A Critical Assessment of $X_{H_2O_2}$ as a Figure of Merit for Oxygen Reduction Electro catalysts in Aqueous Electrolytes

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Certain aspects of the interpretation of rotating ring-disk electrode, RRDE, data for the oxygen reduction reaction, ORR, in aqueous electrolytes have been examined. In particular, the classical mechanism proposed by Damjanovic et al. [J. Chem. Phys. 45, 4057 (1966)] predicts that at a fixed potential, a plot of the ratio of the disk to the ring currents for the ORR vs $\omega^{-1/2}$, where $\omega$ is the rotation rate of the disk, should be linear. According to this analysis, the slope of this line is proportional to $k_1/X_{H_2O_2}$, where $k_1$ is the rate constant for the reduction of solution phase hydrogen peroxide, $H_2O_2(aq)$, and $X_{H_2O_2}$ is the fraction of the disk current that generates $H_2O_2(aq)$, the magnitude of which can be determined from the line intercept. Illustrations of this theoretical framework are provided for ORR data reported in the literature for experiments involving Pt-based electrodes and collected in our laboratories for Pt in aqueous acid solutions. Critically emphasized is the need to perform ring disk measurements at multiple rotations rates in order to determine reliable values of $X_{H_2O_2}$, which can be used as figures of merit for ranking the efficacy of ORR electrocatalysts.

The analysis presented in this section assumes, as originally proposed by Damjanovic et al., that the ORR proceeds either via a four-electron or a two-electron pathway generating $H_2O_2(aq)$, a species that can subsequently escape into the bulk electrolyte, or be further reduced via a two-electron process to yield water as the final product (see Scheme 1).

Where $I_i$ are the rates of the corresponding processes expressed as currents. On this basis, the molar fraction of $O_2$ that generates $H_2O_2(aq)$, denoted as $X_{H_2O_2}$, may be written as follows:

$$X_{H_2O_2} = \frac{2}{I_2N/I_1 + 1}$$

where $I_1$ is the ring current as measured with the ring polarized at a potential positive enough for $H_2O_2(aq)$ to be oxidized under strict diffusion limited control, and $N$ is the collection efficiency of the RRDE assembly. It thus follows from Eq. 1 that if $X_{H_2O_2} = 0$, the reaction proceeds strictly by a four-electron pathway, i.e. no $H_2O_2(aq)$ being detected by the ring, and if $X_{H_2O_2} = 1$, the ORR generates exclusively $H_2O_2(aq)$. As will be shown herein, reliable values of $X_{H_2O_2}$ cannot be obtained by performing measurements at a single rotation rate, a common practice in research published in the literature. In fact, the classical mechanism for the ORR predicts a linear relationship between the ratio of the disk and ring currents collected with a RRDE assembly, and the reciprocal of the square root of the rotation rate, $\omega$, from which one can in principle determine the rate constant for the reduction of $H_2O_2(aq)$ on the disk.

Experimental

Measurements were performed in an all-glass, three-compartment cell, filled with $O_2$-saturated (Air Gas) 0.1 M HClO4 solutions (75 ml) prepared from ultrapure perchloric acid (Ultrapure, EMD), and ultrapure, UHP water generated by a Barnstead system (18.3 MΩcm, EASYpureUV) containing 10 μM KBr (Fisher Scientific, IR grade, > 99%). Experiments were carried out using a polycrystalline Pt(poly)/Pt(poly) ring-disk electrode (Pine Instruments, disk diameter: 0.457 cm; ring inner diameter 0.493 cm; gap, G = 180 μm and ring outer diameter: 0.538 cm, or, correspondingly, disk and ring areas of 0.164 cm² and 0.037 cm², respectively, and a collection efficiency, N = 0.22) and a Pt wire and a reversible hydrogen electrode (RHE) as counter and reference electrodes, respectively. The disk and ring potentials, $E_{disk}$ and $E_{ring}$, respectively, were controlled with a bipotentiostat (Pine Instruments, Model AFTCPB1) and the rotation rate of the RRDE, $\omega$, adjusted with a commercial rotator (Pine Instruments, Model AFMSRX). All the data were recorded using a National Instruments acquisition card (USB-6009) programmed in Labview.

