Redox-active ligands in artificial photosynthesis: a review

Tímea Benkó¹ · Dávid Lukács¹ · Mingtao Li² · József S. Pap¹

Received: 6 December 2021 / Accepted: 1 April 2022 / Published online: 29 April 2022
© The Author(s) 2022

Abstract
Given the rising socioeconomic issues of fossil fuels, efficient artificial photosynthesis would be an important milestone toward a sustainable world. A key step of photosynthesis is the catalytic photooxidation of water by photosystem II, which has a mean lifetime of 30 min under full sunlight. Since the efficiency of photosystem II is controlled by redox-active tyrosine–histidine pairs that regulate the light-induced flow of charges, research has recently focused on the utilization of redox-active ligands in artificial systems. Here we review the molecular catalysis of water oxidation with emphasis on redox cooperation modes between ligands and metal centers. Molecular systems involving redox-active ligands could achieve up to 100% efficiency with respect to oxygen production, overpotential of 200–300 mV and turnover frequency above 100 s⁻¹, which is comparable to the natural process. Nonetheless, molecular catalysts are often prone to degradation of the organic ligand. The oxidative activation of ligands can contribute to the water oxidation reactivity of a metal–ligand complex, or lead to controlled catalyst film formation. We discuss the design of functional analogs to the tyrosine–histidine pair that for the most part rely on abundant elements and exploit redox-active molecular moieties to assist the catalytic centers. We highlight analogies with the cooperation between the natural oxygen-evolving complex and the redox-active tyrosine–histidine pairs found in photosystem II.

Keywords Artificial photosynthesis · Water oxidation · Oxygen evolution reaction · Redox-active ligand

1. Introduction

Natural oxygenic photosynthesis is a singular process that has been fundamentally shaping the image of the biosphere on earth since the advent of the first light-powered life forms. Solar-to-chemical energy conversion by living organisms involves carbohydrate molecules as chemical energy carrier that capacitate them to fuel their own life processes as needed through cellular respiration (Dau et al. 2017). A substantial part of the photosynthesized organic compounds has been fossilized in millions of years that nowadays represents an essential energy source as fossil fuel and feedstock for the modern human society (Balzani et al. 2008). While in many respects, fossil fuels mean safety and comfort, on the other hand the extensive use of these non-renewable energy carriers presents the greatest threat humankind ever faced caused by itself (Pachauri et al. 2015). The extent of greenhouse gas emission, pollutants released into the environment, wasteful thinking about the available resources all root from a wrong perception that has prevailed for decades, if not for a century, for we have thought that nature could withstand the increasing load.

In part because of the extensive use of non-renewable energy carriers, the search for clean and renewable energy resources has become more urgent than ever. However, the availability of renewable energy resources is diffuse and intermittent that demands advanced storage technologies. The straightforward use in fuel-cell technology to generate electricity and the clean combustion properties make hydrogen gas a promising storage material and true alternative to fossil fuels. Moreover, the energy density of hydrogen in a compressed gaseous or liquid form is compatible with a broad range of applications. The global hydrogen production accounts for approximately 7.7 EJ/year, which may rise to
10 EJ/year by 2050, but only 4% of the hydrogen is produced via water electrolysis (Arregi et al. 2018; Hamza et al. 2020). Therefore, increasing the hydrogen production based on renewable technologies is a timely need.

With the above reasons in mind, we note that without feedback or simply, suitable coupling neither natural nor artificial functionalities will create a balanced renewable system, no matter how efficient or profitable individual, functional parts were put together. We believe that this is an important, if not the most important piece of knowledge that can be deciphered from natural photosynthesis for observers, beyond the obvious aim to create artificial systems based on renewable resources, which we can use on our own benefit (Nocera 2012; Faunce et al. 2013; Pantazis 2021; Osman et al. 2021). Or should we rather be the plummet that needs to be taken off the scales to rebalance? The importance of studying artificial photosynthesis lies in the systematic approach that starts with understanding the natural process.

Plants harvest solar energy by photosystem, produce O$_2$ from water molecules, and as a coupled system, convert CO$_2$ into carbohydrates in the course of the Calvin cycle (Krewald et al. 2015; Pantazis 2021). A Z-shaped energy diagram is generally used to illustrate the cascade of electron transfer steps. The energy to drive this reaction cascade is supplied by light absorption of the photosystem II primary electron donor P680, and the photosystem I primary electron donor P700 (Grimes et al. 2008). Indeed, photons are absorbed by the chlorophyll-containing antenna system in the thylakoid membrane as shown in Fig. 1, furnishing photosystem II with very high quantum efficiency. The oxidized primary electron donor of photosystem II gives electrons to an external quinone to form hydroquinone. Electron vacancies are filled by water oxidation producing O$_2$ as byproduct, carried out by the oxygen-evolving complex, which contains an oxo-bridged tetramanganese calcium cluster Mn$_4$O$_5$Ca.

Several in-depth analyses have been published discussing the structure and operating mechanism of photosystem II and that of the oxygen-evolving complex (McEvoy and Brudvig 2006; Umena et al. 2011; Kärkäs et al. 2014; Shen 2015; Zhang and Sun 2019; Zabret et al. 2021). Herein, we would like to emphasize two details that are worth considering. First, an oxygen-evolving complex has a certain average lifetime of circa 30 min under full sunlight, because light quanta induce degradation, and the molecular integrity eventually breaks down (Inoue et al. 2011). Thus, the oxygen-evolving complex has to be protected but also continuously rebuilt by repair mechanisms strongly coupled to energy conversion. Note that the Mn$_4$O$_5$Ca cluster itself binds to the protein and assembles spontaneously from free Mn$^{2+}$ and Ca$^{2+}$ in solution under visible light, a process called photoactivation (Dasgupta et al. 2008).

![Fig. 1](image_url) The light-dependent reactions of photosynthesis at the thylakoid membrane. The electron transfer chain is displayed in blue. The molecular components of the system are embedded in the thylakoid membrane. The water oxidation process at the oxygen-evolving complex is triggered by the light absorption of photosystem II primary electron donor. Quinone molecules transport the released electrons to the cytochrome complex and to plastocyanin that functions as electron donor to photosystem I. This electron transfer requires another photoexcitation process by the primary electron donor of photosystem I. The electrons directed to the lumen are used up in nicotinamide adenine dinucleotide phosphate reduction. Abbreviations: PS II is photosystem II, P680 is the photosystem II primary electron donor, OEC is the oxygen-evolving complex of photosystem II, Q is quinone, H$_2$Q is hydroquinone, b$_6$f is the cytochrome complex, Pc is the blue copper protein plastocyanin, PS I is photosystem I, P700 is the photosystem I primary electron donor, Fd is ferredoxin, FNR is the ferredoxin-NADPH reductase, NADP$^+$ is nicotinamide adenine dinucleotide phosphate and NADPH is the reduced form of nicotinamide adenine dinucleotide phosphate (Pantazis 2021)
From the perspective of the many artificial catalytic systems, where the longest possible lifespan is desired, a similar feedback mechanism at the expense of robustness and maximal energy efficiency might seem rather counterproductive. Nevertheless, the question arises, why this natural system has subsisted a very long evolutionary process, but still remains the best practice in natural energy conversion. Perhaps this feature of the natural oxygen-evolving complex inspired the idea of a Co-based self-healing oxygen-evolving catalyst (Costentin and Nocera 2017) that has to do historically with the century-old attempt of determining the potential for the CoIII/II couple (Coehn and Gläser 1902). In any case, the electrochemical behavior of cobalt has certainly not changed in a hundred years, which may give cause for optimism in terms of the flexibility of the human approach.

The second detail, which is the starting point of our focused review, is that photosystem II contains redox-active organic cofactors close to the inorganic cluster. As integral part of the oxygen-evolving complex a redox-active tyrosine-Z residue coupled to a hydrogen-bonded histidine-Z unit is found near the Mn4O5Ca cluster, shuttling proton-coupled electron transfer and synchronizing the light-induced Kok cycle with the distal transport of the charge carriers between the oxidized primary electron donor of photosystem II and the cluster (Kok et al. 1970). Another tyrosine–histidine pair, tyrosine-D and histidine-D is in redox contact with both tyrosine-Z and Mn4O5Ca. Both redox cofactors are present in every known oxygen-evolving organism; therefore, no photosynthesis as we witness today would be possible without these small molecular fragments.

Our review focuses on the catalysis of the water oxidation reaction that lies at the heart of artificial photosynthesis. Irrespective of the design of the whole system, that is photocatalytic, photoelectrocatalytic or photovoltaic plus electrocatalytic, the function of the system has subsisted a very long evolutionary process, that is photosynthesis as we witness today would be possible without these small molecular fragments.

2. Effect of tyrosine on the mechanism of the natural oxygen evolution reaction

In nature metal cofactors and perhaps to a lesser extent, yet, of comparable effect redox-active organic moieties are key components to enzymatic catalysis to facilitate biochemical redox reactions. In this context, the evolutionary role of the phenolic sidechain of tyrosine cannot be over-emphasized. The oxygen-evolving complex strongly relies on two tyrosine residues found in its protein backbone, tyrosine-Z and tyrosine-D (Siegbahn and Blomberg 2004; McEvoy and Brudvig 2006; Styring et al. 2012; Narzi et al. 2014; Nakamura et al. 2020). The tyrosine residues are involved in the regulation of the sequential transfer of electrons and protons between the oxidized primary electron donor of photosystem II and the Mn4O5Ca.

The oxidation of H2O molecules may take place in four different ways producing HO·, H2O2, O2−, or O2, depending on the number of electrons removed. The 4e− oxidation pathway yielding triplet O2 as product is the lowest in energy although, still energetically uphill and the most complex reaction of all at the molecular level, since four O–H bonds from two water molecules have to be broken and an O–O bond must be formed. This 4e− oxidation occurs at the oxygen-evolving complex of photosystem II.

2.1 Mechanism of the oxygen-producing Kok cycle

The catalytic center has been conceived as progressing in a cycle of five oxidation states, S0 to S4, since Kok has proposed that a trapping center or an associated catalyst successively accumulates oxidizing equivalents to link the 1e− progression in photoexcitation to the 4e− and 4H+ abstraction from two H2O molecules to yield O2 (Kok et al. 1970) (Fig. 2). In the S1 state the system is stable in the dark, while O2 is produced only after reaching the S4 state, during a single photon-induced S1 → S0 transition. The e− to H+ stoichiometry over the four steps corresponds to 1:0:1:2 (Fürster and Junge 1985). The photo-induced charge separation in photosystem II generates the strongest oxidant known in biology, the oxidized form of the primary electron donor of photosystem II, for which the estimated redox potential is circa +1.2 V versus the normal hydrogen electrode (Rappaport and Diner 2008). This potential is enough to drive each of the transitions in the Kok cycle and ultimately extract electrons from water molecules. At the same time, interfacial tyrosine regulators are required to adjust the sequential charge accumulation in the Mn4O5Ca cluster.
Outstanding achievements have led to the presently known detailed models for O₂ formation from water by the oxygen-evolving complex, including valence and spin state analysis of the Mn ions in various S states (Cox et al. 2013; Krewald et al. 2016; Pantazis 2018). In conjunction with spectroscopic and kinetic investigations, structural analysis using femtosecond X-ray pulses, with improved spatial and temporal resolution, selective characterization of the different states resulted in the native structure of photosystem II (Suga et al. 2015) and the structural analysis of the intermediates in the Kok cycle (Kern et al. 2018).

A thorough overview on the evolution of structural and kinetic models of photosystem II and oxygen-evolving complex has been provided recently (Junge 2019). We rely on the current works cited therein, including the stepwise S state structural analysis (Krewald et al. 2016; Kern et al. 2018), and further considerations made on tyrosine-Z (Nakamura et al. 2020), in order to explain the role of the tyrosine–histidine pairs at the different stages of the Kok cycle.

2.1.1. Structure of the Mn₄O₅Ca cluster and the initial S states

The structure of the Mn₄O₅Ca cluster is often depicted as a distorted chair since the first atomic resolution crystal structure of photosystem II has been reported (Umema et al. 2011) (Fig. 3a). This metal cluster along with the surrounding protein scaffold is very stable, and the expected structural changes during the cycle are subtle (Zhang et al. 2017a); thus, the positions of the primary electron donor of photosystem II, tyrosine-Z, tyrosine-D and the Mn₄O₅Ca cluster vary very little. In states S₀ and S₁ the cluster adopts low spin configurations with 1/2 and 0 total spin, respectively. In S₀ the O5 bridge (Fig. 3a) is protonated, one Mn³⁺ and the Ca²⁺ ion both have aqua ligands.

All remaining ligands in the first coordination sphere are carboxylate groups of glutamic acid, aspartic acid and alanine derived from structural polypeptides except for a nitrogen-donor histidine ligand, which coordinates to a Mn ion. The peptide ligands were omitted from Fig. 3a for clarity. The changes taking place in the coordination mode of O5 are of particular importance because spectroscopic results implicated that O5 originates from one of the two reacting substrate water molecules.
Fig. 3  

a Structural changes of the Mn₄O₅Ca cluster during the S₀-S₄ states. The most reduced state is S₀ with a single Mn⁴⁺ and three Mn³⁺ ions. One Mn³⁺ in S₀ is oxidized by one electron to provide S₁ with a proton dissociating from the O₅ oxygen atom. The next oxidation generates another Mn⁴⁺ ion to give a low and a higher spin S₂ structural isomer. Only S₂ can progress to S₃ that is facilitated by tyrosine-Z⁺. In this step a water molecule coordinates to the cluster that loses one proton. In the S₃ state two oxygen atoms get close to each other and participate in O–O bond formation upon reaching subsequent S₄ state (tyrosine-Z⁺)Mn⁴⁺ upon the final photoexcitation.

b The redox transition of tyrosine-Z/tyrosine-Z⁺ and the proximal histidine-Z residue that acts as neighboring base. Abbreviations: ST is the total number of unpaired electrons that defines the spin configuration, hv represents the incident photons, P₆₈₀ is the primary electron donor of photosystem II, P₆₈₀⁺ is the oxidized primary electron donor of photosystem II, Tyr-Z and Tyr-D are the respective tyrosine residues, His-Z and His-D are the respective histidine residues.

The cycle is closed by the evolution of O₂ and the coordination of H₂O.
The photogenerated oxidized primary electron donor cation is coupled to the Mn₄O₅Ca cluster via the intermediary redox-active tyrosine-Z, which works as a 1e⁻ rectifier (Fig. 2). Initial electron transfer between the oxidized primary electron donor cation and tyrosine-Z occurs on a nanosecond timescale, whereas the subsequent electron transfer between tyrosine-Z⁺ and Mn₄O₅Ca occurs on a micro- to millisecond timescale, depending on the actual S-state. Fast reversible redox transition of tyrosine-Z/tyrosine-Z⁺ is an intrinsic property originating from the proximal histidine-Z residue that acts as base, stabilizing the deprotonated tyrosine-Z (Fig. 3b), while structured water molecules bound to the Ca²⁺ ion also tune the redox potential of this molecular moiety. Tyrosine-Z⁺ is a strong oxidizer with a redox potential greater than +0.9–1.0 V versus the normal hydrogen electrode (Vass and Styring 1991). Due to the proximity of the Mn₄O₅Ca cluster tyrosine-Z⁺ is reduced very fast (Babcock et al. 1976), by means of an S-state-dependent kinetics; therefore, a direct detection is complicated.

2.1.2 The S₂ state

The most characterized state of the catalytic cycle is undoubtedly S₂, in which the cluster is oxidized by 1e⁻ compared to S₁. The manganese oxidation states in S₂ are Mn³⁺Mn⁴⁺, leading to a 1/2 spin configuration that is detectable by electron paramagnetic resonance spectroscopy. Importantly, S₂ can adopt a low and a higher spin form exhibiting 1/2 total spin for the open cube-like form S₂⁻ and 5/2 total spin for the closed cube form S₂⁺ (Fig. 3a).

At this point in the cycle a spin state interconversion takes place on a microsecond timescale under physiological conditions with a low energy barrier for the O₅ translocation, thus enabling the conversion of S₂⁻ to S₂⁺ that in turn can progress to S₃ (Styring et al. 2012; Pantazis et al. 2012; Bovi et al. 2013). The low spin configuration up to the S₂⁻ state of the oxygen-evolving complex has been suggested to prevent short circuiting of the 4e⁻ oxidation at a 2e⁻ level of peroxide formation that may help to increase the lifetime of the complex (Rutherford 1989).

In order to proceed further to the low spin S₂ tyrosine-Z⁺ state Ca²⁺ is also indispensable, facilitating the S₂⁻ to S₂⁺ interconversion and the stabilization of the S₁ state. Deprotonation of the coordinating water molecule is coupled to the Mn⁴⁺→Mn³⁺ oxidation in S₂⁺ which occurs after formation of tyrosine-Z⁺ (Retegan et al. 2016). The reorientation of the electric dipole of the Mn₄O₅Ca cofactor supports the coupled charge transport.

2.1.3. The S₃ and S₄ states

In the S₃ state, all Mn ions adopt oxidation state IV. Note that the structure of S₃ in Fig. 3 may not represent the final state. This is because the S₃ to S₄ transition is a multistep process including manganese oxidation, substrate deprotonation, internal rearrangement and water binding. The resulting S₄ has been described as (tyrosine-Z)Mn⁴⁺ or (tyrosine-Z⁺) Mn⁴⁺₃Mn³⁺ (Retegan et al. 2014; Cox et al. 2014). In S₃ two oxygen sites are close to each other and may couple together in the subsequent S₄ state (tyrosine-Z⁺)Mn⁴⁺ upon the final photoexcitation.

The protonation states of the water-derived ligands have not been established yet for each intermediate and vivid ongoing research aims at resolving the deprotonation sequences (Yang et al. 2021). According to computational studies on the O–O bond formation, an oxyl radical is likely to be formed in the S₃ state, most probably a terminal oxyl, which subsequently couples with an oxo bridge to form the O–O bond (Siegbahn 2009). Upon O₂ formation the release of the first proton takes place in the time range of 100 μs followed by a slower deprotonation step at 1 ms ( Förster et al. 1981). The latter timescale also limits a set of inseparable events from the deprotonation, namely the 1e⁻ transfer to tyrosine-Z⁺–H⁺-histidine, the reduction of three manganese ions, the release of O₂ and the uptake of an H₂O molecule. The exact order of the events is subject to ongoing research.

