ABSTRACT

The diffusivity of \( \text{H}_2\text{O}_2 \) was assessed by using a bare and Nafion filmed Pt rotating disk electrode (RDE). The \( \text{H}_2\text{O}_2 \) oxidation currents at the bare and filmed electrode were measured at various electrode rotation frequencies, \( \omega \), for solutions that were 1mM in \( \text{H}_2\text{O}_2 \) and 0.5 M in \( \text{HClO}_4 \) at 25°C. The diffusion coefficient of \( \text{H}_2\text{O}_2 \) in a thin film was estimated to be \( 6 \times 10^{-7} \text{ cm}^2/\text{sec} \). This investigation was undertaken in order to aid in the development of a new test method for studying \( \text{H}_2\text{O}_2 \) generation under more realistic fuel cell conditions. Dual microband electrodes (DMBE) were fabricated and demonstrated as a viable tool for examining \( \text{H}_2\text{O}_2 \) generation as the result of \( \text{O}_2 \) reduction (ORR). The DMBE was operated in generator/collector mode in quiescent, \( \text{O}_2 \) saturated 0.5 M \( \text{HClO}_4 \). Linear seep voltammetry of the generator microband electrode demonstrated that a steady-state ORR current can be obtained. Simultaneous potentiostatic control of the collector microband electrode demonstrated that a \( \text{H}_2\text{O}_2 \) signal can be measured, which relies primarily on physical diffusion.

INTRODUCTION

The electrochemical reduction of oxygen (ORR) has received a great deal of research attention over many years. Specific attention has been paid to the application of the ORR as the cathodic half cell reaction in the polymer electrolyte membrane fuel cell (PEMFC). Even though many researchers have attempted to examine this reaction from a fundamental standpoint, its exact mechanism is still being scrutinized. The ORR occurs by means of several elementary steps, including multiple electron and proton transfer steps as well as O-O bond breaking. A fundamental aspect of the ORR of particular interest, and motivation of this work, is the production and prevalence of \( \text{H}_2\text{O}_2 \). The concern regarding the prevalence of \( \text{H}_2\text{O}_2 \) is raised because of its role as a possible agent leading to chemical degradation of polymeric components in PEMFCs.

It is well-established that oxygen reduction in aqueous acidic media can occur by both a direct four electron path and a two electron path. The latter of these paths, the two electron reduction, results in \( \text{H}_2\text{O}_2 \) as a product (1). In acid solution, the direct four-electron path is:

\[
\text{O}_2 + 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2\text{O}
\]  

[1]
with a thermodynamic reversible potential $E_0 = 1.229 V$ vs. NHE. The two-electron, or peroxide path, is given as:

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

with a thermodynamic reversible potential of $E_0 = 0.67 V$ vs. NHE. It should be kept in mind that realistic PEMFC conditions employ, vapor-equilibrated electrolyte. It is the ultimate aim of this work to develop a test methodology for studying $H_2O_2$ production under these realistic conditions. However, current research efforts rely almost entirely on the use of aqueous, acidic ionic conducting media to study the fundamentals of the ORR. These studies routinely employ the thin-film rotating-ring-disk electrode methodology (thin-film RRDE) (2-3). Factors limiting the thin-film RRDE experiment’s ability to mimic the fuel cell interfacial environment include modification of the pre-exponential coverage dependent term in Butler-Volmer type rate expressions, interfacial water management and the further reduction or decomposition that $H_2O_2$ can undergo. In an aqueous ionic conducting media, further reduction of the $H_2O_2$ intermediate can occur according to:

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$$  \[3\]

with a thermodynamic reversible potential of $E_0 = 1.77 V$ vs. NHE. The decomposition of peroxide can also occur via a disproportionation reaction:

$$2H_2O_2 \rightarrow 2H_2O + O_2$$  \[4\]

With the limitations of the most common research methodology for examining ORR concerns in mind, it is clear that the development of a test method for detecting $H_2O_2$ produced as the result of the ORR under realistic fuel cell conditions is desirable. The motivation of the work being discussed here is the development of a test method that can be used to examine fundamentals associated with the ORR, in particular $H_2O_2$ production, under the most realistic fuel cell conditions. However, it is necessary to study $H_2O_2$ detection and transport in order to design such a test method. Two major initial tasks in the development of the new test method will be highlighted here. The first such task is the assessment of $H_2O_2$ diffusivity in polymer films. The second task is the testing of so-called dual microband electrodes (DMBE). These devices will eventually serve as a new test methodology for examining fundamental ORR concerns employing only a vapor-equilibrated polymer electrolyte. Liu demonstrated that a single microband electrode could be used under such conditions to obtain kinetic parameters and $O_2$ transport parameters that are comparable to a Pt/phosphoric acid system (4).

