Recently, Zhou et al. reported an ingenious method for detecting solution phase superoxide ion $O_2^−(aq)$ generated by the oxygen reduction reaction, ORR, on the surface of a polycrystalline Pt microelectrode, $\mu$-Pt(poly), in an aqueous electrolyte. The specific strategy employed relies on the use of a nanoneedle filled with an $O_2$-saturated benzotrifluoride, BTF, solution, an electrolyte immiscible with water, immersed in the aqueous solution, with its tip placed nanometers away from the $\mu$-Pt(poly) surface. This arrangement made it possible to measure the current associated with the migration of $O_2^→(aq)$, a relatively short-lived species, across the liquid-liquid interface. Based on their proposed mathematical model, the half-life of $O_2^→(aq)$ in the aqueous solution was estimated to be on the order of μs, and thus much shorter than well-accepted values published in the literature.

This communication provides evidence obtained from measurements performed with a Pt(poly)/Pt(poly) rotating ring-disk electrode, RRDE, that BTF can dissolve in the aqueous phase and undergo subsequent adsorption on the Pt surface. As evidenced by data collected with a Pt/Pt rotating ring disk electrode, this effect induces significant changes in the kinetics and mechanism associated with the ORR on the otherwise bare electrode, a factor that might limit the overall utility of this tactic as a reliable tool for elucidating detailed pathways involved in this important redox process. Also included in this communication is a mathematical model that allows for the concentration of $O_2^→(aq)$ next to the disk of a RRDE to be determined during the ORR based on the magnitude of the current collected with a Au ring specifically functionalized to detect exclusively $O_2^→(aq)$, using data reported earlier in our laboratories for a glassy carbon disk electrode and a model system.

Results and Discussion

Voltammetric measurements in Ar-purged solutions.—Shown in Panel A, Fig. 1, are cyclic voltammetric curves collected with the disk of the Pt/Pt RRDE in Ar-purged 0.1 M Na$_2$SO$_4$ (J. T. Baker, 99.9%) and ultrapure water (UPW, 18.3 MΩ cm, EASYpure UV system, Barnstead) yielding a pH of ca. 5.5. Oxygen (Airgas, 99.99% research grade), and hydrogen peroxide (Fisher Scientific, certified ACS, 31.5%) were used as received. A gold wire (ca. 5 cm$^2$ area) and a Ag/AgCl (3.5 M KCl) were used as counter and reference electrodes, respectively. In order to mimick the conditions of the original experiments reported by Zhou et al., an amount of BTF (Sigma Aldrich, anhydrous 99.9%) just sufficient to yield, upon full dissolution, a concentration of 100 ppm (0.68 mM), and thus below the solubility limit of BTF in pure water, i.e. 451 ppm (3.1 mM) at 25°C, was added to the 0.1 M Na$_2$SO$_4$ aqueous solution in which the electrochemical measurements were performed. As one might have expected based on the lack of miscibility with water and its higher density, ca. 1.19 g/cm$^3$ at 20°C, most of the BTF fell to the bottom of the cell forming a droplet. The actual concentration of BTF in the aqueous phase was then determined from standardized UV visible spectra recorded with a Cary 50 spectrophotometer using BTF solutions in 0.1 M Na$_2$SO$_4$ of concentrations in the range 0.04 to 0.33 mM, yielding a value of 0.23 mM (see Fig. S1 in the Supplementary Material). For these spectroscopic measurements, a homogeneous 0.33 mM BTF in 0.1M Na$_2$SO$_4$ stock solution was prepared by brief ultrasonic agitation. Additional experiments were also carried using Na$_2$SO$_4$ (Fisher, 99% + purity) to examine the role of a lower quality chemical on the electrochemical results.

Experimental

All measurements were carried out using a Pt(poly)/Pt(poly) ring-disk electrode (RRDE, Pine Instruments, Model AFE7/88PTPF, disk diameter: 0.457 cm; ring inner diameter 0.493 cm; ring outer diameter: 0.538 cm, yielding a theoretical collection efficiency, N = 0.22). The disk and ring potentials, $E_{\text{disk}}$ and $E_{\text{ring}}$, respectively, were controlled with a bipotentiostat (Pine Instruments, Model AFCBP1), 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.

