



Four-Electron Reduction of Dioxigen with Molecular Copper Complexes on Graphite

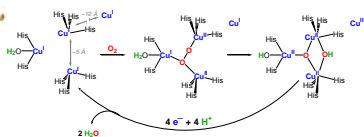
Charles C. L. McCrory, Matthew A. Pellow, Xavier Ottenwaelder, Anando Devadoss, Vennesa O. Williams, T. Daniel P. Stack, and Christopher E. D. Chidsey



Stanford University, Department of Chemistry

Copper Based Oxygen Electrode: Motivation and Biological Precedent

Fungal laccase enzymes provide biological precedent for molecular Cu catalysts for the 4-electron reduction of O₂ to H₂O.¹ They reduce O₂ directly to water at a trinuclear copper site at overpotentials as low as -40 mV from the thermodynamic potential of O₂ reduction at pH 7.¹



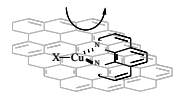
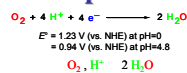
Heller and colleagues have recently reported high current densities of ca. 5 mA/cm² at overpotentials of only -70 mV from the thermodynamic potential of O₂ reduction with specially designed laccase modified electrodes at pH 5.³ This current density corresponds to a turnover rate of 2.1 O₂ reduced per laccase s⁻¹ or 0.7 O₂ per Cu s⁻¹.

In contrast, Pt nanoparticle catalysts reduce O₂ with rates of about 0.25 O₂ per Pt s⁻¹ at overpotentials of -350 mV.⁴

Adsorbed Mononuclear Cu Complexes

Cu complexes of 1,10-phenanthroline (phen) derivatives have been shown to catalyze the 4 e⁻ reduction of O₂ when adsorbed onto edge-plane pyrolytic graphite (EPG) electrodes.⁴

Cyclic voltammograms (shown below) of some Cu complexes adsorbed onto EPG were taken under an N₂ purge (—) and in air-saturated solutions (—).

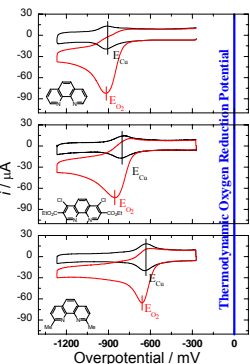


4e⁻ Graphite Electrode

Under N₂, the peaks are due to the reduction and Oxidation of the Cu-center.

The large reduction current in the air-saturated solution is indicative of the catalytic O₂ reduction.

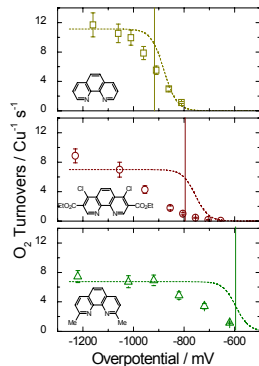
The onset of the catalytic current occurs at or negative of the onset of the Cu^{II} reduction to Cu^I, suggesting the Cu^{II} reduction precedes O₂ reduction. Thus, the O₂-reduction potential can be shifted by changing E_{Cu}.



The rate of O₂ reduction can be determined by rotating disk voltammetry. From this technique can be measured the number of electrons (n) in the reduction and the rate of the O₂ reduction in the absence of mass-transfer effects.

The O₂-reduction rates for three Cu complexes are shown right. The vertical bars are E_{Cu} for the given complex. The dashed curves are the expected rates of O₂-reduction if O₂ binding were rate limiting.

This suggests that there is some electron-transfer step that limits the rate of O₂ reduction. This step may be the reduction of a Cu-bound partially-reduced oxygen species.



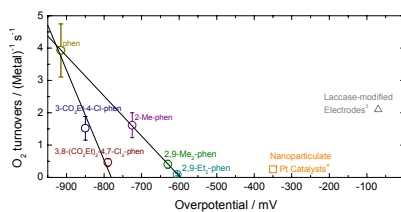
Adsorbed Cu Complexes:

Summary of Ligands Investigated*

Overpotentials of the E_{Cu} and E_{O₂} in mV, and k_{O₂} measured at E_{Cu} in Cu^I s⁻¹

E _{Cu} -920 mV E _{O₂} -930 mV k _{O₂} —	E _{Cu} -925 mV E _{O₂} -930 mV k _{O₂} 3.9 ± 0.8 s⁻¹	E _{Cu} -890 mV E _{O₂} -900 mV k _{O₂} —	E _{Cu} -865 mV E _{O₂} -900 mV k _{O₂} —
E _{Cu} -850 mV E _{O₂} -875 mV k _{O₂} 1.5 ± 0.4 s⁻¹	E _{Cu} -790 mV E _{O₂} -810 mV k _{O₂} 0.5 ± 0.1 s⁻¹	E _{Cu} -725 mV E _{O₂} -735 mV k _{O₂} 1.6 ± 0.4 s⁻¹	E _{Cu} -655 mV E _{O₂} -665 mV k _{O₂} —
E _{Cu} -630 mV E _{O₂} -650 mV k _{O₂} 0.4 ± 0.1 s⁻¹	E _{Cu} -605 mV E _{O₂} -635 mV k _{O₂} 0.09 ± 0.04 s⁻¹	E _{Cu} -600 mV E _{O₂} -680 mV k _{O₂} —	E _{Cu} -550 mV E _{O₂} -860 mV k _{O₂} —

The magnitude of the overpotential decreases as electron withdrawing groups are added to the phen-backbone remote from the Cu-binding site and as the size of the substituents adjacent to the Cu-binding site increases. The steric effects near the Cu-binding site and the electronic effects remote from the Cu-binding site can be combined, as in the case of 5-NH₂-2,9-Me₂-phen and 5-NO₂-2,9-Me₂-phen.