**EXPERIMENTAL**

**Measurement of $H_2O_2$ Oxidation Currents**

The oxidation waves for dilute, acidic $H_2O_2$ solutions were measured via rotating-disk electrode (RDE) voltammetry. A bare and polymer (Nafion) filmed Pt RDE were used to measure the oxidation waves for 1 mMol $H_2O_2$ in 0.5 $M$ HClO$_4$. The solutions were
prepared from 11.7 N HClO₄ (70%) and 30 % unstabilized H₂O₂ obtained from Fisher Scientific. Ultra high purity (UHP) Ar and N₂ gases were obtained from Praxair and used to purge/blanket the solution. It should be noted that unstabilized H₂O₂ was used because the stabilizing molecule, sodium stannate, may have an affinity to adsorb to the Pt electrode. The stock H₂O₂ solution concentration was determined via titration by potassium permanganate, which was standardized with oxalic acid. The concentration of peroxide in 30 wt % H₂O₂ is approximately 10 M. Therefore, 25 µL of the stock solution was diluted to a final volume of 250 mL with 0.5 M HClO₄ in order to prepare peroxide solutions for study.

Prior to the experiment, 0.5 M HClO₄ was de-aerated with UHP Ar and blanketed with UHP N₂. The bare Pt electrode was then potential cycled between 1.4 and 0.05 V vs. RHE for about 1 hr. Filmed RDE’s were produced by rotating the RDE in the range of 500 – 1000 RPM for 5 min after pipetting about 25 µL of a 5% Nafion solution, obtained from Fisher Scientific. The Nafion solution was pipetted onto the RDE immediately after cold storage. The filming procedure is essentially that developed by Porchet et al (5). After allowing the filmed electrode to dry for 12 hr, it was immersed in 0.5 M HClO₄ for 1 hr, at which point the electrode was potential cycled between 1.4 and 0.05 V vs. RHE. The potential cycling described here corresponds to recording the cyclic voltammogram of the electrode in acid solution. The potential was swept at 50 mV/sec between the sweep limits given above.

After verification that the electrode surface was not undergoing any further changes, the solution was changed for the dilute H₂O₂ solution described above. Once the bare or filmed Pt RDE was introduced to the dilute H₂O₂ solution, the solution was de-aerated with UHP Ar and blanketed with UHP N₂ for 20 min. This procedure was followed for every oxidation wave measurement, except only 5 min was used between each measurement. This methodology was used in order to drive dissolved O₂ out of the H₂O₂ solution in order to prevent any significant electrochemical response due to the H₂O₂/O₂ couple. The measurement of H₂O₂ oxidation was carried out by sweeping the potential from 1.3 to 0.8 V vs. RHE at 5 mV/sec. 3 measurements of each oxidation wave were measured at each electrode rotation frequency. Electrode rotation frequencies in the range of 200 – 3600 RPM were examined.

**DMBE Fabrication and Testing**

DMBE devices were fabricated by common photolithographic, metal thin film deposition techniques in the Electronics Design Center (EDC) at Case. Approximately 200 nm of Pt was deposited on a Ti interlayer on a Pyrex substrate. Prior to aqueous testing, the devices were cleaned by immersing them in 1 M HNO₃ and 30 wt % H₂O₂ for 5 min at 80°C, respectively. Liu et al fabricated single microband electrodes that served as a design basis for the DMBE devices (6).

A proof of principle demonstration of the DMBE device was performed in 0.5 M HClO₄. Cyclic voltammetry was performed on the microband electrodes to assess the quality of the Pt electrode. These experiments were conducted after the acid electrolyte was purged with UHP Ar and blanketed with UHP N₂, as above. The potential was scanned at 50 mV/sec between 1.4 and 0.05 V vs. RHE.