Theoretical Formalism

The symbols $I_1$ and $I_2$ in this equation represent the currents as specified in Scheme 1. In particular, if the disk electrode displays no activity for $H_2O_2(aq)$ reduction, i.e. $I_1 = 0$ in Scheme 1, $X_{H_2O_2}$ reduces to Eq. 1, where $I_2 = I_1 + I_2$ and $I_1 = I_2N$.

Yet another parameter often used to assess the activity of a given electrocatalyst for the ORR is $n_e$, also known as the selectivity defined as

$$n_e = \frac{4}{I_r/(I_2N) + 1}$$

which may be regarded as the effective number of electrons transferred per $O_2$ molecule, e.g. 4 or 2, depending on whether the process

$O_2 \xrightarrow{\frac{1}{2}} H_2O$

$O_2 \xrightarrow{\frac{1}{2}} H_2O_2 \xrightarrow{\frac{1}{2}} H_2O$

Scheme 1.

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generates exclusively water or H$_2$O$_2$(aq), respectively. Rather surprisingly, however, hardly any attempts have been made to determine the validity of the assumptions upon which Eq. 1 is based, casting doubts regarding the reliability of $X_{H_2O_2}$ calculated on such basis. This brief communication reexamines theoretical aspects of Scheme 1 to shed light into some of these issues.

As reported by Damjanovic et al., the currents in Scheme 1 are related by the following set of equations:

$$I_d = I_1 + I_2 + I_3 \quad [4]$$

$$I_2 = I_3 + I_4 \quad [5]$$

$$I_2 = I_1 / N \left(1 + 1.61 k_3 D_{H_2O_2}^{-2/3} v^{1/6} \omega^{-1/2}\right) \quad [6]$$

$$I_k = I_1 / N \quad [7]$$

where $k_3$ is the rate constant for the reduction of H$_2$O$_2$(aq) at the disk, assumed to be first order process, $D_{H_2O_2}$ is the diffusion coefficient of H$_2$O$_2$(aq), and $v$ the kinematic viscosity of the solution. These relationships allow a more general form of $X_{H_2O_2}$ to be derived, namely,

$$X_{H_2O_2} = \left(1 + 1.61 k_3 D_{H_2O_2}^{-2/3} v^{1/6} \omega^{-1/2}\right) \frac{2}{I_d N/I + 1} \quad [8]$$

which, as expected, reduces to Eq. 1 when $k_3 = 0$. This expression bears striking similarity to that proposed recently by Ke et al. to account for the ORR behavior of thin films of catalyst nanoparticles homogeneously distributed on the surface of a glassy carbon electrode for the ORR in 0.1 M HClO$_4$, namely,

$$X_{H_2O_2} = \frac{1}{1 - P_{re}} \times \frac{2}{2 N / I + 1} \quad [9]$$

As described by these authors, $P_{re}$ is an empirical parameter that relates to the percent of desorbed peroxide that can readorb and react on the disk to yield water as the final product, so that if there is no affinity of H$_2$O$_2$(aq) for sites of the electrode surface, Eq. 9 reduces to Eq. 1.