2.2 Role of tyrosine residues

All photosynthetic events could take place without tyrosine-D, yet this structural component is found in every natural photosynthesizing species. Tyrosine-D has a redox potential of circa +0.7–0.8 V versus the normal hydrogen electrode (Vass and Styring 1991). This residue is very stable as a radical located farther from the cluster than tyrosine-Z and remaining in the oxidized state from the first sunlight into the dark night hours.

In the D₂ protein of photosystem II, the oxidized tyrosine-D⁺→H⁺-histidine-D can elevate the potential energy of the oxidized primary electron donor of photosystem II via coulombic interaction (Rutherford et al. 2004). Thus, the oxidation of tyrosine-Z is accelerated, and the highly oxidizing charges will be located only in the D₁ protein side of photosystem II, suppressing side events. Further, tyrosine-D⁺ can oxidize the S₀ state to S₁ in the dark but can also deactivate the S₂ and S₃ states by reduction, preventing other unwanted reductants from interfering with the S state cycle ( Feyziyev et al. 2003). Finally, tyrosine-D also plays an important role in the repair cycle of photosystem II, since in the absence of electrons from the Mn₄O₅Ca cluster tyrosine-D can serve as electron–hole carrier in equilibrium with the oxidized primary electron donor of photosystem II and tyrosine-Z⁺.
3. Redox-active ligands in artificial water oxidation catalysts

3.1. General considerations on the mechanism of the catalytic oxygen evolution reaction

Synthetic catalysts for the oxygen evolution reaction must deal with the removal of four electrons and four protons from two molecules of water according to Eq. (1).

$$2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4e^- \quad (1)$$

Transition metal complexes have rich redox chemistry due to a variable d electron configuration making the utilization in catalysts for the oxygen evolution reaction appealing. Upon reversible 1e− oxidation of a metal–aqua complex of general formula $\text{M}^{n+}\text{–OH}_2$ the aqua ligand becomes more acidic and may lose a proton; thus, multiple-site electron–proton transfer can generate the corresponding oxidized form, $\text{M}^{(n+1)+}\text{–OH}$ (Weinberg et al. 2012). In a next oxidation $\text{M}^{(n+2)+}\text{=O}$ can be obtained in a similar fashion (Fig. 4). For example, the aqua-Ru-polypyridyl complexes can reach high oxidation states within a narrow potential range in this way, due to the $\sigma$- and $\pi$-donation character of the $\text{M}=\text{O}$ group (Sala et al. 2014; Matheu et al. 2019). The possibility of multiple-site electron–proton transfer prevents the buildup of positive charges that would otherwise strongly destabilize the oxidized forms and separate the consecutive oxidation steps by high differences in potentials. Instead, the coupling between electron and proton transfer steps allows for a redox leveling that favors rapid kinetics for the whole oxygen evolution process. An excellent example is the histidine base effect in the tyrosine–histidine pairs of the natural oxygen-evolving complex.

Without histidine acting as acceptor site for the proton, electron transfer is unfavorable and slowed down by a factor of 200 (Diner et al. 1991) and the oxidation of tyrosine cannot outcompete the reverse electron transfer from the quinone radical anion to the oxidized primary donor of photosystem II (Hoganson et al. 1995) (see the electron transfer chain in Fig. 1). Another example taken from photosystem II is the proposed multiple-site electron–proton transfer reaction in the S0 to S1 transition of the Kok cycle (Fig. 3a). The S0 to S1 step involves 1e− oxidation of the Mn$_2$O$_2$Ca cluster with electron transfer to tyrosine-Z$^{*+}$ in concert with two proton transfer events: one taking place from a Mn–OH$_2$ moiety to a neighboring aspartate base and another at the electron acceptor site tyrosine-Z$^{*+}$H–histidine-Z providing tyrosine-Z–H–histidine-Z.

In addition to the removal of electrons and protons, the oxidation of water to $\text{O}_2$ also requires the formation of an $\text{O}–\text{O}$ single bond that is generally a purely chemical step in nature and takes place after the second oxidation step of the catalyst. Molecular catalysts for the oxygen evolution reaction follow two main types of mechanism, depending on whether an external $\text{H}_2\text{O}$ molecule participates in the formation of the $\text{O}–\text{O}$ bond, or two M–O units react. The former mechanism corresponds to water nucleophilic attack abbreviated as WNA, while the interaction of two M–O units is called I$_2$M, as shown in Fig. 5. The chemical O–O bond formation step that creates a metal-peroxide intermediate is generally regarded as the bottleneck of the overall process, whereas the follow-up reaction steps proceed rapidly toward the closing of the catalytic cycle.

A recent review covered the role of redox-active and redox non-innocent ligands in water splitting with a categorization based on the way of activation, that is electrochemical, photochemical or chemical, collecting examples of catalysts for both the hydrogen evolution reaction and the oxygen
The evolution reaction (Singh and Indra 2020). The same review paid attention to structural mimics and briefly discussed the possible effects of redox-active ligands on a catalytic process in general. Another work categorized molecular transition metal catalysts as mono- and binuclear complexes, containing redox non-innocent ligands, and emphasized their role in supplying electrons or binding protons at different stages of the corresponding mechanism, such as the water nucleophilic attack or the interaction of two M–O units, leading to a more efficient reaction (Sutradhar et al. 2021). Similarly to the previous reviews, we follow the definition of a ligand being non-innocent, if the oxidation states of the central atom cannot be defined unequivocally (Jørgensen 1966). According to this definition, intramolecular electron transfer may occur between the ligand and the metal center in complexes containing non-innocent ligands, allowing for different valence tautomeric forms (Tezgerevska et al. 2014). However, redox-active ligands are those, in which well-defined changes in the redox state also alter the reactivity of the complex in a favorable direction.

In the case of the oxygen evolution reaction, participation of redox-active ancillary ligands in one or more of the oxidation steps is likely, if this change in the electronic structure of the complex makes the concerned steps energetically favorable. Obviously, those ligands, which can accelerate O–O bond forming or reduce the potential barrier in this manner, are expected to play most attention to. At the same time, catalytic efficiency is occasionally disfavored by intervening ligands. Attention should be paid to unexpected effects, as these may occur in new systems, and account for the specific behavior. Such redox activity also contributes to a more complete picture.

Herein we focus on catalysts for the oxygen evolution reaction, seeking analogies if apply, with the cooperation between the oxygen-evolving complex and the tyrosine–histidine pairs found in photosystem II with the notion that several redox-active ligands have been explored in hydrogen evolution reaction catalysis (Singh and Indra 2020). We bring representative examples on the possible outcome of the redox state change in ancillary ligands during catalysis, keeping in mind that there may be crosstalk between molecular catalysts and oxides, the other main group of synthetic catalysts for the oxygen evolution reaction. The following ligand types will be discussed, irrespective of the metal content, the nuclearity of the complex, or the way of activation:

(i) Those accumulating electron vacancy to assist catalysis;
(ii) Those possessing protic sites to facilitate proton-coupled electron transfer;
(iii) Those participating in the O–O bond formation step and get recovered;
(iv) Those undergoing redox transformation, thus making the complex an efficient precursor of the true catalyst.

### 3.2 Electron vacancy on redox-active ligands to assist catalysis

#### 3.2.1. Robust ruthenium catalysts

Although an early work pointed out that oxygen evolution from water is possible using transition metal complexes as catalysts (Elizarova et al. 1981), the first thoroughly characterized molecular catalysts for water oxidation were Ru-polypyridyl complexes, starting with the blue dimer cis-[(H₂O)Ru³⁺(2,2'-bipyridine)₂(μ-O)Ru³⁺(2,2'-bipyridine)₂(OH₂)]⁴⁺ (Gersten et al. 1982) (Fig. 6). Ruthenium complexes are robust, inert toward ligand substitution and their higher oxidation states required for water oxidation are indeed accessible (Matheu et al. 2019). Moreover, typical Ru-based catalysts do not require redox-active ligands for efficient operation.

The water oxidation mechanism by the blue dimer has been subject to a fruitful debate (Liu et al. 2008; Moonshiram et al. 2012) incorporating electrochemical and chemical activation using Ce⁴⁺ in highly acidic media, and photochemical studies near pH 7 using photosensitizing ruthenium complexes in the S₂O₅²⁻ and blue dimer molecular system. In the latter case the sequential addition
of two $H_2O$ molecules has been suggested to the bipyridine ligands that may couple to generate $O_2$ (Yamada and Hurst 2000; Cape and Hurst 2008). However, the pathway following the $2e^-$ oxidation of the $OH^-$ adducts results in decomposition of bipyridine (Liu et al. 2008). The decomposition ultimately gives $CO_2$ as a product after several redox cycles, since the partly oxidized rings are kinetically susceptible to further oxidation.

Upon electrochemical activation of Ru catalysts, generally the Ru centers and the water-derived ligands eject electrons rather than the ancillary ligands. The blue dimer that carries four electron vacancies relative to the $Ru_{III}$ resting state is thermodynamically capable of water nucleophilic attack, instead of the coupling of the two oxo ligands. On the bottom: the dinuclear complex along with the proposed catalytic pathways. In this case, electron transfer from the redox-active quinone ligands facilitates the intramolecular formation of the $O-O$ bond. Abbreviations: bpy is 2,2′-bipyridine, BTPYAN is 1,8-bis(2,2′-terpyridyl)anthracene, Q is 3,6-di-tert-butyl-1,2-benzoquinone and SQ is 3,6-di-tert-butyl-1,2-benzoquinone.
at + 1.70 V versus the normal hydrogen electrode in water at pH 4, producing O2 by 95% charge efficiency and reaching a turnover number of 6730 (Wada et al. 2000) (Table 1). Upon the O–O coupling the quinones act as oxidants via intramolecular electron transfer. In this reaction step two protons dissociate from the complex and (SQ)RuII(O–O)RuII(SQ) is formed, where SQ is 3,6-di-tert-butyl-1,2-benzosemiquinone−. Two features were found indispensable to a successful catalysis: the two hydroxide ligands located close to each other due to the structural constraint by the two terpyridine moieties, and the two quinone ligands helping intramolecular coupling of the OH ligands to form the O–O bond.

The semiquinone ligands undergo oxidation to quinone at + 0.4 V versus the normal hydrogen electrode, furnishing (Q)RuII(O–O)RuII(Q)2+ that is followed by metal oxidation to RuIII at + 1.2 V versus the normal hydrogen electrode. Valence tautomerism of the produced (Q)RuIII(O–O)RuIII(Q)4+ complex generates (Q)RuII(O=O)RuII(Q)4+ from which O2 liberates upon replacement by two H2O molecules. Note that a theoretical study identified [Ru2(O2−)(Q−1.5)2(BTPYAN)] as a key intermediate and the most reduced catalyst species that is formed by removal of all four protons before 4e− oxidation takes place (Muckerman et al. 2008). The studies on Ru-quinone catalysts signified that the O–O bond formation is attainable at a low oxidation state of the metal and this observation has very important consequences on first row transition metal catalysts.

### Table 1

| Complex | Electrolyte | Turnover frequency (s−1) | Turnover number | Reference |
|---------|-------------|--------------------------|-----------------|-----------|
| [Ru(OH2)(quinone)(terpyridine)]2+ | 0.5 M potassium phosphate, pH 4 | n.d | 6730 | Wada et al. (2000) |
| [RuII(O)2(OH2)(3,6-di-tert-butyl-1,2-semiquinone)2(1,8-bis(2,2′-terpyridyl)anthracene)]2+ | 1.0 M potassium phosphate, pH 4 | n.d | 33,500 | Wada et al. (2001) |
| ([2-(2-carboxyphenyl)-1H-benzo[d]-imidazole-4-carboxylate]-RuIII(OH2)2(picolinate)]2+ | 0.1 M sodium phosphate, pH 6.0 | n.d | 600 | Abdel-Magied et al. (2016) |
| | 0.1 M sodium phosphate, pH 7.2 | n.d | 330 | |
| | 0.1 M trifluoroethanol, trifluoromethanesulfonic acid, pH 1.0 | 0.08 | n.d | |
| ([3,5-bis(4-carboxy-1H-benzimidazol-2-yl)-pyrazole]Ru2II,III(picolinate)]2+ | 0.1 M sodium phosphate, pH 6.2 | 0.5 | 800 | Experimental: Laine et al. (2015a), calculation: Abdel-Magied et al. (2016) |
| | 0.1 M sodium phosphate, pH 7.2 | 1.3 | 470 | |
| [Ru(2-(2-hydroxy-5-R-phenyl)-1H-benzo[d]imidazole-7-carboxylate)(picolinate)]3+ | R=Me | 0.1 M sodium phosphate, pH 7.2 | 0.86 | 460 | Kärkäs et al. (2016) |
| | R=H | 3.1 | 1700–4000 | |
| | R=F | 2.2 | 1520 | |
| | R=Br | 1 | 850 | |

#### 3.2.2. First row transition metal catalysts

Ruthenium centers can undergo multiple oxidation steps in a relatively narrow potential range due to effective proton-coupled electron transfers. The situation can be very different when water oxidation involves first row transition metals that often exhibit high propensity toward ligand substitution and the access to higher oxidation states demands high potentials. The rapid ligand substitution is an intrinsic property that stands as major challenge in the design of catalysts and require careful selection of catalytic conditions. Moreover, the release of four protons in one catalytic cycle may easily cause ligand protonation and subsequent dissociation from the metal center as a competing process.

Stabilization of a catalytically active, highly oxidized first row transition metal center demands strong electron-donating ligands. However, this requirement can be circumvented if redox-active ligands are utilized and reversibly oxidized to cooperate with the metal center in storing electron vacancies needed for the water oxidation reaction. Ligand redox activity has been documented in complexes bearing rigid, planar macrocyclic or semi-macroyclic ligands with extended π-conjugation capable of carrying unpaired electrons. Different families of tetra-amidate ligands were used in Fe (Ellis et al. 2010), Co (Du et al. 2018), Ni (Lee et al. 2020) and Cu (Garrido-Barros et al. 2015, 2017, 2020) complexes. The main experimental parameters and the catalytic performance of the selected complexes discussed herein are listed in Table 2, where the different compounds are listed according to the metal content.
Table 2 Molecular catalysts of the water oxidation reaction that contain first row transition metals and redox-active ancillary ligands, reported reaction conditions and catalytic performance

| (Ancillary ligand)metal assembly | Solution or electrolyte | Overpotential or onset potential (V) | Turnover frequency (s\(^{-1}\)) | Turnover number | Faraday efficiency | Reference |
|----------------------------------|------------------------|-------------------------------------|---------------------------------|----------------|-------------------|-----------|
| (tetra-amido macrocycle)iron(III) | 0.147 M ceric ammonium nitrate, pH 0.7 | n.a | 1.3 | n.d | n.a | Ellis et al. 2010; Liao et al. (2014) |
| [5,10,15-tris(pentfluorophenyl)-corrole]manganese(III) | 0.1 M sodium phosphate, pH 11 | n.d | 0.47 | 19,000 | 82% | Schöfferberger et al. (2016) |
| (phthalocyanine)manganese(III) | water; acetonitrile (1:3), 0.25 M tetraethylammonium perchlorate | n.d | 0.2–0.5×10\(^{-3}\) | n.d | n.d | Mousazade et al. (2019) |
| (tetra-amido macrocycles) cobalt(III) | 0.1 M sodium phosphate, pH 7 | 0.38 | 7.53–8.81 | n.d | > 90% | Du et al. (2018) |
| [5,10,15,20-tetrakis(1,3-dimethylimidazolium-2-yl)porphyrin]cobalt(III) | 0.2 M sodium phosphate, pH 7 | n.d | n.d | 1200 | 85–90% | Wang and Groves (2013) |
| [2-[bis(pyridin-2-ylmethyl)]amino-N-quinolin-8-yl-acetamidate]cobalt(III) | 0.1 M sodium phosphate, pH 8 | 0.50 | 85 | n.d | 81% | Biswas et al. (2020) |
| [N,N-bis[20-pyridinecarboxamide]-1,2-benzene]cobalt(II) | 0.25 M sodium phosphate, pH 8.6 | 0.56 | 81.54 | n.d | n.d | Wang et al. (2015) |
| (β-tetra-amidate macrocycle) cobalt(III) | 0.1 M sodium phosphate, pH 9.2 | ~0.6 | 5.68 | n.d | n.d | Das et al. (2016) |
| [5,10,15-tris(pentfluorophenyl)-corrole]cobalt(III) | 0.1 M sodium phosphate, pH 7.0 | 0.53 | 0.2 (at 0.78 V) | n.d | n.d | Lei et al. (2014) |
| (corrole)cobalt(II) | 0.1 M sodium phosphate, pH 12 | 0.53 | n.d | n.d | n.d | Mondal et al. (2020) |
| [meso-tetra(4-N-methylpyridyl)porphyrin]cobalt(II) | 0.1 M sodium phosphate, pH 11 | n.d | 88.7 | 0.118 | n.d | Nakazono et al. (2013) |
| [meso-tetakis(4-carboxyphenyl)porphyrin]cobalt(II) | n.d | 103.4 | 0.138 | n.d | |
| [meso-tetakis(4-sulfophenyl)porphyrin]cobalt(II) | n.d | 121.8 | 0.17 | n.d | |
| (5,10,15,20-tetra(2,6-difluoro-3-sulfophenyl)porphyrin) cobalt(II) | 0.1 M sodium borate, pH 9 | 0.57 | 1.1 | n.d | n.d | Nakazono et al. (2015) |
| (tetraphenylporphyrin)cobalt(II) | 0.5 M potassium borate, pH 9.2 | 0.53 | 0.5 | n.d | n.d | Han et al. (2014) |
| [tetakis(4-bromophenyl)porphyrin]cobalt(II) | 0.5 M potassium borate, pH 9.2 | 0.58 | 0.4 | n.d | n.d | |
| [5,10,15-tris(pentfluorophenyl)-corrole]cobalt(II) | acetonitrile with 4.8% water, 0.1 M tetrabutylammonium perchlorate | 0.2–0.4 | n.d | n.d | n.d | Sinha et al. (2018) |
| Hangman-type (β-octafluorocorrole)cobalt(III) | 0.1 M potassium phosphate, pH 7.0 | ~0.6 | 0.81 (at 0.8 V) | n.d | n.d | Dogutan et al. (2011) |
The complexes with tetra-amido macrocyclic ligands have been studied in detail (Fig. 7). The first report concerned Fe-tetra-amido macrocyclic complexes that could promote O₂-evolution to a highly variable extent, by mixing with excess CeIV in water at pH 0.7 (Ellis et al. 2010).

