Metal Centers Drive Selectivity of Electrocatalytic Oxygen Reduction Reaction Promoted by Tetrapyrazinoporphyrazine Complexes

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Fuel cells represent a promising technology for the future decarbonization of the mobility sector. However, the efficient use of H_2 and O_2 to produce electricity still requires noble metal catalysts such as platinum and ruthenium. In particular, the Oxygen Reduction Reaction (ORR) is complex and limiting due to its mechanism, which involves the transfer of four electrons and four protons to produce water. The search for alternative catalysts exhibiting high selectivity is progressing at a rapid pace. In this context, this group previously unveiled a homogeneous catalyst based on titanium-centered tetrapyrazinoporphyrazines (TPyzPz) for the ORR, noting a certain modularity in the selectivity toward either a two- or four-electron reduction reaction. In this study, the influence of different metal centers (magnesium (Mg), cobalt (Co), copper (Cu), and zinc (Zn)) and various substituents is investigated on the tetrapyrazinoporphyrazine ring. The findings indicate a strong dependence of activity and selectivity on these modifications. Notably, cobalt and copper catalysts exhibit a selectivity greater than 90% toward H_2O production in the ORR. However, alterations to the macrocycle structure significantly affected the reactivity of these catalysts. These new insights highlighted the importance of careful structural design in the development of the next generation of ORR catalysts.

1. Introduction

Among the challenges facing humanity, the search for clean, inexpensive, and environmentally friendly energy sources and vectors is gaining increasing attention due to the ever-growing demand for energy.[1] In this context, fuel cells may represent a promising alternative to fossil fuels, as they are able to convert chemical energy into electrical energy through electrochemical reactions.[2] Key to the operation of these devices is the optimization of the oxygen reduction reaction (ORR) at the fuel cell cathode. Among the approaches pursued to improve the ORR and to direct this process toward a four-electron reduction of molecular oxygen (O_2) to water (H_2O), the use of catalysts has proved to be the most effective[3] and in line with the 9th principle of green chemistry.[4] Despite the performance of platinum in catalyzing the four-electron process, the cost of this metal is very high[5] and its storage is limited.[3] Moreover, given the slow kinetics of the ORR process,[6] finding an alternative catalyst to platinum may represent a challenge. In addition to transition metal oxides,[7] phosphides,[8] nitrides,[9] carbides,[10] and sulfides[11,12] transition metal/nitrogen-doped carbon materials,[13] inspired to bio-based structures, such as metal-containing porphyrins,[14] corroles and phtalocyanines,[15] have emerged as a promising alternative.[16] Besides being less expensive than noble metals, their activity can be easily modified by tuning not only the central metal site, but also tailoring the coordination environment[17] or introducing groups able to orientate the oxygen in close proximity to the metal center.[16a,18] Pyrolysis and heteroatom doping of the material can be also undertaken.[19] Besides these macrocycles, the aza-analog of phtalocyanines, namely tetrapyrazinoporphyrazines (TPyzPzs) are attracting attention, finding many applications as catalysts, pigments, photoactivators, and electronic components also in electrochemical devices.[20] Nevertheless, the usage of TPyzPzs as ORR catalysts is still limited to simple structures adsorbed on glassy carbon electrodes or supported on nanotubes and complexed with metals such as iron (Fe (II)), cobalt (Co (II)), or zirconium (Zr (IV)).[21] In order to contribute to the achievement of the 6th and 7th sustainable development goals (clean water and sanitation / affordable and green energy), our group has recently unveiled homogeneous titanium (Ti)-based TPyzPzs as alternative electrocatalysts in the ORR process.[22] It is noteworthy that the

