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Reconsideration of the quantitative characterization of the reaction intermediate on electrocatalysts by a rotating ring-disk electrode: The intrinsic yield of H_2O_2 on Pt/C

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ABSTRACT

To solve the problem of the catalyst-loading-effect on quantifying the reaction intermediates on the surface of electrocatalysts with a rotating ring-disk electrode, we studied the formation of hydrogen peroxide in the oxygen reduction reaction on Pt/C with various sample loadings and then proposed an extrapolation model for measuring the intrinsic yield of H_2O_2 , which can quantitatively reflect the characteristics of the surface of a given catalyst. In the extrapolation model, the catalyst loading effect can be compensated by taking the catalyst loading-dependent probability of the re-adsorption + further reaction of the desorbed H_2O_2 into consideration. The core concept in this extrapolation model is that the probability of the re-adsorption + reaction of the desorbed H_2O_2 . The intrinsic yield of H_2O_2 by extrapolation was much higher than that measured by the conventional model, in which the re-adsorption + reaction of the desorbed H_2O_2 is not considered, and thus the catalyst loading-dependent apparent yield of H_2O_2 does not properly reflect the intrinsic characteristics of the surface of a given catalyst.

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1. Introduction

In fundamental studies of catalytic processes, quantifying the reaction intermediates can provide some key hints concerning the reaction mechanism [1–4]. In corresponding applied research, the yield of the intermediate could be used as a criterion for evaluating the performance of the catalyst [5,6].

It is widely known that, in the oxygen reduction reaction (ORR) on platinum, the predominant reaction proceeds via a four-electron pathway [7] (Eq. (1) [8]) with a two-electron side reaction (Eq. (2)) [8]. Even for the two-electron reaction, hydrogen peroxide (H_2O_2) can be further reduced according to Eq. (3) [8]. A disproportion reaction could also occur, as shown in Eq. (4). The disproportion reaction is generally electrochemically undetectable and is thus neglected.

 $O_2 + 4H^+ + 4e^- = 2H_2O$ $E^0 = 1.229V$ (1)

 $O_2 + 2H^+ + 2e^- = H_2O_2$ $E^0 = 0.67 V$ (2)

 $H_2O_2 + 2H^+ + 2e^- = 2H_2O$ $E^0 = 1.77V$ (3)

 $2H_2O_2 = 2H_2O + O_2 \tag{4}$

In developing electrocatalysts for polymer electrolyte fuel cells (PEMFCs) [4,9–11], it is known that H_2O_2 tends to attack the membranes [12–15] and accelerate the dissolution of Pt, leading to a deterioration of the durability. Therefore, ORR electrocatalysts with high selectivity for the four-electron pathway are desired. In contrast, in developing electrocatalysts for H_2O_2 production [16,17], high selectivity for the two-electron pathway is desired. In either case, it is important to understand the intrinsic characteristics of the surface of a given catalyst by quantifying the yield of H_2O_2 (referred to as $X_{H_2O_2}$, the molar ratio of produced H_2O_2 to the total of all reduced oxygen).

The rotating ring-disk electrode (RRDE) technique is widely used to characterize the intermediates or side-products. $X_{H_2O_2}$ has been conventionally derived as below (from Eq. (5) to Eq. (11)) for decades [18–21]. An underlying assumption for the conventional quantification model is that no further reaction occurs on the disk for the desorbed H_2O_2 before it reaches the ring.

The definition of $X_{H_2O_2}$ is expressed in Eq. (5) by the reaction rate of the oxygen molecule reduced via a two-electron pathway ($v_{2e^-}^{con}$) and a four-electron pathway (v_{4e}^{con}) assumed in the conventional model. In the conventional model, one actually cannot distinguish the two reaction pathways (Eq. (1) or Eq. (2)+Eq. (3)) from each other and treats both as four-electron pathways. One is the real four-electron pathway occurring on the same active site, and the other is first a reduction of O₂ to H₂O₂ via a two-electron path-



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way on one active site and then a desorption, re-adsorption and reduction of the produced H_2O_2 to H_2O_2 on a different active site.

$$X_{\rm H_2O_2} = \frac{v_{\rm 2e^-}^{\rm con}}{v_{\rm Q_2}^{\rm reduced}} = \frac{v_{\rm 2e^-}^{\rm con}}{v_{\rm 4e^-}^{\rm con} + v_{\rm 2e^-}^{\rm con}}$$
(5)