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After an initial assessment of the cyclic voltammetry of the DMBE device in 0.5 M 
HClO₄ was carried out, the device was operated in generator/collector mode, analogous 
to a RRDE experiment. The inner and outer bands were independently potentiostated. 
The potential of the inner band of the electrode was swept from 0.85 to 0.2 V vs. RHE at 
5.3 mV/sec. This was done in order to use the inner band as the generator electrode at 
which the ORR was taking place. The potential of the outer band was held constant at 
1.2 V vs. RHE in order to collect any products formed, and having a long enough lifetime 
to reach the outer electrode of the device. The inter-electrode spacing used was 20 μM. 
After performing the cyclic voltammetry of the DMBE device as described above, the 0.5 
M HClO₄ solution was saturated with O₂ (obtained from Praxair) for 20 min. After the 
20 min period expired, the O₂/0.5 M HClO₄ solution was then blanketed with O₂ for 5 
min while allowing the bulk solution to experience no disturbance. At the end of this 5 
min period the gas supply for the blanket was shut off. Careful attention to saturation and 
blanketing procedure was paid. This procedure was developed on the basis that even 
very small mechanical disturbances in and above the solution significantly affected the 
ORR current value and stability in the region of mass transport control during operation 
of the DMBE device.

RESULTS AND DISCUSSION

H₂O₂ Diffusivity

The oxidation waves for H₂O₂ in 0.5 M HClO₄ were measured for various electrode 
rotation frequencies and are depicted in figure 1. The disk voltammograms offered in 
figure 1 have three important features that are immediately obvious. An apparent 
limiting current plateau seems to emerge at disk potentials more positive than 1.2 V vs. 
RHE. This point will be explored more thoroughly later. Another feature of the 
voltammograms in figure 1 is that they appear to be characteristic of a complicated, 
sluggish electrochemical process. This observation is based on the fact that the current 
does not appear to drop rapidly with decreasing potential, and a pre-anodic limiting 
current feature that seems to occur around 0.90 V vs. RHE. Westbroek and Temmerman 
(7) also observed an additional anodic wave feature, which they attributed to two 
peroxide oxidative mechanisms that operate simultaneously. Their work utilized a glassy 
carbon RDE to oxidize dilute, basic H₂O₂ solutions. The third feature of the 
voltammograms is that they converge on a zero-current value of the potential of about 
0.82 V vs. RHE. This zero-current value of the potential is about 150 mV larger than the 
thermodynamic reversible potential, 0.67 V vs. RHE, given in equation 2. The potential 
observed may be larger than the thermodynamic reversible potential due to the deviation 
of peroxide oxidation from a reversible, Nernstian process, or the dominance of one 
particular electrochemical couple in a mixed potential scenario.

In figure 2 the total current, I, at 1.2 and 1.3 V vs. RHE is plotted against the square 
root of the electrode rotation frequency, ω₁/₂. A linear plot of I vs. ω₁/₂ indicates that the 
current is mass transfer limited and the slope can be used to obtain the peroxide 
diffusivity, according to the Levich equation:

\[ I = 0.62nFAD^{2/3}ν^{-1/6}Cₐω^{1/2} \]  [5]
where \( n (= 2 e^- \text{ in this work}) \) is the number of electrons transferred, \( F (= 96,485 \text{ C/mol}) \) is Faraday's constant, \( A (= 0.196 \text{ cm}^2) \) is the electrode area, \( D \) is the species diffusivity, \( \nu (= 0.01 \text{ cm}^2/\text{sec}) \) is the solution kinematic viscosity, \( C_b \) (1 x 10^{-5} \text{ mol/cm}^3) is the solution species concentration, and \( \omega \) (rad/sec) is the electrode rotation frequency. Figure 2 shows that the current at 1.2 and 1.3 V is indeed linear in \( \omega^{1/2} \). Besides the linearity of the plots in figure 2, the negligible y-intercept demonstrated indicates that \( I \) is related to \( \omega^{1/2} \) by equation 5. Using the slope of the plot for \( I \) at 1.2 V vs \( \omega^{1/2} \) yields \( D = 1.1 \times 10^{-5} \text{ cm}^2/\text{sec} \).