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straightforward alteration of the Ti-precursor quantities during the synthesis of the complex enabled us to modify the ORR selectivity, directing it toward the two- or four-electron reduction reaction. To further extend the application of tetrakis-2,3-[5,6-di-R$_8$-pyrazino]porphyrazines as sustainable and efficient ORR electrocatalysts, we have synthesized and evaluated a series of substituted TPyzPzs exploring both the influence of different non-noble transition metals (M = Mg, Cu, Co, and Zn) and substituents (e.g., phenyl, 4-methoxyphenyl and 4-bromophenyl, 2-pyridyl groups) on the macrocycle framework. In regard to the selection of the metal center, Co,[23] Cu,[24] and Zn[25] complexes are well documented to be active ORR electrocatalysts. Magnesium, despite being less prevalent in such applications,[26] has been demonstrated to possess an appropriate affinity for oxygenated species, as evidenced by the pivotal role of Mg-based cofactors in numerous enzymes.[27]

2. Experimental Section

2.1. Synthesis of Metal Complexes

As reported in the Supporting Information, metal-based complexes of tetrakis-2,3-[5,6-di-R$_8$ pyrazino]porphyrazine] **3a-e-M** were obtained either by cyclotetramerization of the starting material **1a-e** at high temperature or by complexation of the corresponding ligand **2a-e** (see **Scheme** 1).

Substituted 2,3-dicyano-1,4-pyrazines **1a-e** were synthesized following a modified procedure reported by Mørkved from diaminomaleonitrile and a suitable α-diketone in acetic acid as the solvent.[28] The synthesis of magnesium (**3a-Mg**) and copper (**3a-e-Cu**) complexes was achieved through the cyclotetramerization of the corresponding starting material **1a-e**, conducted in the presence of magnesium amylate or metallic copper powder. In contrast, the formation of cobalt (**3a, c-e-Co**) and zinc (**3a-Zn**) complexes was accomplished through the complexation of suitable macrocycles **2a-e**. The latter were synthesized from **1a–e** by autocyclotetramerization at high temperatures employing 1,8-diazabiciclo[5.4.0]undec-7-ene (DBU) as a catalyst. After Soxhlet purification the ligand was reacted with cobalt or zinc acetate in refluxing pyridine in order to obtain the corresponding complex. Following purification, the resulting greenish/bluish solids from all metal complexes **3a-e-M** were collected by centrifugation and dried under vacuum until reaching a constant weight.

2.2. Electrochemical Characterization

Cyclic voltammetry (CV) experiments were carried out at room temperature with a standard electrochemical setup, composed of a computer-controlled potentiostat, AUTOLAB PGSTAT12. The electrochemical cell was a three-electrode cell with:

- Electrodes: glassy carbon disc 5 mm diameter (working electrode), rotating ring-disc electrode (RRDE) with platinum (Pt) disc 5 mm diameter and Pt ring (working electrode in RRDE experiments), glassy carbon rod (counter electrode), Ag/AgCl/NEt$_4$Cl 0.1 м in acetonitrile (reference electrode).

Since a non-aqueous electrolyte was employed, the redox couple ferrocene/ferrocenium was used as an additional reference. In the conditions employed, 0.40 м H$_2$SO$_4$ in DMSO, the latter redox couple resulted to be 465 mV more positive than the reference electrode.

- Electrolyte: 0.40 м H$_2$SO$_4$ in DMSO.
- Scan Rates: 10, 50, 100, and 200 mV s^{-1}.
- N$_2$ or O$_2$ atmosphere, with a continuous gas flow of 100 mL min^{-1}.

Bulk electrolyzes were performed on a glassy carbon plate electrode with an active surface of 10 cm^2. Prior to each measurement, the electrolyte (0.4 м H$_2$SO$_4$ in DMSO) containing the metal complex **3a-e-M**, at a concentration of 1 mм, was saturated with O$_2$. During the electrolysis, the potential was kept constant at −0.3 V versus Ag/AgCl for 8 h while the solution was stirred and purged with O$_2$.

