

Supporting Information

Electrocatalytic O₂ Reduction by Covalently Immobilized Mononuclear Copper(I) Complexes: Evidence for a Binuclear Cu₂O₂ Intermediate

Charles C. L. McCrory, Anando Devadoss, Xavier Ottenwaelder, Randall D. Lowe, T. Daniel P. Stack,* Christopher E. D. Chidsey*

Synthesis of 3-ethynyl-1,10-phenanthroline (3-ethynyl-phen). 3-bromo-1,10-phenanthroline was prepared by the route established by Tzalis, et al.¹ 3-bromo-1,10-phenanthroline was separated from other major products via elution through an alumina column with dichloromethane saturated in ammonia. The bromo-compound was first converted to 3-trimethylsilanylethynyl-1,10-phenanthroline as reported by Michel et al,² followed by a deprotection with strong base to form 3-ethynyl-phen.³ ¹H NMR (CDCl₃): 3.34 (s, 1H), 7.58 (dd, 1H), 7.66 (d, 1H), 7.73 (d, 1H), 8.15 (dd, 1H), 8.27 (d, 1H), 9.14 (dd, 1H), 9.17 (d, 1H).

Other Chemicals. For this study, acetonitrile, chloroform, dimethyl sulfoxide (DMSO), hexanes (HPLC grade), and glacial acetic acid were purchased from Fisher Scientific. Sodium azide (NaN₃) and 1,10-phenanthroline (phen) (99+%) were purchased from Sigma-Aldrich. Cupric sulfate (CuSO₄) was purchased from EM Science, anhydrous sodium acetate was purchased from JT Baker, and ascorbic acid from Tokyo Chemical Industry, Co. Iodine monochloride (ICl) was purchased from Riedel-de Haen. All water used in this study was deionized water.

O₂-saturated solutions were made by bubbling 100 mL solutions for ca. 20 mins with ultra-high purity (grade 4.3) O₂(g) from Praxair. O₂-saturated solutions were then blanketed with O₂ during analysis. Ar-purged solutions were purged by bubbling 100 mL solutions for ca. 20

mins with compressed Ar (g) from Praxair. Ar-purged solutions were then blanketed with Ar during analysis.

Analytical Instrumentation. X-ray photoemission spectroscopic (XPS) analysis was done with a Physical Electronics PHI 5000 Versaprobe spectrometer with Al K α radiation (1486 eV). The angle between the sample surface plane and the analyzer was 45°. Analysis of the spectra was done using the Physical Electronics Multipak software package.

Electrochemical measurements were recorded with a Pine Instrument Company AFCBP1 bipotentiostat with a MSR rotator, an auxiliary Pt-mesh electrode and a Ag/AgCl/KCl(sat) reference electrode. The Pine Instrument Company E6 series ChangeDisk Pt rotating-ring-disk-electrode assembly held the surface modified HTGC samples as the disk electrode. Data was recorded using the Pine Instrument Company AfterMath software package. The reference was calibrated against both an Accumet Glass Body Ag/AgCl/4.0M KCl(aq) electrode and an Accumet Glass Body saturated calomel electrode (SCE). All reported values are referenced to the normal hydrogen electrode (NHE). The aqueous electrolyte solution used for all electrochemical measurements was 1 M NaClO₄, 0.05 M sodium acetate and 0.05 M acetic acid. The pH was measured to be 4.7 using a Corning pH meter 140 with an Accumet Glass Body Ag/AgCl/4.0 KCl(aq) pH electrode.

Iodine azide solution preparation. (Warning: Azides are explosive in nature and proper precautionary steps should be undertaken while handling them). The preparation of an iodine azide solution was adapted from a procedure described in acetonitrile by Devadoss and Chidsey.⁴ Iodine azide (IN₃) is prepared in-situ from sodium azide and iodine monochloride. 5 μ L of ICl added to 0.02 g of NaN₃ in 10mL of hexanes in a glass scintillation vial under vigorous stirring. An immediate appearance of a reddish brown color is believed to correspond to the formation of

IN₃, although significant solid (presumably unreacted NaN₃ and product NaCl) is left undissolved at the bottom of the vial. The solution was used immediately upon preparation.