It thus follows from Eqs. 8 and 9 that in fact,

$$P_{re} = 1 - \frac{1}{1 + 1.61 k_3 D_{H_2O_2}^{-2/3} v^{1/6} \omega^{-1/2}} \quad [10]$$

A more useful relationship between the actual observables can be obtained by rearranging Eq. 8, i.e.

$$\frac{I_d}{I_r} = \left(\frac{3.22 k_3 D_{H_2O_2}^{-2/3} v^{1/6}}{X_{H_2O_2} N}\right) \omega^{-1/2} + \left(\frac{2 X_{H_2O_2}}{X_{H_2O_2} N} - \frac{1}{N}\right) \quad [11]$$

In particular, and provided the ORR follows strictly the mechanism in Scheme 1, this equation predicts that a plot of $I_d/I_r$ vs $\omega^{-1/2}$ would be linear, and that $X_{H_2O_2}$ and $k_3$ can, in principle, be determined from the intercept and the slope, $S$, of data collected at a fixed potential, $E$. Specifically, the slope would be zero, and thus independent of $\omega$ if $k_3 = 0$, and positive otherwise.

Recently, L. Zhang et al. attempted to address the same issues as those in this work by including explicitly the oxidation of H$_2$O$_2$(aq) in Scheme 1.

In their analysis, Zhang et al. assumed correctly at first that $I_d$ has four contributions as specified in Scheme 2 above; later in their work, however, they mistakenly rewrote $I_d$ as originating solely from the four-electron and two-electron pathways, namely,

$$\frac{4 I_d}{n_e} = 4 F \pi r^2 (k_1 + k_2) C^n_{H_2O_2} \quad [12]$$

where $n_e$ (denoted in their work simply as $n$) is the selectivity, which led to mathematical expressions of questionable validity. It must be stressed that Eq. 12 should not be confused with that reported by Antoine and Durand, namely,

$$\frac{4 I_d}{n_e} = I_1 + 2 I_2 \quad [13]$$

As these authors correctly stated in their paper, this expression only applies provided the series pathway is neglected, i.e. $k_3 = 0$, or is included in the four-electron disk current. Furthermore, a closer examination of Zhang et al.’s contribution revealed yet another error (cf. Eq. 15 in Ref. 7) which, when corrected, predicts $k_3 = k'_3$, an equality that would only be valid if both quantities were zero at all potentials.

In fact, a rigorous analysis of Scheme 2 may be shown to yield the following expressions for $X_{H_2O_2}$ and $I_d/I_r$:

$$X_{H_2O_2} = \frac{2 I_2}{I_1 + 2 I_2} = \frac{2 \left[1 + 1.61 (k_2 + k_3) D_{H_2O_2}^{-2/3} v^{1/6} \omega^{-1/2}\right]}{I_d N/I + 1 + 3.22 k_2 D_{H_2O_2}^{-2/3} v^{1/6} \omega^{-1/2}} \quad [14]$$

and

$$\frac{I_d}{I_r} = \frac{3.22 D_{H_2O_2}^{-2/3} v^{1/6}}{X_{H_2O_2} N} \left[rac{k_2 (1 - X_{H_2O_2}) + k_3}{X_{H_2O_2} N} \right] \omega^{-1/2} + \frac{1}{N} \left[\frac{2}{X_{H_2O_2}} - 1\right] \quad [15]$$

where $k_3$ represents the rate constant for the reduction of H$_2$O$_2$(aq), assumed to be a first-order process. Hence, for high overpotentials for H$_2$O$_2$(aq) reduction, $k_3 \gg k_2$, and Eqs. 14 and 15 correctly reduce to Eqs. 8 and 11 above.

From a general perspective, the vast majority of papers published over the past two decades have reported values of $X_{H_2O_2}$ in 1–5, 10, 11, 15, 16 as defined in Eqs. 1 and 3, respectively, either at a single, or at multiple rotation rates, but failed to perform the required tests to assess the validity of the assumptions upon which their mathematical expressions are based.