Figure 3 presents a more detailed analysis of the anodic currents measured via RDE voltammetry for a bare Pt disk electrode from figure 1, and a polymer film RDE. The plots were constructed in a Koutecky-Levich fashion, where the inverse of \( I \) was plotted vs. the inverse of \( \omega^{1/2} \) at 1.2 and 1.3 V vs. RHE. For both cases, bare and polymer filmed RDE, straight line plots resulted. In the case of the bare RDE the straight line relationship that is evident is of the following form:

\[
\frac{1}{I} = \frac{1}{I_{i,a}} + \frac{1}{I_k} = \frac{1}{0.62nFAD^{2/3}\nu^{-1/6}C_b\omega^{1/2}} + \frac{1}{I_k}.
\]

\( I \) is the total current at the respective voltage and electrode rotation frequency, \( I_{i,a} \) is the mass transfer dominated anodic current, and \( I_k \) is the current that would flow in the absence of mass transfer limitations. In the case of the bare RDE the straight line plot in figure 3 gives a slope that also yields a peroxide diffusivity of 1.1 x 10^{-5} \text{ cm}^2/\text{sec} in acidic solution. However, it is evident that the current at these large anodic potentials is under mixed control. This conclusion is drawn from the value obtained for \( I_k \), which is the current that would flow in the absence of mass transfer limitations. The extrapolated value of \( I_k \) is 7.1 mA, corresponding to the current at infinite electrode rotation frequency. Examination of the straight line plots for the polymer filmed RDE in figure 3 suggest that the data follows the membrane model:

\[
\frac{1}{I} = \frac{1}{I_{i,a}} + \frac{1}{I_F}.
\]

\( I_{i,a} \) is the mass transfer dominated anodic current due to reactant diffusion in solution and \( I_F \) is the reactant diffusion current due to mass transfer in the polymer film. The diffusivity of H2O2 can be determined from the film diffusion current, which has the following form:

\[
I_F = \frac{nFAD\kappa C_b}{\delta_F}.
\]

\( \kappa \) is the partition coefficient and \( \delta_F \) is the polymer film thickness. In this work it is assumed that mass transfer resistance of H2O2 into the polymer film from the solution is negligible. This means that it is assumed that \( \kappa = 1 \), which would imply that the concentration just inside the polymer film takes on its greatest value, \( \kappa C_b \). This value of
the concentration inside the polymer film is also indicative of mass transfer resistance in
the solution being negligible, which would occur at infinite electrode rotation frequency.
A calculation of peroxide diffusivity in the polymer film using this model is dependent on
the film thickness being known accurately and $k = 1$. The thickness of the polymer film
was determined using the empirical correlation of Porchet and Javet (4). Using $\delta_F = 0.4$
$\mu$m, the diffusivity of $H_2O_2$ in a film of Nafion 1100 equivalent weight was calculated to
be $6.0 \times 10^{-7}$ cm$^2$/sec. The calculated value of the $H_2O_2$ diffusivity in a polymeric
material is extremely sensitive to the degree to which $\delta_F$ is known. Further work will
include a simultaneous, in-situ measurement of the film thickness.

DMBE Testing

Figure 4 shows a schematic representation of the DMBE device. The DMBE used for
testing in 0.5 $M$ HClO$_4$ had an inter-microband electrode spacing of 20 $\mu$m. Figure 5
depicts cyclic voltammograms recorded for both generator and collector microband
electrodes. In general, the cyclic voltammograms shown in figure 5 exhibit the features
expected for a Pt electrode in acid. A typical cyclic voltammogram for a Pt electrode
exhibits regions of oxide formation and reduction, as well as $H^+$ adsorption/desorption.
This behavior is evident in figure 5, but some differences are apparent. It was necessary
to take the generator microband electrode out to 1.4 V vs. RHE, well into the region of
surface oxide formation, in order to observe a large surface oxide reduction peak, near
0.8 V vs. RHE. This behavior may be the result of introduction of organic matter to the
microband electrode by the application of Kapton tape to protect it during its preparation
for test. The onset of $H^+$ adsorption at potentials lower than 0.4 V vs. RHE, during the
scan from positive to negative, that usually appears as two large $H^+$ adsorption peaks is
not evident. Furthermore, the three $H^+$ desorption features that occur between 0 and 0.4
V vs. RHE, during the scan from negative to positive, are not well defined. The two
latter deviations from ideal Pt in acid cyclic voltammetry have caused difficulty in
determining the true area of the generator and collector microband electrodes. After
correcting for the 90 nA background current associated with double layer charging, the
current corresponding to $H^+$ desorption was integrated with respect to time in order to
compute the electrode surface area. The generator microband area was computed to be $6$
$\times 10^{-3}$ cm$^2$, which is about 33% larger than its geometric area, $4 \times 10^{-3}$ cm$^2$. It is not
understood at this point if the discrepancy is due to electrode morphology or its
electrochemical behavior.

