Exploring Advanced Oxygen Reduction Reaction Electrocatalysts: The Potential of Metal-Free and Non-Pyrolyzed Covalent Organic Frameworks

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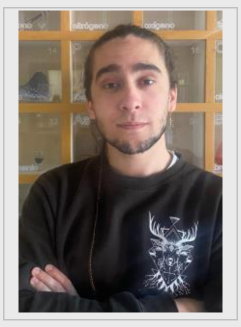
Abstract: Oxygen reduction reaction (ORR) electrocatalysis is an area of increasing interest for the *in-situ* production of H_2O_2 or the development of energy-related devices such as hydrogen fuel cells. Although pyrolyzed catalysts still offer the best performances to date with reference to the organic-based catalysts, metal-free and non-pyrolyzed covalent organic frameworks (COFs) stands out as promising alternatives candidates due to their favourable characteristics such as crystallinity, porosity, and organic composition, allowing the study of structural-property relationships. Herein, we present the design principles and recent advances in COFs-based ORR electrocatalysts, demonstrating how composition influences the activity and electronic pathway of the oxygen reduction process.



Marcos Martínez Fernández received his BS degree in chemistry (2019) at UCM and his MS degree in Organic Chemistry (2020) under the UAM, UCM and USC MQO program. Now, he is finishing his PhD thesis at the UCM under the supervision of José L. Segura. His research is focused on the synthesis of COFs for catalytic applications and controlling the morphology of the crystalline phases.

José L. Segura obtained his PhD in Organic Chemistry at the UCM in Madrid working in Organic Materials. After a stay in W. Dailey's group (Univ. Pennsylvania) he performed postdoctoral stays in the groups of M. Hanack (Univ. Tübingen), F. Wudl (UCSB) and P. Bäuerle (Univ. Ulm). In 1995 Prof. Segura joined the faculty at the Complutense University in Madrid where he is currently Full Professor and is leading the group of Macromolecular and Heterocyclic Organic Materials. Current research interest involve synthesis, photophysical and electrochemical characterization of organic materials including covalent organic frameworks. Results have been published in more than 170 scientific contributions.

Introduction

Oxygen is the third most abundant chemical element in the universe, and the dioxygen molecule is the second most abundant component of the atmosphere, accounting for 23.1% of its mass. Despite the relatively high bond energy of the O=O molecule (498 kJ/mol)[1] the cleavage of this bond is the driving force behind aerobic respiration.[2] Thus, inspired by nature and leveraging the abundance of O_2, the oxygen reduction reaction (ORR) was proposed as an ideal counter reaction for energy conversion technologies such as metal-air batteries or hydrogen fuel-cells.[3] However, to overcome the slow kinetics of this green process, both natural and artificial ORR requires the assistance of catalysts to lower the energy barrier of this process. Best performing materials are Pt-based catalysts, but they present several drawbacks such as scarcity, high-prices or the poisoning possibilities.[4]

Beyond metallic electrocatalysts, the pursuit of novel metal-free ORR electrocatalysts has gained increasing interest since the first publication of a metal-free pyrolytic carbon, which demonstrated good electrochemical performance.[5] However, in order to mitigate the associated costs of pyrolytic treatments[6] and to elucidate the structural-property relationships of the ORR process,[1] Covalent Organic Frameworks (COFs) emerge as promising candidates for the production of non-pyrolyzed and metal-free electrocatalysts, despite the low conductivity or stability of some linkages. COFs represent a relatively recent class of polymers that are characterized by notable properties such as crystallinity, porosity and pre-designability[7] rendering them attractive for heterogeneous applications.[8] Inspired by organic-derived carbons, COFs have been increasingly employed as metal-free and non-pyrolyzed ORR electrocatalysts since the prominent work of Jishan Wu et al. reported in 2018.[9] Since then, these framework materials have demonstrated significant potential for ORR electrocatalysis, offering modulable activity and selectivity depending on the units or linkers constituting the polymeric skeleton, thereby opening up a new research frontier with endless possibilities.

