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Electrochemical reduction of oxygen using a Metal-Organic complex of Cu^{2+}

Carla M. Ormachea, José L. Fernandez, Pedro M.E. Mancini, and María N. Kneeteman

IQAL (UNL-CONICET), Laboratorio Fester – QUÍMICA ORGANICA (FIQ), Universidad Nacional del Litoral, Santa Fe, Argentina.

* *Correspondence: jlfernan@fiq.unl.edu.ar; Tel.: +543424571164*

Abstract: A biphenyl-based copper complex was evaluated as electrocatalyst for the oxygen reduction reaction (*orr*), for a possible application as cathode material in fuel cells. To carry out this evaluation, the complex was supported on Vulcan carbon and deposited as a film on a glassy carbon rotating disk electrode by drop-casting a 1-µL drop of a suspension of carbon in a solution of the complex in DMSO containing Nafion as ionic conductive binder, and drying under vacuum. The cyclic voltammogram in 0.1 M NaOH solution showed voltammetric peaks between 0.8 and 1.0 V vs. Reference Hydrogen Electrode, which suggest the existence of electron transfer processes from/toward the ligand. The *orr* was tested in oxygen-saturated (1 atm) solution by linear sweep voltammetry, which showed significant *orr* current at relatively low overpotential (around -0.4 V), demonstrating the ability of the complex to efficiently electrocatalyze the *orr*.

Keywords: oxygen reduction reaction, electrocatalysis, metal-organic complex.

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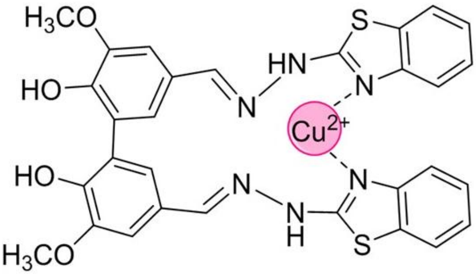
1. Introduction

The design and synthesis of metal-organic complexes (biphenyl structures) for transition metal cations of the p block, is an important topic due to their promising application in systems that imitate the enzyme activity as an alternative catalyst to replace expensive materials based on noble metals. Specifically, the cupric cation (Cu^{2+}) complexes have an important function in the reduction of oxygen.

The electrochemical reduction of oxygen to water ($O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$), usually known as oxygen reduction reaction (*orr*), is an important reaction that participates in many natural and technological processes. Specifically, this is the reaction that operates at the cathode in most types of fuel cells [1], being one of the main factors that limit the performance of low-temperature fuel cells [2] due to the serious kinetic limitations of most catalysts that are being currently used [3,4]. In contrast, natural organisms carry out this reaction very efficiently by using copper-based metalloproteins, such as bilirubin oxidase and laccase [5], which have Cu(II)-based poly-nuclear active sites that are coordinated by nitrogen groups from amino acids. The active centers of these metalloproteins constitute ideal models to mimic, and are the sources of inspiration for the design of new types of electrocatalysts modified by organo-metallic complexes that are potentially active for the *orr* [6]. Although the use of transition metal complexes to reduce oxygen began to be investigated in the middle of the last century with the introduction of Fe(II) and Co(II) porphyrins and phthalocyanines [7], the study of Cu(II) complexes inspired by enzymes is more recent. The pioneering works in this type of approach were carried out by Anson and collaborators and were oriented especially to Cu complexes with substituted 1,10-phenanthroline [8]. They received renewed interest in the middle of the last decade by the group of Chidsey and collaborators [9], who demonstrated a very marked effect of the nature of the substituents on the Cu(I/II) potential and on the *orr* potential onset. While there were several isolated reports of synthesis and evaluation of a variety of Cu complexes with N-linked aromatic ligands (e.g. based on poly-L-histidine [10], pyrrole [11], and imidazole groups [12], among others [13]), the works of Gewirth et al. with ligands of the tris (2-pyridylmethyl) amine type (TPA and related) and with substituted triazoles [6,13-15] are more promising for the *orr*. This group has reported the most efficient Cu electrocatalyst to date in an alkaline medium, which is a Cu complex with 3,5-diamino-1,2,4-triazole ($Cu_2(Hdatzr)_2^{2+}$) [15]. Although the performance of these complexes is still much lower than that of the metalloproteins, these studies shed some light on some fundamental aspects. For example, the nature, substitution, and topology of the ligand is crucial for the performance of the complex to catalyze the *orr*.

Recently the design and synthesis of a novel biphenyl-based chromogenic chemosensor derived from 5,5'-*bis*-vanillin for the determination of Cu^{2+} was reported [16]. In this context, this work presents an electrochemical application study of this copper complex shown in Scheme 1, where the Cu(II) ion is coordinated by nitrogen groups. This complex was evaluated as a potential electrocatalyst for the *orr*.



