Analysis of Adsorption Effects on a Metal-Nitrogen-Carbon Catalyst Using a Rotating Ring-Disk Study

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A steady-state, rotating ring disk study of the oxygen reduction reaction (ORR) was conducted in acid environment using a pyrolyzed metal/nitrogen/carbon (MNC) electrocatalyst. Analysis of peroxide generation indicates that ORR proceeds both via a direct four-electron pathway to water at high potentials and an indirect peroxide pathway at low potentials. Above 0.6 V vs RHE, the direct four-electron pathway to water without a desorbing intermediate dominates oxygen reduction because peroxide generation is inhibited due to site availability. In contrast, at potentials below 0.6 V, oxygen reduction begins to shift to the indirect peroxide pathway due to fast kinetics and higher site availability. The net peroxide generation remains relatively low over the entire range due to reduction of peroxide to water.

The need for less expensive electrocatalysts for the oxygen reduction reaction (ORR) in low temperature fuel cells has impeded commercialization of these devices for transportation applications. Metal/nitrogen/carbon (MNC) compounds represent a major focus in the search for platinum alternatives.1-4 These compounds involve the combination of metal and nitrogen components immobilized in a conductive carbon matrix, and are typically pyrolyzed to enhance activity and stability.4 Although the structure of the MNC active site is poorly understood due to complexities introduced by pyrolysis on high surface-area supports, an increased understanding of mechanism provides evidence for possible structures, as well as direction for further engineering optimization of these catalysts for fuel cell applications. In the present work, a rotating ring-disk electrode analysis is conducted to increase understanding of oxygen and peroxide reactions occurring on a pyrolyzed MNC catalyst.

The oxygen reduction reaction is considered here to be composed of two pathways (Fig. 1).5-10 The first pathway represents direct four-electron reduction to water without a desorbing intermediate (k1 in Fig. 1). The second pathway represents incomplete reduction of oxygen to hydrogen peroxide (k2), which can desorb from the surface (k3), disproportionate to water and oxygen, or reduce to water (k4). Jaouen found that disproportionation was insignificant for his Fe-N-C catalyst and that disproportionation reaction rates would have to be orders of magnitude higher that experimental values to account for the low peroxide yield found in these catalysts.1 We therefore neglect disproportionation in the present work.

Rotating ring-disk electrode (RRDE) experiments are used to distinguish between the above two pathways. The RRDE allows for controlled, well-characterized transport to and from the catalyst layer at steady state.11 An analysis can be performed considering the figure of merit, IP/NIR, vs. ω−1/2 where IP is disk current, NIR is ring electrode collection efficiency, IR is ring current, and ω is rotation speed.6,8,10 The figure of merit, IP/NIR, represents a ratio of disk current to flux of intermediates from the disk, and indicates the electronic efficiency of the catalyzed reaction. This parameter can easily be connected to Koutecky-Levich relationships that are mathematically developed to fast kinetics and higher site availability. The net peroxide generation remains relatively low over the entire range due to reduction of peroxide to water.

The difficulty in applying these models to the present system is that they assume a planar electrode. The present MNC catalysts are porous electrodes with nonzero thickness, adding transport effects that are not considered in the above models.

Previous RRDE studies of non-precious metal catalysts for oxygen reduction1,12-17 generally show an increase in peroxide generation by one to two percent per 0.1 mg/cm² decrease in loading.13,17,18 This suggests that peroxide detection at the ring could be artificially low because inner layers may further reduce peroxide to water, decreasing peroxide at the ring and increasing total disk current. Additionally, more active catalysts have been found to produce less peroxide; this is found both by varying metal content19 and morphology of the carbon support. Such considerations motivate the need for increased understanding of the ORR mechanism using MNC catalysts. For the present work we take steady-state measurements in order to insure uniform transport characteristics as well as minimizing unstable intermediates. This has significant implications especially due to the impact of transport phenomena on peroxide and oxygen availability at the electrode surface.

In the present work, an analysis of the MNC catalyst is attempted via the figure of merit, IP/NIR. This method is revised to isolate the indirect ORR pathway and establish a new figure of merit, CIR/NIR. Finally, this new figure of merit is utilized to understand the kinetic and adsorption limitations of the MNC catalyst in the context of Langmuir Hinshelwood kinetics.

