From Biomimicking to Bioinspired Design of Electrocatalysts for CO₂ Reduction to C₁ Products

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\[ x\text{CO}_2 + n\text{H}^+ + ne^- \rightarrow \text{Products} + y\text{H}_2\text{O} \]

CO₂RR
Abstract: The electrochemical reduction of CO₂ (CO₂RR) is a promising approach to maintain a carbon cycle balance and produce value-added chemicals. However, CO₂RR technology is far from mature, since the conventional CO₂RR electrocatalysts suffer from low activity (leading to currents <10 mA cm⁻² in an H-cell), stability (<120 h), and selectivity. Hence, they cannot meet the requirements for commercial applications (>200 mA cm⁻², >8000 h, >90 % selectivity). Significant improvements are possible by taking inspiration from nature, considering biological organisms that efficiently catalyze the CO₂ to various products. In this minireview, we present recent examples of enzyme-inspired and enzyme-mimicking CO₂RR electrocatalysts enabling the production of C₁ products with high faradaic efficiency (FE). At present, these designs do not typically follow a methodical approach, but rather focus on isolated features of biological systems. To achieve disruptive change, we advocate a systematic design methodology that leverages fundamental mechanisms associated with desired properties in nature and adapts them to the context of engineering applications.

1. Introduction

1.1. Fundamentals of CO₂ Reduction

Electrocatalytic reduction of CO₂ (CO₂RR) offers a compelling avenue to address growing concerns about our carbon footprint, as it offsets carbon emissions and produces value-added products.[1] It is a multiple proton and electron transfer reaction (Eq. 1) resulting in the formation of several products and water (Figure 1)

\[ k_{CO_2} + n(H^+ + e^-) \rightarrow \text{Product} + mH_2O \]  

where \( k \), \( n \), and \( m \) are the reaction coefficients (e.g., \( k = 1 \), \( n = 2 \), \( m = 1 \) when Product = CO; \( k = 2 \), \( n = 12 \), \( m = 3 \), when Product = CH₄, CH₃OH, etc.).[2] If the reduction of CO₂ involves the transfer of two electrons and protons (\( n = 2 \)), then the overall reaction is reversible, since the employed electrocatalyst can catalyze the corresponding reactions in both directions. On the contrary, if CO₂RR occurs via the transfer of more electrons and protons (\( n > 2 \)), then additional intermediates are formed and the overall reaction becomes irreversible, as the binding energy of each intermediate follows linear scaling relationships.[3] These scaling relationships are due to the presence of similar chemical bonds between adsorbed species and catalytic surfaces imposing a high overpotential for the reduction of CO₂. Examples include the scaling relationship between *OCHCH₂, *OCHCH₃, and *OCH₃CH₂ intermediates for the reduction of CO₂ to CH₄, CH₃OH, *OH and *OCHCH₂ intermediates for the reduction of CO₂ to C₂H₆, etc.[2]

1.2. Electrocatalyst Design: The Heart of The Challenge

Several noble (Au, Ag) and non-noble (Cu, Ni, Bi, Fe, Mn, etc.) metals, alloys, oxides, and transition metal chalcogenides are employed as CO₂RR electrocatalysts.[3] Among them, copper is the most widely used electrocatalyst, since it can directly reduce CO₂ to hydrocarbons and alcohols, such as methane, ethanol, CO, and formate.[4] However, Cu based electrocatalysts exhibit poor selectivity and large overpotentials, due to the complexity of the reaction pathway for hydrocarbon production involving several proton and electron transfer steps.[4]

Noble metal based electrocatalysts (such as Au, Pd, Ag, etc.) have also been used for the reduction of CO₂ to CO and formate.[5] Even though these electrocatalysts exhibit high selectivity towards the production of CO (FE CO > 90 %) for Au and Ag based electrocatalysts[6] and formate (FE formate > 97 % for Pd based electrocatalysts),[7] their high cost and scarcity makes them less attractive for large scale production.