Design and selectivity of the COF-based ORR electrocatalysts.

The most prevalent mechanism of the ORR process begins with the adsorption of oxygen on the surface of the electrocatalyst (*), then occurs an electron transfer, yielding the *OOH intermediate whose ΔG_{ads} will determine the two- or four-electron pathway selectivity:

Initiation:

$$O_2 + * \rightarrow O_2*$$

$$O_2 + H_2O + e^- \rightarrow HOO* + OH^-$$

Two-electron pathway:

$$HOO* + H_2O + e^- \rightarrow H_2O_2 + OH^-$$

Four-electron pathway:

$$HOO* + e^- \rightarrow O* + OH^-$$

$$O* + H_2O + e^- \rightarrow HO* + OH^-$$

$$HO* + e^- \rightarrow OH^-$$

For organic compounds, this mechanism is mainly studied in basic media, where there are two primary locations where oxygen can be adsorbed (*) and subsequently electrochemically reduced. These sites, referred to as active sites (AS), may be generated by the incorporation of sp^2 Carbon-Heteroatom bonds (referred to as Polarized active sites; PAS, Figure 1) or by the introduction of distortive defects, such as five or eight membered rings, through the introduction of tension in the C-C bonds (Tensioned active sites; TAS, Figure 1).[5]

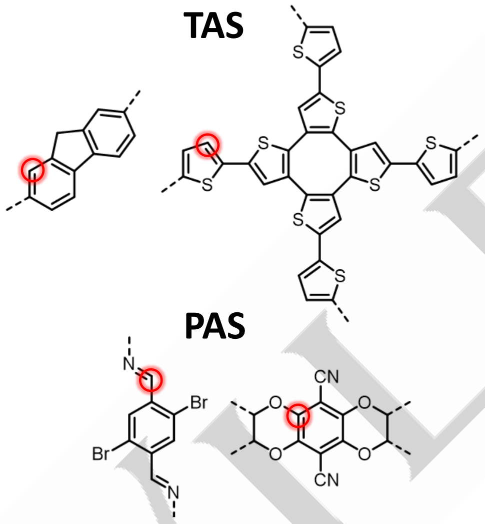


Figure 1. Exemplification of TAS and PAS. Active sites of the different moieties are highlighted.

For COFs both strategies have been employed. However, due to the reversibility requirements of the linkages necessary to obtain organic crystalline phases,[7] purely TAS COF-based electrocatalysts have not been reported to date. Leveraging the pre-designability of COFs, several studies have incorporated PAS or TAS moieties in the extended network, systematically investigating ORR performance experimentally and computationally due to the defined structure of the framework. Furthermore, it has been demonstrated that, despite the limited electrical conductivity of most COFs, their electrocatalytic response can be enhanced by molecular design. This involves employing different co-monomers to increase ORR performance by adjusting the accessibility,[10] or mass transfer[11] of dioxygen species to the active sites. Such enhancements can be achieved through molecular design by expanding the pore size (Figure 2A), or by introducing active sites in the pore positions, rather than the backbone positions (Figure 2B).

One of the most important findings of the studies encompassing this concept, is the dependency of selectivity on the active sites comprising the framework. ORR could occur through two different electronic pathways. On one hand, a two-electron pathway produces hydrogen peroxide, which is interesting for in situ H_2O_2 generation.[12] On the other hand, the four-electron pathway produces water, which is preferred for energy-related applications.[4a]