By combining the Faraday's Law-based equations (Eqs. (6) and (7)) with Eq. (5), one can express $X_{\text{H}_2\text{O}_2}$ with the reduction current due to the assumed two-electron pathway ($I_{2e^-}^{\text{con}}$) and the four-electron pathway ($I_{2e^-}^{\text{con}}$), as shown in Eq. (8).

$$I_{\Delta e^-}^{\rm con} = 4F \nu_{\Delta e^-}^{\rm con} \tag{6}$$

 $I_{2e^{-}}^{\rm con} = 2F\nu_{2e^{-}}^{\rm con} \tag{7}$

$$X_{\rm H_2O_2} = \frac{2I_{2e^-}^{\rm con}}{I_{2e^-}^{\rm con} + 2I_{2e^-}^{\rm con}}$$
(8)

In RRDE evaluation, there are only two current values experimentally obtainable, disk current (I_d) and ring current (I_r) . In the conventional quantification model, I_d and I_r can be expressed as given in Eqs. (9) and (10), respectively:

$$I_{\rm d} = I_{\rm 2e^-}^{\rm con} + I_{\rm 4e^-}^{\rm con} \tag{9}$$

$$I_{\rm r} = I_{\rm 2e^-}^{\rm con} \times N \tag{10}$$

where *N* stands for the collection efficiency of the RRDE. By combining Eqs. (9) and (10) with Eq. (8), one generally expresses $X_{H_2O_2}$ as Eq. (11).

$$X_{\rm H_2O_2} = \frac{\frac{2l_{\rm r}}{N}}{l_{\rm d} + \frac{l_{\rm r}}{N}} = \frac{2}{\frac{l_{\rm d}}{l_{\rm r}} \times N + 1}$$
(11)

Up to now, $X_{H_2O_2}$ has been derived according to the conventional model (Eq. (11)) with the experimentally obtainable I_r , I_d , and electrode-geometry-determined N [20]. N is also experimentally measurable [21].

In both applied and fundamental research, $X_{H_2O_2}$ has been widely recognized as a characteristic parameter for a given catalyst. Therefore, $X_{H_2O_2}$ is supposed to have a constant value under certain conditions (such as potential, temperature, electrolyte and so on) for the surface of a given catalyst. The $X_{H_2O_2}$ values obtained according to Eq. (11), however, are reported to depend significantly on the catalyst loading [19,22–24]. $X_{H_2O_2}$ tends to decrease with increasing catalyst loading, and this was attributed to further reaction of the produced H₂O₂ on active sites different from those where they are produced [19]. As to the further reaction, a mechanism of 'desorption + re-adsorption + reaction' was reported in the literature [24]. In this mechanism, the probability for the re-adsorption + reaction of the desorbed H₂O₂ depends on the catalyst loading and electrolyte flow in a thin-layer flow cell [24]. The higher the loading or the lower the electrolyte flow, the higher is the probability for re-adsorption.

The dependence of the conventionally-derived $X_{H_2O_2}$ on catalyst loading clearly indicates that the value of the conventional $X_{H_2O_2}$ does not realistically or quantitatively reflect the intrinsic characteristics of the surface for a given electrode in terms of the reaction rate of the 2e⁻ pathway, because it is dominated not only by the surface properties of a given catalyst but also by the structure of the electrode (essentially determined by catalyst loading), as illustrated in Fig. 1. Although both factors are important for a real fuel cell electrode, it is important to distinguish them from each other for a clear understanding, and then a reliable design, of the catalysts and electrodes. In particular, a parameter such as $X_{H_2O_2}$ that can quantitatively reflect the intrinsic characteristics of the surface of a given catalyst is critical in investigating the reaction mechanism and comparing the surfaces of different catalysts. To the best of our knowledge, however, there is no report on a quantitative model for characterizing reaction intermediates with the characteristics of the surface distinguished from the catalyst loading-dominated structure of the electrode.

In this work, we reconsider the quantification model by taking the probability of the re-adsorption+reaction of the H_2O_2 into consideration and then establish an extrapolation model in which the catalyst loading (essentially, the number of active sites, referred as n_{as} hereinafter) effects can be compensated for to achieve the $X_{H_2O_2}$ intrinsic to a given surface (as illustrated in the schematic diagram shown in Fig. 1).