Glassy Carbon Surface Modification. Sigradur G glassy carbon disk inserts with a 0.195 cm² geometric surface area were purchased from HTW Hochtemperatur-Werkstoffe GmbH. The disks were polished with 240-grit TufBak Durite SiC sand paper from Grindwell Norton followed by sonication in water and drying in an N₂ stream. The disks were heated in a fused silica-lined furnace at 1000°C for 90 mins under a forming gas purge (5% H₂ in N₂ from Praxair, flow rate = 5 L·min⁻¹), and then allowed to cool under a forming gas purge. This surface treatment resulted in a substantial decrease of the oxygen content on the carbon surface as measured by XPS.

After reaching room temperature, the samples were immediately placed into iodine azide solution and held in the dark for 1 hr. A characteristic XPS signature with two N peaks at 399 eV and 403.9 eV in a 2:1 ratio confirmed the formation of an azide-terminated heat-treated glassy carbon surface (N₃-HTGC).⁴

Covalent Attachment of Ethynyl-complexes to Azide Modified Surfaces. The azide-modified heat-treated glassy carbon (N₃-HTGC) surfaces were reacted to ethynyl-terminated molecules using the Cu(I)-catalyzed 1,3-Huisgen dipolar cycloaddition commonly known as the click reaction.^{5,6} The N₃-HTGC surface was immersed in a click solution of 1 volume DMSO to 1 volume H₂O containing 0.5 mM of the ethynyl-terminated molecule, 1.1 mM of CuSO₄, 1 mM of the water-soluble accelerating ligand tris-(ethylacetyltriazolyl)methylamine (TTMA),⁷⁻⁹ and 10 mM ascorbic acid for 10-14 hrs. TTMA was prepared according to a literature procedure.⁷ After surface modification with the ethynyl-terminated molecule, the samples were rinsed with acetonitrile, sonicated for 2 mins each in DMSO, chloroform, and water, then rinsed with

ethanol, and finally dried in a stream of N₂ gas. Control experiments with analogous non-ethynyl-terminated compounds showed no physisorbed species after this cleaning procedure.

Procedure for Stripping Cu. Previous results have shown that exposing covalently immobilized Cu complexes to a chelating agent such as ethylenediaminetetraacetic acid or sodium diethyldithiocarbamate results in the removal of Cu from the surface.^{10,11} In this work, Cu was successfully stripped from the surface by rotating the Cu(phen^C) surface at 3000 rpm for ca. 10 mins in saturated sodium diethyldithiocarbamate in MeOH. The surface was rinsed with copious amounts of water before being placed back in an electrolyte solution for analysis. Analogous results were obtained by rotating the Cu(phen^C) surface at 3000 rpm for ca. 40 mins in saturated ethylenediaminetetraacetic acid in MeOH.

Controlling Surface Coverage of Clicked Cu(phen^C). The strategy employed to control the surface coverage of clicked Cu(3-ethynyl-phen) was to dilute the solution used for the azide-modification of glassy carbon. First, a standard solution is prepared in which 5 μL of ICl is added to 0.02 g of NaN₃ in 10 mL of hexanes. Note that significant solid (presumably unreacted NaN₃) is left undissolved at the bottom of the vial. The resulting solution was agitated to mix in the undissolved solid, and the resulting suspension was then diluted in hexanes by dilution fractions ranging from 1:1 to 1:20 solution-to-hexanes to produce new azide-modification solutions. Glassy carbon surfaces were exposed to the different solution concentrations for the same reaction time. After the surface-azidification, the surfaces were rinsed and subjected to normal click procedures.

Coverage Dependence of Cu(phen^C) at High Overpotential. An analogous coverage dependence analysis to that reported in the paper but at high overpotential (-150 mV vs. NHE) was conducted for Cu(phen^C). Background-corrected kinetic currents were collected in an

analogous manner to that explained in the text. The plot of $\Delta i_K(-150)$ in O_2 -saturated solutions, corrected for background, as a function of Cu coverage (Δq) shows an intermediate order between a 1st and 2nd order dependence in Cu coverage (Figure S1). A log-log plot of the same data shows a slope of 1.51.

