



Review Article

Strategies to improve the catalytic activity and stability of bioinspired Cu molecular catalysts for the ORR

Karina Muñoz-Becerra¹, José H. Zagal²,
Ricardo Venegas² and Francisco J. Recio³

Abstract

The oxygen reduction reaction (ORR) is essential for energy conversion devices such as fuel cells and metal-air batteries. The use of expensive and scarce noble metal materials to catalyze the ORR is a limitation for the massification of these energy conversion technologies. Copper molecular catalysts that mimic the active sites of metalloenzymes such as laccase are under continuous development. In this minireview, we present the strategies to increase the activity and stability of the copper catalysts for the ORR. The flexibility, lability, and electronic character of the ligands are crucial to promote the ORR. In addition, the use of polymers as backbone for multi-copper catalysts and the synthesis of copper carbon-based pyrolyzed catalysts present remarkable results with promissory applications.

Addresses

¹ Universidad Bernardo O'Higgins, Centro Integrativo de Biología y Química Aplicada (CIBQA), General Gana 1702, Santiago, 8370854, Chile

² Facultad de Química y Biología, Universidad de Santiago de Chile, Av. Libertador Bernardo O'Higgins 3363, Santiago, Estación Central, Región Metropolitana, Santiago, Chile

³ Departamento de Química Física Aplicada, Facultad de Ciencias, Universidad Autónoma de Madrid, C/Francisco Tomás y Valiente 7, 28049, Madrid, Spain

Corresponding authors: Recio, Francisco J (javier.recio@uam.es); Venegas, Ricardo (ricardo.venegas@usach.cl)

Current Opinion in Electrochemistry 2022, 35:101035

This review comes from a themed issue on **Organic and Molecular Electrochemistry**

Edited by **Guobao Xu, Ismael Díez-Pérez and Francesco Paolucci**

For a complete overview see the [Issue](#) and the [Editorial](#)

Available online 3 May 2022

<https://doi.org/10.1016/j.coelec.2022.101035>

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Keywords

Copper molecular catalysts, Oxygen reduction reaction, Catalytic activity, Stability, Reactivity indexes.

Introduction

The widespread use of energy conversion and storage devices such as fuel cells and metal-air batteries is hampered by the high cost associated with the need to use Pt-based electrocatalysts in the cathode. Over the past decades, several strategies to replace expensive and scarce noble metal catalysts with earth-abundant elements have been proposed, the so called “Platinum Group Metal-free Electrocatalysts” [1–4]. Among these materials, the rational design of bio-inspired molecular electrocatalysts that mimic the active sites of metalloenzymes for activation of the dioxygen molecule is one of the most explored strategies. The electronic structure of metal centers and their electrocatalytic properties can be tuned through both the electronic character of the ligands and their interaction with electrode surfaces [5,6].

The metalloenzymes-mediated O₂ activation has been extensively studied in the field of bioinorganic chemistry and has served as inspiration for the development of new catalysts [7]. Enzymes involved in the respiratory chain and other biological processes, such as cytochrome *c* and laccase present highly specific active sites capable of overcoming the spin restriction of O₂ on organic substrates [8–10]. Moreover, when some enzymes, such as laccase, are immobilized on electrode substrates, they efficiently reduce oxygen via 4-electrons to water at almost no-overpotential in pH 5 (1.2 V vs RHE) [11]. Nevertheless, the lack of stability and large molecular sizes of metalloenzymes results in a low current density and durability for practical applications. For this reason, the synthetic routes are focused not only on the modulation of electrocatalytic properties but also on the stability of molecular catalysts.