2. Experimental

2.1. Controlling n_{as} on thin-film electrodes

For carbon-supported platinum (Pt/C), n_{as} can be expressed by the electrochemically active surface area (ECSA) of Pt (i.e., n_{as} = ECSA).

By using an in-house-developed automated thin-film-electrode preparation system [25], we controlled n_{as} by homogeneously coating a glassy carbon (GC: 5 mm dia.) disk with various Pt loadings (μ g_{Pt}/cm²_{GC}: 11.7, 7.83, 5.2, 3.91, 2.61, 1.31) of a commercial Pt/C (Tanaka Kikinzoku, 46.1 wt% Pt, 2.7 nm mean diameter of Pt particles).

2.2. Controlling the structure of the thin-film electrode

In order to obtain structure-reproducible thin films of catalyst nano-particles homogeneously distributed on the GC and highly dispersed, with minimal agglomeration, an ultrasonicated suspension of the catalysts in ethanol was transferred to controlled positions (~1 µm precision) on the GC surface in tiny droplets $(\sim 3 \text{ nL in volume})$. As a result of the electrode preparation process, the particles could be homogeneously distributed on the GC surface in the form of micro-islands (less than 2-3 µm in thickness even for the thickest part for the heaviest loading in this study) or submicro-islands. Compared with the slow mass transport through the overall diffusion layer (on the order of 10 µm in thickness at rotation rates used in this study [20]) via onedimensional diffusion, mass transport within such micro-islands or submicro-islands can proceed quickly via three-dimensional quasi-hemispherical diffusion. This fast quasi-hemispherical diffusion makes the effect of the mass transport-limit within the micro-islands or submicro-islands negligible, and thus the thinfilm electrode behaves like a smooth bulk electrode. Further details about the thin-film electrodes will be systematically reported elsewhere [25].

2.3. Electrochemical measurements

The 0.1 M HClO₄ electrolyte was prepared from high-purity Grade reagent (Ultrapur, Kanto Chemicals). The glass cell was treated in hot concentrated nitric acid and then rinsed with high purity Milli-Q water. A platinum mesh was used as the counter electrode and a reversible hydrogen electrode (RHE) was used as the reference electrode.

Cyclic voltammograms (CV) of the electrodes were obtained at $30 \,^{\circ}$ C from argon-deaerated electrolyte to characterize the ECSA of Pt and then from oxygen-saturated electrolyte to quantitatively characterize the H₂O₂ formation.



Fig. 1. Schematic diagram for detecting hydrogen peroxide formation in oxygen reduction on the RRDE and models for deriving the yield of hydrogen peroxide.

3. Results and discussion

3.1. Confirmation of the problem in the conventional model: dependence of $X_{H_2O_2}$ on n_{as}

The voltammograms are shown in Fig. 2 (in argon-deaerated electrolyte) and Fig. 3 (in oxygen-saturated electrolyte). The ECSA of Pt was calculated from the hydrogen underpotential deposition charge.

With I_d and I_r shown in Fig. 3 and N=0.474, one can derive $X_{H_2O_2}$ according to the conventional model, as shown in Eq. (11). Fig. 4 clearly shows that the conventionally-derived $X_{H_2O_2}$ depends on the ECSA (i.e., n_{as}). The higher is n_{as} , the lower is $X_{H_2O_2}$. This trend agrees well with that reported in the literature [19,22–24] and can be qualitatively explained, as shown below, by the readsorption + reaction of the desorbed H_2O_2 before it is finally swept completely away from the disk. A higher n_{as} means a higher probability for the H_2O_2 to re-adsorb on other reaction active sites, with a

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Fig. 2. Voltammograms in Ar-deaerated electrolyte. (Note: the potential sweeping between 0V and 1.2V was conducted at 500 mV s^{-1} for 50 cycles to pre-condition the surface before obtaining the voltammograms in this figure).