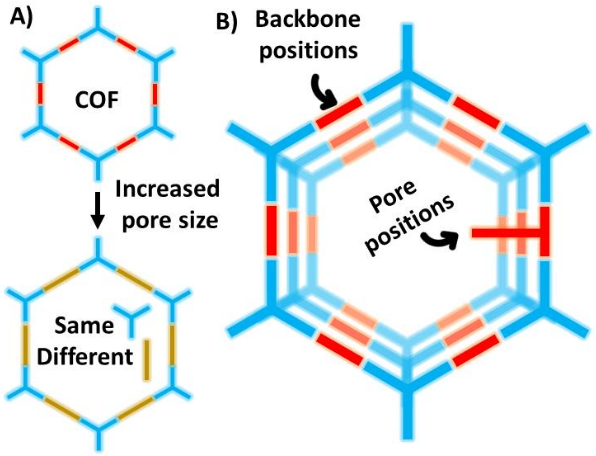


Figure 2. Schematization of A) the variation of the pore size and B) the location of the active sites.

It has been experimentally and computationally demonstrated that COFs with different composition selectively catalyzed the ORR in different ways (Figure 3).[13] Additionally, experimental findings align well with certain molecular arrangements explored in derived carbons,[14] such as the pathway selectivity offered by thiophene moieties.[11] Furthermore, this pattern is reinforced by other five-membered-ring derivatives containing other chalcogen group atoms,[15] and many of them favor the $4e^-$ pathway, consistent with the observations found for the pyrolyzed carbons. However, this trend contrasts with the selectivity provided by pyridine active sites,[4a, 16] with some COFs bearing this unit exhibiting divergent pathway selectivity (as seen in COF-Tz). [17] Similarly, the same findings were observed for halogenated COFs,[12a, 18] demonstrating significant selectivity for the two electron pathway, contrasting with the selectivity found for other halogenated pyrolized carbons.[12a] In other words, due to the presence of various active-site configurations coexisting within the pyrolized carbon matrix, identifying the respective contributions to the ORR becomes challenging. Thus, these observations reinforce the notion of the suitability of the COF platform as model compounds for the development of structural-property relationships.[4a]

Activity descriptors and AS comparison.

The electrochemically driven reactions occur at different thermodynamic potentials depending on the redox pair. However, in real systems the observed potential differs from the theoretical values due to energy losses, resulting in an overpotential.

Catalysts are employed to reduce this gap, aligning the observed and theoretical values.[19] The most common method to analyse the “turn-on” of the reaction is the potential onset, typically determined visually using the tangent method. However, these values are sensitive to the amount of catalyst and the range of data employed, providing primarily qualitative data.[20] Thus, Turnover frequency (TOF), Tafel slope or mass activity are important activity descriptors used for ORR characterization. Among them, TOF is the most relevant parameter for comparing the activity of different COF materials.[21] It can be calculated as follows (Eq. 1):

$$TOF = \frac{J*A}{e*F*n} \qquad \text{(Eq.1)}$$

Where “J” represents the current density at a given potential (commonly 0.7 V and 0.5 V vs RHE for the 4e$^-$ and 2e$^-$ pathways, respectively), “A” denotes the surface area of the electrode, “e” signifies the number of electrons per mole of O_2, F is the Faraday constant, and “n” indicates the number of moles of active centers in the samples. COFs exhibit a well-defined chemical and topological structure, and the identification of active sites can be conducted through DFT calculations. However, some disparities exist in the literature regarding the calculation of “n”.[12a, 15a, 18, 22] Hence, for the purpose of comparing materials studied by various research groups, we propose the following theoretical approximation, wherein an ideal ratio of mol of active site to deposited mass of catalyst can be calculated (Eq.2):

$$\frac{mol}{mass} = \frac{mol\ active\ site}{\sum(m\ linkers) - m\ subproduct} \qquad \text{(Eq.2)}$$

where “mol active site” represent the number of moles of the active site (linker) employed in the polymerization reaction, “m linkers” denotes the mass in milligrams of the linkers utilized in the COF synthesis and “m subproduct” signifies the mass of the byproduct formed during the polymerization (e.g. water in a Schiff’s base condensation reaction). It is important to note that this approach considers all catalytic carbons as active, thus representing the lower limit of this descriptor. Additionally, it can only be applied after the calculation of the most suitable sorption active sites. Furthermore, despite the potential for one linker to present more than one active site due to molecular symmetry, such instances are counted only once due to statistical and electronic considerations. Consequently, we conducted TOF calculation for various metal-free COF electrocatalysts employing the same methodology when the working electrode area was reported in the study. Current densities were measured using WebPlotDigitizer for the two- and four-electron oxygen reduction reactions. To identify the most active catalyst reported to date, we plotted TOF against selectivity values for the two- and four-electron ORR (Figures 4 and 5, and tables S1 and S2, respectively).