Loss of activity was associated with oxidative and hydrolytic...
inactivation pathways, also confirmed by control reactions using other Fe-ligand combinations. The rate of the biphasic O₂ evolution correlated with the addition of electron-withdrawing substituents to the ligand.

The highest measured turnover frequency was 1.3 s⁻¹ for the ligand with R₁/R₂=Cl and R₃=F that was sufficiently large to be limited by the kinetics of bubble formation and release (Table 2). Based on theoretical calculations, the formation of a key intermediate, (tetra-amidate macrocyclic radical)FeV=O was suggested (Ertem et al. 2012; Liao et al. 2014). In the latter study, this species was proposed to undergo water nucleophilic attack, or nucleophilic attack by a nitrate ion, the water attack being more favored. According to the results, nitrate may function as a co-catalyst by first donating an oxygen atom to the oxo group to form O₃ and a nitrite ion, which can then be re-oxidized to regenerate a nitrate ion. Competing pathways were suggested to modify the ligand such as water and nitrate attack as well as ligand amide oxidation, leading to the opening of the benzene ring and fast catalyst degradation.

Efficient electrocatalytic oxygen evolution in neutral aqueous solution was reported by stable CoIII-tetra-amidate macrocyclic complexes (Fig. 5) that were confirmed as molecular catalysts under the working conditions (Du et al. 2018). The catalytic cycle was examined in detail by electrochemical methods and density functional theory calculations. As the working potential was increased, the triplet complex was first oxidized via ligand-centered 2e⁻ + H⁺ transfer in the presence of water. The oxidation of the ligand was clearly indicated by the changes in the C−C bond length of the benzene ring and the N-aryl ring bond lengths, corresponding to the structural change expected in the oxidation of an o-phenylenedicarboxamido ligand to benzoquinonedi-carboxamido form.

The CoIII-OH intermediate was further oxidized to the CoIV=O form, which could react with water to form an O–O bond in a buffer-assisted water nucleophilic attack. The influence of H₂PO₄⁻ on the process revealed by theoretical calculation was in good agreement with the observed buffer effect. Analysis of the calculated structure revealed that both the oxo moiety and the cobalt center bear significant spin densities corresponding to a more correct CoIII−O• assignment. The water nucleophilic attack afforded the quartet hydroperoxo complex, CoII−OOH that was oxidized to the superoxo complex CoIII(O₂·−) through proton-coupled electron transfer, to finally release an oxygen molecule and regenerate the resting state (Fig. 8). The turnover frequency values calculated for the different complexes were very similar, between 7.53 and 8.81 s⁻¹, but no catalytic activity could be observed for a complex with a non-redox-active ligand homolog (the benzene ring was substituted by an aliphatic bridge), indicating that the redox-active ligand played a critical role in this multi-electron catalytic cycle. This work underlined the interplay of ligand- and metal-centered redox activity could be a benefit for water oxidation catalysts.

A NiII-tetra-amidate macrocyclic complex was characterized as electrocatalyst of the oxygen evolution reaction at neutral pH in phosphate buffer (Lee et al. 2020) (Fig. 7, R₃ = CH₃). The HPO₄²⁻ anion served as proton acceptor to accelerate the formation of the O–O bond following atom-proton transfer pathway. The electrochemical activation of the complex started with a reversible, pH-independent
NiII to NiIII oxidation at +0.68 V versus normal hydrogen electrode, followed by two irreversible oxidation peaks at +1.03 V and +1.51 V versus the normal hydrogen electrode. The first irreversible and pH-dependent oxidation was associated with a 2e− + H+ transfer to produce an intermediate NiIII−OH species, while the second one was assigned to produce NiIV=O. Oxygen evolution took place at 93% Faraday efficiency and the calculated turnover frequency was 0.32 s⁻¹. The proposed catalytic cycle is shown in Fig. 8. The first-order dependence of the catalytic current on catalyst concentration clearly indicated a single-site mechanism.

The above catalysts could possibly exploit the one- and two-electron oxidation of the applied tetra-amido macrocycle ligand according to Fig. 9 thanks to the available formal o-phenylene-, benzosemiquinone- and benzoquinonedicarboxamido redox forms. A similar amidate group has been suggested to facilitate the redox activation of a mononuclear CoIII-complex, [Co(2-[bis(pyridin-2-ylmethyl]-N-quinolin-8-yl-acetamidate)(Cl)]Cl (Biswas et al. 2020). Efficient molecular electrocatalysis was reported to occur at a 500 mV overpotential and pH of 8.0. The redox-active amidate ligand facilitated catalysis through the formation of a reactive oxo-metal species (Costentin et al. 2012a, b) (Fig. 10). According to the mechanism proposal, water nucleophilic attack on this putative intermediate formed the O=O bond through a base-assisted proton transfer reaction.

In the case of copper, planar 4 N− donor coordination sites like in tetra-amido macrocycles are well suited for stabilizing an oxidized CuIII metal center and perhaps this metal has been studied the most thoroughly with respect to the utilization of redox-active ligands. The N,N′-(1,2-phenylene)bis(3-methoxyhydroxamide) ligand family shown in Fig. 7 as PBOA demonstrated opportunities in using redox-active ligands to advance Cu-based water oxidation (Garrido-Barros et al. 2015). Introducing electron-donating R1 and R2 substituents at the benzene ring of PBOA allowed reducing the overpotential in electrocatalytic water oxidation by 530 mV.

The energy of the highest occupied molecular orbital in the ligand correlated with the observed overpotential, indicating that the electron-donating substituents increase the overall energy of the highest occupied molecular orbital and favor the oxidation of the ligand. Density functional theory analysis revealed a new mechanism progressing toward the rate-limiting O=O bond formation in single-electron

Fig. 9 Possible redox states of a phenylenediamide moiety. This structural feature is found in all tetra-amidate macrocycles and (1,2-phenylene)bis(oxalamide) ligands. When the closed-shell, dianionic form loses one electron a radical anion is formed. This radical is stabilized due to spin delocalization over the benzene ring and the two amidate functions. Upon losing a second electron, the molecule becomes closed shell again by adopting a neutral, benzoquinonedicarboxamido structure. The two oxidation steps are typically separated by ~0.5 V.
transformations and generating a peroxide intermediate with no formal M–O bond (Funes-Ardoiz et al. 2017) (Fig. 11). The theoretical and experimental results led to a new, general mechanistic proposal, the so-called single-electron transfer water nucleophilic attack.

A derived complex utilizing the ligand 4-pyrenyl-$N_j N_j'$-(1,2-phenylene)bis($N_2$-methyloxalamide) (py-PBOA) was designed to extend the $\pi$-conjugation (Garrido-Barros et al. 2017). Both catalysts have been studied in the homogeneous phase and immobilized by $\pi$-stacking on graphene-based electrodes. In the homogeneous phase the electronic perturbation provided by the pyrene substituent reduced the overpotential by 150 mV and increased the catalytic rate by more than 20 times to achieve a turnover frequency of 128 s$^{-1}$. Spectroscopic investigations on the one-electron oxidized form in aqueous solution confirmed that the oxidation process concerns the pyrene moiety in contrast to the parent complex, in which the oxidation remained metal-centered. (The differences are highlighted in red in Fig. 11.) The better performance of the pyrenyl derivative was associated with the lower oxidation potential of the ligand due to the pyrene group together with a large stabilization of the putatively charged oxidized species in the aqueous environment.

Immobilization on a graphene surface provided additional delocalization that improved the catalytic performance of both catalysts; however, the py-PBOA complex was more active. The overpotential of 538 mV, turnover frequency of 540 s$^{-1}$ and turnover number over 5300 demonstrated that rational design and a redox-active ligand can dramatically increase the stability of first row transition metal catalysts.

The same group underlined in a later work that elucidating the actual sites affected by consecutive oxidations and subtle changes perturbing the delocalization of electron density are of high importance. They developed two new ligands with 13- and 14-membered rings that can be regarded as dibenzo-tetra-amido macrocycles, or shortly dibenzo-TAML as shown in Fig. 7 (Garrido-Barros et al. 2020) in addition to the above-discussed semi-macrocyclic $N_j N_j'$-(1,2-phenylene)bis($N_2$-methyloxalamide). They found...
Fig. 11 Proposed mechanism of the electrocatalytic water oxidation by the Cu complex formed with N,N’-(1,2-phenylene)bis(N,N’-methyloxalamide) abbreviated as PBOA for clarity. The structure is shown in Fig. 7. The resting state on the top of the cycle undergoes a pH-independent one-electron oxidation and Cu$^{III}$ is stabilized by the strong donor $4\,N^–$ equatorial ligand environment. In the next step, the PBOA ligand is oxidized that requires higher potential, and hydroxide coordinates to the metal center. This step is followed by a rate-limiting chemical reaction that is a single-electron transfer water nucleophilic attack to result in the reduction of the PBOA ligand and an H$_2$O$_2$ species with a formal $-1.5$ oxidation state of each oxygen atom. The further oxidation steps are fast at the applied potential. The homolog ligand 4-pyrenyl-N,N’-bis(1,2-phenylene)bis(N,N’-methyloxalamide) is abbreviated as py-PBOA. The structure of the (py-PBOA$^{4–}$) Cu$^{II}$ complex is found in Fig. 7 with the pyrenyl group at the R$_2$ position. The differences in the oxidation potentials and the structure of the key intermediate are highlighted in red.

that a mere one-atom change in the ring size and a change in solvent polarity were enough to shift the delocalization of electron density from the metal over the ligand $\pi$-system.

Valence tautomerism exerted by the solvent interaction evidenced the energetic near degeneration in the frontier orbitals and the subsequent easy access to the different oxidation states, corresponding to metal-centered, $d$-orbital oxidation or ligand centered oxidation. For example, the coordinated 13-membered dibenzo-tetra-amido macrocycle was involved in two $1e^–$ oxidations due to the high delocalization of spins (Fig. 12) resulting in two energetically levelled oxidation steps within an $80\,mV$ potential window. In contrast, this metal–ligand redox cooperativity was missed from the complex containing the 14-membered dibenzo-tetra-amido macrocycle, where the $\pi$-conjugation between both phenylene moieties was broken due to the presence of two dimethylmalonamide bridges with $sp^3$ carbons and the saddle distortion of the ligand (Fig. 7, R=CH(CH$_3$)$_2$).

The addition of only one member group to the macrocycle structure fundamentally determined the fate of the catalysts upon electrolytic water oxidation, since the stability of the spin multiplicities at the different oxidation states relied strongly on the extent of $\pi$-delocalization. The complex bearing the larger macrocycle ligand decomposed during catalysis, whereas the one containing the 13-membered macrocycle (Fig. 12) remained stable and highly active thanks to the evidenced redox cooperativity between the metal and the ligand. The highly oxidized reactive form thus becomes more stable due to the delocalization of the accumulated charges. The proposed mechanism and charge delocalization in the different oxidation states are shown in Fig. 12.

Importantly, this way the high-energy oxidized states that are located only on either the ligand or the metal center have been avoided. This strategy neglects both the ligand oxidative degradation and high-valent metal centers that exist only at large potentials and frequently result in the formation of metal oxides. In addition, the two ligand-based oxidations in a narrow potential window were essential to enable water oxidation at pH 7. As a result, catalysis proceeded with a turnover frequency of $140\,s^{-1}$ at an overpotential of only $200\,mV$.

A comparison was also made in this context with a catalyst featuring electronic delocalization limited to a single phenylene moiety, formed with the $N,N’$-(1,2-phenylene) bis(N,N’-methyloxalamide) ligand (Fig. 7, $R_1=R_2=H$) (Garrido-Barros et al. 2015). In this case, the catalytic cycle at pH $12$ proceeded via metal oxidation followed by ligand oxidation (Fig. 12). However, the acrylic ligand was prone to acidic demetallation below pH $10$ that prevented application in water oxidation at neutral pH, in sharp contrast to the macrocyclic complex. This observation underlined the advantage of the cooperative metal–ligand design approach to find more stable and efficient molecular catalysts for redox reactions. The authors also emphasized that irreversible precatalytic electrochemical oxidation features may hinder substantial changes in the pre-catalysts upon oxidation and may indicate degradation.

Following simple logic, we can conclude that shutting down the redox activity of the metal center in parallel with triggering that of the ligand is possible by appropriate ligand design. Indeed, recently a new family of dianionic [2,2’-bipyridine]-6,6’-dicarboxamide ligands (Fig. 13), substituted with redox-active phenyl or naphthalene moieties have been described (Gil-Sepulcre et al. 2021). The electrocatalytic oxygen evolution process involving only ligand-based redox events was a consequence of two features of the ligand. First, a Cu$^{III/II}$ redox couple at relatively low potentials necessitates highly anionic, strongly $\sigma$- and $\pi$-donating ligand environment. In the case of the bipyridyl-dicarboxamide ligands, the two neutral N donors of the bipyridine and the anionic N donors of the amide groups had insufficient electron-donating capacity to stabilize the oxidized metal center.

 Springer
below or at the onset potential of catalysis. Second, the two redox-responsive phenyl or naphthyl groups attached to the ligand and conjugated with the amide donors were able to accommodate two distal electron vacancies. Upon oxidation, one of the aryl-amide groups could be detached from the metal, opening a quasi-equatorial coordination site for an OH\(^-\) ligand.

A detailed electrochemical analysis at pH 11.6 revealed a large electrocatalytic current associated with O\(_2\)-evolution at an overpotential of 830 mV for the complex shown in Fig. 13. The experimental and computational results supported a catalytic cycle progressing toward the active form through single-electron transfer steps, including intramolecular single-electron transfer steps (Fig. 13, shown as I\(_{SET}\) steps). Upon the first oxidation, a triplet Cu\(^{II}\) complex is formed with a radical cation mainly centered on one of the aryl-amidate moieties. Evidence for this possibly rate-limiting ligand-based electron transfer was provided by the correlation between the substituent effect on the aryl groups and the observed onset potential of catalysis.

Accordingly, the turnover frequency values were in the range of 5–35 s\(^{-1}\) and the Faraday efficiencies were between 40 and 76%, both related to the structure of the ligand and the stability of the oxidized moiety. The Cu\(^{II}\) center served as a scaffold for the two bipyridyl-amide groups bonded to the metal center. At the same time OH\(^-\) coordination and activation could take place.

According to the proposed mechanism, the hydroxyl group is attacked by an external hydroxide via a radical-nucleophilic pathway, generating a Cu-(HOOH) species.
Since this process involves an intramolecular single-electron transfer event between the aryl radical cation and the hydroxyl group, the metal center is responsible for placing the two groups sufficiently close so that fast electron transfer can occur (Gil-Sepulcre et al. 2021). The role for the aryl substituent was clearly discussed from a thermodynamic perspective, because the substitution tuned the overpotential for oxygen evolution reaction. The kinetic perspective was apparent in the low reorganization energy of extended polyacenes upon electron transfer ensuring fast kinetic processes. Considering the high versatility in ligand design, the low efficiency obtained for the above complexes that is due to competitive deactivation pathways can be solved in the future.

Due to cyclic π-delocalization porphyrins and corroles are capable of stabilizing electron vacancies (Han et al. 2014). In addition, the two or three negative charges at the N donor groups, respectively, can stabilize the coordinated metal center in higher oxidation states (Nakazono et al. 2013, 2015). Thus, porphyrins and corroles represent an exciting redox non-innocent and potentially redox-active ligand platform with rich possibilities in derivatization as indicated in Fig. 14. The advantages of porphyrins and corroles have been discussed earlier (Zhang et al. 2017b). In context with the present overview, we emphasize that metalloporphyrin catalysts for the oxygen evolution reaction are generally proposed to undergo first a 1e⁻ oxidation concerning the ligand that is followed by 1e⁻ oxidation of the metal center. Metallocorroles can behave in a similar fashion upon oxidative activation (Zhang et al. 2017b). In metallocorroles the stabilization of high-valent metal ions by corroles is viable through a combination of short metal-nitrogen bonds and large metal out-of-plane displacements (Gross 2001). A key difference from metalloporphyrins is the wider prevalence of non-innocent electronic structures and full-fledged corrole²⁻ radicals among metallocorroles (Ghosh 2017). There is gathering evidence that the non-innocent or redox-active behavior of this ligand family is prevalent (Dogutan et al. 2011; Lemon et al. 2016; Schöfberger et al. 2016; Sinha et al. 2018, 2020; Garai et al. 2018; Mondal et al. 2020). Moreover, the high adsorptivity of the planar molecules to various surfaces (Schöfberger et al. 2016)
makes their utilization in (photo)electrodes directly available (Zhang et al. 2017b). Generation of hydrogen peroxide from water by using metalloporphyrins with redox silent metal centers like Al, or Sn has been also addressed as viable alternative strategy for artificial photosynthesis systems (Kutlassery et al. 2018) as well as light-driven oxidation of halide anions by metallocorroles (Mahammed and Gross 2015). Importantly, corrole and porphyrin ligand architectures are suitable for surface immobilization through covalent linkers or axial coordination of the metal center by tether ligands grafted onto the surface. Phthalocyanines are expected to exhibit advantages like those of porphyrins and corroles in the catalysis of the oxygen evolution reaction (Fig. 14). For example, photocatalytic water oxidation in the presence of a water soluble CuII-phthalocyanine complex was proposed to follow the interaction of two metal–oxygen units mechanism (Fig. 5) in borate buffer at pH 9.5 (Terao et al. 2016). According to computations, upon 1e− oxidation of the complex a phthalocyanine radical is generated instead of an oxidized metal center, thus the CuIII oxidation state generally leading to complex photodegradation does not occur. Importantly, competitive ligand exchange between chloride ions and water molecules for the fifth coordination site inhibits the reaction, calling attention to the potential detrimental effect of impurities.

