A mechanistic model is herein presented for the reduction of H$_2$O$_2$(aq) in aqueous electrolytes on a rotating disk electrode that considers the possible heterogeneous dismutation of H$_2$O$_2$(aq). A theoretical analysis of this model predicts Koutecky-Levich plots that deviate from linearity at high rotation rates depending on the relative values of the rates constants of the processes involved, in agreement with the behavior found for a variety of electrode materials.© The Author(s) 2016. Published by ECS. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, http://creativecommons.org/licenses/by/4.0/), which permits unrestricted reuse of the work in any medium, provided the original work is properly cited. [DOI: 10.1149/2.0211608jes] All rights reserved.

Manuscript received April 22, 2016. Published May 17, 2016.

The search for inexpensive, non-noble-metal-based electrocatalysts for the oxygen reduction reaction (ORR) has ignited renewed interest in the study of the redox properties of hydrogen peroxide, H$_2$O$_2$, in aqueous electrolytes. As is well known, solution-phase H$_2$O$_2$ is often found to be an intermediate in the ORR, leading to losses in the operational voltage of hydrogen/oxygen fuel cells and also to the progressive degradation of proton-exchange membranes. Despite considerable efforts, certain aspects of the reduction of H$_2$O$_2$(aq) have not as yet been fully elucidated. In particular, no satisfactory explanation has as yet been given for the non-linear behavior of Koutecky-Levich (KL) plots found for this reaction, 1−7 although the possible involvement of a heterogeneous dismutation of H$_2$O$_2$ has indeed been raised. 8 This brief communication presents a theoretical model that considers explicitly such possibility, and predicts that the direction and extent of the bending depends critically on the values of the rate constants associated with all the processes involved.

**Theoretical**

The mechanistic pathways for H$_2$O$_2$(aq) reduction to be considered herein (see Scheme 1) 9−10 assumes that none of the species involved displays any affinity for the electrode surface, i.e. the possible role of adsorbed reaction intermediates is fully neglected. As shown in the scheme, H$_2$O$_2$(aq) present in a region immediately adjacent to the electrode surface, denoted as H$_2$O$_2^\text{*}$(aq), can be reduced via a two-electron process to yield water, i.e. 2e$^-$ + H$_2$O$_2$ → 2H$_2$O. In addition, H$_2$O$_2^\text{*}$(aq) can undergo a surface-catalyzed disproportionation generating water and O$_2$(aq), i.e. 2H$_2$O$_2$ → 2H$_2$O + O$_2$, which, in turn, can be reduced, regenerating H$_2$O$_2^\text{*}$(aq) via a two-electron process, i.e. 2e$^-$ + O$_2$ → H$_2$O$_2$, or producing water via a four-electron reaction, i.e. 4e$^-$ + O$_2$ → 2H$_2$O. Also specified in the scheme are the rate constants associated with each of processes involved, as well as the mass transport contributions, denoted as (D/δ)$_j$, j = H$_2$O$_2$(aq) and O$_2$(aq), where D$_j$ is the diffusion coefficient of species j, δ = 1.61(D$^{2/3}$η$^{-1/3}$)$^{1/6}$, the diffusion boundary layer thickness, η, the kinematic viscosity of the solution, and the superscript ∞ refers to the bulk concentration. On this basis, and assuming all of the reactions are first order in the reactant, as assumed originally by Bagotskii et al., 9 the mass balances for O$_2^\text{*}$(aq) and H$_2$O$_2^\text{*}$(aq) can be shown to be given by:

\[
\text{ki}[\text{H}_2\text{O}_2(aq)]^\infty = [O_2(aq)]^\infty (k_1 + k_2 + (D/\delta)_{O_2}) \tag{1}
\]

and

\[
\text{ki}[O_2(aq)]^\infty + ([H_2O_2(aq)]^\infty - [H_2O_2(aq)]^\text{*}) (D/\delta)_{H_2O_2} = (k_1 + 2k_2)[H_2O_2(aq)]^\text{*} \tag{2}
\]

respectively, from which explicit expressions for O$_2^\text{*}$(aq) and H$_2$O$_2^\text{*}$(aq), can be derived, namely,

