We have synthesized a copper-based catalyst for the oxygen reduction reaction in low temperature fuel cells. Catalysts were prepared by covalently attaching a phthalocyanine-type ligand to a carbon black surface, and adding Cu(OAc)$_2$. The phthalocyanine-type ligand provides the nitrogen to form the presumed catalytic centers with the Cu metal. Rotating ring disk electrode experiments revealed that the catalytic activity of the as-synthesized material is greatly enhanced after one-step pyrolysis under inert atmosphere, reaching an onset potential of 0.82 V vs. RHE in acidic environment after thermal treatment at 950 °C, making this the best copper-based ORR catalyst in acid reported to date.

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State of the art proton exchange membrane fuel cells (PEMFCs) use Pt as the catalyst for oxygen reduction reaction (ORR) at the cathode. Due to the high cost of Pt, minimizing the Pt content of the PEMFC has become a major endeavor to make feasible the mass commercialization of PEMFC. While a number of efforts seek to achieve this by improving the activity and utilization of Pt-based catalysts, the most direct approach is replacing Pt with non-precious metal catalysts (NPMC). Synthesis of NPMCs is often inspired by natural systems: enzymes, such as laccase, are very efficient ORR catalysts. Such Cu oxides are known to reduce oxygen at approximately 1.2 V vs. the reversible hydrogen electrode (RHE) under mild pH conditions. The ORR in these enzymes is known to occur in a three or four Cu-atom active site. Since Jasinski first reported the use of Cu-phthalocyanine as a catalyst for ORR, a prolonged effort has been devoted to developing ORR catalyst materials based on transition metal complexes. The best NPMCs to date are based on Fe and Co, and can be unsupported or supported on carbon. In general their catalytic activity increases with increasing Fe content, at pH 4.8, of non-pyrolyzed Cu-3-ethynyl-1-10-phenanthroline covalently attached to an azide-modified glassy carbon electrode via a “click” reaction, allowing controlled catalyst coverage on the carbon surface, finding evidence that to achieve O$_2$ reduction to water by an adsorbed Cu catalyst, two proximal Cu sites are required.

In a previous study we reported the synthesis and RDE characterization of Cu-triazole catalysts adsorbed, and covalently attached (via diazonium coupling) to a carbon black support. Immobilized catalysts showed higher stability than adsorbed ones in acidic environment, as demonstrated by RDE cycling in O$_2$ saturated electrolyte. Few researchers have investigated pyrolyzed Cu catalysts for ORR. Galbiati et al. reported the catalytic activity of materials prepared from a mixture of glucose and histidine with Cu and Fe in acidic media. Catalysts were prepared in a two-step pyrolysis, the first at 600 °C, followed by a second treatment at 900 °C, both in a N$_2$ atmosphere. The Cu to Fe ratio in the materials was varied from 0 to 100% in 25% increments. The pure Cu sample presented an RDE onset potential of 0.58 V vs. normal hydrogen electrode (NHE), with the catalytic activity increasing as a function of the Fe content, reaching a maximum onset potential of 0.8 V vs. NHE for the sample containing 100% Fe.

In this work we report the synthesis and characterization of a novel pyrolyzed Cu-based catalyst for ORR. Catalysts were prepared by covalently attaching a phthalocyanine-type ligand to a carbon black surface, via diazonium coupling using Cu(OAc)$_2$ salt as the metal source. RRDE studies were carried out to determine the catalyst activity and its dependency on loading, catalyst stability and aspects of its electron transfer mechanism. X-ray powder diffraction (XRD), energy-dispersive X-ray spectroscopy (EDS) and scanning electron microscope (SEM) techniques were used to gain insight into the catalyst composition.

**Experimental**

Catalysts were prepared using a two-step process. In the first step, 1,2-benzenedinitrile was covalently anchored to the carbon support by a “click” reaction, allowing controlled catalyst coverage on the carbon surface, finding evidence that to achieve O$_2$ reduction to water by an adsorbed Cu catalyst, two proximal Cu sites are required.