In nature, multicopper oxidases (MCOs), such as laccases or bilirubin oxidases, exhibit polynuclear sites where dioxygen is effectively reduced to water via 4 electrons. MCOs take advantage of the O₂ oxidizing capacity to degrade organic substrates through the structure of their active sites, where the Type-1 site (T1) picks up the electrons from the organic substrate

and transport them to a trinuclear cluster, formed by one T2 and two T3 coppers, where O₂ is efficiently reduced to water in a concerted mechanism [9,11,12]. Interestingly, the intermetallic distance of Cu atoms is dynamic, which allows the entry of O₂ and the exit of water [13]. Inspired by MCOs, a variety of Cu-complexes have been studied as electrocatalysts for ORR. Nevertheless, Cu-based molecular catalysts still show low catalytic activities compared to the state-of-the-art Pt/C due to the synthetic challenges to modulate their electronic structures and electron transfer. Over the past decades, mononuclear Cu-complexes with ligands such as porphyrins, phthalocyanines, substituted triazoles, amino-alkyl ligands, and other aromatic N-donor ligands have been studied as electrocatalysts for the ORR and were extensively reviewed by Thorset et al. [14]. The present minireview focuses on the new advances to improve the catalytic activity and stability of mono- and multi-copper molecular electrocatalysts for the ORR.

Mononuclear Cu-catalysts for ORR

Although MN4 molecular catalysts are considered as paradigm molecules for the study of the electrocatalytic properties for electrochemical reactions, Cu-phthalocyanines and Cu-porphyrins exhibit limited catalytic activity for the ORR [5]. This can be explained by the interaction between the dioxygen and the active-copper site, which is conditioned by the electronic dz^2 density of the metal center orbitals, since it modulates the O₂-M binding energy [15]. In other words, frontier orbitals should have a “*d*” character to facilitate the O₂-M interaction. Unlike the Fe, Mn, and Co phthalocyanines, the full-filled dz^2 orbital of the Cu-phthalocyanines is detrimental to the O₂-M interaction, as it was demonstrated, in an original way, for Cu phthalocyanines attached to Au(111) surfaces via axial ligands [16,17]. Another limitation is the macrocycle ligand rigidity of phthalocyanines and porphyrins, which hinders the Cu(II)-square-planar \rightleftharpoons Cu(I)-tetrahedral structural change associated with the redox transitions. Therefore, the catalytic activity for Cu-complexes depends on an additional structural factor that requires flexible or labile ligands to diminish the Cu(II)/Cu(I) reorganizational energy, similar to the lacasse dynamic active center [13]. In such a manner, the study of mononuclear Cu catalyst in homogeneous and heterogeneous catalysis has been performed with chelating ligands such as 1,10-phenanthrolines (phen), tris(2-pyridylmethyl)amine (tmpa), and their derivatives (Figure 1a).

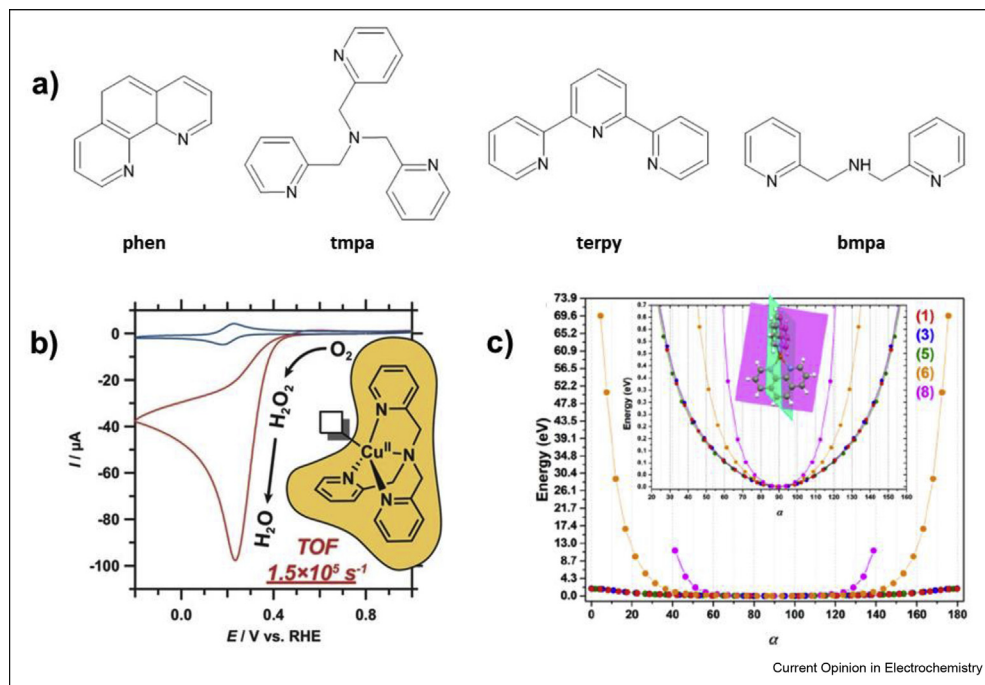
One way to increase the catalytic activity is by the study of the ligands lability, which play an important role since it can help to the Cu(II)/Cu(I) conformational change and the creation of vacancies on the Cu(I) site, favoring the adsorption of O₂ [18]. Ma et al. [19] analyzed two mononuclear copper(II)-complexes