unless otherwise specified, all experiments were performed in Ar (Airgas, PP300, 99.998%)-purged 0.1 M Na$_2$SO$_4$ prepared from Na$_2$SO$_4$ (J. T. Baker, 99.9%) and ultrapure water (UPW, 18.3 MΩ cm, EASYpure UV system, Barnstead) yielding a pH of ca. 5.5. Oxygen (Airgas, 99.999% research grade), and hydrogen peroxide (Fisher Scientific, certified ACS, 31.5%) were used as received. A gold wire (ca. 5 cm$^2$ area) and a Ag/AgCl (3.5 M KCl) were used as counter and reference electrodes, respectively. In order to mimic the conditions of the original experiments reported by Zhou et al., an amount of BTF (Sigma Aldrich, anhydrous 99.9%) just sufficient to yield, upon full dissolution, a concentration of 100 ppm (0.68 mM), and thus below the solubility limit of BTF in pure water, i.e. 451 ppm (3.1 mM) at 25°C, was added to the 0.1 M Na$_2$SO$_4$ aqueous solution in which the electrochemical measurements were performed. As one might have expected based on the lack of miscibility with water and its higher density, ca. 1.19 g/cm$^3$ at 20°C, most of the BTF fell to the bottom of the cell forming a droplet. The actual concentration of BTF in the aqueous phase was then determined from standardized UV visible spectra recorded with a Cary 50 spectrophotometer using BTF solutions in 0.1 M Na$_2$SO$_4$ of concentrations in the range 0.04 to 0.33 mM, yielding a value of 0.23 mM (see Fig. S1 in the Supplementary Material). For these spectroscopic measurements, a homogeneous 0.33 mM BTF in 0.1M Na$_2$SO$_4$ stock solution was prepared by brief ultrasonic agitation. Additional experiments were also carried using Na$_2$SO$_4$ (Fisher, 99% + purity) to examine the role of a lower quality chemical on the electrochemical results.

Certain aspects of the nanoelectrochemical method reported by Zhou et al. (J. Am. Chem. Soc., 137, 6517 (2015)) for the detection of solution phase superoxide, $O_2^→(aq)$, generated by the oxygen reduction reaction, ORR, on polycrystalline Pt in aqueous electrolytes, have been critically assessed. Experiments performed under conditions similar to those employed by these authors have shown that upon formation of the liquid-liquid interface, as required by this technique, benzotrifluoride, BTF, undergoes partial dissolution into the aqueous phase and subsequent adsorption on the Pt electrode. As evidenced by data collected with a Pt/Pt rotating ring disk electrode, this effect induces significant changes in the kinetics and mechanism associated with the ORR on the otherwise bare electrode, a factor that might limit the overall utility of this tactic as a reliable tool for elucidating detailed pathways involved in this important redox process. Also included in this communication is a mathematical model that allows for the concentration of $O_2^→(aq)$ next to the disk of a RRDE to be determined during the ORR based on the magnitude of the current collected with a Au ring specifically functionalized to detect exclusively $O_2^→(aq)$, using data reported earlier in our laboratories for a glassy carbon disk electrode and a model system. © The Author(s) 2017. 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: 10.1149/2.0241704jes] All rights reserved.
Figure 1. Panel A. Cyclic voltammetric curves collected with the disk of the Pt/Pt RRDE in 0.1 M Na₂SO₄ at a scan rate ν = 10 mV/s under stagnant conditions over two different potential ranges (blue and black) as indicated. The curve in red was collected under otherwise the same conditions following addition of an equivalent of 100 ppm BTF (0.68 mM). Panel B. Same as Panel A with the electrode rotating at ω = 900 rpm, where the dotted lines were used as a background for determining the extent of blockage induced by adsorbed BTF.

**Figure 2.** First (initial potential E = 0.0 V, red) and subsequent cyclic voltammetric curve (blue) collected with the disk of a Pt/Pt RRDE in 0.1 M Na₂SO₄ after addition of 100 ppm BTF (0.68 mM) recorded at ν = 10 mV/s and ω = 900 rpm.