\[
[O_2(aq)]^\infty = \frac{k_1(D/\delta)_{O_2}[\text{H}_2\text{O}_2(aq)]^\infty}{(k_1 + k_2 + (D/\delta)_{O_2})(k_3 + 2k_d + (D/\delta)_{H_2O_2}) - k_2k_d} \tag{3}
\]

\[
[H_2O_2(aq)]^\infty = \frac{(k_1 + k_2 + (D/\delta)_{O_2})(D/\delta)_{H_2O_2}[\text{H}_2\text{O}_2(aq)]^\infty}{(k_1 + k_2 + (D/\delta)_{O_2})(k_3 + 2k_d + (D/\delta)_{H_2O_2}) - k_2k_d} \tag{4}
\]

The current density, i, will be given by the sum of the three electrochemical processes in Scheme 1, i.e.

\[
i = F \left[ 4k_1[O_2(aq)]^\infty + 2k_2[O_2(aq)]^\text{*} + 2k_3[H_2O_2(aq)]^\text{*} \right] \tag{5}
\]

where F is Faraday’s constant. Substituting Eqs. 3 and 4 into Eq. 5, the reciprocal current density can be expressed as:

\[
\frac{1}{i} = \frac{1}{2F[H_2O_2(aq)]^\infty} \left[ \frac{1}{(D/\delta)_{H_2O_2}} + \frac{2(D_{O_2}/D_{H_2O_2})^{2/3} + (k_1 + k_2 + (D/\delta)_{O_2})/k_4}{(2k_1 + k_2 + k_3)[k_1 + k_2 + (D/\delta)_{O_2}] / k_d} \right] \tag{6}
\]

As expected, for k$_1$ = 0, i.e. no H$_2$O$_2^\text{*}$(aq) dismutation, Eq. 6 will reduce to a conventional Koutecky-Levich (KL) expression for the two-electron reduction of H$_2$O$_2$(aq) proceeding at a rate proportional to k$_1$:

\[
\frac{1}{i_{k_1 \to 0}} = \frac{1}{2F[H_2O_2(aq)]^\infty} \left( \frac{(D/\delta)_{H_2O_2}}{2F[H_2O_2(aq)]^\infty} + \frac{2F[H_2O_2(aq)]^\infty}{k_1} \right) \tag{7}
\]

\[
\text{Scheme 1. Reaction pathways for the reduction of H}_2\text{O}_2\text{(aq) considered in this work, where k}_1\text{ is rate constant for the reduction of oxygen to water, k}_2\text{ and k}_3\text{ are the rate constants for the reduction of solution phase oxygen, O}_2\text{(aq), to solution phase peroxide, H}_2\text{O}_2\text{(aq), and water, respectively, k}_d\text{ is the first-order rate constant for the catalytic disproportionation of H}_2\text{O}_2\text{(aq), and b}_j\text{ is the diffusion boundary layer thickness for species } j = H_2O_2\text{ and O}_2\text{. The symbols } s\text{ and } \infty \text{ represent the region immediately adjacent to the electrode surface and bulk, respectively. We recognize that one or more steps in the mechanism, that involve the transfer of multiple electrons, may be more complex, and, thus, that the first order rate constants would be of a global character.}
\]
terms of a dimensionless parameter $\gamma$ in Panel A, Fig. 1 are a series of $1/i$ vs. the sum of the rate constants for O$_2$(aq) reduction to peroxide and same slope as that in Eq. 7 and an intercept inversely proportional to recorded at a potential $E \approx 0.45$ V vs. RHE (cf. Fig. 3 in Ref. 12). Shown in Panel A, Fig. 1 are a series of $1/i$ vs. $\omega^{-1/2}$ (KL) plots for various $k_d$ based on the parameters provided in the legend, and for values of $D_{O_2}, D_{H_2O_2}$ and $v$ listed in the caption. As clearly evident from these results, the curves obtained for intermediate values of $k_d$ were found to bend upward as $\omega$ increased approaching the limit predicted by Eq. 7 for $k_d \rightarrow 0$ (see gray dashed line).