[Cu(H₂O)₂(HL)]*2H₂O and [Cu(py)₂(HL)] which have the same tridentate ligand (L = 2-OH-4-(OH)-C₆H₂CH = NCH₂CO₂H). The authors proposed a mechanism where the lability of water and py ligands allow the formation of a coordination site for O₂ in both catalysts, being the highest activity of the [Cu(py)₂(HL)] catalysts attributed to the remaining py ligand that stabilizes the ORR intermediate species due to its aromatic nature.

For mononuclear complexes, the highest electroactivity is presented by Cu(tmpa) catalysts, which show the best values on turnover frequency (TOF = $1.5 \times 10^5 \text{ s}^{-1}$) for homogeneous ORR catalysis at pH 7 (Figure 1b) [20]. The high catalytic activity is associated with the flexibility of the ligand that allows the tetrahedral coordination geometry preferred by Cu(I) centers. To prove that the flexibility of the ligands is a key parameter for the catalytic activity, Smits et al. [21] synthesized two copper complexes with lower flexibility than tmpa, using terpy and bmpa tridentate ligands. The results showed lower catalytic activity in terms of onset potential and TOF for the more rigid ligands. Venegas et al. [22], through theoretical calculations show that the higher steric impediment for the conformational transition, quantified as the torsional energy required to reach a Cu(II) square-planar conformation (Figure 1c), shifts the redox potential towards more positive values with a consequent increase in the onset potential. The good activity of these 2,9-substituted complexes could be related to the loss of one ligand during the ORR, which allows adsorption of O₂ on the Cu(I)-active site.

The ORR mechanisms in homogeneous catalysis through a single or binuclear pathway is still a controversial matter. Ali et al. [23] proposed that the ORR on tetradentate mononuclear catalysts, 1,2-phenylene-diimine-dioxime copper-complex, occurs with the formation of the binuclear Cu₂O₂ species during the ORR, which is favored when flexible ligands can withstand metal oxidation states and coordination geometries changes. Langerman et al. present a mechanistic study with Cu(tmpa) [20] for ORR homogeneous catalysis and reveals a 2 × 2 mechanism, which reveals a mononuclear stepwise mechanism avoiding the formation of binuclear species proposed by Karlin's group [24]. The study concludes that the reaction in the mononuclear copper center is faster than the μ -(O₂)-dimer formation. Davydov et al. [25] present a study using γ -irradiation cryoreduction of mononuclear tridentate Cu(I)O₂ complexes to elucidate the mechanism in Cu(tmpa) derivatives. The characterization of the intermediates corroborates the mechanism in a single active site. In heterogeneous catalysis, the mechanism is dependent on the distance among the confined species and generally is considered a mechanism via one active center.

Figure 1



a) Chelating ligands forming mono-nuclear Cu complexes. b) Cyclic voltammetry for Cu(tmpa) in solution in (blue) Ar-saturated electrolyte and (red) O₂-saturated electrolyte. Reproduced from Ref. [20] with permission. Copyright 2019, John Wiley & Sons, Ltd. c) Potential energy profile constructed as a function of the torsional angle (α) for Cu(I)-1,10-phenanthrolines derivatives. Reprinted with permission from Ref. [22]. Copyright 2019 American Chemical Society.