Oxygen reduction.—Insight into kinetic and mechanistic changes induced by the presence of BTF in solution was obtained from rotating Pt/Pt ring-disk experiments performed in 0.1 M Na₂SO₄ (J. T. Baker) in which the ring was polarized at E_{ring} = 0.7 V, i.e. positive enough for the oxidation of solution phase H₂O₂ to proceed under diffusion limited conditions (see Figure S3 in the Supplementary Material). Shown in Panel A, Figure 3, are dynamic polarization curves recorded at ν = 10 mV/s with the Pt disk of the Pt/Pt RRDE in O₂-saturated 0.1 M Na₂SO₄ (Baker) at different rotation rates, before (magenta) and after addition of an equivalent of 100 ppm BTF (blue), where the arrow represents the direction of the potential scans. The corresponding ring currents collected at ω = 1200 rpm, while the potential of the disk was being scanned, are given in Panel B in the same figure. Although no major changes in the diffusion limited currents nor in the onset potential for the ORR could be discerned between the two sets of data, the presence of the surfactant gave rise to two significant effects:

i. A shift in the half-wave potential, E_{1/2}, toward negative potentials as large as 35 mV (see Table I, for 900 rpm) indicative of losses in activity due to the presence of the organic adsorbate. These shifts were even larger when a lower quality Na₂SO₄ (Fisher, 99%+) was used (see values in parenthesis in Table I) and perhaps more pronounced in the even lower quality Na₂SO₄ (Sigma-Aldrich, ≥98% purity) employed in Ref. 1.

ii. An increase in the amount of H₂O₂(aq) and/or O₂ detected by the Pt ring by a factor of two over almost the entire potential range.
examined, which embraces the value at which the measurements reported by Zhou et al. were performed, i.e. −0.5 V vs Ag/AgCl, that in our case, corresponds to the potential at which the current reaches diffusion limited control, i.e. −0.3 V.

Yet another problematic aspect of the work Zhou et al. relates to the values of the life time of $O_2^−$ extracted from mathematical simulations reported in that work, which are orders of magnitude shorter than those widely accepted in the literature for conditions similar to those employed in their experiments.\(^2\) This issue was investigated in this work by analyzing rotating ring-disk data collected with a GC disk and a judiciously modified Au ring displaying high specificity to solution phase $O_2$ (aq) reported in detail in an earlier publication,\(^3\) to be described in what follows.

Although the reasons for the large discrepancy between the values reported by Zhou et al.\(^1\) and those widely accepted in the literature still remain unexplained, the fact that they assumed the disproportionation of $O_2^−$ to be a pseudo first order, as opposed to a second order reaction as experiments have shown,\(^2\) may have been a contributing factor. As is well known, the half-life for a second order reaction depends on the initial concentration of the reactant, whereas for a first order analogue it does not.

### Table I. Half-wave potentials, $E_{1/2}$, for the ORR on Pt in buffered aqueous 0.1 M Na$_2$SO$_4$ (J.T Baker and Fisher) before and after adding BTF at different rotation rates based on Fig. 3.

| $\omega$, rpm | 400 | 900 | 1200 | 1600 |
|--------------|-----|-----|------|------|
| $E_{1/2}$, mV vs Ag/AgCl | −26(−133)\(^*\) | −48(−180) | −70(−175) | −88(−181) |
| neat         |     |     |      |      |
| adding BTF   | −51(−161) | −83(−196) | −100(−236) | −106(−250) |

* The values in parenthesis were found with Na$_2$SO$_4$ (Fisher).

### Table II. Boundaries and Boundary Conditions.

| Boundary | Description | Boundary Condition |
|----------|-------------|--------------------|
| 1        | Center Axis | Axis of Symmetry   |
| 2        | Disk Electrode | $[O_2^-] = [O_2^−]$ disk |
| 3        | Bulk         | Inflow; $[O_2^-]_{disk} = 0$ |
| 4        | Insulator    | No Flux            |
| 5        | Ring         | $[O_2^-] = 0$      |
| 6        | Insulator    | No Flux            |
| 7        | Outflow      | Outflow            |

An alternate method for detecting $O_2^−$ (aq) generated by the ORR in aqueous electrolytes was recently reported by Feng et al.\(^3\) This tactic relies on the use of a RRDE, whereby solution phase $O_2$ is being reduced at the disk of the RRDE to yield $O_2^−$ (aq) (and probably other products as well), which then escapes into the bulk electrolyte where it can undergo homogeneous disproportionation according to

$$2O_2^- + 2H^+ \rightarrow O_2 + H_2O_2$$  \[1\]

and/or be oxidized at a judiciously functionalized Au ring of the RRDE virtually impervious to the presence of peroxide in solution. As will shown in the next section, this strategy makes it possible to determine the concentration of $O_2^−$ (aq) in the neighborhood of the disk electrode based on the values of the ring current for the oxidation of $O_2^−$ (aq), assuming the latter proceeds under diffusion limited conditions.

