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Electrocatalysis

Oxygen Reduction Activity of a Copper Complex of 3,5-Diamino-1,2,4-triazole Supported on Carbon Black**

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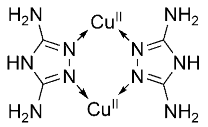
Electrocatalysis of the oxygen reduction reaction (ORR) is currently of widespread interest because of its application in fuel-cell cathodes. Slow reaction kinetics significantly impact the efficiency of fuel cells and, even with Pt catalysts, the onset of the ORR occurs at approximately 1.0 V, which is well below the reversible potential for oxygen reduction of 1.23 V versus the reversible hydrogen electrode (RHE).[1] Multicopper oxidases (exemplified by laccase) activate oxygen at a site containing three Cu atoms with spacings of approximately 3.5 Å and exhibit remarkable ORR electroactivity at potentials approaching 1.2 V (versus RHE).[2,3] Given the high cost and limited supply of Pt, a copper-containing complex adsorbed on an electrode surface that exhibited this level of reactivity would be highly desirable.

There are few reports of synthetic Cu complexes that exhibit significant ORR activity. Several mononuclear Cu complexes have been investigated by adsorption onto graphite electrodes.[4–9] Cu^{II} complexes with phenanthroline ligands, which were popularized by Zhang and Anson,[6] are the best-studied to date. McCrory et al. have investigated the Cu complexes of a variety of substituted phenathrolines, the best of which demonstrated an ORR onset of about 0.68 V (RHE) at pH 4.8, and concluded that further increases in activity were unlikely by using this system.[7] Attempts that used putative multicopper complexes include a water-soluble catalyst formed by the coordination of two Cu^{II} ions in a hexaazamacrocyclic ligand,[10] and electrodes modified with solution-cast polymers containing Cu^{II} ions, including a copper–poly(histidine) complex,[11] and a polymeric Cu^{II} oxalato complex.[12] However, the demonstration of polynuclearity when adsorbed on an electrode in any of these systems is lacking. A cytochrome c oxidase model compound with a Cu–Fe site has also been investigated by adsorption onto graphite, but the ORR onset is quite low at about 0.2 V versus RHE and the complex that contains only Fe has similar activity.[13]

The efficacy of laccase led us to wonder if Cu coordination complexes or polymers composed of Cu^{II} coordinated with bridging azole-type ligands, such as the 3,5-diamino-1,2,4-triazole (Hdartz) ligand (Scheme 1),[14] and with other weakly coordinated ligands (such as water or sulfate) might provide stability in addition to multicopper sites that could potentially bind and activate O_2 (as these have Cu···Cu spacings similar to laccase). The combination of aqueous solutions of $CuSO_4$ and a variety of substituted pyrazoles and triazoles led to the precipitation of insoluble compounds. The lack of solubility was encouraging from a stability standpoint, but made them incompatible with the techniques previously used to prepare electrodes for electrochemical characterization which require the use of solution phases.[4–13]



Scheme 1. 3,5-Diamino-1,2,4-triazole (Hdatrz) ligands bridging two copper centers. Typical Cu···Cu spacing is 3.5 Å. Counterions and ligated water are omitted.

Herein, we report a simple method for the evaluation of the electrocatalytic activity of insoluble coordination compounds by direct precipitation onto carbon black (Vulcan XC-72). Utilization of a carbon black support allows the use of electrode fabrication methods and characterization techniques developed for the analysis of carbon-supported Pt catalysts and could also facilitate the transition to practical application in a fuel cell.[1,15] We have applied this method to the evaluation of the ORR activity of the insoluble multicopper complex formed with 3,5-diamino-1,2,4-triazole (Hdatrz).

Figure 1 shows the characterization of the [Cu(Hdatrz)] complex supported on Vulcan and a blank sample of unmodified Vulcan using a rotating ring-disk electrode (RRDE) obtained in an oxygen-saturated electrolyte at pH 7. The disk potential was swept to determine the potential dependence of the ORR and the ring potential was held constant at 1.2 V to observe the oxidation of any generated peroxide intermediate.[15] The collection efficiency of the ring under the conditions of the experiment was calculated to be 0.04 from the ring-to-disk current ratio obtained for the two-electron reduction of O_2 by the unmodified Vulcan. This was used to calculate the fraction of peroxide intermediates formed with a method described elsewhere.[15] The onset of O_2 reduction occurs at a disk potential of 0.73 V (versus RHE)