Experimental

Materials.— Carbon, nitrogen, and iron materials used in catalyst synthesis were Ketjen 600JD carbon black (Akzo Nobel, Chicago, IL), melamine (Alfa Aesar, Ward Hill, MA), and iron (II) acetate (Alfa Aesar, Ward Hill, MA) respectively. Materials used in characterization were perfluorosulfonic acid-PTFE copolymer (5 wt%), reagent grade sulfuric acid (Alfa Aesar, Ward Hill, MA), and oxygen (Airgas, Lansing, MI).

Catalyst synthesis.— Catalysts were synthesized as described previously1,10,15 Briefly, Ketjen (95.7 wt%), melamine (0.8 wt%), and iron (II) acetate (3.5 wt%) were dispersed in ethanol and dried overnight to produce a dry powder. Further melamine was added to the powder in a ratio of 5:9 to increase the nitrogen content to 24 wt%.
Figure 1. Reaction schematic showing two pathways: pathway one ($K_{o,1}$ and $k_1$) is the complete reduction of oxygen to water with no desorbing intermediate and pathway two ($K_{o,2}$ and $k_2$) is the two-electron reduction to a desorbing peroxide intermediate that disperses into the catalyst layer ($K_{p,2}$), but also has the potential to be further reduced to water ($k_3$).

Electrode preparation.— The catalyst ink was prepared by ultrasonically mixing 4 mg catalyst in 50 μL of 5 wt% ionomer and 150 μL 190 proof ethanol as described previously,16 catalyst layers were prepared at loadings of 0.5 to 0.1 mg cm$^{-2}$ by depositing 5 μL of the ink on the 5 mm diameter, glassy-carbon disk of a rotating ring-disk electrode (Pine Research Instrumentation, Raleigh, NC) and drying for 10 min in air. The ink was diluted with ethanol to achieve lower loadings; in this way the drop volume and ionomer to catalyst ratio were held constant for all loadings.

Electrochemical characterization.— Experiments were conducted in oxygen saturated 0.5 M sulfuric acid at room temperature. Potentials were measured relative to a Hg/Hg$_2$SO$_4$ reference electrode that was calibrated with respect to a reversible hydrogen electrode. All potentials were corrected to RHE scale (0.7 V vs. RHE). A platinum wire served as the counter electrode. Potentiostatic measurements were made at 400, 900, 1200, and 1600 rpm in 50 mV increments between 0.2 and 0.9 V vs. RHE.

Fractional peroxide yield, $\chi_p$, was calculated based on the following equation:

$$\chi_p = \frac{2I_R/N}{I_D + I_R/N}$$

Where $I_R$ is the ring current, $N$ the collection efficiency, and $I_D$ the disk current. Collection efficiency, $N$, was calculated from similar potentiostatic measurements in 0.1 M NaOH, 0.01 M K$_3$Fe(CN)$_6$. The collection efficiency was not found to vary significantly with loading, although it did decrease slightly with rotation speed consistent with Claude et al.20 Collection efficiencies were 0.24 ± 0.01, 0.23 ± 0.01, 0.23 ± 0.01, and 0.22 ± 0.01 for 400, 900, 1200, and 1600 rpm respectively.

Results and Discussion

Potentiostatic, steady-state RRDE experiments were conducted at fixed catalyst loading for four different disk rotation speeds, and at fixed rotation speed for five different loadings. Fig. 2a shows polarization disk current and ring current with respect to disk potential at various rotation speeds. Above 0.7 V, both the disk current, $I_D$, and ring current, $I_R$, exhibit exponential (Tafel) dependence on potential. The disk limiting current ($I_{lim}$, the current plateau below 0.6 V) increases with increasing rotation speed, indicating mass transfer limitation. The ring current also increases with rotation speed, but is more weakly correlated than the disk current. This implies that $I_D/N$ increases with rotation speed.

Fig. 2b shows steady state polarization curves at various catalyst loadings. Loading impacts disk current at high potentials, where the
current falls below \( I_{\text{lim}} \), but impacts ring current much more significantly, even at low potentials.

Comparisons can be made between the peroxide generation rate and the overall rate of water production. Fig. 2b shows that above 0.7 V vs. RHE, disk current increases significantly with loading, whereas ring current is relatively constant. The disk current at such high potentials can therefore be primarily attributed to four-electron reduction because the ring current is 500-fold smaller and constant over the same loading range. Hence, the peroxide generating ORR pathway appears to be insignificant at high potentials.

The ring current, \( I_R \), can be thought of in two ways: as a measure of peroxide flux from the disk and as a measure of peroxide concentration at the disk. In the following results and discussion both perspectives will be considered.

