and that the longrange electron transfer occurs between the catalytic site and the electronic conductor. The derived equation was fitted to the data of an ORR at ZrO_xN_v-MWCNT-modified electrodes. The observed data were well reproduced, indicating that the ZrO_xN_y-MWCNT catalyst was suitable for a random distribution model electrode. The effective distance that the catalytic sites work effectively from the conductive material can be estimated to be approximately 1 nm. The homogeneity of the catalytic sites and the rate of utilization of the loaded catalyst can be discussed by the dependence of the kinetic parameters on the catalyst loading on the GC disc electrode. In this analysis method also, it is very important to set the experimental conditions such that the limiting current is less than the diffusionlimiting current.

The present analysis on the random distribution model, it was suggested that βd_0 values might depend on the measuring potential window due to the residual slope characteristics. Some catalytic sites locating far from the electronic conductor might not function effectively within the measuring potential window. The size of the catalysis particles and the attachment of the electronic conductor might become very important factors to minimize the distance between the catalytic site and the electronic conductor and to utilize all catalytic sites effectively.

Appendix I

The concept of the reciprocal sum relationship described in Ref. 1 is overviewed here. Let us consider a monodirectional sequential steady-state reaction consisting of *n*-step reactions:

$$\sum_{i} \nu_{1,i} A_{1,i} \xrightarrow{\text{step } 1} \sum_{i} \nu_{2,i} A_{2,i} \xrightarrow{\text{step } 2} \cdots$$

$$\sum_{i} \nu_{n,i} A_{n,i} \xrightarrow{\text{step } n} \sum_{i} \nu_{n+1,i} A_{n+1,i}, \qquad (A1)$$

where $A_{m,i}$ (m = 1 to n) are the reactants in the *m*-th step reaction, while $A_{n+1,i}$ are the final products. $v_{m,i}$ (m = 1 to n + 1) are the stoichiometric coefficients of $A_{m,i}$. Under the steady-state conditions at a steady-state reaction rate of v_s , the rate of the Gibbs free energy change of the entire reaction (dG/dt) and that of the *m*-th step one (dG_m/dt) are, respectively, given by:

$$\frac{dG}{dt} = \left(-\sum_{i} \mu_{1,i} \nu_{1,i} + \sum_{i} \mu_{n+1,i} \nu_{n+1,i}\right) v_{s} \equiv R v_{s},$$
(A2)
$$\left(R \equiv \sum_{i} \nu_{n+1,i} \mu_{n+1,i} - \sum_{i} \mu_{1,i} \nu_{1,i}\right) \\
\frac{dG_{m}}{dt} = \left(-\sum_{i} \nu_{m,i} \mu_{m,i} + \sum_{i} \nu_{m+1,i} \mu_{m+1,i}\right) v_{s} \equiv R_{m} v_{s}, \\
\left(R_{m} \equiv \sum_{i} \nu_{m+1,i} \mu_{m+1,i} - \sum_{i} \nu_{m,i} \mu_{m,i}\right)$$
(A3)

where $\mu_{m,i}$ (m = 1 to n + 1) is the chemical potential of $A_{m,i}$. R and R_m correspond to negative values of the sum of the partial driving force of the corresponding reactions, but the reaction rate (v_s) of the entire or corresponding process is independent of R and R_m . Therefore, R and R_m may be called the reaction resistance.¹ Considering the fact that $dG = \sum dG_m$ and Eqs. A2 and A3, we can get the following relation on the reaction resistance under the steady-state conditions:

$$R = \sum R_m. \tag{A4}$$

Here we will define the hypothetical limiting steady-state reaction rate ($v_{rds,m}$) of the *m*-th step reaction that is the rate determining step (rds),

$$v_{\mathrm{rds},m} \equiv \lim_{R_m/R \to 1} v_{\mathrm{s}}.$$
 (A5)

The definition (Eq. A5) gives an important relation:

$$R_m v_{\mathrm{rds},m} \left(= \frac{\mathrm{d}G}{\mathrm{d}t} \right) = R v_{\mathrm{s}}.$$
 (A6)