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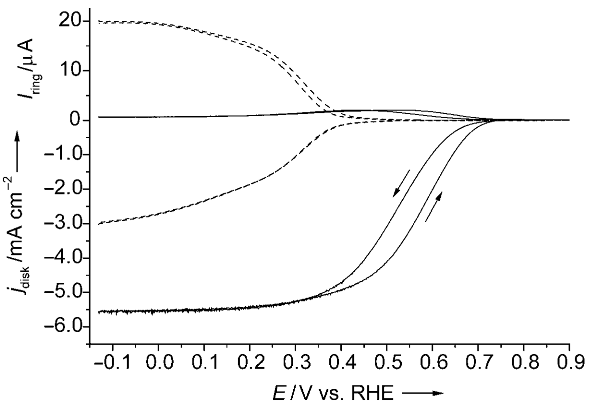

Figure 1. Reduction of O_2 at a rotating Pt ring/glassy carbon disk electrode supporting [Cu(Hdatrz)]/Vulcan (solid line) or unmodified Vulcan XC-72 (dashed line) at 1600 rpm in $NaClO_4$ (0.1 M) and Britton–Robinson buffer (0.04 M, pH 7.0) saturated with O_2. Disk current density (j_{disk}) is shown on the lower half and ring current (I_{ring}) is shown on the upper half of the y-axis. The disk potential was scanned at 5 mVs^{-1}; the ring potential was constant at 1.2 V.

and the reduction current becomes diffusion-limited at approximately 0.35 V. At more negative values, the ring current is less than 1 μA, which corresponds to less than 5% peroxide intermediate generation or almost complete four-electron reduction of O_2 to water. At more positive potentials, the ring current increases until 50% peroxide intermediate formation is observed at approximately 0.7 V, which corresponds to an average of three electrons per O_2 molecule (more detailed analyses, including Koutecky-Levich and Tafel plots are given in the Supporting Information).

The catalyst is sufficiently stable to allow the evaluation of ORR activity over a wide range of pH values (Figure 2). The onset potential was found to increase linearly at a rate of 30 mV per pH unit of the electrolyte (Figure 2), which is equivalent to a −30 mV per pH unit change using a pH-independent reference. This is half the value of −60 mV per pH unit predicted by the Nernst equation for a reaction involving the transfer of one H^+ ion per electron and implies that the rate-determining step involves the transfer of two electrons and one H^+ ion. This is consistent with either the reduction of two Cu^{II} centers and the concomitant protonation of a bridging OH^- or O^{2-} ligand or with the reduction of O_2 to a hydroperoxo (HOO^-) intermediate.

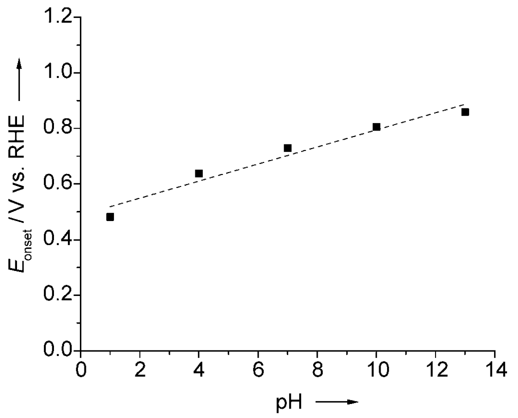

Figure 2. Potentials at which the onset of O_2 reduction occurs at electrodes modified with [Cu(Hdatrz)] in electrolytes of varying pH and a linear fit ((31 ± 4) mV per pH unit slope and (0.49 ± 0.03) V y-intercept). Electrodes were rotated at 1600 rpm in either $HClO_4$ (0.1 M), $NaClO_4$ (0.1 M), and Britton-Robinson buffers (0.04 M, pH 4, 7, or 10) or NaOH (0.1 N) saturated with O_2. Potential scanned at 5 mVs^{-1}. Onset potential chosen as the potential at which the current density reaches −5 μA cm^{-2}.

The observed ORR onset of 0.86 V (versus RHE) at pH 13 represents a reduction of the ORR overpotential to 0.37 V. To the best of our knowledge, this makes the [Cu(Hdatrz)] complex the most efficient synthetic copper-based ORR electrocatalyst reported to date and the first to be evaluated at this pH value. The 0.73 V onset at pH 7 is higher than the 0.67 V onset reported for a Cu complex with a hexaazamacrocycle which was previously the highest onset reported at this or any pH.[10] At more acidic pH values the onset is comparable to the best mononuclear Cu phenanthroline complexes.[7]

At pH 7 the catalyst shows excellent cycle-to-cycle stability; 24 hour stability tests showed a decay of approximately 4% in limiting current (see the Supporting Information). At pH 1 and pH 13 there was a significant decline in activity upon repeated cycling of the applied potential, which is likely to arise from the instability of the complex at these pH values.