Metal nitrogen doped carbon (MNCs) materials are a promising alternative to these electrocatalysts due to their stability and high selectivity towards CO₂RR. Ni based MNCs are the most efficient electrocatalysts to produce CO (FE CO > 90 %) due to the low binding energy of Ni toward H⁺ suppressing the hydrogen evolution (HER) reaction.[8] Further research is needed to improve these materials, as the origin of their activity is not well understood. Thus far, a very low FE CO (≈0.4 %)[9] to produce CH₄ is achieved due to the inability of MNCs to co-adsorb CO⁺ and H⁺ limiting CO protonation.[9] Detailed review about CO₂RR electrocatalysts in general is beyond the scope of this article and the reader is referred to recent, thorough reports in the literature for additional information.[8–11]

From these reviews, it becomes clear that the lack of rational design principles for the development of highly efficient and selective CO₂RR catalysts impedes disruptive progress in CO₂RR devices. Key challenges facing current electrocatalysts are their low selectivity towards desired products and their durability, since a very limited number of electrocatalysts reported thus far can exceed 120 h of continuous CO₂RR without a significant loss in their activity.[1,3,6,12] Additionally, they should mediate multiple proton and electron transfers to CO₂ without resorting to excessive reducing overpotentials, leading to low energy
efficiency. The observed \( \approx 0.36 \text{ V shift in overpotential for } C_2 \) product represents a two-orders of magnitude increase in \( C_2 \) selectivity compared to \( C_1 \) products in that pH range. The \( C_2 \) production is limited by the rate of first proton-electron transfer to the \( O \equiv C \equiv C \equiv C \equiv O \) intermediate (Figure 1) and CO coverage at low and high overpotentials, respectively. On the contrary, \( C_1 \) production is limited by the rate of proton-electron transfer to the \( C \equiv O \equiv H \) intermediate, resulting in a smaller increase in activity with increasing pH, compared to \( C_2 \) formation. A similar trend is observed for noble metal based electrocatalysts to produce CO; the selectivity of Ag electrocatalysts (\( \text{FE}_{\text{CO}} > 85\% \)) is enhanced at local pH values greater than the buffer pH (\( \approx 7 \)) while for Au electrocatalysts, CO selectivity does not depend on local pH as it is limited by the CO\(_2\) adsorption step. For MNCs, pH plays an important role in their selectivity as well. High faradaic efficiency (\( > 80\% \)) toward CO production is achieved for Fe–N–C electrocatalysts at high pH values (\( \geq 7 \)), where the HER is suppressed. Based on the above challenges, it is evident that a novel approach to design CO\(_2\)RR electrocatalysts could drive accelerated innovation. Incremental changes through minor design modifications or alteration of the reaction conditions may not produce the required transformative solutions. An example of such approach is our nature-inspired chemical engineering (NICE) methodology (discussed in more detail in Section 4) which recognizes universal fundamental mechanisms in nature underpinning desired properties (like scalability, efficiency, and resilience), which can be leveraged to achieve similar properties in an applied context. These ubiquitous mechanisms define NICE Themes, of...
which there are presently four: (T1) hierarchical transport networks; (T2) force balancing and nano-confinement; (T3) dynamic self-organization; (T4) ecosystems, networks, and modularity. For example, (T1) includes ubiquitous networks that greatly promote reliably scalable performance across a wide range of length scales, as observed in trees, lungs, and the vascular network. Within or across these themes, NICE deploys a design methodology that comprises four stages to bridge nature with technology in applications, namely: nature-inspired concept, design, prototype, and application (Figure 2). Figure 2 presents an example of the application of the NICE methodology to design lung-inspired flow fields for proton exchange membrane fuel cells (PEMFCs).[19]

Inspiration is derived from the lung (“Nature”) due to its ability to scale-up irrespective of size, providing uniform distribution of oxygen into the blood stream while keeping the thermodynamic losses across its volume at a minimum. This is achieved via its fractal architecture, ensuring that the Péclet number, Pé, is close to 1, and, hence, the convective air flow dominating the upper part of the lung is equal to the diffusive air flow at the lower part of the lung (“Nature-inspired concept”). A mathematical model is built based on these characteristics of the lung to calculate the optimum number of fractal generations in a flow field to achieve Pé ≈ 1 (“Nature-inspired design”), and then, lung-inspired flow fields are created via 3D printing (“Prototype”) exhibiting higher performance (≈ 30% increase in current and power density) and ≈ 75% lower pressure drop than serpentine flow field based PEMFCs (“Application”) minimizing the parasitic power losses.[19]

In terms of CO₂RR electrocatalysts, Nature can be an excellent guide to rational design, as it is full of biological organisms that efficiently catalyze the same reactions as the electrocatalysts and robust structures that are intrinsically scaling. Based on recent literature, we now review opportunities resulting from imitating or taking inspiration from nature to design better catalysts. We focus on C₃ products, since they are important chemical feedstocks to produce fuels and value-added chemicals.