A more detailed mathematical analysis of Eq. 6 reveals that the bending direction of the KL plots or, equivalently, the sign of their first derivative with respect to $\omega^{-1/2}$ in the limit as $\omega \rightarrow \infty$, is governed by the difference between the limiting values of the reciprocal current densities in Eqs. 7 and 8, which can be conveniently expressed in terms of a dimensionless parameter $\gamma$, defined as:

$$\gamma = \ln \left( \frac{1}{k_3} \frac{2(D_{O_2}/D_{H_2O_2})^{2/3}}{(2k_1 + k_2)} \right)$$

$$= \ln \left( \frac{D_{H_2O_2}}{D_{O_2}} \right)^{2/3} \frac{(2k_1 + k_2)}{2k_3}$$

In particular, $\gamma > 0$ if $(2k_1 + k_2)/D_{H_2O_2} > 2k_3/D_{O_2}^{2/3}$, whereas $\gamma < 0$ if $(2k_1 + k_2)/D_{H_2O_2} < 2k_3/D_{O_2}^{2/3}$. In other words (and ignoring the rather small differences in the values of $D_{H_2O_2}$ and $D_{O_2}$), if the rates of oxygen reduction, regardless of the mechanism involved, are larger than the corresponding rates of peroxide reduction, $\gamma$ would be positive, whereas should the opposite be the case, $\gamma$ would be negative. The latter is illustrated in Panel B, Fig. 1, for the set of (fictitious) parameters specified in the legend for which $\gamma$ is the same as in Panel A, but of opposite sign.

In yet another paper, Amirfakhri et al. examined the reduction of H$_2$O$_2$(aq) on metal-free nitrogen-doped graphene nanoflake electrodes in unbuffered 0.1 M Na$_2$SO$_4$ aqueous solutions and found KL plots bending downward (see scattered symbols in Fig. 2 below), where the solid lines are linear fits to the data in the original paper). As indicated, the experimental data displays a curvature which according to our analysis, is consistent with a rate for peroxide reduction that exceeds that of oxygen reduction, i.e. $\gamma < 0$. Assuming, for simplicity, a value of $k_1 = 0$, i.e. total neglect of a four-electron reduction of oxygen to water, a potential independent two-electron reduction of oxygen to peroxide, and a constant value of $k_d$, the best fits to the data based on our model (see Eq. 5; solid lines in Fig. 2), yielded values of $k_2 = 0.0016$ cm/s, and $k_3 = 0.25$ cm/s, which reproduce the curvature observed in the experimental results for all rotation rates, except perhaps the lowest one for the most negative voltage. It should be emphasized that for large $\omega$ our model provides a much better fit than their linear analogue (dotted lines in Fig. 2).

Also included in this report was a thorough theoretical analysis of mechanistic aspects of H$_2$O$_2$(aq) reduction using a similar approach to that employed in this work yielding expressions (cf. Eqs. 13 and 14 in Ref. 1) equivalent to those in Eq. 6. However, the model considered therein assumed that the O$_2$ generated from H$_2$O$_2$(aq) dismutation remained adsorbed on the surface undergoing a subsequent irreversible desorption, which led them to conclude that KL plots would always be linear, a fact that is not supported by their own measurements. These contradictory results stem from their neglect of the mass transport contribution associated with the O$_2$(aq) and thus its dependence on $\omega$.

Summary

The theoretical analysis herein presented has shown that the curvature of Koutecky-Levich plots observed for the reduction of H$_2$O$_2$(aq) in aqueous electrolytes reported in the literature can be accounted for by including the heterogeneous dismutation of H$_2$O$_2$(aq), whereby the direction of the bending depends critically on the values of the rates of the processes involved. On this basis, caution must be exercised when forcing a linear fit to such plots, as the slope and intercept could not be interpreted in the conventional way, and thus yield unreliable results.

Figure 1. Koutecky-Levich plots generated using Eq. 6 for various values of the rate constants for which $\gamma = 2.045$ (Panel A) and $\gamma = -2.045$ (Panel B), assuming $D_{O_2} = 1.3 \times 10^{-5}$ cm$^2$/s and $D_{H_2O_2} = 1.9 \times 10^{-5}$ cm$^2$/s and $v = 0.01$ cm$^2$/s.