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on carbon. After cooling to ambient temperature, the suspensions were centrifuged and the carbons washed with water, acetone, and diethyl ether. The carbons were then dried overnight in a hot bath. This two-step synthetic scheme used to prepare catalysts containing immobilized TrPc ligand is summarized in Scheme 1.

RRDE experiments were carried out using a two-channel VMP3 potentiostat from Bio-Logic, a Pine instruments MSR rotator and RRDE electrode with a 0.2472 cm² glassy carbon disk and Pt ring (320 μm ring-disk gap, 6.25 mm and 7.92 mm ring inner and outer diameter, respectively). The RRDE collection efficiency N was measured experimentally and determined to be 38% (37% is the theoretical value for 100% collection based on the ring-disk geometry). Inks were prepared using a 40/60 weight% ionomer to catalyst ratio and methanol as solvent. For most experiments, aliquots of the inks were solution-cast onto the GC electrode to reach loadings of 600 μg/cm². However, some experiments were conducted with loadings of 400 and 200 μg/cm² to determine the effect of catalyst loading on the apparent, measured catalytic activity. Catalysts were tested in aqueous 0.1 M H₂SO₄ electrolyte. For each experiment the electrolyte was de-oxygenated for at least 30 minutes with ultrahigh purity N₂; voltammograms were collected with the electrode static and rotating at 1600 rpm for background correction. This procedure was repeated in O₂-saturated electrolyte. RDE onset potentials were arbitrarily determined as the potential (vs. RHE) at which the ORR current density reaches a value of 50 μA/cm². Additional experimental details are described in the supporting information.

Results and Discussion

The as-synthesized catalysts showed an onset potential of 0.52 V, comparable to the best reported Cu based catalysts in the literature. After thermal activation under a N₂ atmosphere for 1 hour, the catalytic activity of the catalyst was greatly enhanced, reaching a maximum onset potential of 0.82 V at 950 °C, making our Cu-TrPc/C the best Cu based catalyst in acidic media reported to date. Figure 1 shows RDE plots for the Cu-TrPc/C catalyst before and after thermal activation, with thermal treatment temperature ranging from 600 to 950 °C. A comparison of the Cu-TrPc/C pyrolyzed at 950 °C (Cu-TrPc950) and commercial 30% Pt/C from BASF is shown in figure S1 in the supplementary information.

Another important parameter needed to assess the catalytic reaction is the number of electrons transferred during the ORR, which is an indication of the reaction path. A catalyst that reduces oxygen directly to water through a 4 electron reaction path is desired. The number of electrons transferred n can be determined with the RRDE experiment according to equation 1:

\[
n = \frac{4I_d}{I_d + I_r/N}
\]

Where \(I_d\) is the disk current, \(I_r\) is the ring current and \(N\) the collection efficiency. This method to determine the value of \(n\) as an intrinsic property of the catalyst is based on the assumption that the catalyst layer deposited on the electrode is a very thin film, with no interaction between sites such that, for example, a two-electron product escapes but is further reduced as it moves through the film and then to the ring. Experiments were carried out on the Cu-TrPc/C pyrolyzed at 950 °C (Cu-TrPc950) to determine how the catalytic activity and the value of \(n\) depends on the catalyst layer thickness and thereby to gain a better understanding of the role of these sequential reactions on the observed ORR electron transfer data. Electrodes were prepared with loadings of 600, 400 and 200 μg/cm². Disk and ring current plots in Figure 2 reveal a clear dependency of the ORR activity on the catalyst loading. For loadings of 600 μg/cm² and 400 μg/cm² the calculated...
number of electrons is close to 3.9 in most of the scanned potential range, indicating an apparent reduction of oxygen directly to water as the preferred reaction path. However, at loadings of 200 μg/cm² the calculated number of electrons is circa 3.6 in the low potential range, decreasing to 2 for the higher potential values, indicating a significant production of H₂O₂. The high production of H₂O₂ at the lowest loading indicates the reduction of oxygen to water at higher values of 600 and 400 μg/cm² likely occurs via a two-step process; an initial two electron reduction of oxygen to H₂O₂ followed by a two electron reduction of H₂O₂ to water. This behavior has been reported before for other non-PGM catalysts. Even for the thinnest layer used here, there might still be significant two-step reduction in the catalyst layer.