Fig. 3. Voltammograms in an O_2 -saturated electrolyte. (Note: the voltammograms shown in this figure were obtained by holding E_{disk} at 0.06 V for 30 s and then sweeping E_{disk} between 0.06 V and 1.0 V. Data shown are the positive-going sweep of the second cycle).

concomitant higher probability to be consumed (Eq. (3)), and thus makes the overall reaction appear as if less H_2O_2 forms (Eq. (2)). This indicates that the conventional model for deriving $X_{H_2O_2}$ can underestimate the reaction rate of the $2e^-$ pathway on the surface of a given catalyst. Therefore, the parameter $X_{H_2O_2}$ derived from the conventional model, may lead to misleading results in discussing the difference in surface characteristics of different catalysts, particularly in calculating the kinetic parameters for fundamental research.



Fig. 4. Relation of the yield of hydrogen peroxide $(X_{H_2O_2})$ versus disk potential (E_{disk}) derived from the conventional model (Eq. (11)) and the extrapolation model (Eq. (23)).

3.2. Development of an extrapolation model by considering the re-adsorption + reaction probability

In order to obtain a value of $X_{H_2O_2}$ intrinsic to the surface of a given catalyst and free from the loading effect, we first introduce the probability of the further reaction into the quantification model as below. As illustrated in Fig. 1, if oxygen molecules are reduced on the surface of a given catalyst at a rate of $v_{O_2}^{reduced}$ mol s⁻¹, with the real two-electron pathway proceeding at v_{2e^-} mol s⁻¹, clearly, the yield of hydrogen peroxide can be defined in Eq. (12). One should note that this yield is only governed by the intrinsic characteristics of the surface of the catalyst. Therefore, this yield could be used as a characteristic parameter for the surface and we refer to this yield as $X_{H_2O_2}^{int}$ hereinafter.

$$X_{\rm H_2O_2}^{\rm int} = \frac{\nu_{2e^-}}{\nu_{O_2}^{\rm reduced}} = \frac{\nu_{2e^-}}{\nu_{4e^-} + \nu_{2e^-}}$$
(12)

According to the re-adsorption + reaction mechanism [24], the produced hydrogen peroxide molecule can desorb from the site where it is produced and may re-adsorb at some other site for further reduction. One can imagine that the percentage of the desorbed peroxide for re-adsorption + reaction (referred as $P_{\rm re}$) is proportional to the probability of re-adsorption + reaction. Then, the reaction rate of further reduced hydrogen peroxide, $v_{2e^-}^{\rm re-ad}$, can be expressed in Eq. (13).

$$\nu_{2e^{-}}^{re-ad} = P_{re} \,\nu_{2e^{-}} \quad 0 \le P_{re} \le 1 \tag{13}$$

According the Faraday's Law, one can express the reduction current for the real two-electron reaction (I_{2e^-}) in Eq. (14), the reduction current for the real four-electron reaction (I_{4e^-}) in Eq. (15), and the reduction current due to re-adsorption+reaction ($I_{2e^-}^{re-ad}$) in Eq. (16).

$$I_{2e^{-}} = 2Fv_{2e^{-}} \tag{14}$$

$$I_{4e^{-}} = 4Fv_{4e^{-}} \tag{15}$$

$$I_{2e^{-}}^{re-ad} = 2Fv_{2e^{-}}^{re-ad} \tag{16}$$

One obtains Eq. (17) by combining Eqs. (14) and (13).

$$I_{2e^{-}}^{\rm re-ad} = P_{\rm re}I_{2e^{-}} \tag{17}$$

Furthermore, I_d and I_r can be expressed by Eqs. (18) and (19), respectively. I_{2e^-} can be expressed in Eq. (20) by rearranging Eq. (19).

$$I_{\rm d} = I_{4{\rm e}^-} + I_{2{\rm e}^-} + I_{2{\rm e}^-}^{\rm re-ad} = I_{4{\rm e}^-} + (1+P_{\rm re})I_{2{\rm e}^-}$$
(18)

$$I_{\rm r} = (1 - P_{\rm re}) I_{\rm 2e^-} N \tag{19}$$

$$V_{2e^-} = \frac{1}{N(1 - P_{re})} \times I_r$$
 (20)

One can express I_{4e^-} by Eq. (21) by replacing I_{2e^-} in Eq. (18) with the right hand side of Eq. (20) and then rearranging.

$$_{4e^{-}} = I_{\rm d} - \frac{1 + P_{\rm re}}{1 - P_{\rm re}} \times \frac{I_{\rm r}}{N}$$
(21)

One can express $X_{H_2O_2}^{int}$ with I_d and I_r , as shown in Eq. (22), by combining Eqs. (17)–(21) with Eqs. (12), (14)–(16).

$$X_{H_2O_2}^{\text{int}} = \frac{1}{1 - P_{\text{re}}} \times \frac{2}{\frac{I_d}{I_r} \times N + 1}$$
(22)

Because the conventionally derived $X_{H_2O_2}$ actually depends on n_{as} (Fig. 4), one can clearly see from Eq. (11) that, it is the current ratio of I_d/I_r that depends on catalyst loading (i.e., n_{as}). From Eq. (22), one can naturally see that P_{re} should also be a function of n_{as} , because both $X_{H_2O_2}^{int}$ and N are independent of n_{as} .