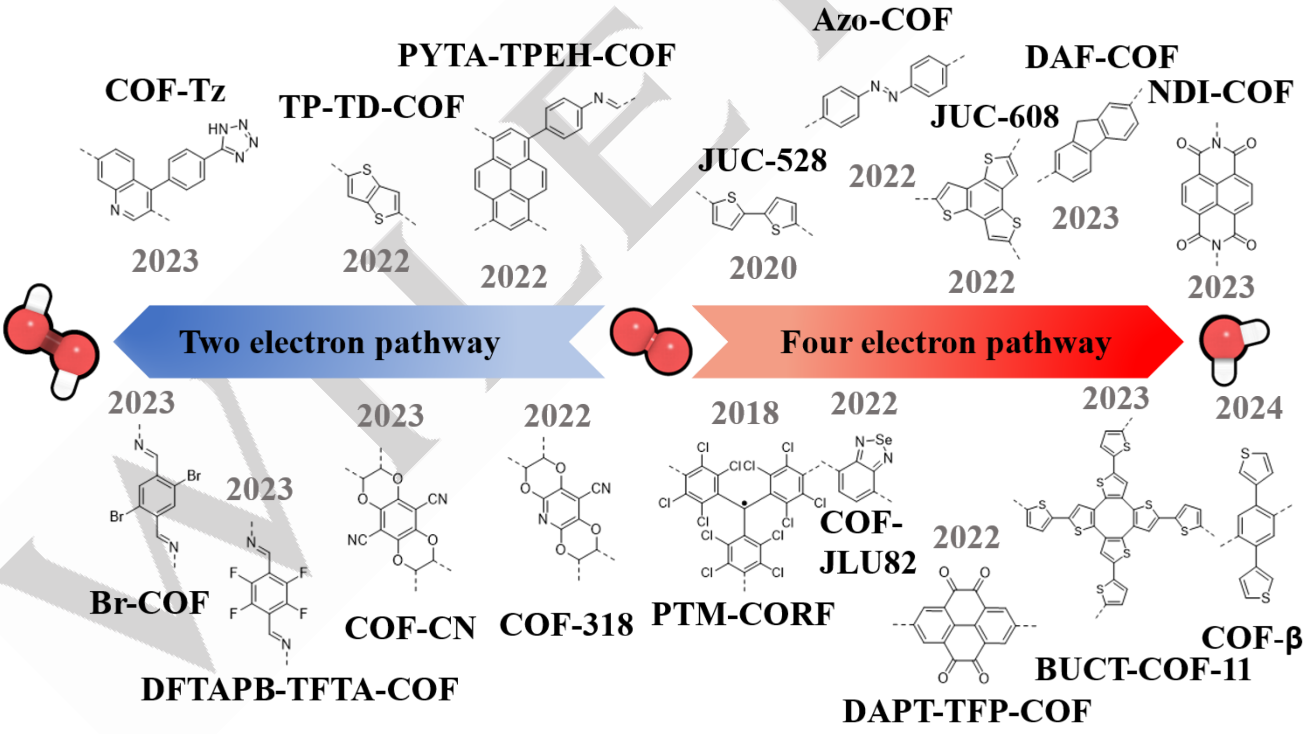


Figure 3. Representation of the two electronic pathways and some AS employed for the ORR electrocatalysis.