2. Biomimetic Electrocatalysts for CO₂ Reduction to C₃ Products

The most widely used source of inspiration for the design of novel electrocatalysts for CO₂ RR are metalloenzymes, which have exceptional catalytic efficiency and selectivity towards the same reactions occurring in electrochemical CO₂ reduction devices. Biomimetic design is focused on isolated features of biological organisms (such as their chemical structure), whereas bioinspired design considers both the structure and function of metalloenzymes recognizing the different context between the biological example and the technological application.

2.1. Enzyme-Mimicking Electrocatalysts

A successful biomimetic design approach is based on the presence of imidazole groups of histidine residues at the active site of carbon monoxide dehydrogenases (CODHs) facilitating proton transfer to and from the active site via the formation of hydrogen bonds with water molecules.[20]

As a result, N,N-di(2-picolyl)ethylenediamine (DPEN), a source of imidazole groups, is incorporated into iron
porphyrin, one of the most active and selective electrocatalysts for CO$_2$ to CO conversion in organic solvents, and its properties are evaluated towards CO$_2$RR in acetonitrile. The poly-pyridine/amine sites of DPEN form hydrogen bonds with water molecules assisting in proton transfer, as they function as multiple proton relays, and the protonated DPEN units are positively charged, stabilizing the negatively charged CO$_2$RR reduction intermediates.

Hence, the iron porphyrin with incorporated DPEN units is highly active towards CO$_2$RR, exhibiting a TOF of $\approx 5 \cdot 10^4$ s$^{-1}$ (acetonitrile (MeCN) electrolyte solution) for CO$_2$ to CO conversion with water as the proton source, four times higher than the activity of DPEN-free iron porphyrin.

Another efficient biomimetic electrocatalyst is pentlandite (Fe$_{4.5}$Ni$_{4.5}$S$_8$), due to its structural resemblance with CODHs, as it contains Fe–Ni sites with a bond length of $\approx 2.6$ Å, similar to the ones in CODHs ($\approx 2.8$ Å), connected via sulfur atoms.[23] The efficiency of CO$_2$RR depends on the concentration of protons (the water content in the chosen solvent to conduct CO$_2$RR) at the surface of the electrocatalyst. The selectivity of the electrocatalyst towards CO$_2$RR increases as the water content decreases (MeCN electrolyte solution), and an $\approx 87\%$ FE for CO is observed at low water concentration ($\approx 24$ ppm H$_2$O).[24] This preliminary result illustrates the potential of aprotic solvents with low water content as electrolytes for CO$_2$RR.[22]

## 2.2. Alveolus-Mimicking Electrocatalysts

The efficiency of CO$_2$RR electrocatalysts can also be improved via an increase of the local CO$_2$ concentration. The ratio of CO$_2$ to H$_2$O molecules in an aqueous solution is $\approx 1:1,300$ at 1 atm pressure; this CO$_2$ concentration can be increased by increasing the pressure,[24] but this is only a temporary solution. To design such electrocatalyst with high gas permeability and low water diffusivity, the structure of the mammalian lung is imitated, where the alveoli are enclosed by several epithelial membranes ($\approx 1$ μm thickness) with high gas permeability and low water diffusivity.[25]

Hence, an artificial alveolus is engineered from a flexible polyethylene (PE) membrane sputtered with a thin layer ($\approx 20$ nm thickness) of gold nanoparticles (Figure 3). The PE membrane is hydrophobic and porous (pore radius $\approx 40–500$ nm) making it impermeable to water but allowing gas transport. Gold serves as the catalyst in this study as it is highly efficient towards the production of CO.[26] This Au/PE composite membrane is rolled into a bilayer structure, and its bottom and top edges are sealed to form a closed pouch-type structure. The activity of this biomimicking electrocatalyst is evaluated in an H-type cell achieving $\approx 92\%$ Faradaic efficiency of CO production (in a CO$_2$-saturated 0.5 M potassium bicarbonate (KHCO$_3$) electrolyte solution).[26]
3. Bioinspired Electrocatalysts for CO₂ Reduction to C₂ Products

