



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

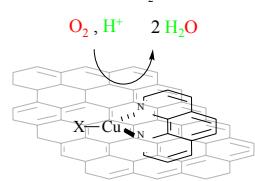
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Copper Based Oxygen Electrode

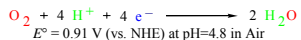
Our motivation is to understand how to design copper-based fuel-cell catalysts for the 4-electron reduction of O₂.



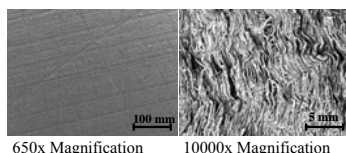
4e⁻ Graphite Electrode

Copper 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) surfaces¹ (shown right):

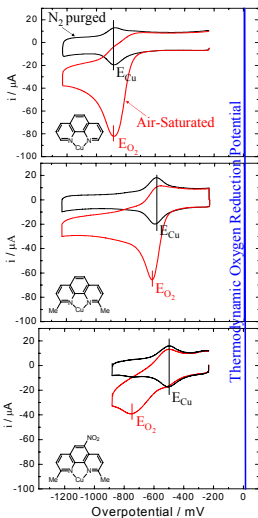
1. Zhang, Anson, *Electrochim. Acta* 1993, 2423
Lei, Anson, *Inorg. Chem.* 1994, 5003



O₂ is a good thermodynamic oxidant, but is kinetically unreactive. In particular, it is a very poor ligand for metal centers. A useful mechanism for binding O₂ is to provide a site on a metal that can donate an electron to the O₂ and then bind the resulting superoxide anion (O₂⁻). The biological O₂ reduction catalysts (cytochrome c oxidase and laccase) work in this manner.



650x Magnification 10000x Magnification



Cyclic voltammograms of the copper complexes adsorbed on EPG were taken under an N₂ purge (—) and in air-saturated solutions (—).

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 oxygen reduction.

The onset of the catalytic 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 the Cu^{II}/Cu^I redox potential.

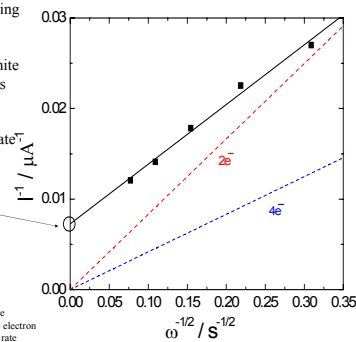
The cyclic voltammogram were taken in a 0.4M acetate buffer solution at pH 4.8 with 0.1M NaClO₄. The scan rate was 100 mV/s

Rate of Oxygen Reduction

The rate of O₂-reduction is obtained by rotating the EPG electrode with the adsorbed Cu catalyst at several rotation rates (ω), and extrapolating the steady-state current to infinite rotation rate. As the electrode rotation rate is increased, the concentration of O₂ at the electrode surface increases and the current increases until the current is limited by the rate of reduction.

$$(K-L \text{ intercept})^{-1} = 4 F A \Gamma_{\text{Cu}} k_{\text{O}_2}$$

F = Faraday's constant
A = electrode area
 Γ_{Cu} = catalyst coverage
 k_{O_2} = O₂ reduction rate in air-saturated solution



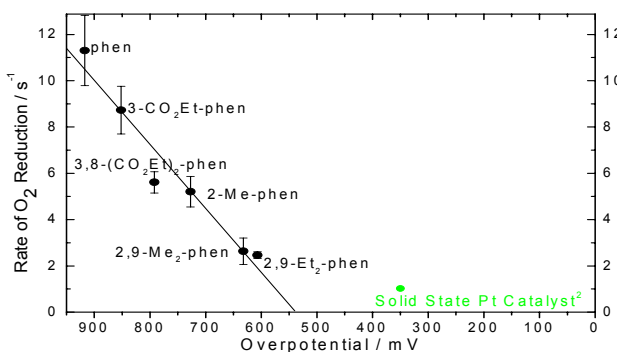
A Koutecky-Levich plot is shown (right). The dashed lines show the calculated responses for the 2 electron reduction (to H₂O₂) and the 4 electron reduction (to H₂O) of O₂ from the Levich Equation. The 2nd order rate constant of the O₂ reduction is calculated from the K-L intercept.