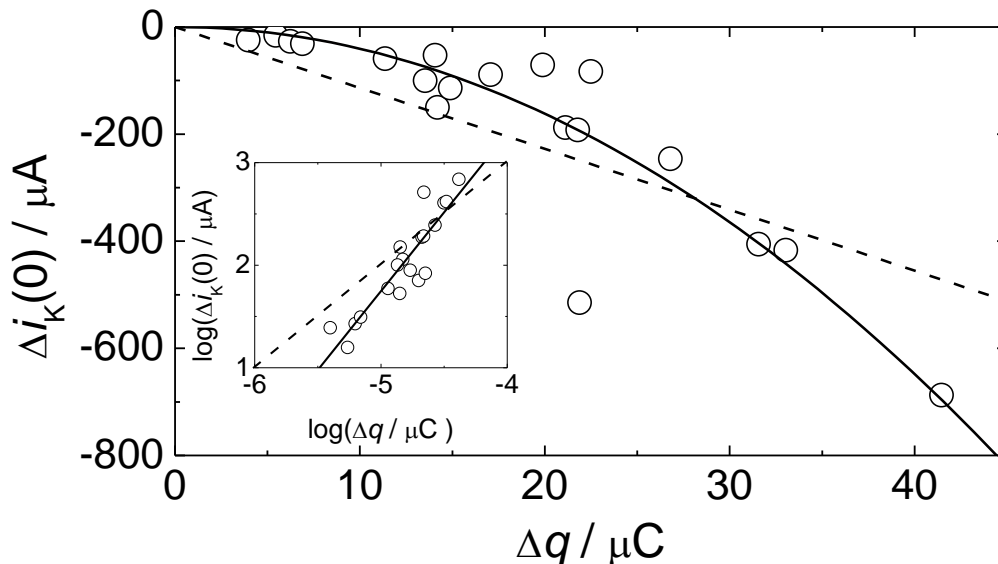


Figure S1. The background-corrected kinetic current measured at -150 mV vs. NHE, $\Delta i_K(-150)$, for O_2 -reduction by $Cu(phen)^C$ on an N_3 -modified glassy carbon electrode at different coverages. The solid line is the best fit of the form $y = Ax^2$. The dashed line is the best linear fit of the form $y = Ax$. The inset is a log-log plot of the same data. The slope of solid line in the inset is 1.51. The dashed line in the inset has a slope of 1.0 and is shown for comparison.

Derivation of Kinetic Model Comprised of Two Potential-Dependent Rates. Given the mechanisms in Equations 1-3 and Equations 5-7 in the main text for the binuclear and mononuclear O_2 -reduction pathways, respectively, we obtain the following expressions for the rate of each pathway:

$$rate = \frac{k_1 k_2 \Gamma_{\{2 Cu^I\}} [O_2]}{k_2 + k_{-1}} \quad (S1)$$

$$rate' = \frac{k_1' k_2' \Gamma_{\{CuI\}} [O_2]}{k_2' + k_{-1}'} \quad (S2)$$

Expressions for k_2 and k_2' shown in equations S1 and S2 are obtained from the Butler-Volmer model:

$$k_2(E) = k_{\{Cu_2O_2\}}^0 \exp\left(\frac{-\alpha F}{RT} (E - E_{\{Cu_2O_2\}}^0)\right) \quad (S3)$$

$$k_2'(E) = k_{\{CuO_2\}}^0 \exp\left(\frac{-\alpha F}{RT} (E - E_{\{CuO_2\}}^0)\right) \quad (S4)$$

F is Faraday's constant, $k_{\{Cu_2O_2\}}^0$ and $k_{\{CuO_2\}}^0$ are the electrochemical standard rate constants, $\alpha = 0.5$ is the transfer coefficient, R is the gas constant, and $T = 298$ K is the electrode temperature.

Therefore, the rates in Equations S3 and S4 can be expressed as:

$$rate = \frac{k_1 \Gamma_{\{2 CuI\}} [O_2] k_{\{Cu_2O_2\}}^0 \exp\left(\frac{-\alpha F}{RT} (E - E_{\{Cu_2O_2\}}^0)\right)}{k_{-1} + k_{\{Cu_2O_2\}}^0 \exp\left(\frac{-\alpha F}{RT} (E - E_{\{Cu_2O_2\}}^0)\right)} \quad (S5)$$

$$rate' = \frac{k_1' \Gamma_{\{CuI\}} [O_2] k_{\{CuO_2\}}^0 \exp\left(\frac{-\alpha F}{RT} (E - E_{\{CuO_2\}}^0)\right)}{k_{-1}' + k_{\{CuO_2\}}^0 \exp\left(\frac{-\alpha F}{RT} (E - E_{\{CuO_2\}}^0)\right)} \quad (S6)$$