Rotating ring disk electrode (RRDE) experiments were performed with the addition of a Metrohm RRDE rotator and a Metrohm RRDE tip (RRDE Pt-Pt) with a 5 mm diameter Pt disc and a Pt ring as working electrode. Ag/AgCl/KCl (3 м) and a Pt sheet were employed as the reference electrode and the counter electrode, respectively. The measurements were executed by cycling the electrode potential between 0.4 V and −1.25 V versus Ag/AgCl with a scan rate of 100 mV s^{-1}. The ring potential was adjusted to 1.2 V versus Ag/AgCl in O$_2$ atmosphere. Rotation rates of 0, 100, 200, 400, 800, 1600, and 3200 rpm were applied while the gas flow was stopped.

RRDE experiments were reported in the Supporting Information. The same RRDE experiment was performed on a solution containing the reversible redox couple [Fe(CN)$_6$]$^{4-}$/[Fe(CN)$_6$]$^{3-}$ to determine the collection efficiency (CE) of the experimental setup (Figure S1, Supporting Information).[29] The couple [Fe(CN)$_6$]$^{4-}$/[Fe(CN)$_6$]$^{3-}$ readily oxidizes/reduces with 100% faradaic efficiency, therefore CE can be obtained as:

$$CE = -\frac{i_r n_r}{i_d n_d} \tag{1}$$

where i_r and i_d are the ring and disc currents, respectively, and n_r and n_d are the electron transferred in disc and ring reactions, respectively. For [Fe(CN)$_6$]$^{4-}$/[Fe(CN)$_6$]$^{3-}$ $n_r = n_d = 1$. With this configuration, a CE value of 0.296 (Figure S2, Supporting Information) is obtained. The fraction of electrons transferred to O$_2$ to form hydrogen peroxide (H$_2$O$_2$) was calculated as:

$$\text{fraction of electrons transferred to form } H_2O_2 = -\frac{i_r}{i_d\, CE} \tag{2}$$

in the potential range +0.10 / −0.30 V versus Ag/AgCl, to avoid the contribution to ORR of the disc electrode itself.

3. Results and Discussion

In order to assess the activation potential of the simplest complexes **3a-M** (M = Mg, Cu, Co, and Zn), which lack substituents on the periphery of the TPyzPzs core structure, and to explore the influence of the metal center on the ORR process, CV measurements were carried out both under N$_2$ and O$_2$ atmosphere.