The catalysts that perform the ORR via direct 4-electrons mechanism are the most desirable for applications in conversion energy devices since this reaction delivers the most energy from ORR. However, the H₂O₂ could be an alternative to O₂ as an oxidant in the development of new fuel cells such as the single compartment hydrogen peroxide fuel cells, where the H₂O₂ acts as both fuel and oxidizer [26]. The mononuclear arrangements promote the 2-electrons pathway in alkaline media as it was reported for the heterogeneous catalysts [Cu(heimp)₂] [27] and [Cu(L) (TfO)] [28]. Moreover, the binuclear [Cu₂(addpa) (CH₃CN)₂(ClO₄)₂](ClO₄)₂ complex also exhibits an ORR mechanism via 2-electrons in homogeneous phase [29].

Multinuclear Cu-catalysts for ORR

Although multicopper catalysts present higher catalytic activity than mononuclear ones, they also present low stability on electrode surfaces for practical purposes. One of the most ORR active binuclear Cu-catalysts reported was obtained using the ligand Hdatz and Cu(II)-salts [30]. However, its low stability under operational conditions of alkaline fuel cells [31] could be related to the electronic configuration of the Cu(I)-active sites, which has no crystalline field stabilization and can exchange stabilizing ligands during the Cu(II)/

Cu(I) redox process [32]. In an attempt to mimic the MCOs tri-copper active site, Thiagarajan *et al.* [33] rationally designed a tri-copper complex, Cu₃(7-N-Etppz(CH₂OH)), at an optimal Cu–Cu distance. The results show an efficient reduction via a 4-electrons mechanism with superior onset potential. The mechanism involving the transfer of the third electron to the tri-copper center is proposed as the rate-limiting step at pH 7.

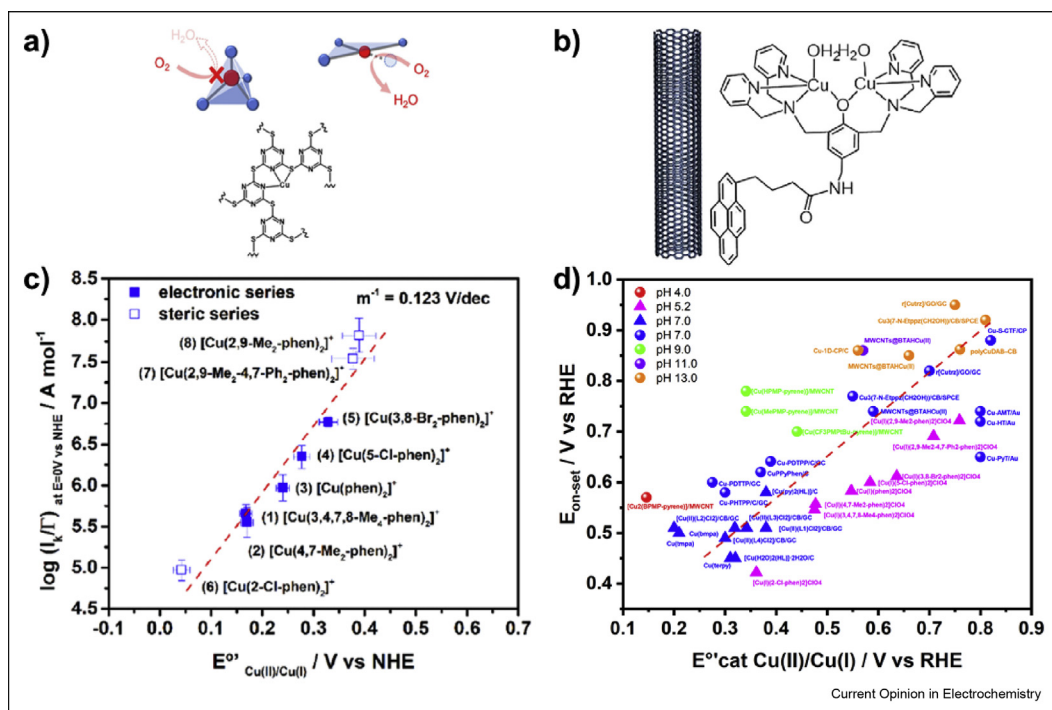
One of the alternatives to increase the activity and stability of the multicopper complexes is the use of polymers that acts as backbone, increasing the conductivity and the π - π interaction with the carbon support. Different conductive polymers have been tested, such as CuPPyPhen/C, Cu-PHTPP, Cu-PDTPP/C/CG, and polyCuDAB–CB [34–37], showing an increase in both activity and stability being potentially applicable as a cathode in microbial fuel-cell [35]. The highest catalytic activity was achieved with the design of periodically extended structures, Iwase *et al.* [38] synthesize an S-linked covalent triazine framework for a distorted three-coordinated configuration around Cu-centers with an accessible coordination site. The authors associate this available site with the remarkable catalytic activity (Figure 2a).