Since these two reaction pathways occur in parallel, then the total rate is the sum of the individual reaction rates. These rates can be expressed as kinetic currents as shown in Equation S7.

$$i_K = \frac{4FAk_1 \Gamma_{\{2 CuI\}} [O_2] k_{\{Cu_2O_2\}}^0 \exp\left(\frac{-\alpha F}{RT} (E - E_{\{Cu_2O_2\}}^0)\right)}{k_{-1} + k_{\{Cu_2O_2\}}^0 \exp\left(\frac{-\alpha F}{RT} (E - E_{\{Cu_2O_2\}}^0)\right)} + \frac{2FAk_1' \Gamma_{\{CuI\}} [O_2] k_{\{CuO_2\}}^0 \exp\left(\frac{-\alpha F}{RT} (E - E_{\{CuO_2\}}^0)\right)}{k_{-1}' + k_{\{CuO_2\}}^0 \exp\left(\frac{-\alpha F}{RT} (E - E_{\{CuO_2\}}^0)\right)} \quad (S7)$$

Here, 4 and 2 are the number of electrons in the binuclear and mononuclear reduction mechanisms, respectively, F is Faraday's constant, and A is the geometric area of the electrode. Equation S7 can be further simplified to Equation S8.

$$i_K = \frac{4FAk_1\Gamma_{\{2\text{Cu}\}}[\text{O}_2]}{1 + \frac{k_{-1}}{k_{\{\text{Cu}_2\text{O}_2\}}} \exp\left(\frac{\alpha F}{RT}(E - E_{\{\text{Cu}_2\text{O}_2\}}^0)\right)} + \frac{2FAk'_1\Gamma_{\{\text{Cu}\}}[\text{O}_2]}{1 + \frac{k'_{-1}}{k_{\{\text{CuO}_2\}}} \exp\left(\frac{\alpha F}{RT}(E - E_{\{\text{CuO}_2\}}^0)\right)} \quad (\text{S8})$$

This expression can be simplified into a 6-parameter kinetic model:

$$i_K = \frac{a}{1 + \exp(b(E - c))} + \frac{d}{1 + \exp(g(E - h))} \quad (\text{S9})$$

The high-coverage potential-dependent kinetic current in Figure 4a was fit by Equation S9 first. Both b and g were fixed at $0.5F/RT$, which is what one might expect from equation S8 for $\alpha = 0.5$. c was set to 0 mV vs. NHE because at that potential half the high-coverage potential-dependent kinetic current is reached. h was initially set to -200 mV, which was picked to be very negative compared to 0 mV vs. NHE and so seemed reasonable for the more negative onset of reduction at the mononuclear sites. Both c and h were allowed to float during the fit and their final values were $c = 22$ mV and $h = -225$ mV. a and d were initially set to 0 and allowed to float. The two parameters reached final values values of $a = -589$ μA and $d = -627$ μA . The low coverage case in Figure 4b was then fit using the fixed values for c and h determined in the high coverage case and allowing only a and d to float. The final values determined by the fit were $a = -3.48$ μA and $d = -165$ μA .

If we assume that $k_1 = k'_1$, then at a given $[\text{O}_2]$, the ratio of a to d is proportional to the fraction of binuclear and mononuclear sites on the surface. Using such an assumption, we find that as the coverage increases from $\Delta q = 4.0$ to $\Delta q = 41.5$ μC , there is a corresponding increase in the fraction of catalytic sites that form binuclear sites from 0.02 at $\Delta q = 4.0$ to 0.48 at $\Delta q =$

41.5 μC . However, because all the data was acquired positive of the putative value of $E_{\{\text{CuO}_2\}}^0 = h = -225 \text{ mV vs NHE}$, Equation S9 is approximately equal to Equation S10.

$$i_K \cong \frac{a}{1+\exp(b(E-c))} + \frac{d}{\exp(g(E-h))} \quad (\text{S10})$$

Here, d and h are convolved, limiting the validity of the above coverage analysis. Nonetheless, the fits are consistent with the experimental data at high and low coverage, and the fit parameters are qualitatively consistent with expectations.