A line connecting the highest TOF value with the pure ORR mechanism was drawn to delineate the most suitable catalysts identified thus far (referred to as the 2024-limit).

For the two-electron ORR, halogenated COFs exhibit significant selectivity and TOF values.[12a, 18] Similarly, it appears that the presence of halogens enhances the selectivity of the process, likely attributed to the increased symmetry of the benzenic system, thereby allowing oxygen to be adsorbed at various positions. Consistently, poly-substituted benzene systems featuring electron withdrawing groups also demonstrate favourable selectivity toward hydrogen peroxide generation, as exemplified by CN-COF.[23] Additionally, J. Hu et al, demonstrated the superiority of 1D COFs over isomeric 2D COFs for electrocatalytic applications, owing to enhanced accessibility of dioxygen species to the active sites.[24] Finally, the "2024 limit" suggests that employing purely PAS in a single-benzenic system favours selectivity towards the 2e$^-$ ORR.

For the four electron ORR, COFs containing thiophene[22] and quinoid-type moieties[25] emerge as promising candidates to achieve high TOF and selectivity. Moreover, it appears that increasing the number of thiophene units improves these descriptors, as evidenced by the comparison of JUC-527[22] with a single thiophene moiety per monomer with other COFs based on multi-thiophene monomers. Additionally, a comparison between JUC 607 and JUC 608, which feature identical benzothieno[3,2-b]thiophene active sites but different pore sizes, demonstrates that oxygen accessibility is an important parameter to consider for improving TOF values without altering the selectivity of the process.[11]

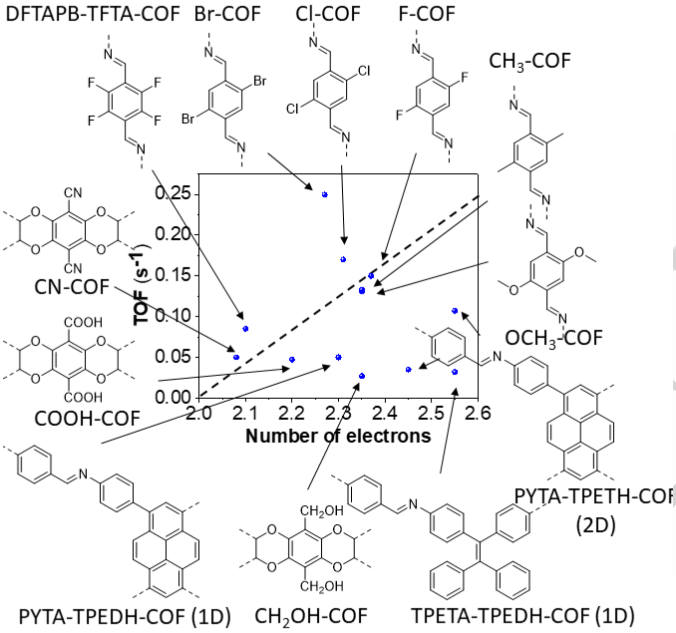


Figure 4. TOF vs. selectivity plot for the two-electron ORR at pH=13.

Additionally, this plot highlights the influence of the active site location, with pore locations being more active than the backbone positions. This is evident when comparing COF-α and COF-β endowed with thiophene moieties in pore positions (Figure 2) with other COFs endowed with thiophene moieties in backbone positions (Figure 2).[26] A similar behaviour is observed by comparing $NDI_{0.17}$-COF[6] with naphthalenediimide (NDI) moieties in pore positions with TAPX-NDI-COFs with NDI moieties in backbone positions.[10, 27] It should be noted that, by comparing JUC-616 and JUC-618,[15a] the importance of the heteroatom substitution can be clearly seen, where the variation of just one atom results in an inverse behaviour between TOF and selectivity.

Finally, the "2024 limit" concept highlights the importance of the strategy used, with the active sites exposed in the pores and the introduction of heteroatom-bearing TAS the most effective catalysts.