Another alternative to overcome the lack of stability of Cu-based heterogeneous systems is to use molecular anchors between the copper complex and the electrode. Gentil et al. [39] designed a binuclear copper complex with a pendant pyrene group to anchor the complex onto the CNT surface ($[\text{Cu}_2(\text{BPMP-pyrene})]$) and constructed a Pt-free H_2/Air bioinspired fuel cell, reaching a power density of 0.15 mW cm^{-2} . The main handicap of using Cu-catalysts in real fuel cells is the lower stability and stability in acid media. However, both parameters improve in alkaline media [31]. Following this study, a new family of unprotected phenolate mononuclear copper-bearing pyrene groups was synthesized to anchor the complexes to MWCTN [40]. These catalysts dimerize on the electrode surface to form binuclear nanostructured catalysts with enhanced ORR activity. This strategy have been also proved with mononuclear copper catalysts, Ham et al. [41] covalently anchor mononuclear Cu-phenanthrolines on a gold surface via a diazonium coupling reaction by the inclusion of a diazo-group in the 5-position of 1,10-phenanthroline ligands, increasing the interaction between the catalyst and the carbon support. In addition, for tridentate copper-complexes substituted with carboxy-derivatives in the

ligand N,N-bis(2-pyridylmethyl)phenylmethylamine increases the catalysts-carbon support interaction [42].

Another family of copper-catalysts that have emerged in the last decade is the pyrolyzed Cu–N–C materials, where the copper atoms are embedded in a nitrogen-doped carbon matrix by a bi-, tri- or tetra-coordination similar to molecular catalysts. These copper catalysts present a good reactivity for several energy conversion reactions as ORR or CO_2 electroreduction [43,44]. Kato et al. [45] reported the synthesis of a very stable catalytic material for the ORR denominated $r[\text{Cutrz}/\text{GO}]$, obtained through short-term pyrolysis of the $[\text{Cu}(\text{II})_3(\text{trz})_3(\mu\text{-OH})]\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ complex, $\text{Cu}(\text{II})\text{trz}$, and graphene oxide. The resulting composite exhibits an onset potential of $+0.82 \text{ V vs. RHE}$ at pH 7.0 and $+0.95 \text{ V vs. RHE}$ at pH 13, being one of the most active Cu catalysts reported so far. He et al. [46] pyrolyze CuSO_4 , carbon black, and two different ligands (N-based ligand BTA and O-based ligand DHQ). The Cu-active sites differ in their first coordination sphere since the Cu in the pyrolyzed-BTA are coordinated to N atoms while in the pyrolyzed-DHQ are coordinated to O atoms. This change in the structure of the active sites

Figure 2



a) Schematic representation of the tri-coordination environment of Cu-centers in the S-linked triazine framework Cu–S-CTF, underlining the activity for the ORR of the tri-coordinated Cu(I) moiety over the tetra-coordinated one. Reprinted with permission from Ref. [38]. Copyright 2018, John Wiley & Sons, Ltd. b) Representation of the $[\text{Cu}_2(\text{BPMP-pyrene})]/\text{MWCTN}$ composite catalysts. Reprinted with permission from Ref. [39], Copyright 2019, Elsevier. c) Linear correlation between the $\log(I_k/I)$ vs. $E^\circ_{\text{Cu(II)/Cu(I)}}$ for Cu-bis-phenanthroline derivatives. Reproduced from Ref. [22] with permission. Copyright 2019 American Chemical Society. d) Correlation between the E_{onset} vs the $E^\circ_{\text{Cu(II)/Cu(I)}}$ of the catalysts revised in this work (Table 1). Triangle represents mononuclear Cu-catalysts and circles represents multinuclear Cu-catalysts.

allows modulating the selectivity for the ORR (4-electrons or 2-electrons mechanism). It is important to note that the pyrolysis process is analogous to the polymerization techniques that allow the synthesis of multiple Cu active sites in a highly conductive carbon-based matrix.