O₂ Reduction by Cu(phen^P) on Edge-plane Graphite. A similar coverage dependence analysis was conducted with physisorbed Cu(phen) on edge-plane graphite, Cu(phen^P). A previously published method was used to prepare Cu(phen^P).¹² Edge-plane graphite surfaces with a 0.195 cm² macroscopic surface area were purchased from Pine Instrument Company. The electrodes were ground by hand with a 600-grit SiC polishing paper (Buehler) followed by sonication in pure water before each ligand deposition. Ligands were physisorbed onto the edge-plane graphite electrode surface by depositing a known quantity of the ligand dissolved in chloroform onto the surface and subsequently allowing the solvent to evaporate. The surfaces were then exposed to saturated CuSO₄ in water for ca. 2 mins. Coverage was determined by an analogous manner to that for Cu(phen^C) on glassy carbon. Background-corrected kinetic currents were collected in an analogous manner to that explained in the text. The plot of $\Delta i_K(0)$ in O₂-saturated solutions, corrected for background, as a function of Cu coverage (Δq) shows first order dependence in Cu(phen^P) coverage (Figure S2). This is confirmed by a log/log plot of the same data that has a slope of 0.91 (Figure S2, inset). This is consistent with previously reported results for the coverage dependence of O₂ reduction by Cu(phen) in air-saturated solutions.^{13,14}

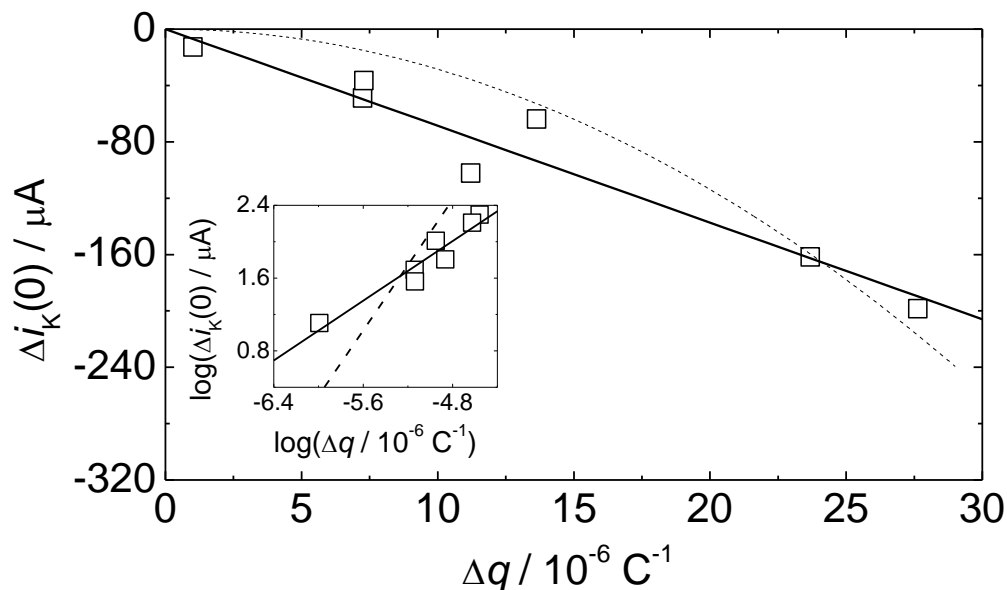
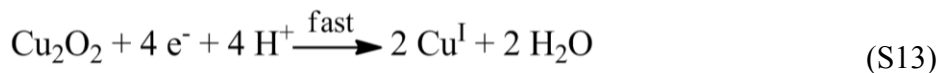
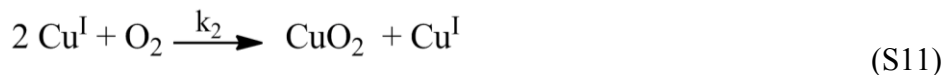


Figure S2. The background-corrected kinetic current measured at 0mV vs. NHE for O₂-reduction by Cu(phen^P) on edge-plane graphite at different coverages. The solid line is a linear fit of the form $y = Ax$. The dashed line is the best fit of the form $y = Ax^2$ and shown for comparison. The inset is a log-log plot of the same data. The slope of solid line in the inset is 0.91. The dashed line in the inset has slope of 2.0 and is shown for comparison.