Copper Complexes with Various Ligands

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

E _{Cu} -895 mV	E _{Cu} -880 mV	E _{Cu} -855 mV	E _{Cu} -850 mV
E _{O₂} -895 mV	E _{O₂} -895 mV	E _{O₂} -865 mV	E _{O₂} -870 mV
k _{O₂} —	k _{O₂} 11.2 ± 1.4 s ⁻¹	k _{O₂} —	k _{O₂} —
E _{Cu} -850 mV	E _{Cu} -830 mV	E _{Cu} -815 mV	E _{Cu} -815 mV
E _{O₂} -860 mV	E _{O₂} -865 mV	E _{O₂} -840 mV	E _{O₂} -840 mV
k _{O₂} —	k _{O₂} —	k _{O₂} —	k _{O₂} 8.7 ± 0.8 s ⁻¹
E _{Cu} -770 mV	E _{Cu} -755 mV	E _{Cu} -690 mV	E _{Cu} -620 mV
E _{O₂} -795 mV	E _{O₂} -775 mV	E _{O₂} -700 mV	E _{O₂} -630 mV
k _{O₂} —	k _{O₂} 5.6 ± 0.6 s ⁻¹	k _{O₂} 5.0 ± 0.6 s ⁻¹	k _{O₂} —
E _{Cu} -595 mV	E _{Cu} -570 mV	E _{Cu} -565 mV	E _{Cu} -515 mV
E _{O₂} -615 mV	E _{O₂} -605 mV	E _{O₂} -645 mV	E _{O₂} -825 mV
k _{O₂} 2.5 ± 0.6 s ⁻¹	k _{O₂} 2.5 ± 0.3 s ⁻¹	k _{O₂} —	k _{O₂} —

Increasing steric bulk near the Cu center leads to a decrease the magnitude of the overpotential of O₂-reduction. Adding electron-withdrawing groups (such as esters and nitro-groups) also decreases the magnitude of the overpotential, and adding electron-donating groups (such as amines) has the opposite effect.



The rate of O₂ reduction decrease as the magnitude of the overpotential decreases, and the difference between E_{Cu} and E_{O₂} increases as the magnitude decreases. There is a clear potential limit of -540 mV for O₂-reduction with mono-Cu catalysts.

It has been shown that the tri-Cu center in fungal laccase reduce O₂ at comparable O₂-reduction rates to phen-based Cu-complexes, but closer to the thermodynamic O₂-reduction potential.³ This suggests that the potential limit reached with mono-Cu catalysts may be overcome with multi-nuclear copper catalysts.

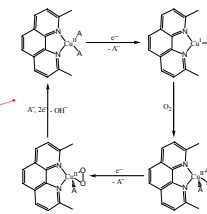
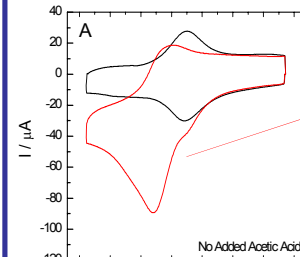
Future work will involve the development of multi-nuclear copper complexes that operate closer to the thermodynamic O₂-reduction potential while maintaining comparable reduction rates.

2. Ralph, T.R.; Hogarth, M.P. *Platinum Metal Reviews* 2002, 46, 3-14.

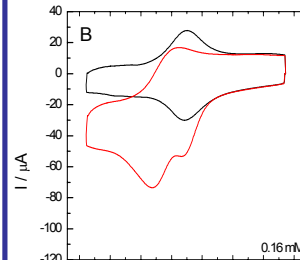
3. Barton, S.C.; Kim, H.H.; Binayamin, G.; Zhang, Y.C.; Heller, A. *J. Am. Chem. Soc.* 2001, 123, 5802-5803

Barton, S.C.; Kim, H.H.; Binayamin, G.; Zhang, Y.C.; Heller, A. *J. Phys. Chem. B* 2001, 105, 11917-11921

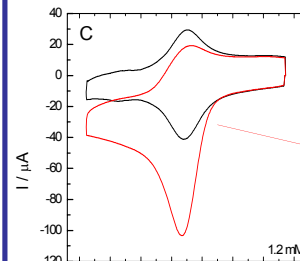
Mechanisms of O₂-Reduction



A. At low acetic acid concentrations, there is a shoulder at the Cu^{II} redox potential and an oxygen reduction peak centered at a 780 mV overpotential.



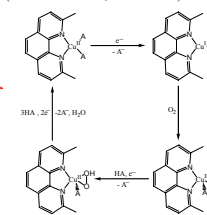
B. As the acetic acid concentration increases, the shoulder at Cu^{II} redox potential grows into a second oxygen reduction peak.



C. At high acetic acid concentrations, only the peak at the 670 mV overpotential is evident.

We have also found that the catalyst releases a bound acetate ion upon reduction from Cu^{II} to Cu^I. Proposed mechanisms for the catalytic cycle are shown in the case of low acetic acid (above) and high acetic acid (below) concentration.

For each run, the acetate concentration was held constant at 100 mM and acetic acid was titrated into solution (0.1M NaClO₄, 100 mV/s).



Conclusions

The overpotential of O₂-reduction can be decreased by developing catalysts with electron-withdrawing substituents and with steric bulk near the Cu-center.

As the overpotential of O₂-reduction is decreased by these ligand effects, there is a corresponding decreases in the rate of O₂-reduction.

Acetic acid facilitates the O₂-reduction by phen-based catalysts. When no acetic acid is present, larger overpotentials are required for O₂-reduction.

Future work will involve the development of multi-nuclear copper complexes that operate closer to the thermodynamic O₂-reduction potential with similar O₂-reduction rates.

Acknowledgements

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