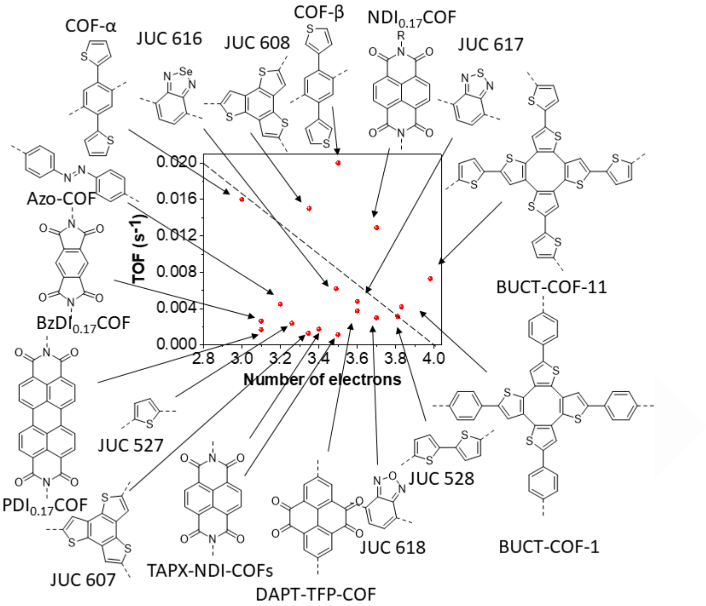


Figure 5. TOF vs. selectivity plot for the four-electron ORR at pH=13. Units with two or more dashed connectors indicate that the unit is part of the skeleton while units with a single dashed line imply the position of this active centre in the pore.

Summary and Outlook

To summarize, active research in the development of metal-free and non-pyrolyzed ORR electrocatalysts has enabled researchers to enhance the activity and selectivity of new materials through the study of new structural-property relationships. Good selectivity and TOF values as high as 2.1 electrons and 0.25 s^{-1} for the two-electron process, and 4 electrons and 0.02 s^{-1} for the four-electron process have been already obtained. Despite of the great selectivity values, the TOF values are still far from those offered by metal-conducting materials for the four-electron process (around 20 s^{-1}).[28] We envisage that the low conductivity of the COFs and the low-stability of the imine-linkage need improvement to develop practical materials for everyday use. For this aspect, the authors envisage that the design of novel COF based metal-free and non-pyrolyzed electrocatalysts should be based on more conductive materials, along the sheets as well as between de different layers. To address this, some linkages could favour the charge mobility, such as C-C obtained by Michael-type condensations or by olefin cross-metathesis. In addition, the stability of the catalyst could be post-synthetically modified by imine-linkage conversion to more stable units such as amide, amine, or different heterocycles as it is recently reported. Additionally, exploring non-solvothermal and scalable procedures for catalyst synthesis is desirable. Finally, investigating acid-media ORR electrocatalysis is crucial for the development of practical energy-related devices such as hydrogen fuel-cells.

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Keywords: COF • electrocatalysis • ORR • H_2O_2 • oxygen

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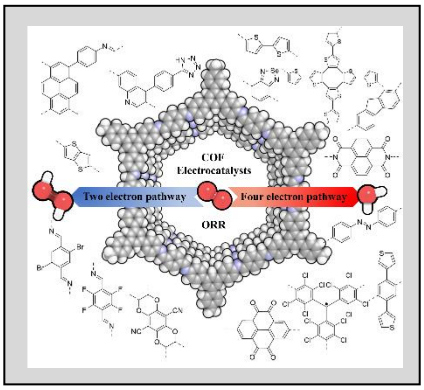

Oxygen Reduction Reaction (ORR) electrocatalysis using metal-free and well-defined Covalent Organic Frameworks (COF) is an interesting approach to study the structural-selectivity of the electrocatalytic process. Thus, in this concept article we review the most important features of COF-based electrocatalysts for designing selective and active ORR.

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Biographic sketch