Consider, for example, the dynamic polarization curves reported by Stamenkovic et al. (cf. Fig. 2) for the ORR on a sputtered Pt/Ni disk electrode of a P|Pt|PtNi RRDE (N = 0.2) in 0.1 M HClO$_4$. These data were recorded for several values of $\omega$, while the disk potential, $E_{disk}$, was being scanned at a rate $\nu = 50$ mV/s toward positive values and the ring was polarized at a potential, $E_{ring}$, positive enough for the oxidation of H$_2$O$_2$(aq) to proceed under diffusion-limited conditions. Shown in Fig. 1 is a plot of $I_d/I_r$ vs $E_{disk}$ using $I_r$ vs $E_{disk}$ results for the two values of $\omega$ reported by these authors, i.e. 1600 and 2500 rpm. Although $I_d/I_r$ over the range 0.075 V $\leq E_{disk} \leq 0.23$ V were found to be quite similar, the corresponding values positive to this range were quite different. This latter behavior indicates that the main assumption upon which their reported values of $X_{H_2O_2}$ were calculated (also provided in Fig. 2 in their work) i.e. no reduction of solution phase H$_2$O$_2$(aq), was not fulfilled. In fact, the values of $X_{H_2O_2}$ determined from their $I_d$ and $I_r$ data using Eq. 1 appear to be inconsistent with those in their figure.

Yet another illustration of the formalism herein developed is provided by dynamic polarization data recorded in this laboratory at a scan rate $\nu = 10$ mV/s for the Pt(poly) disk of a Pt/Pt RRDE in O$_2$-saturated 0.1 M HClO$_4$ containing 10 $\mu$M KBr at various rotation rates (see Fig. 2). Also included in this figure are the corresponding

Scheme 2.

$$O_2 \xrightarrow{h} H_2O$$

$$O_2 \xrightarrow{h} H_2O_2(aq) \xrightarrow{h} H_2O$$

$$\text{solution}$$

where $n_e$ (denoted in their work simply as $n$) is the selectivity, which led to mathematical expressions of questionable validity. It must be

ring currents recorded simultaneously with the ring polarized at \( E_{\text{ring}} = 1.4 \text{ V vs RHE} \) (Panel B). The data in Panels A and B can then be used to generate plots of \( I_d/I_r \) vs \( E_{\text{disk}} \), which, as shown in Panel C in this figure, where in this case the contributions to \( I_r \) derived from the oxidation of bromide and other sources were subtracted (see Appendix A for details). As evidenced from these data, \( I_d/I_r \) was found to be virtually independent of \( E_{\text{disk}} \) over the range \( 0.37 < E_{\text{disk}} < 0.63 \text{ V vs RHE} \). Hence, according to the model herein developed, the bromide-modified surface in this potential region is not active for the direct reduction of \( \text{H}_2\text{O}_2(aq) \), Strong support for this conclusion was obtained from dynamic polarization curves recorded in Ar-purged 1 mM \( \text{H}_2\text{O}_2 \) solutions in the same electrolyte for the Pt(poly) disk of the RRDE assembly (see Fig. 4), for which the very small reduction currents observed in the range \( 0.4 < E_{\text{disk}} < 0.8 \text{ V vs RHE} \), were found to be independent of \( \omega \), i.e. strict kinetic control. Also included in this figure for comparison (see thick line, right ordinate) are data collected at \( \omega = 400 \text{ rpm} \) in the same solution devoid of bromide to underscore the marked reduction in the electrocatalytic activity of Pt(poly) induced by the adsorbed halide.  

Plots of \( I_d/I_r \) vs \( \omega^{-1/2} \) over the same range (see Fig. 3) were found to be linear with an average intercept of ca. 19.5, which based on Eq. 8 would yield a value of \( X_{\text{H}_2\text{O}_2} \) ca. 0.38. However, no clear correlations were found between \( I_d/I_r \) and \( \omega^{-1/2} \) for \( E_{\text{disk}} < 0.4 \text{ V vs RHE} \) affording strong evidence that Scheme 1 is not be operative in this potential range and, therefore, it becomes very difficult to extract values for \( k_3 \) based on this methodology (In fact, it might be much easier and far more reliable to simply determine this parameter from measurements performed in deaerated \( \text{H}_2\text{O}_2 \) solution in the same electrolyte.). This may not be surprising, as it is precisely in this region where bromide desorbs and hydrogen adsorbs introducing complexities in the overall mechanism of the ORR.