Enzyme-inspired electrocatalysts derive their inspiration more broadly from the protein scaffold surrounding the active metal center of metalloenzymes, which is responsible for their high activity and selectivity. Their structural characteristic is the presence of primary and secondary (or outer) coordination spheres, which contribute significantly to the function of metalloenzymes. The primary coordination sphere is dominated by covalent interactions between ligands and metal ions; the number of ligands and the oxidation state of the metal affect spin-state ordering and reactivity.[27] The secondary coordination sphere represents the residues that do not directly bind to the active metal center but interact with the primary ligands via long-range interactions, modulating the catalytic properties of the metalloenzymes. These long-range interactions, such as hydrogen-bonding interactions or a salt-bridge to the substrate or the primary ligands, charge stabilization of a nearby anion or cation binding site, alter the redox potential of the metal, local charge distribution, and electron transfer, tuning the catalytic behavior of the metal center.[27–28]

3.1. Dehydrogenase-Inspired Electrocatalysts

In nature, the enzyme dehydrogenase (such as CODH, formate DH, alcohol DH, etc.) catalyzes the selective reversible conversion of CO₂ to C₂ products (formate and methane, respectively).[29] For Mo–Cu based bio-inspired electrocatalysts, a [(bdt)Mo(VI)(O)S₃Cu(CN)]⁻ complex is used in which Mo and Cu ions are connected via sulfide and benzenedithiolate (bdt) ligands resembling the carbon monoxide dehydrogenase enzyme (CODH).[29a] The reduction (n = 2 e⁻) of [(bdt)Mo(VI)(O)S₃Cu(CN)]⁻ forms CO₂ and the complex [(bdt)Mo(VI)S₃Cu(CN)]⁻ whose protonation creates Mo⁺H hydride intermediates that react with CO₂ to form formate, as revealed by infrared spectroelectrochemical (IR-SEC) studies coupled with density functional theory (DFT) computations.[29a] This Mo–Cu based bio-inspired electrocatalyst exhibits good selectivity for formate over CO (9:1) but low activity (turnover number = 4 in 0.1 M trifluoroethanol (TFE) electrolyte solution), demonstrating that further fundamental research is required to comprehend the interplay between the two metal centers.[29a]

For Ni–Fe based bio-inspired electrocatalysts, a [L²Ni²⁺Fe³⁺(Cp(CO))]⁺ (L²N₂S₂ = 2,2-(2,2-bipyridine-6,6-diy)bis(1,1-diphenylethanethiolate)) complex is used to resemble NiFe dehydrogenase enzyme.[29c] It exhibits high activity (TON₄H₂ = 3.5·10⁵ and TON₅H₂ = 8·10⁴ at pH = 4) and its selectivity is affected by the pH value as the H₂CH₄ product ratio fluctuates between 50:1 and 30:1 at pH = 3 and 5, respectively.[29c] The reaction mechanism is still unknown for this Ni–Fe complex; it is speculated that CO₂ is activated and reduced at one metal site, while the second metal site delivers hydride to the first metal site until CH₄ is produced.[29c]

Thus, the design of such electrocatalysts is extremely challenging, as there are several intertwined factors affecting their activity and selectivity. Their activity is also influenced by the presence of O atoms, and the position of a positively charged group or amide pendant in the outer coordination sphere, while their selectivity is influenced by the size of functional groups in the secondary coordination sphere (Figure 4a and b).