Since the reaction mechanisms involve the binding of the oxygen molecule on one or two copper centers, the binding energy Cu–O₂ is a reactivity descriptor for the ORR on these systems. For the MN_x catalysts and related materials with a similar active center as the M–N–C pyrolyzed catalyst, the experimental formal

Table 1

Electrochemical parameters and experimental conditions for the Cu-complexes revised in this review.

Cu complex	E _{on-set} /V vs. RHE	E ^o _{Cu(II)/Cu(I)} /V vs. RHE	n ^o of e ⁻ transferred	Conditions	Ref.
Cu–S-CTF/CP	0.88	0.82	~ 4.0	pH 7 (PBS)	[38]
r[Cu ₂ (OTf) ₂]/GO/GC	0.82	~ 0.70	~ 4.0	pH 7 (BRS)	[45]
	0.95	~ 0.75	~ 4.0	pH 13 (0.1 M NaOH)	
Cu ₃ (7-N-Etppz(CH ₂ OH))/CB/SPCE	0.77	0.55	3.46	pH 7 (BRS)	[33]
	0.92	0.81	3.5	pH 13 (0.1 M NaOH)	
MWCNTs@BTAHCu(II)	0.74	0.59	~ 3.8	pH 7 (PBS)	[54]
	0.86	0.57	~ 4.0	pH 11 (PBS)	
	0.85	0.66	~ 4.0	pH 13 (0.1M KOH)	
Cu-AMT/Au	0.740	~ 0.8	–	pH 7 (BRS)	[55]
polyCuDAB–CB	0.862	0.760	4.0	pH 13 (0.1 M KOH)	[37]
Cu-1D-CP/C	0.86	0.56	4	pH 13 (0.1 M KOH)	[56]
[Cu(Hdatrz)]/Vulcan	0.73	–	3.9	pH 7 (BRS)	[30]
	0.86	–	–	pH 13 (0.1 M NaOH)	
Cu-HT/Au	0.720	~ 0.8	–	pH 7 (BRS)	[55]
[CuL ₄ (OTf) ₂]/GC	0.72	–	2.19	pH 13 (0.1 M KOH)	[28]
Cu ₃ (7-N-Etppz)/CB/SPCE	0.71	–	3.24	pH 7 (BRS)	[33]
Cu ₃ (7-Dpiy)/CB/SPCE	0.71	–	3.5	pH 7 (BRS)	[33]
Cu-PyT/Au	0.650	~ 0.8	–	pH 7 (BRS)	[55]
Cu-PDTPP/C/GC	0.641	0.389	4.0	pH 7 (PBS)	[36]
Cu ₂ (7-Dpiy)//CB/SPCE	0.64	–	2.84	pH 7 (BRS)	[33]
CuPPyPhen/C	0.62	0.37	3.82	pH 7 (PBS)	[34]
Cu-PDTPP/GC	0.600	0.275	3.8	pH 7 (PBS)	[36]
[Cu(py) ₂ (HL)]/C	0.58	0.38	3.6	pH 7 (PBS)	[19]
Cu-PHTPP/C/GC	0.58	0.30	3.8	pH 7 (PBS)	[35]
[Cu ₂ (BPMP-pyrene)]/MWCNT	0.57	0.146	~ 4.0	pH 4.0 (BRS)	[39]
	0.71	–	–	pH 9.0 (BRS)	
[Cu(II) (L1)Cl ₂]/CB/GC	~ 0.51	0.38	~ 4.0	pH 7 (PBS)	[42]
[Cu(II) (L2)Cl ₂]/CB/GC	~ 0.51	0.20	~ 4.0	pH 7 (PBS)	[42]
[Cu(II) (L3)Cl ₂]/CB/GC	~ 0.51	0.319	~ 4.0	pH 7 (PBS)	[42]
[Cu(II) (L4)Cl ₂]/CB/GC	~ 0.51	0.342	~ 4.0	pH 7 (PBS)	[42]
Cu(tmpa) ^a	0.50	0.21	3.9	pH 7 (PBS)	[20]
Cu(bmpa) ^a	0.49	0.30	2.5–2.7	pH 7 (PBS)	[21]
Cu(terpy) ^a	0.45	0.31	2.7–2.5	pH 7 (PBS)	[21]
[Cu(H ₂ O) ₂ (HL)]·2H ₂ O/C	0.45	0.32	3.7	pH 7 (PBS)	[19]
[Cu(I) (3,4,7,8-Me ₄ -phen) ₂]/ClO ₄	0.546	0.475	3.8	pH 5.2 (ABS)	[22]
[Cu(I) (4,7-Me ₂ -phen) ₂]/ClO ₄	0.557	0.477	3.7	pH 5.2 (ABS)	[22]
[Cu(I) (phen) ₂]/ClO ₄	0.583	0.547	3.1	pH 5.2 (ABS)	[22]
[Cu(I) (5-Cl-phen) ₂]/ClO ₄	0.600	0.584	3.1	pH 5.2 (ABS)	[22]
[Cu(I) (3,8-Br ₂ -phen) ₂]/ClO ₄	0.612	0.636	3.8	pH 5.2 (ABS)	[22]
[Cu(I) (2-Cl-phen) ₂]/ClO ₄	0.422	0.361	2.8	pH 5.2 (ABS)	[22]
[Cu(I) (2,9-Me ₂ -4,7-Ph ₂ -phen) ₂]/ClO ₄	0.691	0.708	2.9	pH 5.2 (ABS)	[22]
[Cu(I) (2,9-Me ₂ -phen) ₂]/ClO ₄	0.722	0.759	2.7	pH 5.2 (ABS)	[22]
[Cu(MePMP-pyrene)]/MWCNT	0.74	0.341	3.6	pH 9.0 (BRS)	[40]
[Cu(HPMP-pyrene)]/MWCNT	0.78	0.341	3.7	pH 9.0 (BRS)	[40]
[Cu(CF ₃ PMP ^{tBu} -pyrene)]/MWCNT	0.70	0.441	3.8	pH 9.0 (BRS)	[40]
Cu-NC	0.909	–	~ 4.0	pH 13 (0.1 M KOH)	[46]
Cu-OC	–	–	~ 2.0	pH 13 (0.1 M KOH)	[46]
[Cu(phen)]/Au	0.40	–	–	pH 4.0 (PBS)	[41]
[Cu(heimp) ₂]	–	0.45	–	pH 7	[27]
	–	0.41	–	pH 13 (KOH)	