0.0

60

38

In order to obtain $X_{H_2O_2}^{int}$, one needs to know the specific values for both P_{re} and I_d/I_r . I_d/I_r is experimentally available. P_{re} , however, is not directly experimentally obtainable.

3.3. Extrapolation of $X_{H_2O_2}^{int}$

For obtaining a specific value for P_{re} , one must re-examine the mechanism [24] of the re-adsorption+reaction of the desorbed H₂O₂. Oxygen is reduced on some active sites, partially producing hydrogen peroxide. The produced hydrogen peroxide desorbs from where it is produced and is transported to another location (neighboring to or away from the production site) to readsorb. Therefore, it is not difficult to imagine that the probability for re-adsorption on other active sites is dominated by two factors: (i) the mass transport rate for the H₂O₂ (i.e., the rate of escape of the hydrogen peroxide before it has absolutely no further opportunity to be captured by the working electrode), and (ii) the number of active sites within the domain accessible by the peroxide.

As to the effect of the rate of escape of the hydrogen peroxide, there are already detailed reports available. According to a study with nanostructured model electrodes in a thin-layer flow cell, under a condition with a given number of active sites (catalyst loading), the higher was the electrolyte flow rate, the greater was the opportunity for the desorbed H₂O₂ to escape into the electrolyte and the lower the opportunity for re-adsorption + reaction [24]. Therefore, one can imagine that if the rate of escape of the hydrogen peroxide is infinitely fast, the opportunity for readsorption + reaction might be negligible (i.e., $P_{re} = 0$ at infinite rate of escape). Therefore, theoretically, $X_{H_2O_2}^{int}$ is measurable if the electrolyte flow rate is infinitely fast. This hypothesis is experimentally supported by an interesting study on micro-electrodes and ultramicro-electrodes of single carbon-supported Pt particles [26]. On the micro-electrodes or ultramicro-electrodes, a high rate of escape of the hydrogen peroxide is realized by particle diameter-determined hemispherical diffusion. When the size of the Pt particle is less than 50 nm, the H_2O_2 formation rate is the highest ($X_{H_2O_2} = 25\%$ at 0.4 V [26]) and appears to become independent of the size, and, however, a size-dependence of H₂O₂ formation is observed between 50 nm and 5 μ m. We believe that the value for the yield of hydrogen peroxide obtained at a diameter of 50 nm is the intrinsic value to the Pt surface and is nearly free from the re-adsorption reaction due to the high rate of escape of the hydrogen peroxide. To achieve such a high rate of escape of the hydrogen peroxide, however, is clearly not feasible for a flow cell or an RRDE cell. Neither is it feasible to evaluate and compare all catalysts with the single particle micro-electrode or ultramicro-electrode due to the difficulty in the experimental handling.

As to the effect of the number of active sites, one can imagine that, at a given rate of escape, the fewer are the available active sites, the lower will be the re-adsorption probability for the desorbed hydrogen peroxide before escaping from the disk. Therefore, if there are close to zero active sites available for the desorbed hydrogen peroxide, the probability for the re-adsorption of the peroxide also tends to approach zero. Consequently, the probability for the further reaction (Eq. (3)) tends to approach zero. In other words, all of the desorbed hydrogen peroxide can survive, with no possible further reaction when there are no other active sites (i.e., under the condition of close to zero catalyst loading) on the disk electrode.

With the hypothetical boundary value at zero catalyst-loading $(n_{as} \rightarrow 0)$ for P_{re} , one can derive X^{int}_{H2O2} from Eq. (22) if the value of I_d/I_r at the boundary condition (i.e., $n_{as} \rightarrow 0$) is also available



Pt loading/µg_{pt}.cm⁻²

76

15.3

E_{disk}

Fig. 5. Voltammograms derived results: linear relation of the current ratio (I_d/I_r) at various E_{disk} versus the number of the active sites (n_{as}) or the catalyst loading.