Copper-phthalocyanine was reported to act as efficient redox mediator in TiO2 nanorod-based photoelectrochemical water splitting (Li et al. 2019). Moreover, conjugation of Cu-phthalocyanine to carbon quantum dots by π-stacking and then coupling with BiVO4 to construct a hybrid water oxidation photocatalyst also seems to be a viable strategy (Xu et al. 2021). A somewhat similar system with Co-phthalocyanine deployed on BiVO4 was also very recently reported to enhance the photocurrent in photoelectrochemical oxygen evolution (Shen et al. 2021). In conclusion, recent findings on the possible application of metallo-phthalocyanines are encouraging.

Polymeric copper and cobalt phthalocyanines were prepared as thin films on fluorine-doped tin oxide from evaporated metal films via chemical vapor deposition process with 1,2,4,5-tetracyanobenzene. The system was successfully operated in 0.1 M KOH electrolyte to generate O2 electrocatalytically (Geis et al. 2016). The phthalocyanines and other types of polymers, like metallated azo-naphthalene diimide-based redox-active porous organic polymer frameworks (Bhat et al. 2018), are encouraging to envision future applications of such materials. On the other hand, the example of a MnII-phthalocyanine complex results in manganese oxide formation upon electrocatalytic water oxidation in acetonitrile–water mixture (Mousazade et al. 2019). The reported decomposition shows that organic ligand platforms may not be suitable under harsh conditions and may undergo hydrolytic degradation.
3.3. Ligands possessing protic sites to facilitate proton-coupled electron transfer

Ancillary ligands with sites occupied by labile protons can facilitate changes in both the number of protons and the electrons during water oxidation catalysis. This feature allows uncommon mechanistic pathways that resembles to the function of tyrosine residues in photosystem II. Some emblematic examples for different ligand design strategies and some recent findings are discussed below.

The 3,5-bis(4-carboxy-1H-benzimidazol-2-yl)-1H-pyrazole ligand framework was reported to form a mixed valence RuIIIRuIII complex with 4-picolines occupying the remaining sites (Laine et al. 2015b, a) (Fig. 15). This complex could carry out water oxidation catalysis by both chemical and photochemical activation and O2 evolution was observed in high turnover number of circa 800–890 (Table 1). The strongly electron-donating 3,5-bis(4-carboxy-1H-benzimidazol-2-yl)-1H-pyrazole ligand not only decreased the redox potentials and enabled the higher metal oxidation states, but also allowed proton transfer and exhibited a non-innocent character. The proposed mechanism based on the calculated lowest energy isomers is shown in Fig. 15. A similar ligand design was also successful in the case of mononuclear Ru complexes (Kärkäs et al. 2016) (see Table 1 for data). Importantly, the mononuclear complexes exhibited catalytic capabilities similar to that of the diruthenium complex.

A relatively simple ligand, 6,6′-dihydroxy-2,2′-bipyridine with pendant hydroxyls to mimic the function of tyrosine-Z in photosystem II was applied in a Cu-based electrocatalyst (Zhang et al. 2014). As an effect of the hydroxyl groups, the oxidation potential of the Cu center was reduced by

Fig. 15 Structure and proposed water oxidation mechanism for the diruthenium complex formed with 3,5-bis(4-carboxy-1H-benzimidazol-2-yl)-1H-pyrazole and picoline that are abbreviated as H2bim2pz and pic herein, respectively (Laine et al. 2015b, a). This complex could be activated by chemical or photochemical methods. The H2bim2pz ligand enabled the higher metal oxidation states. The proton dissociation from the benzimidazoyl group makes this ligand non-innocent, since the deprotonated form lowers the oxidation potential of the RuIII centers. The nature of the O–O bond formation step involving the RuIVV oxidation state remained unclear. Single-site ruthenium complexes were also designed with different ligand substituents (Kärkäs et al. 2016; Abdel-Magied et al. 2016). Those complexes also followed a similar mechanistic pathway, in which the ligand redox non-innocence was a crucial feature.
circa 200 mV according to a direct comparison made by the same authors, but the turnover frequency of 0.4 s\(^{-1}\) was well below that of circa 100 s\(^{-1}\) for the parent 2,2′-bipyridine complex at pH ~ 12.5 (Barnett et al. 2012) (Table 3). According to density functional theory calculations, two oxidations preceded the water nucleophilic attack step (Fig. 16). The second oxidation concerned the redox-active ligand to yield a radical anion at a calculated potential of + 1.4 V versus normal hydrogen electrode. Spin delocalization and stabilization of the corresponding oxidized state were claimed to lower the onset potential but also to reduce the electrophilic character disfavoring water nucleophilic attack.

Importantly, a partially oxidized complex polymer was found on the electrode surface upon electrolysis that could be re-dissolved in pure electrolyte. Crystallographic studies suggested that the film was built up by a one-dimensional coordination polymer with μ–OH bridges and an H-bonding network. Importantly, in cyclic voltammograms the catalytic peak current showed a curving-over behavior at high complex concentrations that has been associated with the film formation due to the local pH drop. Although such electrochemical features are often associated with catalyst decomposition and concomitant metal oxide film formation, coordination polymers may also generate catalytic films that operate at lower overpotential than the parent complex (Cui et al. 2016; Mishra et al. 2017; Kuwamura et al. 2018). These three studies highlighted that the pH-dependent behavior and redox transformations of molecular catalysts may change their surface affinity thus promote immobilization.

Finally, 6,6′-dihydroxy-2,2′-bipyridine in 2:1 stoichiometry to Cu\(^{2+}\) formed the aqua-coordinated \([6,6′-\text{(O)}_2-(2,2′-\text{bipyridine})_2\text{Cu}^{II}(\text{H}_2\text{O})]^{2−}\) like the homolog 2,2′-bipyridine compounds (Gerlach et al. 2014). Beside the catalytic water oxidation, a competing non-catalytic degradation has been identified. The 4,4′-disubstituted analogs were inactive in water oxidation. Thus, the neighboring O\(^−\) or OH groups indeed facilitate proton-coupled electron transfer and H-bonding interactions to promote water oxidation, in addition to the redox non-innocence of 6,6′-dihydroxy-2,2′-bipyridine (Burks et al. 2018) in line with findings on the corresponding Ir\(^{II}\)-complex (DePasquale et al. 2013).

The tridentate bis(arylimino)isoindoline pincer ligands can bind metal ions in neutral or anionic form owing to exocyclic imine functions that can act as internal proton acceptor site (Csonka et al. 2015; Saha et al. 2021) (Figs. 14 and 17). The rigid isoindolines occupy three co-planar sites around metal centers and often support both stability and reactivity, because variable coordination sites are available for substrate binding and activation.

Recently, Fe\(^{III}\)- and Cu\(^{II}\)-bis(arylimino)isoindoline complexes were reported to catalyze water oxidation (Al-Zuraiji et al. 2020b, 2021; Benkő et al. 2021). The

---

**Table 3** Performance and reaction conditions of molecular electrocatalysts for the water oxidation reaction that contain redox-active ancillary ligands with protic sites to facilitate proton-coupled electron transfer step in the catalytic process

| (Ancillary ligand) | Solution or electrolyte | Overpotential (V) | Turnover frequency (s\(^{-1}\)) | Turnover number | Faraday efficiency | Reference |
|-------------------|-------------------------|-------------------|-------------------------------|-----------------|-------------------|-----------|
| (6,6′-dihydroxy-2,2′-bipyridine)copper(II) | 0.1 M sodium hydroxide, acetate, pH 12.4 | 0.64 | 0.4 | ~400 | 85% | Zhang et al. (2014) |
| (2,2′-bipyridine) copper(II) | 0.1 M sodium hydroxide, acetate, pH 12.5 | 0.75 | 100 | ~30 | 90% | Barnett et al. (2012) |
| [1,3-bis(2′-thiazolylimino)-isoindolinate] iron(III) drop-casted on indium tin oxide | 0.1 M sodium borate, pH 8.3 | 0.86 | 0.014 | 228 | ~94% | Al-Zuraiji et al. (2020b) |
| [1,3-bis(2′-benzthiazolylimino)-isoindolinate] iron(III) electrodeposited on indium tin oxide | 0.1 M sodium borate, pH 8.3 | 0.95 | 0.4 | >5000 | 83% | Al-Zuraiji et al. (2021) |
| [1,3-bis(2′-pyridyl)-iminooisoindolinate] copper(II) drop-casted on fluorine-doped tin oxide | 0.2 M carbonate, pH 10 | 0.97 | ~0.002 | 139 | 69% | Benkő et al. (2021) |

Additional ligands that dissociate from the pre-catalytic form and coordinated substrate molecules are omitted for clarity.
[FeIIICl2(1,3-bis(2′-thiazolylimino)isoindolinate−)] complex (Váradi et al. 2013) was pre-catalyst to efficient water oxidation when immobilized on indium tin oxide electrodes and applied in borate buffer at pH 8.3 (Al-Zuraiji et al. 2020b). Product analysis indicated more than 80% Faraday efficiency and a turnover number of 193 (Table 3). Surface analysis before and after electrolysis and re-dissolution tests suggested that an immobilized molecular catalyst was responsible for catalysis and deactivation occurred by depletion of the metal.

The catalytically active form was claimed to arise by the exchange of chloride ligands to water molecules, while the pincer ligand rendered water-insolubility to the Fe(1,3-bis(2′-thiazolylimino)isoindolinate−) assembly. Electrochemical and spectroscopic investigations in homogeneous water–acetone mixtures indicated a single-site molecular catalysis. Both ligand oxidation and intramolecular hydrogen-atom transfer were suggested to occur, as all three forms in Fig. 17 should be capable of metal binding. The latter conclusion relied on electrochemical detection of an intermediate in re-dissolved and chloride-free samples from drop-casted indium tin oxide that was previously exposed to long-term electrolysis. Interestingly, the ligand exchange occurring in water–organic mixtures could be exploited to develop a material saving electrodeposition method to form chloride-depleted catalyst ad-layers for efficient water oxidation electrocatalysis (Al-Zuraiji et al. 2021). Changing the thiazolyl arms to benzothiazolyl increased the durability of the catalytic films (Table 3), highlighting that the ancillary ligands play a crucial role in the stabilization of surface-adsorbates.

A more insightful, theoretical and experimental study on the possible combined redox-active and proton acceptor role of isoindoline-based pincer ligands was published very recently (Benkó et al. 2021). A pre-catalyst complex, [CuII(1,3-bis(2′-pyridyl)imino-isoindoline)(OClO3)(NCCH3)]+ was immobilized on indium tin oxide to generate O2 electrocatalytically for over 20 h at pH 10 in carbonate buffer, reaching a turnover number of 139 with no signs of CuOx or Cu(OH)2 formation (Table 3). The experimental results in turn indicated that a [CuII(1,3-bis(2′-pyridyl)iminoisoindolinate−)(OH)] complex form dissolved in the aqueous phase might be responsible for catalysis. In order to identify the actual catalyst, [CuII(1,3-bis(2′-pyridyl)iminoisoindolinate−)(OClO3)(OH)2] was isolated and

Fig. 16 Suggested water oxidation mechanism for the CuII-complex containing the redox-active 6,6′-dihydroxy-2,2′-bipyridine ligand (Zhang et al. 2014). The 6,6′-dihydroxyl functions participate in a hydrogen-bonding network involving the two coordinated water molecules as seen on the top of the cycle. A proton-coupled electron transfer facilitates the oxidation to CuIII. The next oxidation step is pH-independent and concerns the ligand. The ligand radical anion is stabilized by π-delocalization. However, the same stabilization reduces the catalytic rate by lowering the electrophilic character of the coordinated OH ligands. The presence of the hydroxyl groups also induces in situ polymerization of the complex on the electrode surface. Degradation was reported pointing out limited stability dependent on catalytic conditions (Gerlach et al. 2014)

Fig. 17 Metal binding by bis(arylimino)isoindoline ligands in the radical, anionic and neutral, protonated forms. Several complexes have been characterized structurally, in which the ligand is anionic. In this case the two imine –C=N− groups exhibit symmetrical bond distance pattern that contributes to the rigid, planar structure and intense π−π* intra-ligand charge transfer absorption bands in the visible spectral region. Only a few complexes were characterized with neutral ligands, where one of the imine groups is protonated. The presence of this proton causes a characteristic change in the bonding pattern and shifts the intra-ligand charge transfer bands in the electronic spectrum. The radical form of the ligand is expected to be reactive and no structurally characterized complex is known. The protonation site and the redox-activity may create a suitable platform to facilitate proton-coupled electron transfer by this ligand family

[FeIIICl2(1,3-bis(2′-thiazolylimino)isoindolinate−)] complex (Váradi et al. 2013) was pre-catalyst to efficient water oxidation when immobilized on indium tin oxide electrodes and applied in borate buffer at pH 8.3 (Al-Zuraiji et al. 2020b). Product analysis indicated more than 80% Faraday efficiency and a turnover number of 193 (Table 3). Surface analysis before and after electrolysis and re-dissolution tests suggested that an immobilized molecular catalyst was responsible for catalysis and deactivation occurred by depletion of the metal.

The catalytically active form was claimed to arise by the exchange of chloride ligands to water molecules, while the pincer ligand rendered water-insolubility to the Fe(1,3-bis(2′-thiazolylimino)isoindolinate−) assembly. Electrochemical and spectroscopic investigations in homogeneous water–acetone mixtures indicated a single-site molecular catalysis. Both ligand oxidation and intramolecular hydrogen-atom transfer were suggested to occur, as all three forms in Fig. 17 should be capable of metal binding. The latter conclusion relied on electrochemical detection of an intermediate in re-dissolved and chloride-free samples from drop-casted indium tin oxide that was previously exposed to long-term electrolysis. Interestingly, the ligand exchange occurring in water–organic mixtures could be exploited to develop a material saving electrodeposition method to form chloride-depleted catalyst ad-layers for efficient water oxidation electrocatalysis (Al-Zuraiji et al. 2021). Changing the thiazolyl arms to benzothiazolyl increased the durability of the catalytic films (Table 3), highlighting that the ancillary ligands play a crucial role in the stabilization of surface-adsorbates.

A more insightful, theoretical and experimental study on the possible combined redox-active and proton acceptor role of isoindoline-based pincer ligands was published very recently (Benkó et al. 2021). A pre-catalyst complex, [CuII(1,3-bis(2′-pyridyl)imino-isoindoline)(OClO3)(NCCH3)]+ was immobilized on indium tin oxide to generate O2 electrocatalytically for over 20 h at pH 10 in carbonate buffer, reaching a turnover number of 139 with no signs of CuOx or Cu(OH)2 formation (Table 3). The experimental results in turn indicated that a [CuII(1,3-bis(2′-pyridyl)iminoisoindolinate−)(OH)] complex form dissolved in the aqueous phase might be responsible for catalysis. In order to identify the actual catalyst, [CuII(1,3-bis(2′-pyridyl)iminoisoindolinate−)(OClO3)(OH)2] was isolated and

Fig. 16 Suggested water oxidation mechanism for the CuII-complex containing the redox-active 6,6′-dihydroxy-2,2′-bipyridine ligand (Zhang et al. 2014). The 6,6′-dihydroxyl functions participate in a hydrogen-bonding network involving the two coordinated water molecules as seen on the top of the cycle. A proton-coupled electron transfer facilitates the oxidation to CuIII. The next oxidation step is pH-independent and concerns the ligand. The ligand radical anion is stabilized by π-delocalization. However, the same stabilization reduces the catalytic rate by lowering the electrophilic character of the coordinated OH ligands. The presence of the hydroxyl groups also induces in situ polymerization of the complex on the electrode surface. Degradation was reported pointing out limited stability dependent on catalytic conditions (Gerlach et al. 2014)

Fig. 17 Metal binding by bis(arylimino)isoindoline ligands in the radical, anionic and neutral, protonated forms. Several complexes have been characterized structurally, in which the ligand is anionic. In this case the two imine –C=N− groups exhibit symmetrical bond distance pattern that contributes to the rigid, planar structure and intense π−π* intra-ligand charge transfer absorption bands in the visible spectral region. Only a few complexes were characterized with neutral ligands, where one of the imine groups is protonated. The presence of this proton causes a characteristic change in the bonding pattern and shifts the intra-ligand charge transfer bands in the electronic spectrum. The radical form of the ligand is expected to be reactive and no structurally characterized complex is known. The protonation site and the redox-activity may create a suitable platform to facilitate proton-coupled electron transfer by this ligand family

[FeIIICl2(1,3-bis(2′-thiazolylimino)isoindolinate−)] complex (Váradi et al. 2013) was pre-catalyst to efficient water oxidation when immobilized on indium tin oxide electrodes and applied in borate buffer at pH 8.3 (Al-Zuraiji et al. 2020b). Product analysis indicated more than 80% Faraday efficiency and a turnover number of 193 (Table 3). Surface analysis before and after electrolysis and re-dissolution tests suggested that an immobilized molecular catalyst was responsible for catalysis and deactivation occurred by depletion of the metal.
Structurally characterized in the solid state. Spectroscopy and density functional theory calculations were conducted to reveal a distorted equatorial coordination plane with three nitrogen atoms and one oxygen atom around copper in solution in close resemblance to that suggested by others for a similar redox-active ligand containing system (Gil-Sepulcre et al. 2021). Each catalytic intermediate was tested with different spin multiplicities and the most stable states were identified. The proposed mechanism is shown in Fig. 18. In acetonitrile–water solutions, experimental findings supported by theoretical calculations suggested that the 1,3-bis(2′-pyridyl)-iminoisouindoline\(^-\) ligand was oxidized while the Cu\(^{II}\) center remained redox-silent in the proposed catalytic cycle.