^a Homogeneous catalysts.

potential is also used as a reactivity descriptor for a myriad of reactions [2,47–53], since the formal potential is related directly with the M–O₂ binding energy [38,47]. The use of the redox potential as a reactivity descriptor can be useful for the rational design of new catalysts. Venegas et al. synthesized 1,10- and 2,9- Cu-bis-phenanthrolines to evaluate which effect, the structural or the electronic one, is most relevant to increase the catalytic activity [22]. The results showed that the steric effect (in 2,9-substituted-bis-phen) to hinder the confirmation changes Cu(II)/(I) is more pronounced than the electron-withdrawing effect of the ligand (Figure 2c). The hindering effect essentially shifts the Cu(II)/(I) redox potential to more positive values. In spite of the lower impact of the electron-withdrawing effect, there is a positive linear relationship between the activity with the redox potential for the ORR. Table 1 summarizes the selection of the studies presented in this work, indicating the experimental conditions, the redox potential, and the onset potential. In order to compare the electrocatalytic parameters among the different pH media, the potential values have been converted to RHE scale. To evaluate the catalytic activity among the revised catalysts, Figure 2d presents the formal Cu(II)/(I) redox potential versus the onset potential for the ORR. As can be observed, the catalytic activity increases when the pH becomes more alkaline. The highest activity has been reached for the pyrolyzed catalyst, followed by the trinuclear Cu-complex with the optimal configuration of their active sites, demonstrating in each case the role of the conductive matrix and its electronic effect on the Cu_Nx activity towards the ORR, and also the synergism of multiple active Cu-sites that favors the breaking of the O=O bond. However, there are clear exceptions with the use of S-linked covalent triazine frameworks at pH 7 [38] and the mononuclear 2,9-bis-phen with a steric restriction at pH 5.2 [22], in which the lability of the ligands and the hemilability of the Cu(I) centers are crucial. Considering the nuclearity of the copper catalyst, it seems to be clear that the multinuclear arrangement presents better catalytic activity, which can be associated with the proximity of the active sites to bind the O₂ molecule as it was proposed for the benchmark binuclear Cu-complex, [Cu(Hdtraz)] [30].