To investigate the effect of the position of a positively charged group (such as arginine, histidine, or lysine) in the outer coordination sphere on CO₂ hydrogenation to formate, several artificial enzymes have been synthesized as variants of the active catalyst Rh-LmrR (Rh-bisdiphosphine complex [Rh(PN³⁰⁰⁰⁰⁰⁰⁰P)₆] covalently incorporated into a 119-residue protein (LmrR-factocell multidrug resistant regulator).[29d] Proton NMR measurements reveal that the D100 position is influential in catalysis, with the D100R mutant exhibiting a three-fold increase in catalytic activity compared to Rh-LmrR (~0.7 and 0.2 h⁻¹ TOF, respectively).[29d] In D100R mutant, aspartic acid is replaced by arginines, which are placed near the active metal center; this positively charged group attracts CO₂, increasing its concentration near the metal center and, hence, enhancing the reaction rate. Even though the position of a positively charged group affects the activity of these artificial enzymes, there are several additional factors that must be considered as well: the accurate positioning of the charged group may be inhibited due to the presence of hydrogen bonds or salt...
bridges, which prohibit the incorporation of residues near the active metal center and, thus, do not increase the reaction rate. Water distribution around the active metal center may influence the catalytic activity too, according to molecular dynamic simulations. Preliminary results demonstrate that the population of water around the most active center may influence the catalytic activity too, according to reaction rate. Water distribution around the active metal center and, thus, do not increase the formation of formate in the presence of –OH (FEHCOO ≈ 68 %) using 0.1 M TBAPF₆ in DMF as electrolyte solution.[32] Hence, the utilization of moieties in the secondary coordination sphere to improve metal-ligand interactions and proton transfer to the active metal center is a powerful strategy for tuning the activity and selectivity of the electrocatalyst.[32a]

In terms of the selectivity of the bio-inspired electrocatalyst (Figure 4b), the size of the functional groups[33] and their combined tuning with the active metal center[34] are crucial parameters.

Small pyridyl-based groups promote selective H₂ evolution, since the transfer of hydride to protons is facile, resulting in a ≈78 % FE for H₂ production.[35] The active metal center of this bio-inspired electrocatalyst is [Fe₃N(CO)₉L]⁺ where the parent iron cluster [Fe₃N(CO)₉]⁺ is an effective electrocatalyst for the selective reduction of CO₂ to formate (≈95 % FE) at pH = 7 and L represents the secondary coordination sphere groups containing phosphine ligands functionalized with aprotic functional groups of different sizes.[36] On the contrary, large N,N-dimethylamine groups support selective formation of formate, as they hinder protonation of the active site and selectivity for hydride transfer to CO₂ is increased, resulting in the production of formate with ≈70 % FE (0.1 M n-Bu₄NBF₄ in MeCN/H₂O (95:5) as electrolyte solution).[37]

The incorporation of bipyridine-modified ligands, in which two benzylic amines are positioned in the secondary coordination sphere of the active metal center can alter the selectivity of the electrocatalyst towards specific products of CO₂ reduction. These benzylic amines serve as proton transfer relays and form ([Metal]-H) units, which, in turn, create “formato” compounds ([Metal]-O,CH) upon interaction with CO₂, resulting in the formation of formic acid (HCOOH). If the active metal center is rhenium (Re) or ruthenium (Ru), the binding of CO₂ onto the metal is more favorable than the formation of ([Re/Ru]-H) and it exhibits...
high selectivity towards CO production (FE\textsubscript{CO} ≈ 80 % in a 0.2 M Bu\textsubscript{4}NB\textsubscript{F}, in MeCN electrolyte solution).[34] On the contrary, if Mn serves as the active metal center, then the formation of ([Mn]-H) compound is more favorable than the binding of CO\textsubscript{2} onto the metal and it results in high selectivity towards the production of HCOOH (FE\textsubscript{HCOOH} ≈ 80 %, TOF > 4000 s\textsuperscript{-1}, 0.2 M Bu\textsubscript{4}NB\textsubscript{F} in MeCN electrolyte solution).[34]