According to the suggested mechanism, the first proton-coupled electron transfer step would oxidize the isoindolate ligand to produce [Cu\(^{II}\)(1,3-bis(2′-pyridyl)iminoisoxindole\(^-\))(OH)]\(^+\) that is followed by a second oxidation to generate the oxyl radical, instead of Cu\(^{III}\). The separation of the two oxidized sites explained the appearance of the second event only after adding H\(_2\)O. The redox silence of Cu\(^{II}\) could be attributed to the spatial configuration of the complex, since the steric hindrance made difficult the formation of a square planar field around copper and stabilize the d\(^8\) Cu\(^{III}\) configuration. The oxyl radical was found capable of single electron transfer water nucleophilic attack resulting in [Cu\(^{II}\)(1,3-bis(2′-pyridyl)iminoisouindoline)(OOH)]\(^+\). In this step, the electron from the attacking water molecule reduces the oxidized ligand and the ancillary ligand could then act as internal proton acceptor before an external base caught the released proton and restored again the anionic ligand form.

The spatial aspect of this proton capture was also considered. Since the N–H(Cu–OOH) distance was 4.82 Å in the [Cu\(^{II}\)(1,3-bis(2′-pyridyl)iminoisouindoline\(^-\))(HOOH)]\(^+\) intermediate, the assistance of a carrier is necessitated to transport a proton to the ligand N, asynchronous

![Fig. 18 Proposed catalytic cycle of electrocatalytic water oxidation starting from [Cu\(^{II}\)(1,3-bis(2′-pyridyl)iminoisouindoline\(^-\))(OH\(_2\))]\(^+\) in acetonitrile–water mixture (Benkő et al. 2021). The cycle proceeds counterclockwise through proton-coupled electron transfer steps. The first oxidation generates a ligand radical stabilized by spin-delocalization over the central NCNCN structural motif. According to density functional theory calculations the next step generates a Cu\(^{II}\)-oxy species that can undergo water nucleophilic attack. Hydrogen atom transfer to the ligand radical generates the neutral form 1,3-bis(2′-pyridyl) iminoisouindoline along with the O–O bond formation. Following this step, the cycle proceeds through rapid oxidations and closed by O\(_2\) evolution. Crossing between the quartet and doublet spin states plays an important role in the O–O bond formation that is a similar feature to the S\(^{A}\), S\(^{B}\) spin multiplicity change in the oxygen-evolving complex of photosystem II](attachment://image.png)
1 3
way with the formation of the O–O bond. Note that the [Cu\text{II}(1,3-bis(2′-pyridyl)iminoisindolyl•)(O•)]^+ form contains three unpaired electrons, one at the ancillary ligand, one at the d^9 Cu\text{II} center and one at the oxyl ligand giving rise to different available spin multiplicities. Importantly, the calculated energy diagram of the system during the O–O bond formation clearly displayed crossing between the quartet and doublet states with the O–O distance near 2.0 Å. Note that spin multiplicity changes in the S state cycle of the natural oxygen-evolving complex of photosystem II is crucial to regulate the relative rates in the reaction sequence. Therefore, the utilization of redox-active ancillary ligands bearing labile protons may have prominent role in the advancement of future molecular catalysts for water oxidation.

3.4. Ligands participating in the oxygen–oxygen bond formation step

So far, the participation of ligands in the key O–O bond formation step has been limited to those oxanions, which may in principle form peroxo-metallocycles with transition metals. These ligands are carbonate and borate, both having rich literature on reactivity as perhydrate and persalt, respectively (Pizer and Tihal 1987; Tsoler 1999; Durrant et al. 2011; Deary et al. 2013; Liu et al. 2021). The presence of carbonate or borate anions by a catalyst in a sufficiently high concentration is naturally expected only in electrolytes; thus, this section will include electrocatalytic examples.

In a catalytic cycle producing O_2 from two H_2O molecules, involving a single-site catalyst and inner-sphere coordination of oxanions, one can imagine two general pathways. In Fig. 19, the cycle on the top starts from the aquo-metal assembly highlighted with a frame in the middle of the figure. This aquo-metal complex is oxidized and lose an electron and a proton, while the assisting L_A ligand seen in blue remains coordinated through an oxygen donor. The next oxidation step concerns L_A, in which a reactive oxyl radical is formed that in turn attacks the hydroxyl function, resulting in a peroxo-metallocycle and eventually O_2 evolution.

The second option is the generation of higher metal oxidation state with oxyl radical M^{ox−}O* as shown in the cycle at the bottom of Fig. 19. In this case, the oxyl radical attacks a hydroxyl of L_A forming peroxo intermediates. Stabilization of the M^{ox−} state generally requires suitable ancillary ligands (L in green, Fig. 19). The ancillary ligand can be also an oxanion, as carbonate is known to stabilize higher oxidation states of metal ions in solution. The following examples may fit with one of the two general scenarios; however, as will be seen, there are ongoing debates about the dominant mechanisms.

![Fig. 19 Two possible mechanistic routes leading to O_2 formation.](image)

3.4.1. Participation of carbonate in the oxygen–oxygen bond formation

An early report on copper based, electrocatalytic water oxidation introduced an astonishingly simple solution equilibrium system. Different copper salts were added to a NaHCO_3
buffer at pH 8.2 or at pH 6.7 saturated with CO₂. When high anodic potentials were applied to an inert indium tin oxide, fluorine-doped tin oxide or glassy carbon working electrode immersed into the solutions the electrocatalytic process yielded O₂ with high charge efficiency (Chen and Meyer 2013). Complex formation between the metal and bicarbonate–carbonate in high excess was clear from the characteristic shifts of the d-d transitions in the electronic spectra.

Later, density functional theory calculations indicated that carbonate is a non-innocent, reactive ligand forming a peroxocarbonate metallo-cycle (Winikoff and Cramer 2014). This mechanism would be compatible with the cycle on the top of Fig. 19. The peroxocarbonate is then oxidized rapidly to yield O₂ and CO₂. The high reactivity was explained by means of a low energy singlet–triplet splitting in the 3e⁻ oxidation of CuII to CuIII upon which no carbonate anions are required to stabilize the NiIII oxidation state (Ariela et al. 2017). Consequently, the concomitant oxidation of [NiII(1,4,8,11-tetraazacyclotetradecane)(CO₃)₂]⁻ to a catalytically active NiIV species is either preceded by a slow exothermic carbonate-to-H₂O ligand exchange to provide [NiIV(1,4,8,11-tetraazacyclotetradecane)(CO₃)(OH)]⁺, or a bond breaking produces [NiIV(1,4,8,11-tetraazacyclotetradecane)(CO₃)₂(O)]⁻ + CO₂ from [NiIV(1,4,8,11-tetraazacyclotetradecane)(CO₃)₂]⁻. In the upcoming steps, the [NiIV(1,4,8,11-tetraazacyclotetradecane)(CO₃)₂(O)]⁻ + [NiIV(1,4,8,11-tetraazacyclotetradecane)(CO₃)₂(OH)] coupling would produce a NiIII–O–O–NiIII species that in turn would release H₂O₂ (Table 4).

Alternative proposals argued in favor of reaction steps leading to short circuiting the catalytic cycle at the stage of peroxide formation that corresponds to a 2e⁻ + 2e⁻ mechanism. According to a combined experimental and theoretical study, O₂COO–CO₂²⁻ is produced from two CuIII-carbonate complex units (Mizrahi et al. 2018). This means the electrochemical oxidation of CuII to CuIII upon which no CO₃⁻ radical anion should occur. Instead, the hydrolysis of C₂O₆²⁻ that is O₂COO–CO₂²⁻ gives H₂O₂ that reacts with the CuIII complexes producing O₂. However, below pH 8.2 the electrocatalytic reaction was found to be first order in copper. This is not in line with the above conclusions that are rather compatible with a second order in copper. Note, on the other hand that second order kinetics in copper has been found in concentrated CO₂²⁻ or HPO₄²⁻ and PO₄³⁻ buffers at pH 10.8 on the analogy to the known copper peroxide chemistry (Lewis and Tolman 2004; Elwell et al. 2017), but the rate-limiting step was the formation of a CuO–OCu intermediate.

There are gathering arguments on the viability of similar mechanistic pathways for other first row transition metals like cobalt and nickel (Mizrahi and Meyerstein 2019; Patra et al. 2020a, b). In the case of planar NiIV(1,4,8,11-tetraazacyclotetradecane) complexes with an aliphatic 4N donor environment two axially coordinated carbonate anions are required to stabilize the NiIII oxidation state (Ariela et al. 2017). Consequently, the concomitant oxidation of [NiIII(1,4,8,11-tetraazacyclotetradecane)(CO₃)₂]⁻ to a catalytically active NiIV species is either preceded by a slow exothermic carbonate-to-H₂O ligand exchange to provide [NiIV(1,4,8,11-tetraazacyclotetradecane)(CO₃)(OH)]⁺, or a bond breaking produces [NiIV(1,4,8,11-tetraazacyclotetradecane)(CO₃)₂(O)]⁻ + CO₂ from [NiIV(1,4,8,11-tetraazacyclotetradecane)(CO₃)₂]⁻. In the upcoming steps, the [NiIV(1,4,8,11-tetraazacyclotetradecane)(CO₃)₂(O)]⁻ + [NiIV(1,4,8,11-tetraazacyclotetradecane)(CO₃)₂(OH)] coupling would produce a NiIII–O–O–NiIII species that in turn would release H₂O₂ (Table 4).

If [NiIV(1,4,8,11-tetraazacyclotetradecane)(CO₃)₂(O)]⁻ reacts with an external HCO₃⁻, then O₂COO–CO₂²⁻ or HCO₃⁻ is produced, which leads again to H₂O₂ release. All mechanistic scenarios producing peroxide may be conceived as a short circuiting of the 4e⁻ process due to a disfavored metal promotion of cyclization as shown by the reaction steps with grey background in Fig. 19. The rest of the oxidation steps take place away from the inner sphere of the original complex.

Whichever is the case, the results underline that carbonate ions are not only ligands that stabilize NiIII, but also active,

### Table 4: Performance of molecular water oxidation electrocatalysts binding buffer anions that participate in the O–O bond formation step and the required experimental conditions

| Catalyst | Solution or electrolyte | Overpotential or onset potential (V) | Turnover frequency (s⁻¹) | Turnover number | Faraday efficiency | Reference |
|----------|-------------------------|-------------------------------------|--------------------------|-----------------|---------------------|-----------|
| Cu²⁺ in sodium carbonate buffer | 1.0 M sodium carbonate, bicarbonate, pH 10.8 | ~0.7 | n.d | ~16 | 97% | Chen and Meyer (2013) |
| (1,4,8,11-tetraazacyclotetradecane)nickel(II) | 0.2 M sodium bicarbonate, pH 7.0 | ~0.68 | n.d | n.d | n.d | Ariela et al. (2017) |
| CuSO₄ in borate-containing buffer | 0.45 M sodium borate and 1.0 M Na₂SO₄, pH 7.0 | 0.75 | ~2.8×10⁻³ | ~3 | ~100% | Huang et al. (2017) |
| Cu-peptidomimetic complex | 0.2 M sodium borate, pH 9.35 | ~0.6 | 129 | ~52 | 95% | Ruan et al. (2021) |

Additional ligands that dissociate from the pre-catalytic form and coordinated substrate molecules are omitted for clarity, n.d. means not determined.
non-innocent participants in the redox process. Note that the occurrence of a \(\eta^2\)-peroxo-monocarbonate metallo-cycle has been considered for manganese in catalytic epoxidation (Lane et al. 2002) and importantly, the X-ray structure of an L\(_3\)Fe\(^{III}\)-peroxomonocarbonate complex (Hashimoto et al. 2002) illustrated that such entities should not be eliminated from mechanistic speculations. The redox non-innocent scenarios for carbonate are especially fascinating since L-M compounds involved in water oxidation are known to bind carbonate (Chen et al. 2017; Benkó et al. 2021), and efficient material systems are also known with this anion (Ji et al. 2018).

### 3.4.2. Participation of borate in the oxygen–oxygen bond formation

With respect to borate only a few examples are known to date, in which this anion was suggested to participate in the O–O bond formation step, including an electrocatalytic system under neutral conditions using copper (Huang et al. 2017). The in situ formation of a stable Cu-borate catalytic film has been described earlier with a catalytic performance comparable to that of Ni-borate, but somewhat lower than that of Co-borate (Yu et al. 2015). In the study by Huang et al., the addition of borate to a 1 M solution of sulfate resulted in a soluble complex and UV–visible spectrophotometric evidence confirmed a ternary sulfate-Cu-borate catalyst species, in which sulfate acted as ancillary ligand. Electrocatalytic oxygen evolution at pH 7 was stable and no catalytically active deposit could be detected on the surface of the working electrode after several hours of electrolysis. The observed first-order dependences in both borate and copper suggested single-site catalysis relying on proton-coupled electron transfer steps.

The lack of a protium over deuterium kinetic isotope effect ruled out the participation of the inner sphere tetrahydroxyborate ligand in the rate-limiting step as a proton acceptor. Instead, the enhanced rate of electrocatalysis (Table 4) was associated with the participation of tetrahydroxyborate in the rate-limiting O–O bond formation step as oxygen donor, on the grounds of density functional theory calculations. This mechanism may be conceived as that shown in Fig. 19 (cycle on the bottom). In the key step, the 2e\(^-\) oxidized form, Cu\(^{III}\)-O\(^*\) attacks a hydroxyl group on the coordinated (HO\(_3\)BO\(^-\)) ligand providing an energetically favorable pathway for the O–O bond formation.

In the presence of different N-donor ligands, for example 2,2’-bipyridine, various tripeptides and a dinucleating peptidomimetic ligand, borate was also reported to coordinate to copper (Huang et al. 2017; Lukács et al. 2019; Ruan et al. 2021). However, the outcome of the electrochemical oxidation seems to depend strongly on the ancillary ligand. In the case of mononucleating tripeptides the formation of [LCu\(^{III}\)OOB(OH)\(_3\)]\(^2+\) has been proposed upon electrochemical oxidation, leading to complex degradation and in situ CuO deposition (Lukács et al. 2019). As for the di-copper complex formed with the peptidomimetic ligand results implied that borate coordination occurred upon Cu\(^{II}\)→Cu\(^{III}\) oxidation (Ruan et al. 2021). In the rate-limiting step the Cu\(^{III}\)-O\(^*\) attacks the neighboring (HO)\(_3\)Br(O)Cu\(^{III}\) tethered by the peptidomimetic ligand (for data see Table 4). In essence, considering the rate-limiting chemical step this mechanism corresponds to that shown in the bottom cycle of Fig. 19 noting that the order of the proton and electron transfers may be shuffled.

Nickel complexes have been scarcely studied in the presence of borate to our knowledge, and even in those cases the complex was unstable under catalytic conditions, and thus, the role of borate has not been discussed (Aligholivand et al. 2019). Recent studies conducted under alkaline conditions eventually concluded that nickel complexes undergo degradation and NiOx is formed under catalytic conditions no matter of what buffer was chosen (Feizi et al. 2018; Garrido-Barros et al. 2019). If one regards this general tendency of the nickel complexes, a similar mechanism to that in Fig. 19 is rather unlikely with this metal. On the other hand, one might wonder about the role of borate anions in water oxidation catalysis by nickel oxide surfaces.

The growth of nickel oxide films from borate electrolyte have been known for long (MacDougall and Graham 1981) and their utilization as efficient heterogeneous water oxidation catalyst was an important milestone in this field (Dinca et al. 2010). The role of borate has been studied in particular (Bediako et al. 2013). Bediako’s and Dinca’s studies elucidated that in borate-buffered electrolyte borate anions occupy the active surface sites and prior to commence the catalytic cycle their reversible dissociation from the domain edge of NiO\(_x\) octahedron is required.

A later study spectroscopically confirmed that an increase in the number of NiO\(_x\) domains is necessary to achieve an efficient water oxidation catalyst (Yoshida et al. 2015). Lately, a Ni\(_3\)(BO\(_3\))\(_2\)-Ni\(_3\)S\(_2\) amorphous-crystalline heterostructure has been identified as an efficient bifunctional catalyst for both the hydrogen and the oxygen evolution reactions (Sun et al. 2020). Although the authors constructed schematic models of –OH, –O, and –OOH surface-bound intermediates on varied sites of Ni\(_3\)(BO\(_3\))\(_2\), Ni\(_3\)S\(_2\), and Ni\(_3\)(BO\(_3\))\(_2\)-Ni\(_3\)S\(_2\) in order to calculate the free energy for each elementary step, the possible role of a peroxoborate intermediate was not discussed explicitly.

With respect to other first row transition metals, a few cobalt (Shagaghi et al. 2021) and iron (Al-Zuraiji et al. 2020a, b, 2021) complexes have been studied in borate electrolyte. Moreover, Mn\(_2\)OBO\(_3\) (manganese-oxoborate) was an efficient surface catalyst under neutral conditions (Elmaci et al. 2021). However, the possible role of borate in
the O–O bond formation step has not been fully elucidated. The above examples illustrate that due to a similar, supportive function in the O–O bond formation step the use of carbonate or borate could be beneficial in advanced electro-, photoelectro- or photocatalytic water splitting and integrated CO₂ reduction systems (Fu et al. 2019, 2020a, b; Liu et al. 2019a; An et al. 2019; Cao et al. 2020, 2021; Hamza et al. 2020; Feng et al. 2020; Chen et al. 2020; Li et al. 2020) to further improve efficiency.

3.5. Ligand redox transformations leading to surface catalysts

3.5.1. General degradation pathways of molecular catalysts and related analysis methods

Potential molecular catalysts of the oxygen evolution reaction can undergo degradation in rather general ways that are shown in Fig. 20. First row transition metal complexes can be especially prone to spontaneous hydrolytic degradation, or sensitive to the acidification of the solution that occurs at the anode upon catalytic oxygen evolution. In such cases, the hydrolytic dissociation of the complex does not require redox events, and in principle, the produced aqua or hydroxide complexes can serve as precursors to metal oxide or hydroxide surface catalysts (Fig. 20). However, this scenario is normally unwanted, since the solubility of metal oxides and hydroxides is limited and the bulk precipitation of the metal content makes this approach inefficient and less controllable. Therefore, spontaneous hydrolytic degradation should be avoided by proper ligand design. Other complexes act as precursors to catalytic films only when the oxidation state of either the metal center or the ligand is changed (Fig. 20). The use of redox-active precursors results in a much more controlled strategy for surface catalyst fabrication because the redox event produces the precursor species right at the target electrode surface.