Conclusions and perspectives

During the last three years there have been considerable improvements on the catalytic activity and stability of copper molecular catalysts. The high onset potentials reached in alkaline and neutral media demonstrates the possible applicability of these compounds as electrocatalysts for the ORR, and the results in operando conditions are promising. However, there are some technical issues related to the low stability and activity in acid media of molecular Cu-complexes for scaling up to an industrial level. Therefore, the state of the art for

their massive applications in energy conversion devices such as H₂/air fuel cell has reached the proof-of-concept stage in alkaline media.

Among the different synthetic alternatives, the use of conducting polymers as a network to host multicopper structures is the most favorable option since it increases both the catalytic activity and stability of the molecular catalysts. Another important advance was performed with the synthesis of pyrolyzed copper carbon-based catalysts with remarkable activity and stability, in these materials the copper active sites are embedded in highly conductive graphitized carbon matrix. However, the total control on the synthesis of copper active sites such as the final copper coordination needs to be improved.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work has been supported by FONDECYT 11221073, FONDECYT 1221798, FONDECYT Postdoctoral Project 3170330 and Anillo Project ACT-192175.

Abbreviations

7-Dpiy	3,3'-(1,4-diazepane-1,4-diyl)bis(1-(bis(pyridin-2-yl)methyl)amino)propan-2-ol)
7-N-Etpyz	3,3'-(1,4-diazepane-1,4-diyl)bis(1-(4-ethylpiperazin-1-yl)propan-2-ol)
7-N-Etpyz-(CH ₂ OH)	3,3'-(6-(hydroxymethyl)-1,4-diazepane-1,4-diyl)bis(1-(4-ethylpiperazin-1-yl)propan-2-ol)
ABS	Acetate Buffer Solution
AMT	3-amino-1,2,4-triazole-5-thiol
BPMP-pyrene	2,6-bis[(bis(2-pyridylmethyl)amino)methyl]-phenol ligand functionalized with a pyrene moiety
BRS	Britton–Robinson Buffer Solution
BTAH	1,2,3-benzotriazole
CB	Carbon black
Cu-1D-CP	[Cu ₃ (bpy) ₃ (μ-OH) ₂ (μ-CO ₃) ₂] _n polymer
GC	Glassy carbon
L1	N,N-bis(2-pyridyl-methyl)phenylmethylamine
L2	(2-{[bis(2-pyridylmethyl)amino]methyl}benzoic acid
L3	3-{[bis(2-pyridylmethyl)amino]methyl}benzoic acid
L4	4-{[bis(2-pyridylmethyl)amino]methyl}benzoic acid
L _q	6-(quinolin-8-yl)-6,7-dihydro-5H-dibenzo[<i>c,e</i>]azepine
H	1,2-phenylene-diimine-dioxime
Hdtraz	3,5-diamino-1,2,4-triazole
Heimp	2-[(2-Hydroxyethyl)iminomethyl]phenolato
HL	2,4-dihydroxybenzaldehyde

HT	1H-1,2,4-triazole-3-thiol
HPTP	(10,12-bis(4-hexylthiophen-2-yl)thieno[3',4':5,6]pyrazino[2,3-f][1,10]phenanthroline)
PBS	phosphate buffer solution
PDTPP	poly(2,7-dimethyl-10,12-di(thiophen-2-yl)thieno[3',4':5,6]pyrazino[2,3-f][1,10]phenanthroline)
Py	pyridine
PyT	5-(2-pyridyl)-4H-1,2,4-triazole-3-thiol
S-CTF	S-linked covalent triazine frameworks
SPCE	Screen-printed carbon electrode
Trz	1,2,4-triazole

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* of special interest

** of outstanding interest

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