XRD performed on the Cu-TrPc/C catalyst is shown in Figure 3 (experimental details are given in the supporting information). It can be seen that after pyrolysis at 600 °C and 700 °C very sharp Cu° peaks are detected, indicating the formation of large Cu metal particles during pyrolysis. As the pyrolysis temperature increases above 800 °C a mixture of Cu° and Cu oxide (Cu₂O) is detected. The XRD peak widths are rather narrow, approximately 0.19 degrees (FWHM) for the Cu(111) peak and 0.34 degrees (FWHM) for the Cu₂O(111) peak in the sample pyrolyzed at 950 °C. These correspond to Scherrer domain widths of 45 nm and 24 nm, respectively. However, using SEM imaging we detect many much larger domains of Cu-Cu₂O, frequently approaching 1–2 microns in width. It is likely that the domain size obtained via Scherrer analysis is more akin to a grain size than a particle size, and not an appropriate measure of the latter quantity. SEM and EDS were carried out using a Hitachi TM-3000 SEM at a 15 kV accelerating voltage. The EDS spectra shown in Figure S2 are normalized to the carbon peak and, indicate the presence of Cu, N and O in the as-synthesized catalyst. Qualitatively, the content of Cu, N and O decreases after pyrolysis. SEM images also reveal a high content of metallic Cu particles in the samples and that the Cu particles are homogeneously distributed on the carbon surface.

Figure 2. (a) Disk current and (b) number of electrons transferred n for Cu-TrPc950 at different

Figure 3. XRD pattern of Cu-TrPc catalyst before and after pyrolysis from 600 °C to 950 °C.

Figure S3. To determine if the catalytic activity is mainly due to the presence of Cu and Cu oxide in the carbon surface, we prepared a control sample consisting of Cu(OAc)₂ adsorbed on the BP2000 and pyrolyzed at 950 °C. RDE experiments demonstrated that the catalytic activity of the sample without the TrPc ligand is very low compared to the CuTrPc950 catalyst, Figure S4, which is an indication that the metal-ligand complexes are necessary for the formation of catalytic centers.

RDE stability experiments conducted on the Cu-TrPc950 catalysts are shown in Figure 4. Voltammograms are collected at 20 mV/s in N₂ saturated electrolyte, cycling repeatedly from 0.6 to 1.0 V vs. RHE at pH 1 according to protocols reported by Zelenay's and Popov's groups for NPMCs. After 4000 cycles the catalyst shows good stability.

It is worth emphasizing the importance of the ligand immobilization on the catalytic activity. Heat treatment at high temperatures incorporates species derived from the metal-ligand complexes on to the carbon surface, forming the catalytic centers. Covalent attachment, in contrast to adsorption, strongly bonds the metal-ligand complexes to the carbon surface, facilitating the incorporation onto the carbon support. Moreover, because the immobilization approach that we used is not limited to (limited and randomly spaced) oxygen functionality on the surface, we can achieve a more homogeneous distribution of the ligand on the carbon surface and a higher ratio of ligand to carbon. This translates to the formation of more catalytic centers. RDE experiments comparing catalysts that are respectively adsorbed or immobilized CuTrPc/C pyrolyzed at 950 °C are shown in figure S5. The
catalyst from immobilized CuTrPc/C showed higher catalytic activity than the adsorbed catalyst.

Conclusions

We have synthesized a novel Cu-based material that catalyzes the ORR, making it suitable as the air electrode for application in low temperature fuel cells and related electrochemical devices. The maximum activity is reached after a one-step pyrolysis at 950 °C under inert atmosphere. This catalyst is the best Cu based NPGM material yet reported in terms of onset voltage (0.82 V vs. RHE measured at 50 μA/cm²). XRD, SEM and EDS indicate the presence of high metallic Cu content. Ongoing work in our laboratory is devoted to control the Cu content and creating Cu alloys with other transition metals to determine the impact of these parameters on the catalytic activity. RDE data showed that ligand immobilization on the carbon surface helps to increase the catalytic activity with respect to adsorbed catalysts; this is potentially due to an increased formation of catalytic centers during the pyrolysis of immobilized ligand-based materials.

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