Figure 2. Koutecky-Levich plots reproduced from the data reported by Amirfakhri et al. (see scattered symbols) and fits according to our analysis (solid lines). The dotted lines are linear fits provided in Ref. 1. See text for additional details.
values for the rate constants for H$_2$O$_2$(aq) reduction. One possible means of avoiding this problem is by measuring the rate constant for the heterogeneous dismutation of H$_2$O$_2$(aq) under the same identical conditions as those employed in the electrochemical experiments and include those in the mechanistic analysis.

Acknowledgments

This work was supported by a grant from NSF, CHE-1412060.

References

1. S. J. Amirfakhri, J.-L. Meunier, and D. Berk, *Electrochim. Acta*, **114**, 551 (2013).
2. S. J. Amirfakhri, P.-A. Pascone, J.-L. Meunier, and D. Berk, *J. Catal.*, **323**, 55 (2015).
3. S. J. Amirfakhri, J.-L. Meunier, and D. Berk, *J. Power Sources*, **272**, 248 (2014).
4. N. Labat-Allietta and D. R. Thevenot, *Biosens. Bioelectron.*, **13**, 19 (1998).
5. Y. Okawa, N. Yokoyama, Y. Sakai, and F. Shiba, *Anal. Chem. Res.*, **5**, 1 (2015).
6. R. C. Pena, J. C. M. Gambra, M. Bertotti, and T. R. L. C. Paixao, *Int. J. Electrochem. Sci.*, **6**, 394 (2011).
7. K. L. Stewart and A. A. Gewirth, *Langmuir*, **23**, 9911 (2007).
8. E. R. Vago and E. J. Calvo, *J. Electroanal. Chem.*, **339**, 41 (1992).
9. V. S. Bagotskii, V. Y. Filinovskii, and N. A. Shumilova, *Elektrokhim.*, **4**, 1247 (1968).
10. K. L. Hsueh, D. T. Chin, and S. Srinivasan, *J. Electroanal. Chem. Interfacial Electrochem.*, **153**, 79 (1983).
11. A. Mudhukrishnan, Y. Nabae, T. Okajima, and T. Ohsaka, *ACS Catal.*, **5**, 5194 (2015).
12. N. Uehara, A. Ishihara, T. Nagai, M. Matsumoto, H. Imai, Y. Kohno, K. Matsuzawa, S. Mitsushima, and K. Ota, *Electrochim. Acta*, **182**, 789 (2015).
Erratum: Communication—Hydrogen Peroxide Reduction in Aqueous Electrolytes: Influence of a Heterogeneous Decomposition Step [J. Electrochem. Soc., 163, H630 (2016)]

Nicholas S. Georgescu and Daniel A. Scherson

Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106-7078, USA

© 2017 The Electrochemical Society. [DOI: 10.1149/2.0401706jes] All rights reserved. Published March 15, 2017.

The diffusion coefficients of peroxide, \( D_{H_2O_2} \), and oxygen, \( D_{O_2} \), were accidentally interchanged when calculating the data shown in Fig. 1. The correct values are \( D_{O_2} = 1.9 \times 10^{-5} \text{ cm}^2/\text{s} \) and \( D_{H_2O_2} = 1.3 \times 10^{-5} \text{ cm}^2/\text{s} \). These values have been used to generate a new Fig. 1 as shown here, which is in qualitative agreement with those reported in the original paper and, as such, do not affect the conclusions drawn from the analysis provided therein. Note that Fig. 2 was obtained using the correct diffusion coefficients for the species in question and therefore was not compromised by the error noted.

---

**Figure 1.** Koutecky-Levich plots generated using Eq. 6 for various values of the rate constants for which \( \gamma = 1.54 \) (Panel A) and \( \gamma = -1.54 \) (Panel B), assuming \( D_{O_2} = 1.9 \times 10^{-5} \text{ cm}^2/\text{s} \) and \( D_{H_2O_2} = 1.3 \times 10^{-5} \text{ cm}^2/\text{s} \) and \( \nu = 0.01 \text{ cm}^2/\text{s} \).