The exponential increase of ring current with decreasing potential near 0.7 V vs RHE (Fig. 2) suggests that peroxide generation is limited by the kinetics of the first 2e\(^-\) reduction step, because the reduction of oxygen to hydrogen peroxide coincides with that potential. Decreasing ring current below the maximum at 0.5–0.6 V suggests either the onset of step 3 (further reduction of peroxide to water) or competition between the two different oxygen reduction reactions (steps 1 and 2). A detailed analysis of the 2e\(^-\) + 2e\(^-\) reaction pathway (\( I_3 \) and \( I_2 \)) is necessary to compare these two phenomena, via the figure of merit, \( I_{D2}/I_{R} \).

By assuming a reaction mechanism, an expression for \( I_{D2}/I_{R} \) can be obtained in terms of fundamental rate constants plus the rotation rate.\(^{5,6}\) Without considering adsorption (ignoring \( K_{i,1} \) and \( K_{i,2} \)), the expression for the mechanism displayed in Fig. 1 is:

\[
i_{D2}/I_{R} = 1 + 2k_1k_2 + \frac{2 + 2k_1/k_2}{z_p} k_3 \omega^{-1/2} \]

[2]

where \( k_1, k_2, \) and \( k_3 \) are the rate constants for reduction of oxygen to water, reduction of water to hydrogen peroxide, and reduction of hydrogen peroxide to water, respectively. The parameter \( z_p = 0.62D_0^{2/3}v^{-1/6} \) is an abbreviation for the group of constants in the Levich equation:

\[
i_{\text{mt}} = 0.62nFC_{b}D^{2/3}v^{-1/6} \omega^{1/2} \]

[3]

where the mass transport limited current at a rotating disk, \( i_{\text{mt}} \), is a function of \( n \) is the number of electrons per mole electrode, \( F \) is Faraday’s constant, \( C_b \) is a bulk concentration, \( D \) is diffusivity, \( v \) is viscosity, \( \omega \) is the rotation speed. The parameter \( z_p \) is calculated from a mass transfer limiting current and \( \omega^{-1/2} \). Based on a bulk oxygen concentration of 1 mM\(^{21} \) and a viscosity of 0.01 cm\(^2\)/s,\(^{22} \) the resulting \( z_p \) values indicate diffusivities of \( 2.17 \pm 0.07) \times 10^{-5} \) cm\(^2\)/s for oxygen (which is in the range of reported values: \( 1.87 \times 10^{-5} \) to \( 2.12 \times 10^{-5} \) cm\(^2\)/s\(^{21} \) and \( 1.28 \pm 0.25) \times 10^{-5} \) cm\(^2\)/s for hydrogen peroxide (reported value: \( 1.71 \times 10^{-5} \) cm\(^2\)/s).\(^{23} \)

The figure of merit, \( I_{D2}/I_{R} \) for the current data set was regressed with respect to the inverse square root of the rotation speed, and sample regressions are shown in Fig. 3a, with a plot of slope vs intercept given in Fig. 3b. One issue with the application of this analysis is that Eq. 2 shows negative slope.

A requirement for the validity of Eq. 2 is first order kinetics.\(^5 \) In order to test this requirement, the variation of disk and ring currents with oxygen concentration is explored as shown in Fig. 4. Assuming a Nernst boundary layer at the disk surface, \( C_{o} \) can be calculated from the bulk oxygen concentration and the ratio of the total reduction current at a given potential and the mass transfer limiting current:

\[
C_{o} = C_{o,b} \left( 1 - \frac{I_{D} - I_{R}}{I_{\text{lim}}} \right) \]

[4]

where \( C_{o,b} \) represents oxygen concentration in the bulk electrolyte, \( C_{o} \) is dissolved oxygen concentration at the catalyst surface, and \( I_{\text{lim}} \) the diffusion limited current. At high potential (0.7 V vs RHE), where the peroxide reduction rate is small, \( I_{R} \sim I_{D2} \). This correlation with oxygen (\( I_{1} \sim I_{D} \) and \( I_{2} \sim I_{R}/N \)) shows that neither reaction pathway appears to show first order kinetics (\( \propto C_{o} \)).