Under catalytic conditions, degradative side-reactions may affect any of the oxidized molecular catalysts to some extent that has been subject of several studies using advanced in situ techniques to reveal the true nature of water oxidation catalysis (Li et al. 2017). The technical advancements gave impetus to a gradual shift from the concept of traditional homogeneous and heterogeneous classification of catalysts to an evolutionary concept of dynamic catalyst transformations (Eremin and Ananikov 2017), ranging from molecules over nanoparticles and leaching-derived catalysts to complex catalyst mixtures.

A recent manuscript underlined that the combination of some main critical tests is crucial to elucidate the molecular nature of an electrocatalyst by the example of a known pentanuclear iron complex (Okamura et al. 2016). Rigorous analysis of several catalytic cycles in voltammetry and in parallel, X-ray absorption spectroscopy of the initial complex in frozen acetonitrile and that of the glassy carbon electrode surface used in voltammetry clearly demonstrated the in situ formation of iron oxides from the complex (Pelosin et al. 2020). Obviously, tracking such possible conversions of metal complexes to the corresponding oxides is of major concern from the perspective of drawing structure–activity relationships with respect to the molecular catalyst. However, the ex situ and in situ methods can be just as useful from the perspective of efficient precursor design; therefore, we listed typical techniques along with the experimental considerations and expected results in Table 5. Laboratory-scale application of classical spectroscopic, electroanalytical and separation-based analytical methods can be very helpful for basic distinctions between molecular and heterogeneous water oxidation processes. Further, direct tracking of the reaction mechanisms and intermediate species requires advanced in situ techniques that are pronouncedly resource
intensive and only possible with the involvement of special areas of expertise. Finally, the ex situ analysis of the electrode surface is a classical approach that remains invaluable to provide a more complete understanding of a catalytic system.

3.5.2. Possible ways of ligand-based redox transformations leading to surface catalysts

Herein, we would like to show a few examples on redox transformation of the ancillary ligand that can lead to an active surface catalyst in order to point out further perspectives. Importantly, the utilization of metal–ligand assemblies may be justified by special requirements, such as solubility limit of the precursor, narrow redox stability of the substrate material, need for size-control of the deposited catalyst material or surface morphology preserving method.

Electrocatalytic CoOx films that can be directly deposited from a number of cobalt complexes in situ are revealing examples. The organic ancillary ligands include oximes (Han et al. 2013), salen derivatives (Chen et al. 2015) and porphyrins (Daniel et al. 2017). The precise structure of the coordinating salen ligand had an especially strong influence on the catalytic performance of the resulted film. This established a strong link between molecular catalyst construction and precursor design for heterogeneous catalysts. Note that the oxide films produced from the above Co-complexes showed superior performance over those resulted from simple cobalt salts that clearly underlines the advantage of using organic ancillary ligands (Table 6). The above studies did not discuss the possible role of ligand oxidation in the catalytic film formation; however, oximates, salen and porphyrin ligands are all capable of chemical redox state changes in complexes (Wang and Groves 2013; Fu et al. 2014; Dinda et al. 2022). Therefore, the option of utilizing redox-active ligands in precursors should not be ruled out and worthy of further investigations.

Ligand degradation through redox transformation is obvious, if the identification of any resulting by-product is possible (Lu et al. 2016), but in most of the cases the initiating event cannot be revealed perfectly, because only a minute part of the molecular catalyst undergoes degradation and acts as precursor. Copper-diglycylglycine, which is a copper-tripeptide complex known since 1955 (Dobbie and Kermack 1955) is a good example. In fact, this water-soluble and stable complex can be precursor to a heterogeneous oxide catalyst, possibly due to anodic current density limited by a chemically destabilizing density of surface CuIII-oxyl functions. The dynamics of the deposition and re-dissolution processes, the dependences on pH, buffer anion and type of the electrode all highlight the immensely prospective application of molecular precursors involving redox-active components in catalyst film fabrication.

Another example involves nickel complexes with substituted 1,2-phenylenebis(oxalamidate) (PBOA) ligands that were investigated as molecular water oxidation catalysts at basic pH (Fig. 7, R1=R2=H, R1=R2=CH3 and R1=H, R2=OCH3) (Lin et al. 2017; Garrido-Barros et al. 2019). Electrochemical studies revealed that the first oxidation wave corresponded to the NiII/NiIII redox couple. At pH 10–13 a second oxidation wave was observed due to the generation of a phenyl radical cation associated with the coordination of a hydroxide anion to form [NiIII(PBOA)(OH)]−, which was responsible for the O–O bond formation and O2 release. The dimethyl and methoxy substituted 1,2-phenylenebis(oxalamidate) complexes also exhibited two oxidation processes. The electronic perturbation by the more electron-donating ligands resulted in a decreasing overpotential for water oxidation, 0.5 V for the parent 1,2-phenylenebis(oxalamidate) complex, 0.17 V and 0.22 V for the substituted ones, respectively.

At pH 12 and suitable absolute concentration copper-diglycylglycine exhibited a purely homogeneous water oxidation catalysis, but at lower pH, heterogeneous features appeared. Post-catalytic surface analysis revealed that a black amorphous Cu2O, CuO and Cu(OH)2 deposit was responsible for a smaller overpotential and efficient O2-evolution (Table 6). The produced spherical surface nanoparticles as well as their in situ generation from bio-degradable complexes are known in the literature, but the surface instability to overpolarization has remained unmentioned.

Operando spectroelectrochemical investigations revealed that anodic overpolarization on indium tin oxide may induce excessive oxidation of the nanoparticles ending up in the total destruction of the nanostructure and re-dissolution of the copper-oxide catalyst, possibly due to anodic current density limited by a chemically destabilizing density of surface CuIII-oxyl functions. The dynamics of the deposition and re-dissolution processes, the dependences on pH, buffer anion and type of the electrode all highlight the immensely prospective application of molecular precursors involving redox-active components in catalyst film fabrication.

While the oxalamidate complexes were stable in basic aqueous solutions from pH 10 to 13, below this pH the protonation of the amide group caused metal ion release (Garrido-Barros et al. 2019). The 1e− oxidized [NiIII(PBOA)]− complex was fully stable within pH 10−12 on the electrochemical time scale, but at pH 13 the complex underwent progressive substitution in four steps leading to [NiIII(OH)2]−. The doubly oxidized phenyl radical cation [NiIII(PBOA)(OH)]− also suffered from hydroxide substitution processes. Additional degradation occurred through the hydroxylation of the aromatic ring with the OH− present in the medium that in turn was competing with the O–O bond formation.
| Method                        | Type        | Scope and experimental considerations                                                                                                                                                                                                 | Expected result                                                                                                                                                                                                 | Reference                                      |
|-------------------------------|-------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------|
| Cyclic voltammetry            | In situ     | Repeated cycles over the catalytic potential range, high scan rates allow the detection of intermediates, or in situ formed equilibrium species, concentration dependences are informative of molecular versus heterogeneous processes, often combined with a rinse, or re-dissolution test and post-catalytic surface analysis | Changes in redox features of the putative catalyst and the catalytic current indicate conversion between homogeneous, heterogeneous or a dynamic mechanism, indication of film formation                                        | Garrido-Barros et al. (2019), Pelosin et al. (2020) |
| Working electrode rinse test   | Ex situ     | The working electrode is rinsed after voltammetry, then tested in pure electrolyte under identical conditions, insoluble adsorbate films can be detected, passive films are detected through an insulating effect | Identification and electrochemical characterization of surface films, quantification of the catalytic effect                                                                                                           | Lukács et al. (2019)                          |
| Re-dissolution test from the working electrode | Ex situ     | Immobilized or in situ formed films of molecular catalysts are dissolved from the electrode by a suitable solvent, electrochemical and spectroscopic characterization of the re-dissolved sample | Elucidation of the molecular nature of catalyst, substantial differences from the initial properties can be detected                                                                                       | Al-Zuraiji et al. (2020a, b)                 |
| Molecular spectroscopy (UV–visible, Raman, infrared, electron paramagnetic and nuclear magnetic resonance) | Ex situ     | The molecular catalyst is analyzed before and after catalysis tests in solution, direct comparison between the initial and the used form of the molecular catalyst is possible | Differences in the molecular and electronic structure can be defined, quantification of the remnant catalyst over decomposed proportion                                                                        | Sinha et al. (2018), Al-Zuraiji et al. (2020a, b) |
| Mass spectrometry             | Ex situ     | Post-catalytic characterization of molecular catalysts, excess components such as salts, photosensitizers or chemical oxidants complicate analysis, extraction of the catalyst is often needed | Elemental composition of the catalyst residues or complexes in solution                                                                                                                                                             | Asraf et al. (2016)                          |
| On-line mass spectrometry     | In situ     | Mass spectrometry is applied in parallel with electrochemistry, electrolysis, or voltammetry is performed in the catalytic regime                                                                                                       | Real-time detection of the O₂ product in the cell, suitable for CO₂ detection from ligand degradation, ascertains the onset potential of O₂ production                                                              | Kottrup and Hetterscheid (2016), D’Agostini et al. (2021) |
| Dynamic light scattering      | In situ, ex situ | Scattering of monochromatic, polarized light shot through the solution of the catalyst is analyzed, sensitive to nanoparticles present, persistent initial precipitates cause false positive result, suitable for detecting large amounts of nanoparticles, can be combined with post-catalytic filtration and recycling of the solution | Detection and size distribution analysis of nanoparticles from the decomposition of a molecular catalyst                                                                                                           | Li et al. (2017)                              |
| Method                          | Type                        | Scope and experimental considerations                                                                                                                                                                                                                                                                                                                                                           | Expected result                                                                                                                                                                                                                     | Reference                  |
|--------------------------------|-----------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------|
| Spectroelectrochemistry        | In situ                     | Different valence states can be characterized, variation in the solution composition and lower temperatures may help characterizing the electrochemically generated forms, some electrode types allow near-surface analysis                                                                                                                                                                                                                       | Spectroscopic distinction of the different valence states involved in catalysis, intermediates can be detected and related to film formation                                                                                       | Lukács et al. (2019)        |
| X-ray absorption spectroscopy  | In situ                     | Suited to immobilized, or dissolved molecular catalysts, the near edge region is sensitive to valence state and coordination geometry of the absorbing element, the extended fine structure region provides information on the number of neighboring atoms, distances and disorders, unsuitable for a surface atomic layer analysis                                                                                             | Fundamental structural information on the molecular catalyst and the intermediate states, elucidates the structural integrity of the molecules                                                                                   | Cui et al. (2016)           |
| Electrochemical optical waveguide light-mode spectroscopy | In situ                     | Limited to transparent working electrodes, allows the time-resolved tracking of molecular sorption–desorption processes upon electrochemistry, detects the dry mass of surface adsorbed compounds at ng/cm² sensitivity, but sensitive to gas evolution                                                                                                                       | Real-time monitoring of surface mass changes upon electrochemical processes allows quantitative insight into the dynamics of immobilized compounds                                                                       | Farkas et al. (2016)        |
| Spectroscopic ellipsometry     | In situ                     | Vacuum-free, non-destructive optical method to analyze the thickness and porosity of surface films on electrodes, electrical resistivity, electron concentration and mobility, and inter- and intraband transition energy data are available by modeling of the optical spectra                                                                                                                 | In situ optical investigations under catalytic conditions reveal structure–activity correlation for catalyst films, or the adsorption–desorption of molecular catalysts                                                           | Sachse et al. (2020)        |
| Electrochemical quartz crystal microbalance | In situ                     | The electrode is a gold-coated quartz crystal oscillator, mass change at the surface is detected by measuring the resonance frequency change of the quartz crystal, sensitive to mechanical impacts and bubble-formation, oxidation of the surface to gold oxide must be considered                                                                                                    | Decreasing frequency upon voltammetry test tells about the formation of surface adsorbate and its relation to the observed current                                                                         | D’Agostini et al. (2021)    |
| X-ray photoelectron spectroscopy | In situ, ex situ            | Ex situ this technique requires ultra-high vacuum, ambient pressure allows *operando* study of solid–liquid interface, the information depth is the top few nanometers, insulating and porous surfaces may cause complications, ion gun allows depth analysis of layered films                                                                                                         | Ex situ comparison of neat and used catalytic films with respect to chemical state and semiquantitative ratio of each element, elucidates the presence and chemical state of *operando* formed films, or immobilized catalysts | Li et al. (2017)            |
Based on stability measurements as a function of pH, the authors concluded two possible pathways competing with the homogeneous catalytic process: first, the formation of the hydroxylated aromatic species with no water oxidation activity and second the formation of a catalytically active NiOx, that is a nickel oxide film of general formula Ni\textsubscript{3}O\textsubscript{2}H\textsubscript{6}, attached to the surface of the electrode with higher overpotential for water oxidation than the molecular catalyst (Table 6). The dominant process was pH dependent, raising the pH from 10 to 12 promoted NiOx formation. At pH 13, the amount of the initially active NiOx decreased, indicating that the material dissolved during a further, slower process. The impact of the applied potential also proved that slight modifications in the experimental conditions might influence the stability and the catalytically active form of nickel complexes. Importantly, the parent complex could be used effectively as a molecular precursor for the formation of NiFeOx, that is nickel and iron oxides of general formula Ni\textsubscript{x}Fe\textsubscript{1-x}O\textsubscript{y}H\textsubscript{z} that behave as extremely powerful water oxidation anodes (Table 6).

During controlled potential electrolysis at +1.05 V versus the normal hydrogen electrode, at pH 11 no NiOx could be detected, instead oxygen evolved at 94% Faraday efficiency with turnover number of 3.81. Similar experiments with the dimethylated 1,2-phenylenebis(oxalamidate) complex showed a higher stability and lack of NiOx emphasizing the opportunities in fine-tuning the redox properties of the ligand in order to control metal oxide film formation.

The pH-dependent operando formation of nickel oxide from a [N,N’-bis(salicylidene)ethylenediamino]nickel(II) complex was also investigated (Feizi et al. 2018). Here, the applied ligand is often found to play an active role in redox catalysis. However, the complex suffered degradation and a surface deposit containing Ni, P and O in a carbon matrix was formed. The complicated structure of the matrix clearly showed activity that was different from a simple nickel oxide highlighting the unique role of the ligand (Table 6).

No doubt, tunable and well-understood metal oxide formation originated from molecular catalysis should be considered as a practical option, when size- or morphology control of the deposit is important, when a metal oxide component has to be introduced into a system under controlled conditions, or the regeneration of a surface catalyst is required without dismantling the cell. Redox-active ligands should not be omitted from the line of options in such cases.

4. Conclusion

Molecular complexes are often regarded as the chemists’ warm little pond to allow insight into unexplored details of water oxidation and thus into artificial photosynthesis. Indeed, molecular compounds are intrinsically sensitive
Table 6  Examples of molecular precursors with suspected or proven redox-active ligand types that undergo in situ degradation to produce a surface catalyst film

| Compound                  | Electrolyte and applied potential for deposition | Electrode substrate | Catalyst film                          | Catalytic performance of the produced film                                                                 | Faraday efficiency | Reference                      |
|---------------------------|--------------------------------------------------|---------------------|---------------------------------------|------------------------------------------------------------------------------------------------------------|--------------------|---------------------------------|
| Cobaloximes               | 0.1 M sodium borate, pH 9.2, at 1.1 or 1.5 V versus Ag/AgCl | Fluorine-doped tin oxide | Pale yellow, nanostruct. CoOx          | 2.0–5.5 mA/cm² at 1.0 V, 1.5–2.6 mA/cm² at 0.6 V of overpotential, dependent on ligand, min. Tafel slope ~ 66 mV/dec | > 80%              | Han et al. (2013)               |
| Co²⁺                     | 0.1 M sodium borate, pH 9.2, at 1.1 V versus Ag/AgCl | Fluorine-doped tin oxide | Black Co-borate film                  | 0.88 mA/cm² at 0.6 V of overpotential                                                                   | n.d                | Han et al. (2013)               |
| cobalt-salen complexes    | 0.1 M potassium borate, pH 9.2                    | Fluorine-doped tin oxide | Nanostruct. CoOₓ                       | 2.4 mA/cm² at 0.72 V of overpotential, dependent on ligand, min. Tafel slope ~ 62 mV/dec                | > 93%              | Chen et al. (2015)              |
| Cobalt porphyrins         | 0.1 M sodium borate, pH 9.2                       | Fluorine-doped tin oxide, spin-coated with complex | Ultrathin CoOₓ                         | Turnover frequency 20 s⁻¹ at 0.6 V of overpotential                                                    | ~100%              | Daniel et al. (2017)            |
| (Diglycylglycine)-copper(II) | 0.1 M sodium borate, pH 9.2, at 1.05 V versus Ag/AgCl | Indium tin oxide, hematite and Cu(OH)₂ | Nanostruct. CuOₓ                       | 1.0 mA/cm² at 0.61 V of overpotential, min. Tafel slope ~ 90 mV/dec                                    | > 90%              | Lukács et al. (2019)            |
| [1,2-phenylenebis-(oxalamidate)]-nickel(II) | 0.1 M sodium phosphate, pH 13, at 0.85 V versus normal hydrogen electrode | Glassy carbon plates | Low loading NiOₓ                       | ~ 10 mA/cm² at ~0.45 V of overpotential                                                               | ~100%              | Garrido-Barros et al. (2019)    |
| [1,2-phenylenebis-(oxalamidate)]-nickel(II) combined with Fe(ClO₄)₂ | 0.1 M sodium phosphate, pH 13, at 0.85 V versus normal hydrogen electrode | Glassy carbon plates | Low loading NiFeOₓ                      | 11.77 mA/cm² and turnover frequency of ~11 s⁻¹ at 0.35 V of overpotential                             | ~100%              | Garrido-Barros et al. (2019)    |

Ligands that do not play role in the deposition process are omitted for clarity, n.d. means not determined
to degradation; thermodynamics dictates that the harsh oxidative conditions demanded by the endergonic oxygen evolving reaction most often are enough to eventually break up aliphatic bonds or open aromatic rings. Yet, there are examples of ligands accumulating electron vacancies, serving as internal base to facilitate coupling between electron and proton transfer, participating in the O–O bond formation, or allowing true catalyst formation upon redox transformation efficiently. Realization of such phenomena and the concept of self-healing catalytic systems may be guidance for new discoveries and a timely paradigm shift. From the viewpoint of direct practical applications, cost-efficient precursor complexes to surface catalyst films are of utmost importance. The diversity of first row transition metal complexes containing redox-active ancillary ligands is very promising, if refined methods are sought in order to carry out stringent, nanoscale surface modifications on conducting and semiconducting materials.