Scheme 1. Chemical structure of the copper complex studied in this work

It was found that the nitrogens of the benzothiazol moieties coordinate with Cu^{2+} generating two new Cu-N bonds. The Cu^{2+}-N bond length value is 1,88 Å and 1,89 Å for each -N. The GAP value of the ligand decreases from 89,81 Kcal/mol to 13,51 Kcal/mol with the complexation with cupper, stabilizing the system [16].

2. Materials and methods

The Cu complex (CuL) was synthesized from a solution of the ligand (L) in DMSO by adding stoichiometric amounts of copper chloride. For electrode preparation, a DMSO-based ink containing CuL (or just L) and finely dispersed carbon was dropped onto a polished glassy carbon (GC) rotating disk electrode (3 mm diameter), and dried under vacuum at room temperature. This ink was prepared by dispersing 20 mg of Vulcan XC72R (Cabot Co., USA) in 0.5 mL of 20 mM CuL (or L) solution in DMSO, followed by a further addition of 0.1 mL of 5 wt.% Nafion solution (Aldrich, USA) and ultrasonic agitation for 15 min. Electrochemical experiments were carried out in a three-electrode cell using a Reversible Hydrogen Electrode (RHE) as reference electrode and a gold wire as counter-electrode. The GC/C-CuL and GC/C-L rotating disk electrodes (RDEs) were mounted in an EDI 10K rotating disk system (Radiometer, France) and used as working electrodes. Voltammetric and polarization curves were measured using a CHI1140B potentiostat (CH Instruments, USA), which allowed to control the electrode potential (*E*) and measure the electrode current (*i*). All experiments were performed in 0.1 M NaOH solution that was previously saturated either with N_2 (for voltammetric evaluation) or with O_2 (for oxygen reduction evaluation) at 1 atm.

3. Results and Discussion

The cyclic voltammograms (CV) of unrotated GC/C-CuL and GC/C-L electrodes in 0.1 M NaOH solution saturated with N_2 are shown in Figures 1(a) and 1(b), respectively. While the current is mostly governed by the capacitive response of carbon in both electrodes, two oxidation peaks can be clearly detected at c.a. 0.84 V and 0.89 V vs. RHE in the anodic scan of the CuL voltammetric response. The cathodic scan shows only a single peak at 0.7 V vs. RHE, whose background-subtracted integrated charge is about the same of both anodic peaks. Thus, this peak probably involves the irreversible reduction of the surface species that were oxidized in the anodic scan. On the other hand, the CV of the ligand presents two oxidation peaks at more anodic potentials (> 0.9 V vs. RHE), and the respective quasi-reversible reduction peaks. This evidence indicates that the ligand molecule is capable to reversibly exchange electrons, probably by oxidation/reduction of the oxygenated groups of the bis-vanillin molecule [17,18]. However, the presence of Cu ion that is coordinated by the ligand seems to facilitate the oxidation by shifting the oxidation potentials toward more cathodic values, and to make the reduction process more irreversible.

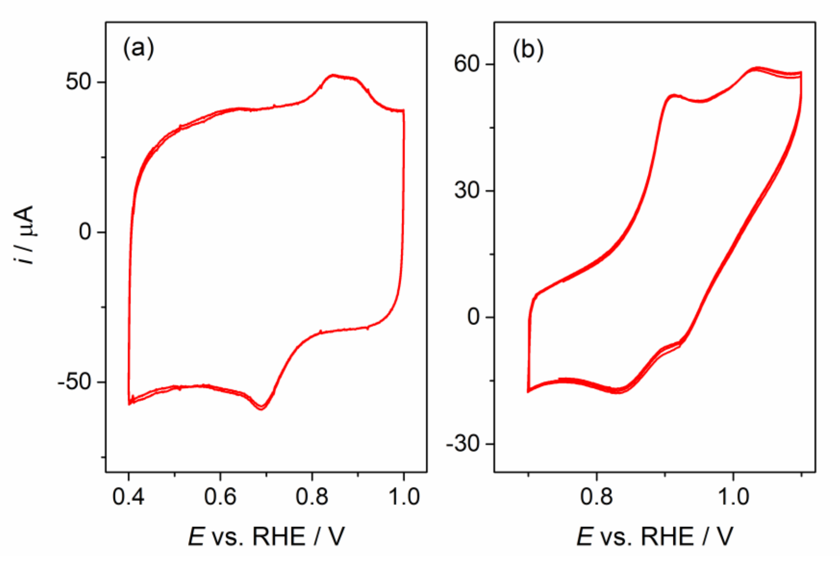


Figure 1. Cyclic voltammograms of GC/C-CuL (a) and GC/C-L (b) electrodes in 0.1 M NaOH solution saturated with N_2 (1 atm). Scan rate: 0.05 V s^{-1}.