If the disk and ring currents were first order, the traces in Fig. 4 would be straight lines that intercept the origin. Because this is not the case, kinetics controlled by surface adsorption were explored. For single constituent adsorption, the Langmuir adsorption coefficient may be defined as:

\[
K_{ij} = \frac{C_{i}}{\theta_{ij}} \]

[5]

where \( K_{ij} \) is the adsorption coefficient for species \( i \) on site \( j \), \( \theta_{ij} \) is the fraction of sites occupied by species \( i \), \( C_{i} \) is concentration of species \( i \) near the surface, and \( \theta_{ij} \) is the fraction of vacant sites. A mass balance on the total number of sites of type \( j \) yields:

\[
1 = \theta_{ij} + \sum_i \theta_{ij} \]

[6]

Then \( \theta_{ij} \) can be solved for and substituted into the adsorption equations to obtain the surface fractions. For a single adsorbent this results in:

\[
\theta_{ij} = \frac{C_{i}}{K_{ij} + C_{i}} \]

[7]

![Figure 3](image-url) 
Figure 3. (a) Plot of \( I_{D2}/I_{R} \) vs rotation speed for two different electrodes at two different potentials, 0.5 M H\(_2\)SO\(_4\), room temperature, oxygen saturated, ring poised at 1.2 V vs. RHE. (b) Slope and intercept plot at various loadings and potentials: 0.5 M H\(_2\)SO\(_4\), room temperature, oxygen saturated, ring poised at 1.2 V vs. RHE.

![Figure 4](image-url) 
Figure 4. Plot of disk and ring current densities vs oxygen concentration (varying rotation speed) for two different loadings at 0.7 V vs RHE, 0.5 M H\(_2\)SO\(_4\), room temperature, oxygen saturated, ring poised at 1.2 V vs. RHE. Dashed lines represent fit of Eq. 8.
If an electrochemical reaction is first order with respect to the surface species, \( \theta_{i,j} \), reaction rate laws can be written as a current:

\[
i = \frac{nFkC_k}{K_{i,j} + C_i}
\]

where \( k \) is a rate constant, and \( nFk \) represents a plateau current density when \( C_i \gg K_{i,j} \), i.e. when the surface is saturated.

Returning to Fig. 4, one can see that Eq. 8 fits the experimental data well. The data are therefore well explained by a site-limited surface reaction, because the current density plateaus as \( C_o \) increases. As mentioned earlier, a high potential was chosen for Fig. 4 to minimize rate 3 (peroxide reduction). The small rate three allows comparison between oxygen adsorption on the direct 4\( e^- \) and indirect 2\( e^- \) active sites. The smaller variation with oxygen concentration in the ring current (representing peroxide generation) as compared to the disk current (dominated by 4\( e^- \) oxygen reduction) suggests that the 2\( e^- \) sites are more saturated than the 4\( e^- \) sites.

One can extend the analysis to lower potentials for the disk current, assuming that \( I_1 \) dominates. Disk current is plotted vs. oxygen concentration at 0.5 V vs RHE in Fig. 5; the disk current displays more linear kinetics, suggesting that the surface concentration is low, \( C_o \ll K_{o,j} \).

The observed adsorption limitation and resulting nonlinear kinetics do not satisfy the requirements for Eq. 2. For this reason, the RRDE data must be reanalyzed assuming Langmuir-Hinshelwood kinetics. In this analysis we will assume that the two reduction pathways occur on different sites. As shown in Fig. 1, site one is responsible for direct 4\( e^- \) reduction of oxygen to water, while site two is responsible for the indirect, 2\( e^- + 2H^+ \) reduction pathway via peroxide. We will obtain an expression for parameter \( C_oN/I_R \), where \( C_i \) is calculated by Eq. 4, and will assume that the rate peroxide generation by reaction 2 is first order with respect to oxygen concentration. Initially, the method will be established assuming linear kinetics (no adsorption limitations), and then extended to consider Langmuir adsorption. For the initial analysis, with linear kinetics (\( C_o \ll K_{o,j} \)) the two-electron oxygen reduction current \( I_2 \) may be expressed as:

\[
I_2 = \frac{nFk_2C_o}{K_{p,2}}
\]

where \( k_2 \) is the associated rate constant, \( K_{p,2} \) is the adsorption equilibrium coefficient for 2+2 pathway surface sites (site 2), and \( C_o \) is oxygen concentration given by Eq. 4. The ring current, \( I_R \), is related to the concentration of peroxide, \( C_p \) at the disk by a Levich-like transport model:

\[
I_R = nFNC_pz_i\omega^{1/2}, \text{ where } z_i = 0.62D_i^{1/3}v^{1/6}
\]