We suggest the following binuclear mechanism for O₂-reduction by physisorbed Cu(phen^P):



We propose that a single Cu(phen^P) initially coordinates O₂ (Equation S11). This is followed by the coordination of a second Cu^I site (Equation S12), and then by rapid reduction and protonation to H₂O (Equation S13). The rate for the proposed mechanism is given by Equation S14.

$$\text{rate} = \frac{k_1 k_2 (\Gamma_{\text{Cu}})^2 [\text{O}_2]}{k_{-1} + k_2 \Gamma_{\text{Cu}}} \quad (\text{S14})$$

In the Cu(phen^P) case, previous results showed that initial O₂-binding (Equation S11) is rate limiting at 0 mV vs. NHE.¹⁵ Thus, Equation S14 simplifies to Equation S15.

$$rate_{\text{physisorbed}} = k_1 \Gamma_{\text{Cu}} [\text{O}_2] \quad (\text{S15})$$

This simplification requires that all Cu(phen^P) are identical and that each Cu site has sufficient lateral mobility such that, if one Cu(phen^P) coordinates O₂, another Cu(phen^P) can rapidly coordinate to form Cu₂O₂ (in Equation S12). Equation S15 is 1st order in Cu coverage. This suggests that the Cu(phen^P) system is a special case of the binuclear mechanism.

Dependence of the Kinetic Current on Buffer Concentration and pH. Kinetic currents were measured for O₂ reduction by Cu(phen^C) on glassy carbon electrodes in air-saturated acetate buffer solutions as a function of pH, buffer concentration, and sodium acetate (NaOAc) concentration (Figure S3). pH was controlled by titrating a standard aqueous acetate buffer electrolyte solution of 0.05 M NaOAc, 0.05M acetic acid, and 1 M sodium perchlorate at pH 4.8 with 1 M perchloric acid or 1 M sodium hydroxide. Buffer concentration was controlled by diluting the standard aqueous acetate buffer solution at pH 4.8 into an aqueous 1 M sodium perchlorate solution. NaOAc concentration was controlled by mixing aqueous 1 M NaOAc and aqueous 1 M sodium perchlorate solutions. There is no observed dependence on pH (Figure S3a), buffer concentration (Figure S3b), or acetate concentration (Figure S3c). This is evidence that the protonation steps are fast compared to the potential-dependent reduction steps in the binuclear O₂-reduction mechanism (Equations 1-3).

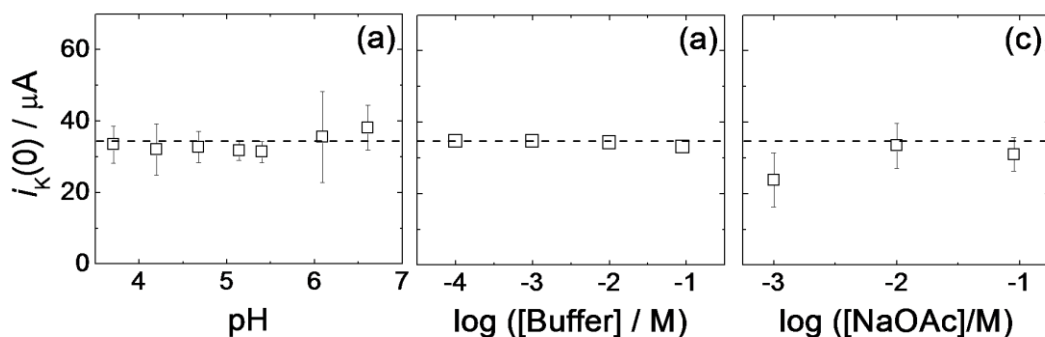


Figure S3. Kinetic current plotted as a function of (a) pH, (b) the log of acetate buffer concentration, and (c) the log of sodium acetate (NaOAc) concentration in air-saturated aqueous solutions.

References

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- (15) Lei and Anson determined O_2 -binding to be the rate limiting step for $\text{Cu}(\text{phen})^{\text{P}}$ on edge-plane graphite surfaces at high overpotentials.¹⁰ This result was confirmed at 0 mV vs. NHE.¹⁹ O_2 reduction by Cu complexes of other substituted-1,10-phenanthroline ligands exhibit first order behavior in Cu coverage at high overpotential as well,¹⁹ but the order in Cu has not been investigated at 0 mV vs. NHE. There is some evidence that O_2 -binding may not be rate limiting at low overpotentials for more easily-reduced Cu complexes with substituted 1,10-phenanthroline ligands.¹⁹