After performing basic cyclic voltammetry, the ability of the DMBE to operate in
generator/collector mode was examined. The operation of the DMBE in
generator/collector mode is analogous to the RRDE experiment, with one marked
difference. In the DMBE experiment the ability of the collector electrode to detect any
by-products due to an electrochemical process at the generator relies on diffusion. This
would assume that quiescent solution conditions exist. The well-defined hydrodynamics
of the RRDE experiment utilize forced convection of the generated species to the
collector electrode. So, in the DMBE test in O$_2$ saturated 0.5 $M$ HClO$_4$ any by product
detected at the collector electrode must have diffused across the 20 $\mu$m gap.

Figure 6 shows the linear sweep voltammetry behavior for the DMBE generator
microband in both de-aerated and O$_2$ saturated 0.5 $M$ HClO$_4$. The linear sweep
voltammogram recorded in de-aerated solution served as a measurement of the
background current for the generator microband electrode. The collector microband electrode was potentiostated while its current was recorded for both de-aerated and O₂ saturated 0.5 M HClO₄. The measurement of the current for the potentiostatic control of the collector microband electrode in de-aerated solution served to establish its background current. These background currents may be attributed to double layer charging and the oxidation/reduction of solution impurities and the Pt surface. It is evident from examining this figure that the background current is quite low for both the generator and collector microband electrodes. Most of the background current for the generator microband electrode is due to some reduction process, and is on the order of -5 nA. The background current at the collector microband electrode was on the order of 120 nA. The initial spike in the generator background current may be due to the stripping of adsorbed hydrogen, and then is dominated by another oxidation process.

The linear sweep voltammogram recorded for the generator microband electrode in O₂ saturated 0.5 M HClO₄ is quite significant in comparison to its background current. It seems that the current is approaching mass transfer limitation at potentials less than 0.3 V vs. RHE. This mass transfer limited current is reproducible employing cell conditions described in the experimental section of this work, and approaches -2.25 μA. The DMBE experiment is very sensitive to the state of the solution, and area above it. That is, the voltammetry of the generator microband electrode, especially in the mass transfer limited regime of the curve, depends greatly on a quiescent solution and no disturbance of the solution surface by the flow of blanketing gas. A limiting current plateau does not occur for a wide potential window. This may be explained by a slow growth of the O₂ depleted region next to the generator microband electrode which relies only on reactant diffusion.

Another interesting feature of figure 6 is the signal obtained at the collector microband electrode, which is held at 1.2 V vs. RHE, when the potential of the generator microband electrode is swept. It is well understood that a prevalent side product of the ORR is H₂O₂. This may occur by reaction in equation 2. If H₂O₂ desorbs and does not undergo further reduction via the reaction in equation 3, it could diffuse across the inter-electrode gap of the DMBE and be oxidized. This oxidation should occur according to the reaction in equation 3. It is clear that the collector microband electrode is detecting an ORR side product. This is based on the current obtained while holding the collector microband potential at 1.2 V vs. RHE while the potential of the generator microband electrode is swept in the cathodic direction. Figure 6 shows that the collector microband signal starts to rise above the background between 0.5 and 0.6 V (generator potential) vs. RHE. This indicates that in the DMBE experiment described, H₂O₂ production starts to occur between 0.5 and 0.6 V (generator potential) vs. RHE. The collector microband signal continues to climb as the generator microband electrode potential is swept in the cathodic direction. This result seems consistent with RRDE work with a poly-crystalline electrode conducted by Paulus et al. (8). Paulus et al. showed that the ring current obtained for RRDE voltammetry in O₂ saturated 0.1 M HClO₄ did not start to rise until the disk potential was below 0.4 V vs. RHE. The ring current obtained in this work increased significantly as the disk potential was swept in the cathodic direction. The collector microband electrode current also continues to rises in a similar fashion as the electrode at which the ORR takes place is swept in the cathodic direction. The main difference in the results is that the DMBE current does not approach a well defined limiting current plateau. This, however, is understood in terms of the nature of quiescent conditions that lead to less well defined mass transfer characteristics in the DMBE experiment than in
the RRDE experiment. The results presented here are promising in the sense that the DMBE device is capable of demonstrating an ORR current which results in a \( \text{H}_2\text{O}_2 \) detection current, even when relying on only the process of physical diffusion. The DMBE will be extended to vapor-equilibrated conditions in order to simulate more realistic PEMFC operating conditions.