where \( n \) is the number of electrons per mole oxygen, \( F \) is Faraday’s constant, \( D \) the diffusivity, \( v \) the viscosity, and \( \omega \) the rotation speed. An equation for \( I_2 \) with respect to ring current can be developed by assuming that \( I_1 \), i.e. the further reduction of peroxide to water is first order with respect to peroxide concentration at the disk:

\[
I_3 = \frac{nFk_3}{K_{p,2}}C_p = \frac{k_3}{K_{p,2}}I_R\omega^{1/2}z_i^{1/2}N
\]

where \( K_{p,2} \) is the adsorption coefficient of peroxide on site two. Eqs. 9 and 11 provide rate expressions for each step associated with the two-by-two reaction pathway (\( I_2 \) and \( I_3 \)) with the only parameters being three rate constant groups (\( k_2/K_{p,2} \) or \( k_3/K_{p,2} \)) and mass transport properties.

A charge balance on peroxide generation/consumption relates the ring current to \( I_2 \) and \( I_3 \):

\[
I_2 = \frac{I_R}{N} + I_3
\]

Here we have neglected bulk disproportionation of peroxide. Combining equations 12 and 11 allows \( I_2 \) to be represented as a function of the ring current and some reaction coefficient \( k_3/K_{p,2} \):

\[
I_2 = \frac{I_R}{N} \left( \frac{k_3}{K_{p,2}}\omega^{-1/2} + 1 \right)
\]

Rearranging Eq. 13 and introducing \( C_o \) via Eq. 9 yields:

\[
\frac{C_oN}{I_R} = \frac{K_{o,2}k_3}{nFk_2K_{p,2}z_i^{1/2}}\omega^{-1/2} + \frac{K_{o,2}}{nFk_2}
\]

In the absence of adsorption limitations, the term \( k_2/K_{o,2} \) can then be calculated from a regression of \( C_oN/I_R \) with rotation speed, allowing the calculation of \( I_2 \) via Eq. 9. Based on the earlier analysis of Fig. 4, the present data indicate limitations due to oxygen adsorption. Therefore, an adsorption model must be incorporated into the reaction system.

For oxygen and peroxide, the Langmuir adsorption coefficients, \( K_{o,2} \) and \( K_{p,2} \), may be defined as:

\[
K_{o,2} = \frac{C_o\theta_{o,2}}{\theta_{o,2}}, \quad K_{p,2} = \frac{C_p\theta_{p,2}}{\theta_{p,2}}
\]

where \( \theta_{o,2} \) and \( \theta_{p,2} \) are the surface fractions of oxygen and peroxide respectively on the sites involved in indirect ORR pathway (site 2), \( \theta_{o,2} \) is the surface availability of this adsorption site, and \( C_o, C_p \) are oxygen and peroxide concentrations near the surface. If the reactions two and three are first order with respect to the surface species (\( \theta_{o,2} \) and \( \theta_{p,2} \)) the rate laws can be re-written:

\[
I_2 = \frac{nFk_2\theta_{o,2}C_o}{K_{o,2}}
\]

\[
I_3 = \frac{nFk_3\theta_{p,2}C_p}{K_{p,2}}
\]

Using these rate laws, Eq. 14 becomes:

\[
\frac{C_oN}{I_R} = \frac{K_{o,2}k_3}{nFk_2K_{p,2}z_i^{1/2}}\omega^{-1/2} + \frac{K_{o,2}}{nFk_2}
\]

Assuming that the surface fractions of oxygen and peroxide are small (that \( \theta_{p,2} \) is near unity) the equation reduces to Eq. 14.

Peroxide reduction experiments were performed by running the same RRDE experiment as above, but in the presence of various concentrations of hydrogen peroxide and saturated with nitrogen. By plotting the current at a given potential as a function of peroxide concentration, the presence of adsorption limitations associated with peroxide reduction can be studied. As demonstrated in Fig. 6, in the absence of oxygen, the observed peroxide reduction rate is linearly dependent on bulk hydrogen peroxide concentration at least to 4 mM. This suggests that \( K_{o,2} \) is large and adsorbed peroxide does not
parameters and the inverse slope represents a rate constant. The resulting reaction rate parameters can be used to calculate surface coverage and rate parameters can be established. These rate parameters can be applied to deduce the adsorption coefficient (Eq. 15) and a mass balance on adsorption sites is necessary. The resulting reaction parameters are: $K_{o,2} = 1.7e-4 \pm 1.1e-4$ M, $k_2 = 4.3e-8 \pm 0.8e-8$ mol s$^{-1}$ mg$^{-1}$ and the Tafel slope is $114 \pm 6$ mV per decade. Conditions: 0.5 M H$_2$SO$_4$, room temperature, oxygen saturated, ring poised at 1.2 V vs. RHE. 