Substituting Eq. A6 into Eq. A4, we can obtain the following general relationship in the reciprocal sum expression for the steady-state reaction kinetics of the *n*-step sequential reaction:

$$\frac{1}{v_{\rm s}} = \sum \frac{1}{v_{\rm rds,m}}.$$
(A7)

For simplicity here, we may consider that each sequential reaction kinetics is pseudo first-order:

$$A_1 \xrightarrow{\text{step 1}} A_2 \xrightarrow{\text{step 2}} \cdots A_n \xrightarrow{\text{step } n} A_{n+1},$$
(A8)

where k_m (m = 1 to n) is the pseudo-first order reaction rate constant of the *m*-th step reaction. In this case, v_s is related to the apparent pseudo first-order reaction rate constant of the entire reaction (k) and k_m :

$$v_{\rm s} = kc^{\circ}{}_{\rm A_1} = k_m c_{\rm A_m, s} \tag{A9}$$

where $c^{\circ}_{A_1}$ and $c_{A_m,s}$ are the initial concentration of A_1 and the steady-state concentration of A_m . On the other hand, $v_{rds,m}$ is given by:

$$v_{\mathrm{rds},m}(=\lim_{R_m/R \to 1} v_{\mathrm{s}}) = \lim_{c_{A_m, \mathrm{s}} \to c^{\circ}_{A_1}} k_m c_{A_m, \mathrm{s}} = k_m c^{\circ}_{A_1} \qquad (A10)$$

Combination of Eqs. 7, 9, and 10 yields the following reciprocal sum relation of the pseudo-first-order reaction rate constants:

$$\frac{1}{k} = \sum \frac{1}{k_m}.$$
(A11)

In the reciprocal sum expression focusing on the hypothetical $v_{rds,m}$, we can derive the reaction kinetics of the sequential steadystate reaction (Eqs. A7 or A11) without the knowledge of $c_{A_m,s}$ (Eq. A10).

In contrast, such steady-state reaction kinetics is frequently derived based on the steady-state assumption that is $dc_{A_m,s}/dt = 0$ ($c_{A_m,s}$ being the steady-state concentration of the intermediate species (m = 2 to n)). Of course, the final equation derived on the reciprocal sum expression is identical with that derived on the steady-state assumption on a given reaction model. However, the reciprocal sum expression method is much simpler than the steady-state assumption method especially for complicated reaction models, since it is very easy to get $v_{rds,m}$ for the hypothetical limiting case. In contrast, one must solve simultaneous equations of $dc_{A_m,s}/dt = 0$ (m = 2 to n) on the steady-state assumption.

Appendix II

When $|i_{d(O)}| \ll |i_{c,r(C)}|$ and at $K_{N(C)} \approx < 1$ (that is, at $E \approx < E^{\circ'}_{rds(C)}$), Eq. 6 is reduced to:

$$\frac{1}{i_{s(O)}} \cong \frac{1}{i_{d(O)}} + \frac{1}{i_{e,r(C)}}.$$

$$(i_{e,r(C)} \equiv -nFAk_{e(CO)}\Gamma_{C})$$
(A12)

Equation A12 means that the steady-state current–potential curve (except the onset region) is characterized by the diffusion property of O and the electrode kinetic property of the reduction of CO on the electrode surface, but without the information of the catalytic property. In addition, Eq. A12 is essentially identical with Eq. 1. So far, RDE responses of ORRs have frequently been analyzed using Eq. 11 or Eq. A12 under the conditions of $|i_{d(O)}| \ll |i_{c,r(C)}|$ (or $i_{s(O)}^{lim} \cong i_{d(O)}$). From such analyses, one could not get any information on the catalytic property of electrocatalysts.

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- Akimitsu Ishihara: Data curation (Lead), Project administration (Equal), Writing original draft (Equal), Writing - review & editing (Equal)
- Masahiro Yamamoto: Conceptualization (Equal), Writing review & editing (Equal) Kohei Miyazaki: Writing – review & editing (Equal)
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Conflict of Interest

The authors declare no conflict of interest in the manuscript.

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