(Eq. (23)).

$$X_{H_2O_2}^{\text{int}} = \frac{1}{1 - \lim_{n_{as} \to 0} P_{re}} \times \frac{2}{\lim_{n_{as} \to 0} (\frac{l_d}{l_r}) \times N + 1}$$
$$= \frac{2}{\lim_{n_{as} \to 0} (\frac{l_d}{l_r}) \times N + 1}$$
(23)

The specific value for $\lim_{n_{as}\to 0} \left(\frac{I_d}{I_r}\right)$ is obtainable by extrapolating the relation of I_d/I_r versus n_{as} to $n_{as} = 0$. Interestingly, a linear relation was experimentally obtained for I_d/I_r versus n_{as} (Fig. 5), making the extrapolation very convenient. The linear relation can be described by Eq. (24):

$$\frac{I_{\rm d}}{I_{\rm r}} = A_0 + A_1 \, n_{\rm as} \tag{24}$$

where, A_1 stands for the slope and A_0 for the intercept at $n_{as} = 0$. Reasonably, A_0 can be mathematically described by Eq. (25).

$$A_0 = \lim_{n_{as} \to 0} \left(\frac{I_d}{I_r}\right) \tag{25}$$

Eq. (23) becomes Eq. (26) by replacing $\lim_{n_{as}\to 0} \left(\frac{l_d}{L}\right)$ with A_0 , as shown in Eq. (25).

$$X_{\rm H_2O_2}^{\rm int} = \frac{2}{A_0 N + 1}$$
(26)

From Eq. (26), one can obtain the specific value for $X_{H_2O_2}^{int}$ at a certain potential. This value reflects the intrinsic characteristics of the surface for a given catalyst in terms of the formation rate of the H_2O_2 intermediate, because the n_{as} -dependent consumption on the disk of the desorbed H₂O₂ has been compensated by the extrapolation.

The extrapolated $X_{H_2O_2}^{int}$ values are shown in Fig. 4. By comparing the $X_{H_2O_2}^{int}$ extrapolated values with the conventionally-derived $X_{\rm H_2O_2}$ values, one can clearly see that the H₂O₂ formation rate on the surface of a catalyst can be greatly underestimated (up to about 10-fold) if the re-adsorption + reaction of the H_2O_2 are not taken into consideration.

The high value of the extrapolated $X_{H_2O_2}^{int}$ agrees with the value obtained at a high rate of escape of the hydrogen peroxide on a 50 nm Pt particle [26], strongly supporting the extrapolation model.



Fig. 6. Voltammogram-derived results: Percentage of the desorbed hydrogen peroxide further reduced via re-adorption + reaction (P_{re}) versus the number of active sites (n_{as}).

3.4. Specific expression of P_{re} in the extrapolation model

Rearranging Eq. (26) further, A_0 can be expressed by Eq. (27).

$$A_0 = \frac{1}{N} \times \frac{2 - X_{\rm H_2O_2}^{\rm int}}{X_{\rm H_2O_2}^{\rm int}}$$
(27)

 $X_{H_2O_2}^{\text{int}}$ in Eq. (22) can be further expressed as Eq. (28) by combining Eqs. (24) and (27).

$$X_{H_2O_2}^{\text{int}} = \frac{1}{1 - P_{\text{re}}} \times \frac{2}{\left(\frac{1}{N} \times \frac{2 - X_{H_2O_2}^{\text{int}}}{X_{H_2O_2}^{\text{int}}} + A_1 \times n_{\text{as}}\right) \times N + 1}$$
(28)

Rearranging Eq. (28), one can express P_{re} by Eq. (29).

$$P_{\rm re} = 1 - \frac{2}{2 + A_1 X_{\rm H_2O_2}^{\rm int} N n_{\rm as}}$$
(29)