Contribute significantly to surface coverage. Considering this approximation, surface fractions for site 2 become $\theta_{o,2} = 1$, and Eq. 18 becomes:

$$ C_o N = \frac{K_{o,2} k_3}{nFk_2} \omega^{1/2} + \frac{C_o + K_{o,2}}{nFk_2} $$

Additionally, at high potentials where $I_3$ is insignificant, Eq. 19 simplifies to

$$ C_o N = \frac{C_o + K_{o,2}}{nFk_2} $$

In these cases the figure of merit $C_o N/k_2$ should scale with $C_o$. Some representative correlations are shown in Fig. 7a. For this correlation the ratio of the intercept to slope indicates an adsorption coefficient, and the inverse slope represents a rate constant. The resulting reaction parameters are: $K_{o,2} = 1.7e-4 \pm 1.1e-4$ M, $k_2 = 4.3e-8 \pm 0.8e-8$ mol s$^{-1}$ mg$^{-1}$ and the Tafel slope is $114 \pm 6$ mV per decade. Conditions: 0.5 M H$_2$SO$_4$, room temperature, oxygen saturated, ring poised at 1.2 V vs. RHE.

Surface coverage at various potentials can be compared as shown in Fig. 8. Surface coverage was calculated via the definition of the adsorption coefficient (Eq. 15) and a mass balance on adsorption sites:

$$ \theta_{o,2} = \frac{C_o}{C_o + K_{o,2}}; \quad \theta_{o,2} = \frac{K_{o,2}}{C_o + K_{o,2}} $$

As shown in Fig. 8, for 0.1 mg cm$^{-2}$ loading, oxygen surface coverage remains above 70% down to 0.6 V vs RHE. Low surface coverage at 0.5 mg cm$^{-2}$ indicates that the high loadings approach mass-transfer-limiting current faster than lower loadings. This is an indication of high catalyst utilization.

The currents for each reaction step can also be compared. Fig. 9 shows currents $I_1, I_2,$ and $I_3$ cumulatively as compared to disk current. It is evident that at high potentials $I_1$ dominates, but $I_2$ becomes significant below 0.7 V and $I_3$ below 0.6 V. The fact that $I_1$ dominates over most of the potential range justifies the use of disk current as a proxy for $I_3$, as was assumed in the context of Fig. 4.

The adsorption limitation may be why $I_2$ is not significant at higher potentials: at high potential, oxygen surface concentration is high and available sites for adsorption limit the 2+2 reaction pathway. At low potential oxygen concentration and surface coverage are mass transfer limited, decreasing adsorption limitations. At these low potentials the 2+2 reaction pathway can compete better with the direct 4-electron pathway.

![Figure 6](image-url)  
**Figure 6.** Correlation of disk current with hydrogen peroxide concentration showing first-order peroxide reduction reaction: slope is $0.0564 \pm 0.0007$ mA cm$^{-2}$ mM$^{-1}$. Hydrogen peroxide concentrations range from 10 μM to 4 mM in 0.5 M H$_2$SO$_4$: room temperature, nitrogen saturated.

![Figure 7](image-url)  
**Figure 7.** (a) Plot of $C_o N/k_2$ vs oxygen concentration at four high potentials with 0.3 mg/cm$^2$ loading, 0.5 M H$_2$SO$_4$, room temperature, oxygen saturated, ring poised at 1.2 V vs. RHE. (b) Plot of peroxide generation parameters $k_2$ and $K_{o,2}$ at various loadings and potentials. Reaction parameters are: $K_{o,2} = 1.7e-4 \pm 1.1e-4$ M, $k_2 = 4.3e-8 \pm 0.8e-8$ mol s$^{-1}$ mg$^{-1}$ and the Tafel slope is $114 \pm 6$ mV per decade. Conditions: 0.5 M H$_2$SO$_4$, room temperature, oxygen saturated, ring poised at 1.2 V vs. RHE.

![Figure 8](image-url)  
**Figure 8.** Fractional surface coverage at two different loadings and at various rotation speeds. Open symbols represent vacant sites, while filled symbols represent occupied sites.
scavenges the peroxide on the catalyst surface decreasing the flux of peroxide from the catalyst layer.

Acknowledgments

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