**Figure 1.** Plots of \( I_d/I_r \) vs \( E_{\text{disk}} \) based on the data reported by Stamenkovic et al. for a sputtered Pt\(_3\)Ni disk electrode of a Pt\(|Pt_3\)Ni RRDE collected at two different rotation rates as indicated.  

**Figure 2.** Panel A. Dynamic polarization curves recorded at a scan rate \( \nu = 10 \text{ mV/s} \) with the Pt(poly) disk of a Pt(poly)|Pt(poly) RRDE in O\(_2\)-saturated 0.1 M HClO\(_4\) solutions containing 10 \( \mu \text{M} \) KBr at various values of \( \omega \), as indicated. Panel B. Ring currents collected while the disk data in Panel A was being collected, with the ring polarized at \( E_{\text{ring}} = 1.4 \text{ V vs RHE} \). Panel C. Plots of \( I_d/I_r \), based on the data in Panels A and B in this figure, after correction for residual current contributions.

**Figure 3.** Plot of \( I_d/I_r \) vs \( \omega^{-1/2} \) based on the data in Panel C in Fig. 2, for the specified values of \( E_{\text{disk}} \), where the solid lines were obtained by a linear fit of the experimental data.

**Figure 4.** Dynamic polarization curves recorded at \( \nu = 10 \text{ mV/s} \) for the reduction of 1 mM H\(_2\text{O}_2\) in 10 \( \mu \text{M} \) KBr in Ar-purged 0.1 M HClO\(_4\) on the Pt(poly) disk of the Pt(poly) RRDE at various rotation rates as indicated. The thick curve was obtained in the same solution devoid of bromide at \( \omega = 400 \text{ rpm} \).
Figure A1. Plot of the average values of the measured ring currents, $i_{\text{ring}}$ vs $\omega^{1/2}$ based on data collected with the Pt|Pt RRDE under the conditions specified in the main text.

In conclusion, the classical mechanism proposed decades ago by Damjanovic et al. for the ORR predicts a linear relationship between the ratio of the disk and ring currents collected with a RRDE assembly, and the reciprocal of the square root of the rotation rate, $\omega$. The formalism presented in this work makes it possible to extract from the intercept of these lines, the fraction of the disk current associated with the generation of H$_2$O$_2$(aq), a figure of merit defined as $X_{\text{H}_2\text{O}_2}$, which can then be used to determine the rate constant for the reduction of H$_2$O$_2$(aq) on the disk. On this basis, reliable values of $X_{\text{H}_2\text{O}_2}$ cannot be obtained by performing measurements at a single rotation rate, a common practice in research published in the literature.

Appendix A

Shown in Fig. A1 is a plot of $i_{\text{lim}}^{\text{ring}}$ vs $\omega^{1/2}$ based on the original data RRDE collected with the Pt$|$Pt electrode under the experimental conditions specified in the main text. The actual $i_{\text{ring}}$ values in this graph represent averages for $E_{\text{disk}} >$ ca. 0.98 V. A linear fit to these data (see solid line) yielded a slope $S = 0.1 \mu\text{A/s}^{1/2}$, within 3% from that predicted from the diffusion limiting current for the oxidation of bromide on a ring electrode, i.e. $S = 0.62nF \pi(\text{r}_d^3 - \text{r}_r^3)^{1/2}D_{\text{Br}^-}^{1/3} \frac{\nu - 1}{6} C_{\text{bulk}}^{\text{Br}^-}$, assuming a value of $D_{\text{Br}^-} = 2.7 \times 10^{-5} \text{cm}^2/\text{s}$ determined independently in this laboratory. Moreover, the value of the intercept was ca. 0.66 $\mu$A and thus very close to that observed in the absence of bromide in solution and can thus be attributed to an instrumental artifact.

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