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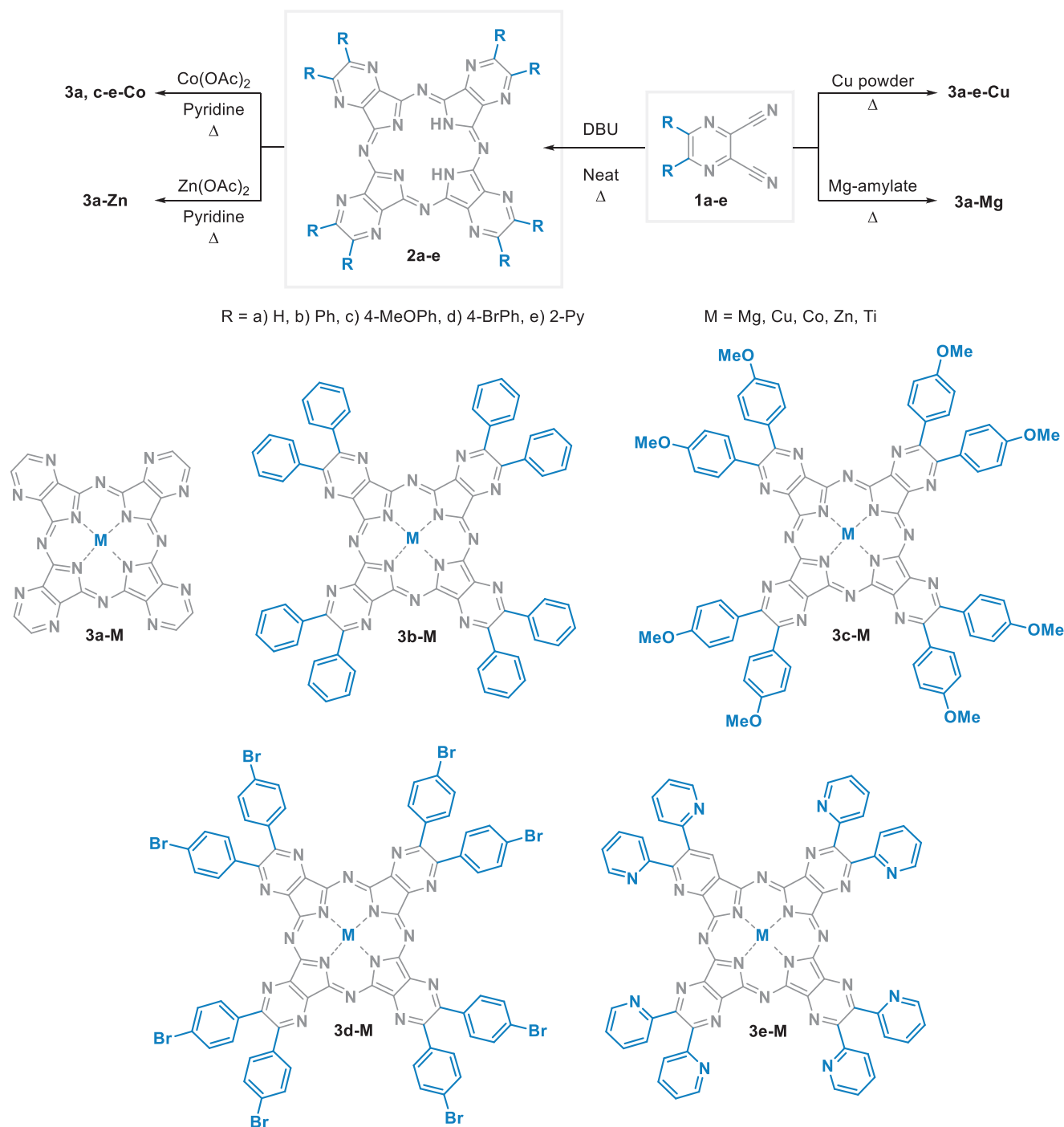
Scheme 1. Top: reaction scheme for the synthesis of metal-based complexes of tetrakis-2,3-[5,6-di-R_8 pyrazino]porphyrazine] **3a-e-M** – R = a) H, b) Ph, c) 4-MeOPh, d) 4-BrPh, e) 2-Py; M = Mg, Cu, Co, Zn, and Ti. Bottom: summary of the structures of metal complexes **3a-e-M** tested in the Oxygen Reduction Reaction.

To detect ORR activity, larger cathodic currents than those under N_2 flow should be observed below 0.25 V (vs Ag/AgCl) under O_2. Moreover, blank experiments must be carried out being the glassy carbon electrodes itself able to reduce molecular O_2 to H_2O_2. Consequently, in order for a complex to be considered a catalyst for the ORR, it must also exhibit a greater current yield

under O_2 atmosphere than that observed in the blank experiment and this reduction should take place at a potential more positive than −0.5 V versus Ag/AgCl, where the working electrode itself starts the reduction of O_2.

As shown **Figure 1**, no activity in ORR was observed for complexes **3a-Mg** and **3a-Zn**. In fact, their CVs in O_2 atmosphere
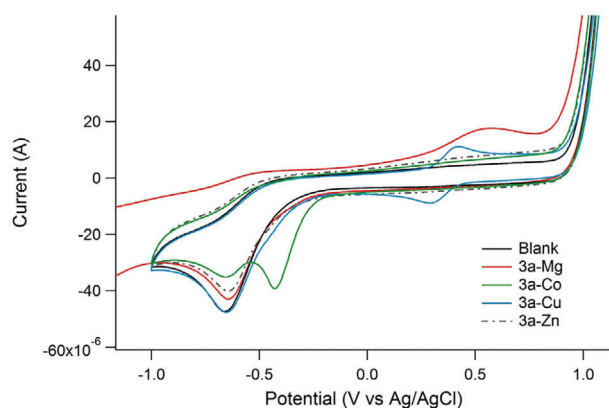
Figure 1. CVs in 0.40 м H_2SO_4 in DMSO under O_2 atmosphere for complexes **3a-M** (M = Mg, Cu, Co, and Zn). For comparison, the blank experiment (electrolyte without any complex) is also reported.