3.2. Dehydrogenase-Inspired Electrocatalysts with Pseudo-Secondary Coordination Sphere

Apart from the utilization of different ligands for the formation of a secondary coordination sphere, another successful strategy is the employment of cationic buffers (such as imidazole, bicarbonate, phosphate, and triethanolamine) replacing the long-chain ligands in the outer coordination sphere of DHases. In this catalyst design, [Ni(cyclam)]\textsuperscript{2+} (cyclam = 1,4,8,11-tetraazacyclotetradecane) is the active metal center which catalyzes the reduction of CO\textsubscript{2} to CO or formate via a proton-coupled, ECEC (electron transfer-chemical step-electron transfer-chemical step) pathway; its activity and selectivity are increased via pyridine- or imidazole-binding.[35] Imidazole preferentially binds to the Ni\textsuperscript{II} of [Ni(cyclam)]\textsuperscript{2+}, stabilizes the divalent oxidation state, and decreases the required reduction potential. Once [Ni(cyclam)]\textsuperscript{2+} is reduced, imidazole buffer plays the role of histidine ligands in DHases, transferring protons to and from the bound substrate, and hence, acting as a pseudo-secondary coordination sphere.[19]

The highest turnover frequencies (TOF\textsubscript{CO}) of ≈50 s\textsuperscript{-1} (100 μM [Ni(cyclam)]\textsuperscript{2+} with 100 mM potassium chloride (KCl) as electrolyte solution) are observed for imidazole (red diamond, Figure 5) and imidazole-derived buffers (purple diamond, piperazine, Figure 5). However, imidazole buffer exhibits the highest negative electrocatalytic over-potential for CO\textsubscript{2} reduction (≈0.77 V vs. NHE), compared to bicarbonate buffer (blue diamond) demonstrating the least negative electrocatalytic potential of ≈0.69 V (vs. NHE), similar to the value for the reduction of CO\textsubscript{2} to CO at pH = 7.[36]

4. Application of NICE Methodology

The above examples do not explicitly use a systematic design framework, as the one provided by NICE, but instead represent a set of isolated inspirations from natural systems.

Our NICE methodology can address this issue, as it deploys a thematic approach that comprises four stages to bridge nature with technology in applications, namely: nature-inspired concept, design, and prototyping for experimental realization (Figure 2).

First, the nature-inspired concept, is identified as a mechanism found commonly in nature, which is the crucial ingredient to solve an issue in nature (e.g., the properties of the hierarchical transport network leading to scalability, within T1) that is also pertinent in the envisioned technological application, despite the often different contexts of nature and technology (e.g., a lung and a fuel cell).[19]

Second, the nature-inspired design stage translates this concept into a design that is specifically formulated for the intended application; hence, an (abstract) mechanism is adopted but its (concrete) realization needs to be adapted for technological use (e.g., the self-similar branching of the lung and the dimensioning of its channels for scalable, minimum entropy production, need to be adapted in the context of the different environment and production requirements of a hydrogen fuel cell flow plate, even though both require scalable, maximally efficient air distribution).

Finally, experimental realization is achieved by manufacturing prototypes based on the nature-inspired, often computationally assisted design through experimental testing and characterization to investigate performance under technologically relevant conditions. Prototyping is an iterative process that embraces new synthesis and (e.g., digital and additive) manufacturing techniques.

The design of bio-inspired CO\textsubscript{2}RR electrocatalysts reported in the literature relates to the T2 theme of NICE methodology (Section 1.2.), namely force balancing, achieved through nano-confinement. The employment of a secondary sphere to modulate active metal center-ligand interactions or forces is indeed a successful strategy (Section 3.1.) for the enhancement of their catalytic activity and selectivity (Figure 6).
**Minireviews**

<table>
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<th>Mechanism</th>
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<td>Active metal center surrounded by coordination sphere</td>
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*Figure 6.* Systematic methodology for the design of nature-inspired CO₂RR electrocatalysts. The unit of \( \text{TOF}_{\text{in}} \) values is \( \text{s}^{-1} \). The figures under “Prototype” and “Application” are reproduced from ref. [30] with permission from the Royal Society of Chemistry.

Are there any additional elements in the design space that could further improve the properties of bioinspired CO₂RR electrocatalysts? NICE could be employed as an innovation accelerator for the design and development of such materials by following each stage of its methodology, and recognising universal aspects captured by the NICE Themes. This allows us to avoid fragmentation in case-by-case catalyst developments.