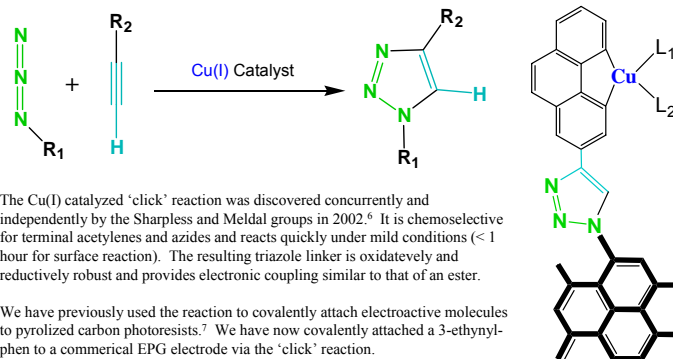


The rate of O₂ reduction (measured at E_{Cu}) decreases as the magnitude of the overpotential decreases. There is no catalytic current expected for mononuclear Cu complexes with overpotentials more positive than -590 mV.

Synthetic multinuclear Cu complexes in which two or more metal centers are situated such that they can interact with O₂ simultaneously may efficiently catalyze the reduction of O₂ at more positive overpotentials.

*This work has been accepted for publication: McCrory, C. C. L.; Ottenwaelder, X.; Stack, T. D. P.; Chidsey, C. E. D. "Kinetic and Mechanistic Studies of the Electrocatalytic Reduction of O₂ to H₂O with Mononuclear Cu(II) Complexes of Substituted 1,10-Phenanthrolines." *J. Phys. Chem. Accepted, 08/28/2007.*

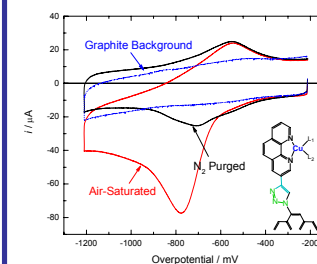
"Clicking" Mononuclear Cu Complexes to Graphite



The Cu(I) catalyzed 'click' reaction was discovered concurrently and independently by the Sharpless and Meldal groups in 2002.⁶ It is chemoselective for terminal acetylenes and azides and reacts quickly under mild conditions (< 1 hour for surface reaction). The resulting triazole linker is oxidatively and reductively robust and provides electronic coupling similar to that of an ester.

We have previously used the reaction to covalently attach electroactive molecules to pyrolyzed carbon photoresists.⁷ We have now covalently attached a 3-ethynyl-phen to a commercial EPG electrode via the 'click' reaction.

"Clicked" Cu Complexes†



Cu(3-ethynyl-phen) is covalently attached to an EPG electrode.

The blue dotted line is the C.V. of the bare EPG background.

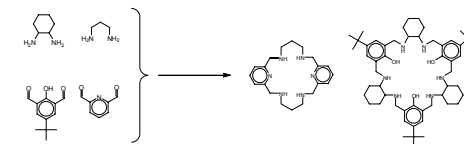
The E_{Cu} of the 'clicked' complex is at an overpotential of -640 mV vs. NHE, 275 mV more positive than that of adsorbed Cu(phen).

Kinetic studies have shown no catalytic activity at E_{Cu}, but O₂ turnovers of ca. 0.25 O₂ Cu⁻¹ s⁻¹ at an overpotential of -740 mV.

†This work is in preparation for publication: McCrory, C. C. L.; Devadoss, A.; Ottenwaelder, X.; Stack, T. D. P.; Chidsey, C. E. D. "Covalent Attachment of Alkyne-Terminated Molecular Electrocatalysts for O₂-Reduction to Edge-Plane Graphite Surfaces by 'Click' Chemistry."

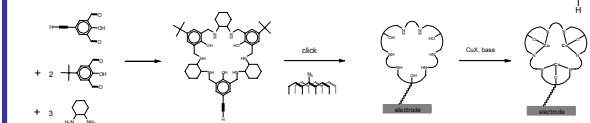
Polynucleating Ligands for O₂-Reduction Catalysts

Future effort toward efficient O₂ reduction will emulate the trinuclear laccase center using highly preorganized polynucleating ligands. The ligand is formed by the reductive amination of an **alkyl diamine** with an **aryl dialdehyde**. Equimolar amounts of these two reagents spontaneously form macrocyclic structures capable of holding two or three metals in close proximity.



Because a variety of diamines and dialdehydes are available, this strategy allows a **modular search** for a coordination environment that facilitates dioxygen reactivity.

Click-ready dialdehydes are accessible from commercial starting materials in three steps.



Acknowledgements

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