Table 1. Charge transferred and TON for the bulk electrolyzes performed on complexes 3a-M (M = Mg, Cu, Co, and Zn).

Complex	Charge transferred [C]	TON[a]
3a-Mg	−2.5	< 1
3a-Cu	−7.3	1.3
3a-Co	−37.5	6.6
3a-Zn	−2.2	< 1

[a] TON values were calculated considering the number of electrons transferred (n) for each molecule of O_2 reduced as $n = 3.9$, based on RRDE evidences.

exhibited no additional features compared with the blank experiment. Conversely, the introduction of cobalt (**3a-Co**) and copper (**3a-Cu**) led to a markedly different behavior in the complex activity. For complex **3a-Cu**, we observed the reversible oxidation and reduction of the couple Cu(I)/Cu(II) at ≈0.4 V versus Ag/AgCl (Figure 1, blue line). Furthermore, the onset of the ORR current at 100÷150 mV was found to be more positive than in the blank, although its current density was only ≈5 µA larger than in the blank. When cobalt was employed, complex **3a-Co** exhibited a 40 µA cathodic current peak 200 mV more positive than the current peak observed in the blank (Figure 1, green line). It is noteworthy that the current peak at −0.6 V versus Ag/AgCl, which is observed in the blank as well as in all other complexes **3a-M**, is less intense in the presence of **3a-Co**. This is due to the depletion of O_2 in the electrolyte in the presence of **3a-Co**, which is already active in the ORR at less cathodic potentials.

In order to gain insights into the selectivity of the O_2 reduction to H_2O or H_2O_2 for the copper and cobalt complexes, RRDE experiments were conducted. During the measurement, the potential of the disk electrode was scanned while keeping the ring electrode at the oxidation potential of H_2O_2. During the ORR the reduction products, H_2O or H_2O_2, diffuse at the ring electrode where no signal is observed when H_2O is produced, while a signal is obtained in the presence of H_2O_2 when it is oxidized back to O_2. Moreover, the RRDE rotation controls the mass transport of the species from the disc to the ring electrode. The recovery efficiency at the ring electrode was evaluated with a standard measurement with the reversible redox couple $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$. The aforementioned RRDE measurements demonstrated that both **3a-Co** and **3a-Cu** can reduce O_2 mainly to H_2O with yields >90%, while less than 5% of the transferred electrons concur to H_2O_2 production (Figures S4 and S5, Supporting Information). It is noteworthy that in the presence of ligand **2a**, the nature of the metal center exerts a significant influence on the selectivity of the reduction products. While the titanyl (TiO^{2+}) complexes, previously reported by our group,[22] produced respectively H_2O_2 (≈80% of the transferred electrons and 90% selectivity as observed in complex **3a-Ti**) or similar amounts of H_2O_2 e H_2O (≈30% of the electrons were transferred to H_2O_2, with 45% selectivity as observed in the pres-

ence of an excess of titanium *tert*-butoxide), complexes **3a-Co** and **3a-Cu** produced H_2O with selectivity above 90%. CV evidences were confirmed by bulk electrolysis at controlled potential (**Table 1**). While the charge transferred to **3a-Mg** and **3a-Zn** was limited at 2.5 and 2.2 C, respectively, **3a-Co** and **3a-Cu** showed a charge transfer of 37.5 C and 7.3 C, respectively. Subsequently, the turnover number (TON) value was calculated based on the reduction products and the quantity of O_2 reduced by each complex. The average number of electrons transferred to an O_2 molecule was determined to be 3.9 from the RRDE experiments (see Supporting Information), with H_2O identified as the primary reduction product. Based on the aforementioned evidence, the TON of **3a-Co** and **3a-Cu** was determined to be 6.6 and 1.3, respectively (Table 1). Because both values are >1, even though by a small margin in the case of **3a-Cu**, we demonstrated the catalytic activity of **3a-Co** and **3a-Cu** toward ORR. The TON value measured for **3a-Co** is even larger than the Ti-complexes previously reported, for which we assessed TON values of 4.5 and 4.4, respectively.[22] Conversely, for **3a-Mg** and **3a-Zn** the TON was less than 1, even employing for its assessment the lowest possible value of electrons transferred, i.e., $n = 2$. Therefore, in accordance with CV results, **3a-Mg** and **3a-Zn** do not shows any measurable activity in ORR.