This overview is merely a short glimpse at the various catalyst types of an ever-evolving field – artificial photosynthesis. On the timescale of human research, the evolution of the natural system might seem static, but let us not forget that evolution has been in motion since the appearance of the first living organism and our species is only a milestone on the path. How many futile exercises shaped the image of biosphere known today, and how many left a mark that is waiting for a prepared explorer; these provoking questions should inspire us to step forward and explore new, advanced artificial systems.

Acknowledgements The National Research, Innovation and Development Office of Hungary, grant numbers NKFI-128841 and TKP2021-NKTA-05 (J. S. Pap), funded this work. M. L. thanks the Basic Science Center Program for Ordered Energy Conversion of the National Natural Science Foundation of China (No. 51888103) for their financial support.

Author contributions All authors contributed to the conception of and literature analysis in the review. The first draft of the manuscript was written by József S. Pap and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

Funding Open access funding provided by Centre for Energy Research. This work was supported by the National Research, Innovation and Development Office of Hungary (Grant numbers NKFI-128841 and TKP2021-NKTA-05). Author M. L. received funding from the Basic Science Center Program for Ordered Energy Conversion of the National Natural Science Foundation of China (Grant No. 51888103).

Declarations

Conflict of interest The authors have no relevant financial or non-financial interests to disclose.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit http://creativecommons.org/licenses/by/4.0/.

References

Abdel-Magied AF, Shatskiy A, Liao R-Z et al (2016) Chemical and photochemical water oxidation mediated by an efficient single-site ruthenium catalyst. ChemSusChem 9:3448–3456. https://doi.org/10.1002/cssc.201601171

Aligholivand M, Shagaghzi Z, Bikas R, Kozakiewicz A (2019) Electro-catalytic water oxidation by a Ni(II) salophen-type complex. RSC Adv 9:40424–40436. https://doi.org/10.1039/C9RA08585H

Al-Zuraiji SM, Benkő T, Illes I et al (2020a) Utilization of hydrophobic ligands for water-insoluble Fe(II) water oxidation catalysts–immobilization and characterization. J Catal 381:615–625. https://doi.org/10.1016/j.jcat.2019.12.003

Al-Zuraiji SM, Lukács D, Németh M et al (2020b) An iron(III) complex with pincer ligand—catalytic water oxidation through controllable ligand exchange. Reactions 1:16–36. https://doi.org/10.3390/reactions1010003

Al-Zuraiji SM, Benkő T, Frey K et al (2021) Electrodeposition of Fe-complexes on oxide surfaces for efficient OER catalysis. Catalysts 11:577. https://doi.org/10.3390/catal11050577

An P, Yang B, Zhang N et al (2019) Hybrid TaON/LaTiO2N photoelectrode for water oxidation. Transp Sa Environ 1:212–219. https://doi.org/10.1093/tse/dza020

Ariela B, Yaniv W, Dror S et al (2017) The role of carbonate in electro-catalytic water oxidation by using Ni(1,4,8,11-tetraazacyclotetradecane)4+. Dalton Trans 46:10774–10779. https://doi.org/10.1039/C7DT02223A

Arrebi A, Amutio M, Lopez G et al (2018) Evaluation of thermochemical routes for hydrogen production from biomass: a review. Energy Convers Manage 165:696–719. https://doi.org/10.1016/j.enconman.2018.03.089

Asraf MdA, Younus HA, Ezugwu CI et al (2016) Cobalt salophen complexes for light-driven water oxidation. Catal Sci Technol 6:4271–4282. https://doi.org/10.1039/C5CY02157J

Babcock GT, Blankenship RE, Sauer K (1976) Reaction kinetics for positive charge accumulation on the water side of chloroplast photosystem II. FEBS Lett 61:286–289. https://doi.org/10.1016/0014-5793(76)81058-7

Balzani V, Credi A, Venturi M (2008) Photochemical conversion of solar energy. ChemSusChem 1:26–58. https://doi.org/10.1002/cssc.200700087

Barnett SM, Goldberg KJ, Mayer JM (2012) A soluble copper–bipyridine water-oxidation electrocatalyst. Nature Chem 4:498–502. https://doi.org/10.1038/nchem.1350

Bediako DK, Surendranath Y, Nocera DG (2013) Mechanistic studies of the oxygen evolution reaction mediated by a nickel-borate thin film electrocatalyst. J Am Chem Soc 135:3662–3674. https://doi.org/10.1021/ja3126432

Benkő T, Lukács D, Frey K et al (2021) Redox-inactive metal single-site molecular complexes: a new generation of electrocatalysts
for oxygen evolution? Catal Sci Technol 11:6411–6424. https://doi.org/10.1039/D1CY01087E

Bhat SA, Das C, Maji TK (2018) Metallated azo-naphthalene diimide based redox-active porous organic polymer as an efficient water oxidation electrocatalyst. J Mater Chem A 6:19834–19842. https://doi.org/10.1039/C8TA00911A

Biswas S, Bose S, Deb Gupta J et al (2020) Redox-active ligand assisted electrocatalytic water oxidation by a mononuclear cobalt complex. Dalton Trans 49:7155–7165. https://doi.org/10.1039/D0DT00838A

Bovi D, Nazri D, Guidoni L (2013) The S2 state of the oxygen-evolving complex of photosystem II explored by QM/MM dynamics: spin surfaces and metastable states suggest a reaction path towards the S1 state. Angew Chem Int Ed 52:11744–11749. https://doi.org/10.1002/anie.201306667

Bursk DB, Vasil’iu M, Dixon DA, Papish ET (2018) Thermodynamic acidity studies of 6,6'-Dihydroxy-2,2'-bipyridine: a combined experimental and computational approach. J Phys Chem A 122:2221–2231. https://doi.org/10.1021/acs.jpcas.7b011441

Cao S, Chan T-S, Lu Y-R et al (2020) Photocatalytic pure water splitting with high efficiency and value by Pt/porous bikoite TiO2 nanoflutes. Nano Energy 67:104287. https://doi.org/10.1016/j.nanoen.2019.104287

Cao M, Li H, Liu K et al (2021) Vertical SrNbO3N nanorod arrays for solar-driven photoelectrochemical water splitting. Sol RRL 5:2000448. https://doi.org/10.1002/solr.202000448

Cape JL, Hurst JK (2008) Detection and mechanistic relevance of Costentin C, Drouet S, Robert M, Savéant J-M (2012b) Correction Costentin C, Drouet S, Robert M, Savéant J-M (2012a) Turnover numbers, turnover frequencies, and overpotential in molecular catalysis of electrochemical reactions. Cyclic

voltammetry and preparative-scale electrolysis. J Am Chem Soc 134:19949–19950. https://doi.org/10.1021/ja3106187

Cox N, Pantazis DA, Neese F, Lubitz W (2013) Biological water oxidation. Acc Chem Res 46:1588–1596. https://doi.org/10.1021/ar3003249

Cox N, Retegan M, Neese F et al (2014) Electronic structure of the oxygen-evolving complex in photosystem II prior to O–O bond formation. Science 345:804–808. https://doi.org/10.1126/science.1254910

Csonka R, Speier G, Kaizer J (2015) Isosindoline-derived ligands and applications. RSC Adv 5:18401–18419. https://doi.org/10.1039/C4RA15379K

Cui S, Qian M, Liu X et al (2016) A Copper Porphyrin-based conjugated mesoporous polymer-derived bifunctional electrocatalyst for hydrogen and oxygen evolution. ChemSusChem 9:2365–2373. https://doi.org/10.1002/cssc.201600452

D’Agostino S, Kottrup KG, Casadevall C et al (2021) Electrocatalytic water oxidation with α-[Fe(mcp)(OTf)]2 and analogues. ACS Catal 11:2583–2595. https://doi.org/10.1021/acscatal.0c05439

Daniel Q, Ambre RB, Zhang B et al (2017) Re-investigation of cobalt porphyrin for electrochemical water oxidation on FTO Surface: formation of CoOx as active species. ACS Catal 7:1143–1149. https://doi.org/10.1021/acscatal.6b01815

Das D, Pattanayak S, Singh KK et al (2016) Electrocatalytic water oxidation by a molecular cobalt complex through a high valent cobalt o xo intermediate. Chem Commun 52:11787–11790. https://doi.org/10.1039/C6CC05773I

Dasgupta J, Ananyev G, Dismukes G (2008) Photoassembly of the water-oxidizing complex in photosystem II. Coord Chem Rev 252:347–360. https://doi.org/10.1016/j.ccr.2007.08.022

Dau H, Fujita E, Sun L (2017) Artificial photosynthesis: beyond mimicking nature. ChemSusChem 10:4228–4235. https://doi.org/10.1002/cssc.201702106

Deary ME, Durrant MC, Davies DM (2013) A kinetic and theoretical study of the borate catalysed reactions of hydrogen peroxide: the role of dioxorhodanine as the catalytic intermediate for a wide range of substrates. Org Biomol Chem 11:309–317. https://doi.org/10.1039/C2OB26842F

DePasquale J, Nieto I, Reuther LE et al (2013) Iridium dihydroxy-bipyridine complexes show that ligand deprotonation dramatically speeds rates of catalytic water oxidation. Inorg Chem 52:9175–9183. https://doi.org/10.1021/ic302448d

Dincer M, Surendranath Y, Nocera DG (2010) Nickel-borate oxygen-evolving catalyst that functions under benign conditions. Proc Natl Acad Sci USA 107:10337–10341. https://doi.org/10.1073/pnas.1001859107

Dinda S, Sarkar K, Panda BK et al (2022) Diarylazooxime complex of cobalt(III): synthesis, structure, ligand redox, DFT calculations and spectral characteristics. Transit Met Chem 47:31–38. https://doi.org/10.1007/s11243-021-00485-1

Diner BA, Nixon PJ, Farchaus JW (1991) Site-directed mutagenesis of photosynthetic reaction centers. Curr Op Struct Biol 1:546–554. https://doi.org/10.1016/S0959-440X(05)80076-4

Dobbie H, Kermack WO (1955) Complex-formation between polyvalent copper ions and peptides and metals. 3. The reaction between cupric ions and diglycylglycine. Biochem J 59:257–264. https://doi.org/10.1042/bj0590257

Dogutan DK, McGuire R, Nocera DG (2011) Electrocatalytic water oxidation by cobalt(III) hangman β-octafluoro corroles. J Am Chem Soc 133:9178–9180. https://doi.org/10.1021/ja201313m

Du H-Y, Chen S-C, Su X-J et al (2018) Redox-active ligand assisted multielectron catalysis: a case of Co10 complex as water oxidation catalyst. J Am Chem Soc 140:1557–1565. https://doi.org/10.1021/jacs.8b00032

Durrant MC, Davies DM, Deary ME (2011) Dioxorhodanine: a highly reactive peroxide that is the likely intermediate in borate
catalysed electrophilic reactions of hydrogen peroxide in alkaline aqueous solution. Org Biomol Chem 9:7249. https://doi.org/10.1039/c1ob06142a

Elizarova GL, Matvienko LG, Lozhkina NV et al (1981) Homogeneous catalysts for dioxygen evolution from water. Water oxidation by trisbipyridylruthenium(III) in the presence of cobalt, iron and copper complexes. React Kinet Catal Lett 16:191–194. https://doi.org/10.1007/BF02065456

Ellis WC, McDaniel ND, Bernhard S, Collins TJ (2010) Fast water oxidation using iron. J Am Chem Soc 132:10990–10991. https://doi.org/10.1021/ja104766a

Elmaci G, Icten O, Ozer D et al (2021) Manganese oxoborate-based nanostructures as novel oxygen evolution catalysts in neutral media. ChemNanoMat. https://doi.org/10.1002/cnma.202100025a

Elwell CE, Gagnon NL, Neisen BD et al (2017) Copper-oxygen complexes revisited: structures, spectroscopy, and reactivity. Chem Rev. https://doi.org/10.1021/acs.chemrev.6b00636

Eremin DB, Ananikov VP (2017) Understanding active species in catalytic transformations: from molecular catalysis to nanoparticles, leaching. “Cocktails” of catalysts and dynamic systems. Coord Chem Rev 346:2–19. https://doi.org/10.1016/j.ccr.2016.12.021

Ertem MZ, Gagliardi L, Cramer CJ (2012) Quantum chemical characterization of the mechanism of an iron-based water oxidation catalyst. Chem Sci 3:1293. https://doi.org/10.1039/c2sc20103o

Farkas E, Sranko D, Kerner Z et al (2016) Self-assembled, nanostructured coatings for water oxidation by alternating deposition of Cu-bridged peptide electrocatalysts and polyelectrolytes. Chem Sci 7:5249–5259. https://doi.org/10.1039/C6CS00595K

Faunce T, Styring S, Wasielewski MR et al (2013) Artificial photosynthesis as a frontier technology for energy sustainability. Energy Environ Sci 6:1074. https://doi.org/10.1039/c3ee40534f

Feihi H, Shiri F, Bagheri R et al (2018) The application of a nickel(II) Schiff base complex in water oxidation: the importance of nanosized materials. Catal Sci Technol 8:3954–3968. https://doi.org/10.1039/c8cy00582f

Feng C, Faheem MB, Fu J et al (2020) Fe-based electrocatalysts for oxygen evolution reaction: progress and perspectives. ACS Catal 10:4019–4047. https://doi.org/10.1021/acs.catal.9b04533

Feyziyev Y, van Rotterdam BJ, Bernát G, Styring S (2003) Electron transfer from cytochrome b559 and tyrosineF to the S2 and S3 states of the water oxidizing complex in photosystem II. Chem Phys 294:415–431. https://doi.org/10.1016/S0301-0104(03)005227

Förster V, Junge W (1985) Stoichiometry and kinetics of proton release upon photosynthetic water oxidation. Photochem Photobiol 41:183–190. https://doi.org/10.1111/j.1751-1097.1985.tb03469.x

Förster V, Hong Y-Q, Junge W (1981) Electron transfer and proton pumping under excitation of dark-adapted chloroplasts with flashes of light. Biochim Biophys Acta (BBA)-Bioenerg 638:141–152. https://doi.org/10.1016/0005-2728(81)90197-3

Fu S, Liu Y, Ding X et al (2014) A mononuclear cobalt complex with an organic ligand acting as a precatalyst for efficient visible light-driven water oxidation. Chem Commun 50:2167–2169. https://doi.org/10.1039/C3CC48059C

Fu J, Liu K, Jiang K et al (2019) Graphitic carbon nitride with dopant induced charge localization for enhanced photoreduction of CO2 to CH4. Adv Sci 6:1900796. https://doi.org/10.1002/advs.20190796

Fu J, Jiang K, Qiu X et al (2020a) Product selectivity of photocatalytic CO2 reduction reactions. Mater Today 32:222–243. https://doi.org/10.1016/j.mattod.2019.06.009

Fu J, Wang S, Wang Z et al (2020b) Graphitic carbon nitride based single-atom photocatalysts. Front Phys 15:33201. https://doi.org/10.1007/s11467-019-0950-z

Funes-Ardoiz I, Garrido-Barros P, Llobet A, Maseras F (2017) Single electron transfer steps in water oxidation catalysis redefining the mechanistic scenario. ACS Catal 7:1712–1719. https://doi.org/10.1021/acscatal.6b03253

Garai A, Sobottka S, Schepper R et al (2018) Chromium complexes with oxidido and correlato ligands: metal-based redox processes versus ligand non-innocence. Chem Eur J 24:12613–12622. https://doi.org/10.1002/chem.201801452

Garrido-Barros P, Funes-Ardoiz I, Drouet S et al (2015) Redox non-innocent ligand controls water oxidation overpotential in a new family of mononuclear Cu-based efficient catalysts. J Am Chem Soc 137:6758–6761. https://doi.org/10.1021/jacs.5b03977

Garrido-Barros P, Gimbert-Suríñach C, Moonshiram D et al (2017) Electronic π-delocalization boosts catalytic water oxidation by Cu(II) molecular catalysts heterogenized on graphene sheets. J Am Chem Soc 139:12907–12910. https://doi.org/10.1021/jacs.7b06828

Garrido-Barros P, Grau S, Drouet S et al (2019) Can Ni complexes behave as molecular water oxidation catalysts? ACS Catal 9:3936–3945. https://doi.org/10.1021/acscatal.8b03953

Garrido-Barros P, Moonshiram D, Gil-Sepulcre M et al (2020) Redox metal-ligand cooperativity enables robust and efficient water oxidation catalysis at neutral pH with macrocyclic copper complexes. J Am Chem Soc 142:17434–17446. https://doi.org/10.1021/jacs.0c06515

Geis C, Schneider SP, Schlettwein D (2016) Polymeric phosphocyanin sheets as electrocatalytic electrodes for water oxidation. J Porphy Pththal 20:1166–1172. https://doi.org/10.1142/S1088424616500826

Gerlach DL, Bhagan S, Crrce AA et al (2014) Studies of the pathways open to copper water oxidation catalysts containing proximal hydroxy groups during basic electrocatalysis. Inorg Chem 53:12689–12698. https://doi.org/10.1021/ic501018a

Gersten SW, Samuels GI, Meyer TJ (1982) Catalytic oxidation of water by an oxo-bridged ruthenium dimer. J Am Chem Soc 104:4029–4030. https://doi.org/10.1021/ja00378a053

Ghosh A (2017) Electronic structure of corrole derivatives: insights from molecular structures, spectroscopy, electrochemistry, and quantum chemical calculations. Chem Rev 117:3798–3881. https://doi.org/10.1021/acs.chemrev.6b00590