The two reported crystal structures containing Cu and the hdatrz ligand are consistent with the bridging coordination mode illustrated in Scheme 1 and consistent with the approximate 1:1 ratio between Cu and Hdatrz shown by elemental analysis.[14] In order to characterize the adsorbed catalyst complex, magnetic susceptibility measurements were undertaken as shown in Figure 3. The expected value of χT for an $S = {}^1\!/_2$ system is 0.374 emu K mol^{-1}, which is independent of the temperature and would indicate the presence of normal spin-only mononuclear Cu sites. The values of χT for the crystalline complexes of Cu with Hdatrz increase with temperature, which is consistent with an antiferromagnetic interaction between Cu^{II} ions with a singlet ground state and a

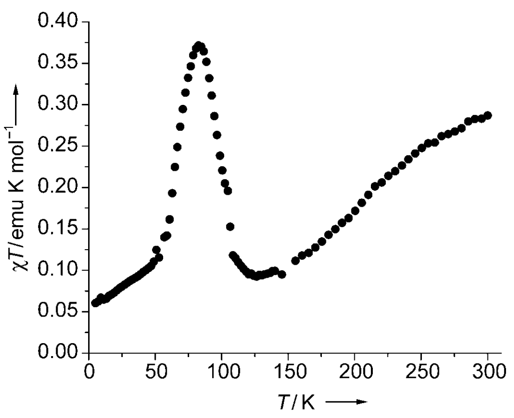

Figure 3. Temperature dependence of the χT value of the [Cu(Hdatrz)]/Vulcan composite. Data are shown per mole of Cu and corrected for the significant diamagnetism of the Vulcan substrate.

thermally populated triplet state.[14] For the adsorbed [Cu(Hdatrz)] complex, we observe the expected low χT value at low temperature. This value increases with temperature to a peak value of 0.372 emu K mol^{-1} at 83 K, which implies that most of the Cu spins are effectively unpaired at this temperature. However, as the temperature is raised further there is a subsequent decrease in the χT value followed by a gradual increase to a value of 0.283 emu K mol^{-1} at 295 K. This complicated behavior indicates that the complex is distinct from those previously crystallized, but indicates that spin pairing between Cu centers occurs and that closely spaced Cu centers must be present.

The development of simple methods to adsorb insoluble Cu complexes onto carbon black opens the possibility of developing other catalysts that are more closely aligned to the three Cu active site of laccase. It also allows the use of ex situ methods to characterize and obtain structural information about the on-electrode catalyst. The observed ORR activity of the [Cu(Hdatrz)] complex is very high for synthetic copper-based electrocatalysts and, given the demonstrated activity of laccase, we believe large increases in activity may be realized upon the development of improved model complexes.

Experimental Section

Preparation of [Cu(hdatrz)]-modified Vulcan XC-72: Vulcan XC-72 (1.00 g, Cabot), Cu(SO$_4$)$_2$·5 H$_2$O (0.200 g, 0.801 mmol, Aldrich, 99.995 %), and water (20 mL, Milli-Q UV Plus, 18.2 MΩ) were combined and sonicated to form a viscous suspension. A solution of 3,5-diamino-1,2,4-triazole (hdatrz, 0.159 g, 1.60 mmol, Aldrich, 98 %) in water (10 mL) was then added dropwise with stirring. The mixture was stirred for 18 h, the solids were collected by suction filtration, dried in vacuo for 3 h at 90 °C, and pulverized with a mortar and pestle. Elemental analysis (%) found: C 85.2, H 0.14, N 5.36, Cu 3.76.

Electrochemical characterization: A catalyst ink containing [Cu(Hdatrz)] (1.0 mg mL^{-1}) on Vulcan and Nafion solution (4 μL mL^{-1} 5 %, Aldrich) was prepared in water and sonicated for 10 min. A 20 μL drop was applied to a glassy carbon disk electrode (0.196 cm^2) with a Pt ring (Pine Instruments, glassy carbon polished with alumina (0.05 μ) and sonicated in water prior to electrode assembly) and dried under a stream of Ar. The Ar flow was adjusted by trial and error until a uniform catalyst distribution across the electrode surface was obtained. Electrochemical measurements were performed using a CHI 760C bipotentiostat (CH Instruments) using with a Pt gauze counter electrode and a "no-leak" Ag/AgCl reference electrode (Cypress Systems), which was separated from the working electrode by a Luggin capillary. The reference electrode was calibrated to the RHE scale after each experiment by saturating the cell with H$_2$ and measuring the open circuit potential at the Pt ring electrode. All potentials are reported versus RHE. Britton–Robinson buffers were used to control the pH at intermediate values and were prepared to contain CH$_3$COOH (0.04 M), H$_3$PO$_4$ (0.04 M), H$_3$BO$_4$ (0.04 M), and NaClO$_4$ (0.1M) and the pH was adjusted with NaOH (0.1N).

Magnetic characterization: The 5 to 300 K magnetic susceptibility, $\chi(T)$, was measured on a Quantum Design MPMS-5XL magnetometer. In order to correct for the diamagnetism of the carbon support, the susceptibility of unmodified Vulcan XC-72 was also measured across the entire temperature range and then subtracted.

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