In order to study the influence of substituents on the macrocycle framework, we synthesized differently substituted Cu- and Co-complexes (Scheme 1). In the case of Cu-based complexes **3b-e-Cu**, the introduction of phenyl (complex **3b-Cu**) or 4-methoxy substituted phenyl (complex **3c-Cu**) substituents on the macrocycle framework was not beneficial for the ORR activity (**Figure 2a,b**). While the deactivating effect was less marked in the presence of 4-bromo substituted phenyl rings (complex **3d-Cu**) and 2-pyridyl groups (complex **3e-Cu**), showing a lower current density (Figure 2c,d), complexes **3d-Cu** and **3e-Cu** resulted to be less efficient than not substituted **3a-Cu** and the Ti-complexes, previously published by our group.[22]

On the compounds **3d-Cu** and **3e-Cu**, which showed activity toward ORR, we performed RRDE experiment to determine the selectivity in the reduction products. For complex **3e-Cu**, bearing 2-pyridyl substituents, the 45 ± 5% of the electrons transferred concurred to H_2O_2 formation, which will therefore be the more abundant product of reduction with 62 ± 8% yield, while H_2O yield will be limited to 38 ± 8% (Figure S7, Supporting Information). Conversely, the presence of 4-bromo substituted phenyl rings on the macrocycle **3d-Cu** reduced to 35 ± 5% the amount of electrons contributing to H_2O_2 formation, with more similar yields for the two reduction products compared with

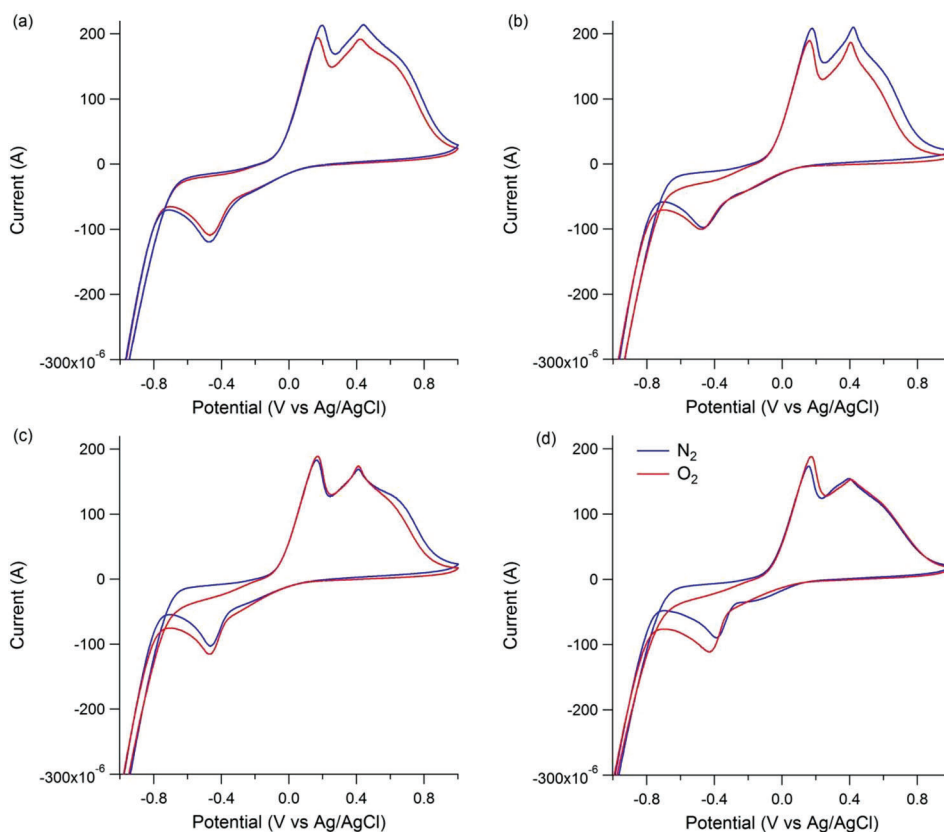**Figure 2.** CVs in 0.40 M H_2SO_4 in DMSO under N_2 and O_2 atmosphere for complexes: a) **3b-Cu**, b) **3c-Cu**, c) **3d-Cu**, d) **3e-Cu**.