For the **nature-inspired concept**, it should be considered that T1 (intercalating transport networks) and T2 (force balancing) harmonically co-exist in natural systems; in particular, enzymes that catalyze the same reactions as CO₂RR electrocatalysts rely on both their coordination sphere and hierarchical transport network to obtain their appealing catalytic properties. The unique structural characteristic of enzymes is the position of the active metal center deep into a substrate channel to effectively separate it from the solution environment. This structural geometry provides control over the chemical environment where the reaction occurs and the transport of products to new active sites for cascade reactions (substrate channeling). A recent example is an ORR electrocatalyst (PtNi) with similar structure to metalloenzymes. Isolated substrate channels are formed between the surface and the center of the nanoparticles, while their exterior surface is passivated by a surfactant to ensure that the electrochemical reactions take place in nanoconfined substrate channels. As a result, this bio-inspired PtNi electrocatalyst demonstrates a twofold increase in ORR activity (acidic media) compared to mesoporous PtNi nanoparticles. The diameter of their substrate channels greatly impacts the activity of these bioinspired PtNi nanoparticles. In the kinetically limited regime where electron transfer dominates (low overpotential), the reaction occurs along the substrate channel and, hence, the smaller its diameter (< 1.5 nm), the higher the activity of the electrocatalyst. On the contrary, at high overpotentials where the reaction is mass transport limited, nanoconfinement does not affect the activity of the electrocatalyst, since the reaction occurs at the entrance of the substrate channel, and, thus, the larger its diameter (> 2 nm) or accessible electrochemically active area, the higher its activity.

Thus, an electrocatalyst consisting of an optimal combination of nanochannels (between 1–4 nm diameter) to leverage nano-confinement, a hierarchical transport network to minimize transport limitations, and a coordination sphere to improve the properties of its active metal center could be highly active and selective towards CO₂RR. Computationally assisted models (nature-inspired design), a step that is often neglected in the reported literature, should be developed first to aid in the design of bio-inspired electrocatalysts. Molecular modelling could help fundamental understanding to achieve customized selectivity through cascade reactions, lowering the free energy barrier of CO₂RR and, hence, its overpotential. Synthesis procedures should then be carefully chosen to create these CO₂RR electrocatalysts and evaluate their activity, stability, and selectivity in a CO₂RR device (prototyping for applications).

### 5. Conclusions and Outlook

In summary, nature is an ideal source of inspiration for the design of artificial CO₂RR electrocatalysts, as there are plenty of biological examples that efficiently catalyze the same reactions and have robust structures, deployed at scale. The examples presented in Sections 2 and 3 demonstrate that bioinspired design prevails over narrow biomimetics (or bio-imitation), since it considers the structure and function of the biological example and the different context between nature and technological applications. However, thus far, most bioinspired examples represent a set of isolated inspirations from natural systems leading to non-optimal...
CO2RR electrocatalysts with high activity and selectivity towards C1 products, but low current density in a CO2RR device (< 10 mA cm−2 in an H-cell) and long-term stability (< 120 h) substantially lower than targets for commercialization (> 200 mA cm−2 over > 8000 h at > 90 % selectivity). [3, 38-39]

The adoption of NICE could lead to a more systematized bioinspired design strategy and accelerate the development of highly efficient bioinspired CO2RR electrocatalysts. The NICE methodology could become even more effective when paired with further advances in the fundamental understanding of the CO2RR mechanism. The complex interplay between the structure (nano- and meso-scale) of the catalyst, its catalytic properties and durability, the electrolyte (pH, buffers), and the mass transport limitations is far from being completely understood. [1-3a] Finally, synthesis protocols viable for mass production must be developed to enhance the low yield of electrocatalysts prepared by conventional approaches.

Apart from electrocatalysts, the commercialization of this technology is also contingent upon the significant improvement of the design of CO2RR devices to enhance their energy efficiency (i.e., high activity and selectivity at low overpotential). Mass transport limitations within the device must be resolved, while product separation and tolerance towards gas inlet purity must be improved. [10] Nature provides examples that can be leveraged to circumvent these issues, through its intrinsically scaling hierarchical transport networks.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

Keywords: Bio-Inspired · Bio-Mimicking · C1 Products · CO2 Reduction · Electro catalysts


A nature-inspired chemical engineering (NICE) approach for the design of nature-inspired electrocatalysts for the reduction of CO$_2$ to C$_1$ products is presented in this Minireview.