Gil-Sepulcre M, Garrido-Barros P, Oldengott J et al (2021) Consecutive ligand-based electron transfer in new molecular copper-based water oxidation catalysts. Angew Chem Int Ed 60:18639–18644. https://doi.org/10.1002/anie.202104020

Grimes CA, Varghese OK, Ranjan S (eds) (2008) Light, water hydro- gen. Springer, Boston

Gross Z (2001) High-valent corrole metal complexes. J Biol Inorg Chem 6:733–738. https://doi.org/10.1007/s007750100273

Hamza MA, El-Shazly AN, Tolba SA, Allam NK (2020) Novel Bi-based photocatalysts with unprecedented visible light-driven hydrogen production rate: experimental and DFT insights. Chem Eng J 384:123351. https://doi.org/10.1016/j.cej.2019.123351

Han A, Wu H, Sun Z et al (2013) Facile deposition of nanostructured cobalt oxide catalysts from molecular cobaloximes for efficient water oxidation. Phys Chem Chem Phys 15:12534. https://doi.org/10.1039/c3cp52275

Han A, Jia H, Ma H et al (2014) Cobalt porphyrin electrode films for electrocatalytic water oxidation. Phys Chem Chem Phys 16:11224–11232. https://doi.org/10.1039/C4CP00523F

Han Y, Wu Y, Lai W, Cao R (2015) Electrocatalytic water oxidation by a water-soluble nickel porphyrin complex at neutral pH with low overpotential. Inorg Chem 54:5604–5613. https://doi.org/10.1021/acs.inorgchem.5b00024
in basic and neutral solutions. ACS Catal 6:77–83. https://doi.org/10.1021acs.catal.5b02173

Lukács D, Németh M, Szyrwić L et al (2019) Behavior of a Cu-Peptide complex under water oxidation conditions – Molecular electro-catalyst or precursor to nanostructured CuO films? Sol Energy Mater Sol Cells 201:110079. https://doi.org/10.1016/j.solmat.2019.110079

MacDougall B, Graham MJ (1981) Growth of thick anodic oxide films on nickel in borate buffer solution. J Electrochem Soc 128:2321–2325. https://doi.org/10.1149/1.2127242

Magnusson A, Rova M, Mamedov F et al (1999) The role of cytochrome b559 and tyrosine D in protection against photoinhibition during in vivo photactivation of Photosystem II. Biochim Biophys Acta (BBA)-Bioenerg 1411:180–191. https://doi.org/10.1016/S0005-2728(99)00044-4

Mahammed A, Gross Z (2015) Metalloco-roles as photocatalysts for driving endergonic reactions, exemplified by bromide to bromine conversion. Angew Chem Int Ed 54:12370–12373. https://doi.org/10.1002/anie.201503064

Matheu R, Garrio-Barros P, Gil-Sepulcre M et al (2019) The development of molecular water oxidation catalysts. Nat Rev Chem 3:331–341. https://doi.org/10.1038/s41570-019-0096-0

McEvoy JP, Brudvig GW (2006) Water-splitting chemistry of photo-catalysts. J Phys Chem B 106:4455–4483. https://doi.org/10.1021/ct0204294

Mildner S, Beleggia M, Mierwaldt D et al (2015) Environmental TEM study of electron beam induced electrochemistry of PbO2-xCaO-xMnO, catalysts for oxygen evolution. J Phys Chem C 119:5301–5310. https://doi.org/10.1021/jp511628c

Mishra R, Ulker E, Karadas F (2017) One-Dimensional Copper(II) coordination polymer as an electrocatalyst for water oxidation. ChemElectroChem 4:75–80. https://doi.org/10.1002/celc.201600518

Mizrahi A, Maimon E, Cohen H et al (2018) Mechanistic studies on the role of [Cu(9)(CO3)]2– as a water oxidation catalyst: carbonate as a non-innocent ligand. Chem Eur J 24:1088–1096. https://doi.org/10.1002/chem.201703742

Mizrahi A, Meyerstein D (2019) Plausible roles of carbonate in catalytic water oxidation. In: Adv Inorg Chem. Elsevier, pp 343–360

Mondal B, Chattopadhyay S, Dey S et al (2020) Elucidation of factors that govern the 2e-/2H+ vs 4e-/4H+ selectivity of water oxidation by a cobalt corrole. J Am Chem Soc 142:21040–21049. https://doi.org/10.1021/jacs.0j05183

Moonshiram D, Jurss JW, Concepcion JJ et al (2012) Structure and electronic configurations of the intermediates of water oxidation in blue ruthenium dimer catalysis. J Am Chem Soc 134:4625–4636. https://doi.org/10.1021/ja208636f

Mousazade Y, Najafpour MM, Bagheri R et al (2019) A manganese(II) phthalocyanine under water-oxidation reaction: new findings. Dalton Trans 48:12147–12158. https://doi.org/10.1039/C9DT01790A

Muckerman JT, Polyansky DE, Wada T et al (2008) Water oxidation by a ruthenium complex with noninnocent quinone ligands: possible formation of an O–O bond at a low oxidation state of the metal. Inorg Chem 47:1787–1802. https://doi.org/10.1021/ic70189z

Nakamura S, Capone M, Narzi D, Guidoni L (2020) Pivotal role of the redox-active tyrosine in driving the water splitting catalyzed by photosystem II. Phys Chem Chem Phys 22:273–285. https://doi.org/10.1039/C9CP04605D

Nakazono T, Parent AR, Sakai K (2013) Cobalt porphyrins as homogenous catalysts for water oxidation. Chem Commun 49:6325. https://doi.org/10.1039/c3cc43031f

Nakazono T, Parent AR, Sakai K (2015) Improving singlet oxygen resistance during photochemical water oxidation by cobalt porphyrin catalysts. Chem Eur J 21:6723–6726. https://doi.org/10.1002/chem.201500716

Narzi D, Bovi D, Guidoni L (2014) Pathway for Mn-cluster oxidation by tyrosine-Z in the S2 state of photosystem II. Proc Natl Acad Sci USA 111:8723–8728. https://doi.org/10.1073/pnas.1401719111

Nocera DG (2012) The artificial leaf. Acc Chem Res 45:767–776. https://doi.org/10.1021/ar2003013

Okamura M, Kondo M, Kuga R et al (2016) A pentanuclear iron catalyst designed for water oxidation. Nature 530:465–468. https://doi.org/10.1038/nature16529

Osman AI, Mehta N, Elgaraby AM et al (2021) Hydrogen production, storage, utilisation and environmental impacts: a review. Environ Chem Lett. https://doi.org/10.1007/s10311-021-01322-8

Pachauri RK, Mayer L. Intergovernmental Panel on Climate Change (eds) (2015) Climate change 2014: synthesis report. Intergovernmental Panel on Climate Change, Geneva, Switzerland

Pantazis DA (2018) Missing pieces in the puzzle of biological water oxidation. ACS Catal 8:9477–9507. https://doi.org/10.1021/acscatal.8b01928

Pantazis DA (2021) Natural and artificial photosynthesis. In: Sun H (ed) Solar-to-chemical conversion, 1st edn. Wiley, pp 41–76

Pantazis DA, Ames W, Cox N et al (2012) Two interconvertible structures that explain the spectroscopic properties of the oxygen-evolving complex of photosystem II in the S2 state. Angew Chem Int Ed 51:9935–9940. https://doi.org/10.1002/anie.201204705

Patra SG, Illes E, Mizrahi A, Meyerstein D (2020a) Cobalt carbonate as an electrocatalyst for water oxidation. Chem Eur J 26:711–720. https://doi.org/10.1002/chem.201904051

Patra SG, Mizrahi A, Meyerstein D (2020b) The role of carbonate in catalytic oxidations. Acc Chem Res 53:2189–2200. https://doi.org/10.1021/acs.accounts.0c00344

Pelinos P, Gil-Sepulcre M, Garrio-Barros P et al (2020) Analysis of the active species responsible for water oxidation using a pentanuclear Fe complex. iScience 23:101378. https://doi.org/10.1016/j.isci.2020.101378

Pizer R, Thal C (1987) Peroxoborates. Interaction of boric acid and hydrogen peroxide in aqueous solution. Inorg Chem 26:3639–3642. https://doi.org/10.1021/ic00268a046

Rappaport F, Diner B (2008) Primary photochemistry and energetics leading to the oxidation of the (Mn)4Ca cluster and to the evolution of molecular oxygen in Photosystem II. Coord Chem Rev 252:259–272. https://doi.org/10.1016/j.ccr.2007.07.016

Retegan M, Cox N, Lubitz W et al (2014) The first tyrosyl radical intermediate formed in the S2–S3 transition of photosystem II. Phys Chem Chem Phys 16:11901. https://doi.org/10.1039/c4cp00968h

Retegan M, Krewald V, Mamedov F et al (2016) A five-coordinate Mn(IV) intermediate in biological water oxidation: spectroscopic signature and a pivot mechanism for water binding. Chem Sci 7:72–84. https://doi.org/10.1039/C5SC03124A

Ruan G, Ghosh P, Fridman N, Maayan G (2021) A Di-copper-peptoid in a noninnocent borate buffer as a fast electrocatalyst for homogeneous water oxidation with low overpotential. J Am Chem Soc 143:10614–10623. https://doi.org/10.1021/jacs.1c03225

Rutherford AW (1989) Photosystem II, the water-splitting enzyme. Trends Biochem Sci 14:227–232. https://doi.org/10.1016/0968-0004(89)90032-7

Rutherford AW, Boussac A, Fuller P (2004) The stable tyrosyl radical in photosystem II: Why? D7 Biochim Biophys Acta (BBA)-Bioenerg 1655:222–230. https://doi.org/10.1016/j.bbabi.2003.10.016

Sachs R, Pflüger M, Velasco-Vélez J-J et al (2020) Assessing optical and electrical properties of highly active IrO2 catalysts for the electrochemical oxygen evolution reaction via spectroscopic ellipsometry. ACS Catal 10:14210–14223. https://doi.org/10.1021/acscatal.0c03800
Saha S, Sahil ST, Mazumder MdMR et al (2021) Synthesis, characterization, and electrocatalytic activity of bis(pyridylimino)isoindolone Cu(II) and Ni(II) complexes. Dalton Trans 50:926–935. https://doi.org/10.1039/D0DT03030A

Sala X, Maji S, Bofill R et al (2014) Molecular water oxidation mechanisms followed by transition metals: state of the art. Acc Chem Res 47:504–516. https://doi.org/10.1021/ar400169p

Schöflberger W, Fasching F, Chattopadhyay S et al (2016) A bifunctional electrocatalyst for oxygen evolution and oxygen reduction reactions in water. Angew Chem Int Ed 55:2350–2355. https://doi.org/10.1002/anie.201508040

Shaghatghiz Z, Aligholivand M, Mohammad-Rezaee R (2021) Enhanced water splitting through different substituted cobalt-salophen electrocatalysts. Int J Hydrog Energy 46:389–402. https://doi.org/10.1016/j.ijhydene.2020.09.162

Shen J-R (2015) The structure of photosystem II and the mechanism of water oxidation in photosynthesis. Annu Rev Plant Biol 66:23–48. https://doi.org/10.1146/annurev-arpla-050312-120129

Shen X, Zhao L, Fan W et al (2021) Efficient photoelectrochemical water oxidation of cobalt phthalocyanine decorated BiVO4 photoanode by improving kinetics. Appl Surf Sci 564:150463. https://doi.org/10.1016/j.apsusc.2021.150463

Siegbahn PEM (2009) Structures and energetics for O2 formation in photosystem II and the mechanism of water oxidation in photosynthesis. Annu Rev Plant Biol 60:377–393. https://doi.org/10.1146/annurev-arplant-032608-120129

Siegbahn PEM, Blomberg MRA (2004) Important roles of tyrosines in photosystem II and cytochrome oxidase. Biochim Biophys Acta (BBA)-Bioenerg 1655:45–50. https://doi.org/10.1016/j.bbabioc.2003.07.003

Singh B, Indra A (2020) Role of redox active and redox non-innocent ligands in water splitting. Inorg Chim Acta 506:119440. https://doi.org/10.1016/j.ica.2020.119440

Singh W, Mizrahi A, Mahammed A et al (2018) Reactive intermediates involved in cobalt corrole catalyzed water oxidation (and oxygen reduction). Inorg Chem 57:478–485. https://doi.org/10.1021/acs.inorgchem.7b02696

Sinha W, Mahammed A, Fridman N, Gross Z (2020) Water oxidation catalysis by mononuclear copper in aqueous bicarbonate solution. J Power Sour 287:50–57. https://doi.org/10.1016/j.jpowsour.2015.05.031

Suga M, Akita F, Hirata K et al (2015) Water oxidation catalyzed by a water-soluble copper phthalocyanine complex. ChemPlusChem 81:1064–1067. https://doi.org/10.1002/cplu.201600263

Tezgeresvka T, Alley KG, Boskovic C (2014) Valence tautoomerism in metal complexes: stimulated and reversible intramolecular electron transfer between metal centers and organic ligands. Coord Chem Rev 268:23–40. https://doi.org/10.1016/j.ccr.2014.01.014

Tsoler U (ed) (1999) Handbook of detergents. M. Dekker, New York

Umena Y, Kawakami K, Shen J-R, Kamiya N (2011) Crystal structure of oxygen-evolving photosystem II at a resolution of 1.9 Å. Nature 473:55–60. https://doi.org/10.1038/nature09913

Váradi T, Pap JS, Giorgi M et al (2013) Iron(III) Complexes with meridional ligands as functional models of intradiol-cleaving catechol dioxygenases. Inorg Chem 52:1559–1560. https://doi.org/10.1021/ic302378r

Vass I, Styring S (1991) pH-Dependent charge equilibria between tyrosine-D and the S states in photosystem II. Estimation of relative midpoint redox potentials. Biochem 30:830–839. https://doi.org/10.1021/bi00217a037

Wada T, Tsuge K, Tanaka K (2000) Electrochemical oxidation of water to dioxygen catalyzed by the oxidized form of the bis(ruthenium – hydroxo) complex in H2O. Angew Chem Int Ed 39:1479–1482. https://doi.org/10.1002/1021/1521-3773(20000417)39:8<1479::AID-ANIE1479>3.0.CO;2-4

Wada T, Tsuge K, Tanaka K (2001) Syntheses and redox properties of bis(hydroxoruthenium) complexes with quinone and bipyridine ligands. Water-Oxidation Catalysis. Inorg Chem 40:329–337. https://doi.org/10.1021/acs.inorgchem.7b02691

Wang D, Groves JT (2013) Efficient water oxidation catalyzed by homogeneous cationic cobalt porphyrins with critical roles for the buffer base. Proc Natl Acad Sci USA 110:15579–15584. https://doi.org/10.1073/pnas.1315383110

Wang Z-Q, Tang L-Z, Zhang Y-X et al (2015) Electrochemical-driven water splitting catalyzed by a water-soluble cobalt(II) complex supported by N,N′-bis(2-pyridinerboxamide)-1,2-benzene with high turnover frequency. J Power Sour 287:50–57. https://doi.org/10.1016/j.jpowsour.2015.04.031

Weinberg DR, Gagliardi CJ, Hull JF et al (2012) Proton-coupled electron transfer. Chem Rev 112:4016–4093. https://doi.org/10.1021/cr2001777

Winikoff SG, Cramer CJ (2014) Mechanistic analysis of water oxidation catalyzed by mononuclear copper in aqueous bicarbonate solutions. Catal Sci Technol 4:2484–2489. https://doi.org/10.1039/C4CY00500G

Xu S, Sun W, Meng X et al (2021) Carbon quantum dot conjugated copper(II) phthalocyanine integrating BiVO4 semiconductor for photocatalytic water oxidation. J Phys Chem C 125:24413–24421. https://doi.org/10.1021/acs.jpcc.1c07491

Yamada H, Hurst JK (2000) Resonance Raman, optical spectroscopic, and EPR characterization of the higher oxidation states of the water oxidation catalyst, cis, cis-[(bpy)3Ru(OH)2]O4+. J Am Chem Soc 122:5303–5311. https://doi.org/10.1021/ja993194y

Yang KR, Lakshmi KV, Brudvig GW, Batista VS (2021) Is deprotonation of the oxygen-evolving complex of photosystem II during the S1→S2 transition suppressed by proton quantum delocalization? J Am Chem Soc 143:8324–8332. https://doi.org/10.1021/acs.jacsat.1c00663

Yoshida M, Mitsuomi Y, Mineo T et al (2015) Direct observation of active nickel oxide cluster in nickel-borate electrocatalyst for water oxidation by in situ O K-Edge X-ray absorption spectroscopy. J Phys Chem C 119:19279–19286. https://doi.org/10.1021/acs.jpcc.5b06102

Yu F, Li F, Zhang B et al (2015) Efficient electrocatalytic water oxidation by a copper oxide thin film in borate buffer. ACS Catal 5:627–630. https://doi.org/10.1021/cs501510e
Zabret J, Bohn S, Schuller SK et al (2021) Structural insights into photosystem II assembly. Nat Plants 7:524–538. https://doi.org/10.1038/s41477-021-00895-0

Zhang B, Sun L (2019) Artificial photosynthesis: opportunities and challenges of molecular catalysts. Chem Soc Rev 48:2216–2264. https://doi.org/10.1039/C8CS00897C

Zhang T, Wang C, Liu S et al (2014) A biomimetic copper water oxidation catalyst with low overpotential. J Am Chem Soc 136:273–281. https://doi.org/10.1021/ja409267p

Zhang M, Bommer M, Chatterjee R et al (2017) Structural insights into the light-driven auto-assembly process of the water-oxidizing Mn₆CaO₅-cluster in photosystem II. eLife 6:e26933. https://doi.org/10.7554/eLife.26933

Zhang W, Lai W, Cao R (2017b) Energy-related small molecule activation reactions: oxygen reduction and hydrogen and oxygen evolution reactions catalyzed by porphyrin- and corrole-based systems. Chem Rev 117:3717–3797. https://doi.org/10.1021/acs.chemrev.6b00299

Publisher’s Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.