3e-Cu: $52 \pm 8\%$ yield for H_2O_2 and $48 \pm 8\%$ for H_2O (Figure S6, Supporting Information). Considering these results, in the case of Cu complexes, the ligand is able to direct the selectivity toward the ORR products, in fact, without substituent H_2O is produced, whereas 2-pyridyl and, even more importantly, 4-bromo phenyl substituents promote the concomitant production of H_2O and H_2O_2.

In the case of Co-based complexes **3c-e-Co**, no activity toward ORR was evidenced from CV results, where no significant differences between the voltammetry in N_2- and O_2-saturated electrolyte between 0 and -0.75 V versus Ag/AgCl was observed (**Figure 3**). Differently from copper, for which we observed weak activity with certain substituted ligands, Co-complexes behave very similarly to TiO^{2+} complexes, for which the unsubstituted
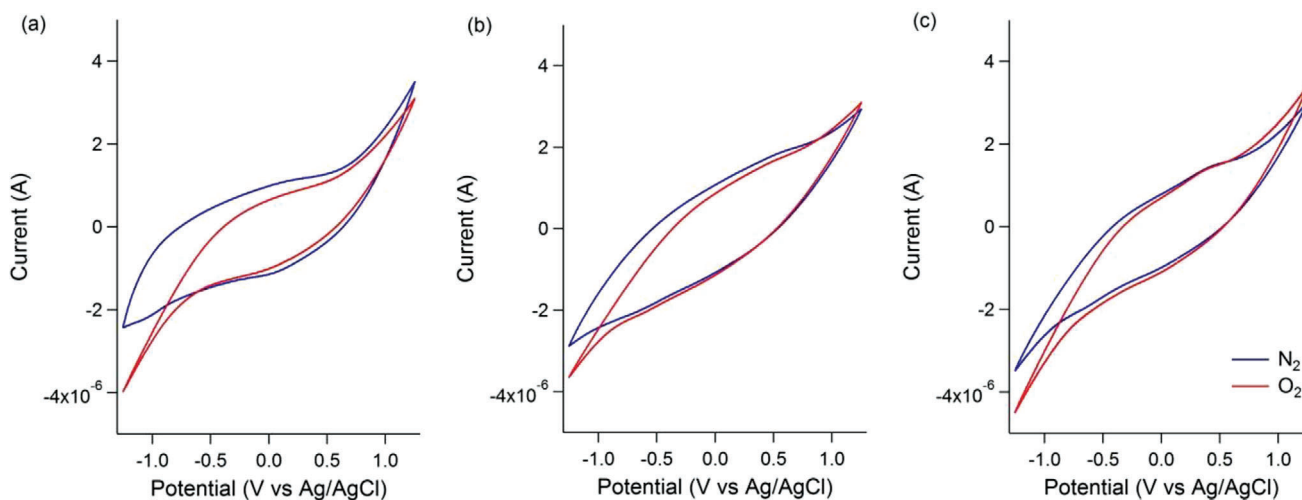
Figure 3. CV in 0.40 M H_2SO_4 in DMSO under N_2 and O_2 atmosphere for complexes: a) **3c-Co**, b) **3d-Co**, c) **3e-Co**.

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