Because $A_1 > 0$ (as shown in Fig. 5), $0 \le X_{H_2O_2}^{int} \le 1$, N > 0 and $n_{as} \ge 0$, one easily estimate from Eq. (29) the value range of P_{re} , i.e., $0 \le P_{re} \le 1$. This result satisfies the condition for P_{re} shown in Eq. (22). Also, from Eq. (29), one can obtain the two boundary values (for $n_{as} \rightarrow 0$, and $n_{as} \rightarrow \infty$) of P_{re} , respectively: $\lim_{n_{as} \rightarrow 0} (P_{re}) = 0$ and $\lim_{n_{as} \rightarrow \infty} (P_{re}) = 1$. The experimentally derived boundary condition value at zero-loading equals the hypothetical boundary condition value. In contrast to zero-loading, at infinite loading ($n_{as} \rightarrow \infty$), the value of P_{re} is 1, indicating that 100% of the desorbed hydrogen peroxide can be consumed due to the high probability for re-adsorption + reaction. These results strongly support the extrapolation model.

 $P_{\rm re}$ can be rearranged into Eq. (30) by combining Eqs. (22) and (26).

$$P_{\rm re} = 1 - \frac{A_0 N + 1}{\frac{l_d}{L} N + 1} = \frac{A_0 N}{(A_0 + A_1 n_{\rm as})N + 1}$$
(30)

By utilizing the extrapolated A_0 and the current ratio of I_d/I_r (Fig. 5), one can obtain the specific value of P_{re} (Fig. 6) and clearly see the dependence of P_{re} on both n_{as} and potential. Under conditions of high n_{as} , P_{re} approaches to a value of 1, which indicates that most of the desorbed H_2O_2 can be consumed by the further re-adsorption+reaction before escaping from the disk. As to the potential dependence, except for the points at 65 mV, which are scattered, probably due to experimental error, there is a clear trend that the higher the potential is, the higher the

value of the slope A_1 will be and the higher the probability of the re-adsorption + reaction. This can be explained by a larger attractive force of the oxygen atoms in the peroxide at more positive potentials. A larger attractive force obviously indicates an easier re-adsorption + reaction at a single re-adsorption opportunity, hence a higher $P_{\rm re}$. Therefore, we believe that, the slope A_1 is a parameter related to the reaction probability of the peroxide during its one opportunity for re-adsorption.

In this work, we first establish an extrapolation model for deriving the intrinsic yield of the hydrogen peroxide on the basis of the thin-film of real catalyst particles. We expect that this extrapolation model could promote the analysis of oxygen reduction mechanism in a more accurate way and that applying the model into some model electrode system [27] may clarify some unknown points for the well known Pt/Co and Pt/Ni alloy catalysts, [5] as well as for particle size effects and inter-particle distance effects.

In characterizing a given nano-sized catalyst with complicated structure (for example, core-shell particles supported on some difficult-to-process material) realized by some unique technique or difficult process, it is quite challenging to study with a model electrode due to the difficulty in fabricating an equivalent catalyst. Thus, the thin-film electrode method in this work is clearly advantageous, because the real catalyst material can be evaluated as it is.

4. Conclusions

In the quantitative characterization of the reaction intermediates on electrocatalysts with the RRDE method, if further reactions of the intermediate occur before it reaches the ring, the yield of the intermediate derived from the conventional model, in which there is an underlying assumption that no further reaction occurs for the produced intermediate, tends to be underestimated and does not correctly reflect the intrinsic characteristics of the surfaces of the electrocatalysts. For a proper quantitative analysis, the probability for the further reactions of the desorbed intermediate should be taken into consideration.

By studying the formation of H_2O_2 in oxygen reduction on highly dispersed Pt/C thin-layer electrodes with various sample loadings, we first propose a quantitative model (Eq. (22)) to compensate for the re-adsorption + reaction of the desorbed H_2O_2 and to extrapolate the intrinsic yield of H_2O_2 on the surface of a given catalyst (shown in Eq. (23)). This model is based on the core concept that, if there are few active sites available (i.e., $n_{as} \rightarrow 0$, or ECSA $\rightarrow 0$, or zero loading) for the re-adsorption + reaction, nearly all of the desorbed reaction intermediate can escape from the disk without further consumption by its re-adsorption + reaction.

The high value obtained by extrapolation for the yield of hydrogen peroxide on Pt/C agrees well with that obtained at high rate of escape of the hydrogen peroxide on an ultramicro-electrode of a Pt single particle (50 nm in diameter) [26], on which we believe that the high rate of escape also ensures the desorbed H_2O_2 to survive with little re-adsorption + reaction on other active sites.

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