### Theoretical Aspects

The primary objective of this section is to determine quantitative correlations between the concentration of $O_2^−$ in the immediate vicinity of the disk and the magnitude of the ring current measured at steady state with a RRDE as a function of pH. The problem so stated involves finding solutions to the time-independent convective diffusion equation for $O_2^−$ (aq) in Eq. 2 below,

$$0 = D_{O_2^-} \left\{ \frac{\partial^2 [O_2^-]}{\partial z^2} + 1 \frac{\partial}{\partial r} \left( r \frac{\partial [O_2^-]}{\partial r} \right) \right\}$$

$$-u_z \frac{\partial [O_2^-]}{\partial r} - u_r \frac{\partial [O_2^-]}{\partial z} = -2R$$  \[2\]

where $[O_2^-]$ and $D_{O_2^-}$ represent the concentration and diffusion coefficient of $O_2^-$, respectively, $u_z$ and $u_r$ are the fluid velocities along the radial, $r$, and axial, $z$, coordinates, and $R$ is the pH-dependent rate of the second-order dismutation of $O_2^−$ given by\(^2\)

$$R = k_{dis} [O_2^-]^2 = \left[ 7.61 \times 10^4 + 1.58 \times 10^6 pH \right] \left[ O_2^- \right]^2$$  \[3\]

where the rate constant $k_{dis}$ is given in units of cm$^3$ mol$^{-1}$ s$^{-1}$. Numerical solutions of Eq. 2, subject to the boundary conditions specified in Table II were obtained using COMSOL, assuming the system could

![Figure 3](https://example.com/figure3.png)

**Figure 3.** Panel A. Dynamic polarization curves recorded at $v = 10$ mV/s with the Pt disk of a Pt/Pt RRDE in O$_2$-saturated 0.1 M Na$_2$SO$_4$ (J.T. Baker, 99.9%) before (magenta) after addition of 100 ppm BTF (blue) at various values of $\omega$ as indicated. The horizontal arrow represents the direction of the potential scans whereas the vertical arrow point to increasing rotation rates, $\omega$, in the sequence 400, 900, 1200 and 1600 rpm. Panel B. Ring currents measured while the disk was being scanned at 1200 rpm with the ring polarized at $E_{ring} = 0.7$ V vs Ag/AgCl.

![Figure 4](https://example.com/figure4.png)

**Figure 4.** Schematic diagram of the two-dimensional domain employed in the simulations.
be accurately represented by the finite 2-dimensional axisymmetric domain shown schematically in Figure 4, and explicit expressions for the fluid velocities as prescribed by the Levich formalism, i.e.:  

\[ u_z = \frac{0.51023}{m} \cdot \left(\frac{\omega}{v}\right)^{1/2} r_z \]  

where \( \omega \) is the rotation rate of the electrode in rad/s, and \( v \) is the kinematic viscosity of the solution, i.e. ca. 0.01 cm\(^2\)/s. Such calculations were performed for a series of rotation rates, in the range of 400 to 1600 rpm and for pH 7.4 and 10.0. As indicated in Figure 4, the height of the domain was assumed to be three times longer the thickness of the diffusion boundary layer, \( \delta \), given by  

\[ \delta = 1.612 D_0^{1/3} v^{1/6} \omega^{-1/2} \]  

where \( D_0 \) = 6.7 \times 10\(^{-6}\) cm\(^2\)/s. \(^{1,10}\) For the simulations, the concentration of \( O_2^- \) immediately adjacent to the disk electrode (boundary 2), \( [O_2^-]_{\text{disk}} \), was assumed to be fixed over a range of values chosen such that the flux did not exceed the flux of oxygen to the surface given the solubility of oxygen in the bulk solution of \( [O_2^-]_{\text{bulk}} = 1 \) mM, i.e. \((1.3 \times 10^{-5} \text{cm}^2/\text{s})^{1/2}/(6.7 \times 10^{-5} \text{cm}^2/\text{s})^{1/2} \). \( [O_2^-]_{\text{disk}} \), and independent of the radial distance along the disk, \( r_1 \). The simulated current for a single-electron process flowing across the ring (boundary 5) is given by:  

\[ I_{\text{ring}}^{\text{ring}} = F D_0 \int_0^\infty \frac{3}{5} \left(\frac{\partial [O_2^-]}{\partial z}\right)_{z=0} 2\pi r dr \]  

where \( F \) is Faraday’s constant, and boundary 5 represents the thickness of the ring electrode.