CONCLUSION

The diffusivity of \( \text{H}_2\text{O}_2 \) was examined in order to aid in the development of a microband electrode device for studying the ORR and \( \text{H}_2\text{O}_2 \) production under realistic PEMFC operating conditions. \( \text{H}_2\text{O}_2 \) oxidation was shown to be under appreciable mass transfer control above 1.2 V vs. RHE. The aqueous \( \text{H}_2\text{O}_2 \) diffusivity was determined to be \( 1.1 \times 10^{-5} \) cm\(^2\)/sec. The oxidation of \( \text{H}_2\text{O}_2 \) is a complicated, sluggish process on Pt. This is evidenced by an additional anodic feature, and a zero-current value of the potential, 0.82 V vs. RHE, being more than 150 mV than the predicted thermodynamic value, 0.67 V vs. RHE. The diffusivity of \( \text{H}_2\text{O}_2 \) in a film of Nafion 1100 equivalent weight on a Pt RDE was calculated to be \( 6 \times 10^{-5} \) cm\(^2\)/sec.

A DMBE device was fabricated and tested in aqueous acid solution. The cyclic voltammetry behavior recorded for the generator and collector microband electrodes was similar to that expected for a poly-crystalline Pt electrode. However, the \( \text{H}^+ \) adsorption/desorption portion of the voltammograms did not mimic the usual behavior of clean well-defined Pt surface. The area of the generator microband electrode was estimated to be \( 6 \times 10^{-3} \) cm\(^2\), which is about 33% larger than its geometric area, \( 4 \times 10^{-3} \) cm\(^2\). The cause of the observed behavior, leading to a larger than expected calculated area, is unknown. Linear sweep of the generator microband electrode in the cathodic direction resulted in the demonstration that this device is capable of producing an ORR current. The ORR current observed appeared to tend toward mass transfer limitation between 0.2 and 0.3 V vs. RHE. This current reached a peak value of -2.25 \( \mu \)A. A \( \text{H}_2\text{O}_2 \) detection signal at the collector microband electrode was also shown to rise appreciably above background levels. This current increased steadily after about 0.4 V (generator potential) vs. RHE. The collector microband electrode current continued to increase, to a value of 0.5 \( \mu \)A, as the generator microband electrode potential was swept in the cathodic direction. These results are consistent with the ORR/\( \text{H}_2\text{O}_2 \) detection behavior observed by other researchers employing the much more robust RRDE experiment. Since an appreciable ORR current and \( \text{H}_2\text{O}_2 \) detection signal that rely strictly on physical diffusion have been demonstrated, the DMBE device will be employed utilizing a vapor-equilibrated polymer electrolyte to study the ORR under more realistic PEMFC operating conditions.

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Figure 1. Voltammogram depicting the oxidation behavior of 1 mM H₂O₂ in 0.5 M HClO₄. The potential was swept from positive to negative at 5 mV/sec. T = 25°C.

Figure 2. Levich plot of the current at 1.3 and 1.2 V vs. RHE (from figure 1) showing that the current at high oxidative potentials is strongly dominated by mass transport control.
Figure 3. Koutecky-Levich and membrane model analysis of the current obtained at 1.2 and 1.3 V for a bare and polymer filmed Pt RDE.

Figure 4. Representation of the DMBE device.
Figure 5. Cyclic voltammograms of the generator and collector microband electrodes in 0.5 M HClO$_4$ recorded at 50 mV/sec.

Figure 6. Voltammograms showing the generator-collector behavior of the DMBE in O$_2$ saturated 0.5 M HClO$_4$.