Electrodes were analyzed in the same solutions saturated with O_2 in order to evaluate their performance for the oxygen reduction reaction (*orr*). While the voltammetric response of the GC/C-L electrode did not significantly vary, the response of the GC/C-CuL electrode evidenced mayor changes over the analyzed potential range. As it is shown in Figure 2(a), by rotating the electrode in order to increase the mass transport rate it was possible to identify significant oxygen reduction currents that approached a mass-transport limiting value, indicating a high electrocatalytic activity of CuL for oxygen reduction. Moreover, Figure 2(b) shows polarization curves measured by slow potentiodynamic scans at different rotation rates, which show a stable behavior of this material to carry out the *orr*. From these curves, it is verified that *orr* currents are detected already at potentials as high as 0.85 V vs. RHE, which means an overpotential close to -0.4 V (calculated taking into account that the equilibrium potential for oxygen reduction is 1.23 V vs. RHE). The reaction operates under near-activated control down to 0.7 V vs. RHE. At $E < 0.7$ V the mass transport rate affects the *orr* current, but no clear limiting current is reached over the analyzed potential range.

It should be noted that the material is able to electro-reduce oxygen only when the potential is, roughly, more cathodic than the oxidation potentials of the surface processes that were detected by cyclic voltammetry. On the other hand, the absence of *orr* current on the GC/C-L electrode indicates an active role of the Cu ion in the reaction. This evidence suggests that the O_2 molecule is reduced by a redox reaction with coordinated Cu(I) ions that, upon oxidation, are further re-reduced by electron transfer from carbon via the functional groups of the ligand.

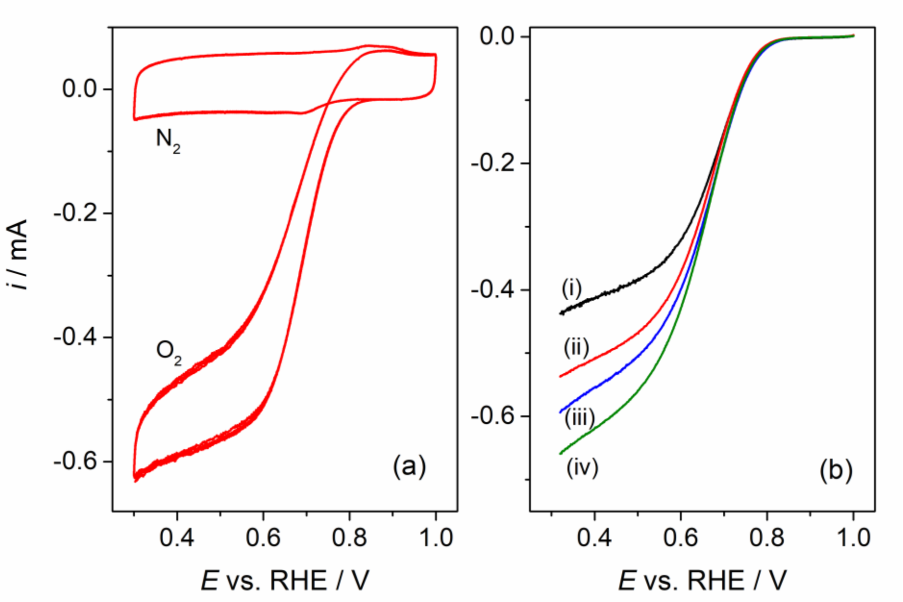


Figure 2. (a) Cyclic voltammograms of a GC/C-CuL RDE rotated at 900 rpm, in 0.1 M NaOH solution saturated with N_2 and O_2. Scan rate: 0.05 V s^{-1}. (b) Steady-state polarization curves measured by slow potentiodynamic scans (scan rate: 1 mV s^{-1}) on a GC/C-CuL RDE rotated at 400 (i), 900 (ii), 1200 (iii), and 1600 (iv) rpm, in 0.1 M NaOH solution saturated with O_2.

4. Conclusions

Copper complexes with biphenyl-based ligands are capable to function as active sites for the electrochemical oxygen reduction. Electron transfer to the ligand molecule can be efficiently performed from an inert conductive electrode, and the electrons can be further transferred to the Cu-based active redox center. Studies seeking to acquire important information about the performance of this new type of electroactive material, such as the effective number of exchanged electrons (relevant to figure out whether the oxygen reduction product is water, water peroxide, or a mixture of both products), and the effect of the ligand functional groups and of the cation, are underway in our laboratories.

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