Figure 5 displays a plot of \([O_2^-]_{\text{disk}} vs I_{\text{ring}}^{\text{ring}}\) for various values of \( \omega \) determined from the simulations, where the solid circles represent experimental values reported in our earlier publication involving a glassy carbon (GC) disk and a modified Au ring of a RRDE specific for the detection of solution phase \( O_2^- \). \(^2\) As indicated, the magnitudes of \([O_2^-]_{\text{disk}}\) are indeed very reasonable and their dependence on pH in line with the relative rates of disproportionation reported in the literature. \(^2\) Also interesting is the dependence of \([O_2^-]_{\text{disk}}\) on \( \omega^{1/2} \), shown in Figure 6, which provides valuable information to elucidate the overall mechanism of the ORR in the disk.

Unfortunately, the actual mechanism of the ORR on many surfaces including carbon is not known with certainty and the rates of the elementary processes involved have not as yet been determined with sufficient accuracy. This scarcity of key information makes it very difficult to gain additional insights regarding the ORR based strictly on the data analyzed in this work.

Conclusions

The information presented in this brief communication raises serious doubts regarding the reliability of the nanoelectrochemical method reported by Zhou et al.\(^1\) for the determination of mechanistic aspects of a surface sensitive reaction, such as the ORR on Pt, owed to the possible adsorption of the organic solvent on the electrode surface. In fact, as shown by Yang and McCreery,\(^{11}\) the presence of an organic on an electrode surface can lead to enhancements in the amount of \( O_2^- \) produced during the ORR. On this basis it is quite possible that a fraction of \( O_2^- \) detected by Zhou et al. may have originated from the presence of adsorbed BTF on Pt. Yet an additional concern regarding this strategy is the magnitude of the half-life of \( O_2^- \) dismutation in the unbuffered aqueous solution reported by Zhou et al., which is orders of magnitude shorter than accepted values in the literature. In contrast, the RRDE method developed by Feng et al. not only avoids many of these complications, but offers rather simple means for the quantitative electrochemical detection of solution phase \( O_2^- \), provided the rates of \( O_2^- \) dismutation are not too fast for its concentration at the ring to drop to negligible values. In closing, and, from a general perspective, the solubility of the organic solvents most commonly employed in the implementation of this SECM capillary method in pure water is relatively high, ranging from 3.1 mM for BTF up to 88 mM for dichloroethane (DCE). It is, therefore, quite likely that their presence in the aqueous phase can alter the properties and behavior of the systems, including interfacial processes, being examined.

Acknowledgments

This work was supported by a grant from NSF, CHE-1412060. The authors thank Prof. M. Mirkin and Prof. C. Amatore for useful discussions.

References

1. M. Zhou, Y. Yu, K. K. Hu, and M. V. Mirkin, J. Am. Chem. Soc., 137, 6517 (2015).
2. B. H. J. Bielski and A. O. Allen, J. Phys. Chem., 81, 1048 (1977).
3. Z. Feng, N. S. Georgescu, and D. A. Scherson, Anal. Chem., 88, 1088 (2016).
4. C. Lin, J. Rodriguez-Lopez, and A. J. Bard, *Anal. Chem.*, **81**, 8868 (2009).
5. A. L. Horvath, F. W. Getzen, and Z. Maczynska, *J. Phys. Chem. Ref. Data*, **28**, 395 (1999).
6. S. C. Valvani, S. H. Yalkowsky, and T. J. Roseman, *J. Pharm. Sci.*, **70**, 502 (1981).
7. J. J. Maul, P. J. Ostrowski, G. A. Ublacker, B. Linclau, and D. P. Curran, *Top Curr. Chem.*, **206**, 79 (1999).
8. S. Budavari, *The Merck Index - Encyclopedia Of Chemicals, Drugs And Biologicals*, Merck and Co., Inc., Rahway, NJ (1989).
9. A. J. Bard and L. R. Faulkner, *Electrochemical Methods: Fundamentals And Applications*, John Wiley & Sons, Inc., New York, NY (2001).
10. M. Okuda, T. Tsuruta, and K. Katayama, *Phys. Chem. Chem. Phys.*, **11**, 2287 (2009).
11. H. H. Yang and R. L. McCreery, *J. Electrochem. Soc.*, **147**, 3420 (2000).