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Review Article

Design principles for homogeneous water oxidation catalysts based on first-row transition metals

Daan den Boer and Dennis G. H. Hetterscheid



Abstract

The development of homogeneous first-row transition metal (FRTM) catalysts for the water oxidation reaction is considerably more challenging than for second and third-row catalysts. Given that FRTM catalysts are, in general, more labile, additional design principles must be considered to develop robust and stable catalysts for the water oxidation reaction. In this review, we highlight important design criteria and summarize important lessons learned for FRTM water oxidation catalysts.

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Keywords

Electrocatalysis, Homogeneous catalysis, Water oxidation, Design principles, First-row transition metals.

Introduction

The increasing worldwide energy demand, the complex geopolitics associated with our current energy infrastructure, and global warming are major challenges that humankind needs to overcome [1–4]. The replacement of fossil fuels with renewable fuels, which are produced from earth-abundant resources such as H₂O and CO₂, is a potential solution to overcome these challenges. The utilization of hydrogen as an energy carrier has gained considerable interest over the last decades, as upon combustion of hydrogen, water is formed as the only byproduct. Hydrogen can be produced by the water-splitting reaction, which consists of the hydrogen evolution ($2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$) and the water oxidation ($2\text{H}_2\text{O} \rightarrow 4\text{H}^+ + 4\text{e}^- + \text{O}_2$) half reactions. The water

oxidation reaction is the bottleneck in this process, wherein multiple proton and electron transfer steps need to take place before two water molecules can be combined and produce an O–O bond. The inability to run all necessary electron transfer steps close enough to the equilibrium potential of water results in a requirement for a significant overpotential. For producing hydrogen in an energy-efficient manner, a robust and stable catalyst is required, which catalyzes the water oxidation reaction at a low overpotential and with high catalytic rates. Homogeneous water oxidation catalysts (WOCs)¹ allow for fine-tuning of the electronic structure and catalytic properties through ligand design, and thereby are very interesting platforms to produce potentially very efficient catalytic systems.

Second and third-row transition metal WOCs

Over the last decades, major developments have been shown in the field of water oxidation chemistry by studying Ru complexes from the blue dimer to Ru(bda) (bda = 2,2'-bipyridine-6,6'-dicarboxylate) systems [5,6]. On the other hand, Ir-based systems have shown to be very active catalysts for water oxidation [7] but can also form IrO_x under operating conditions [8,9]. However, the application of these scarce metals on a large scale is extremely expensive, and therefore, almost impossible. Nevertheless, important design lessons have been learned from studies involving these Ru and Ir-based WOCs:

- By removing electrons from the catalytic center via proton-coupled electron-transfer steps rather than electron transfer steps high-valent metal-oxo species can be obtained without a build-up of charge. This allows for these high oxidation state species to form at relatively mild potentials [10].
- A water nucleophilic attack (WNA) or the interaction between two M–O units (I2M) have been proposed as the two main mechanistic pathways wherein O–O bond formation takes place (Figure 1) [11]. The application of second coordination sphere effects has been shown to be a very useful strategy in facilitating very high turnover frequencies. This has for example been shown for the WNA mechanism wherein the

¹ FRTM – first-row transition metal, I2M – interaction between two M–O units, SET – single-electron transfer, WNA – water nucleophilic attack, WOC – water oxidation catalyst.

formation of the O–O bond is facilitated via intramolecular proton transfer via an internal carboxylic moiety [12]. For the I2M mechanism, it has been shown that preorganization of the two ruthenium sites allows for efficient coupling of oxo ligands via π -stacking interactions induced by axial ligands [13].

- Many ligands are unstable under the oxidative conditions employed. The Cp* (Cp* = pentamethylcyclopentadienyl) group, for example, is linked both to the degradation and the activation of the molecular complexes [7–9]. Despite the decomposition of the ligands, their remnants have been shown to still be of influence on the catalytic performance, both under chemical and electrochemical operating conditions [14–16].

First-row transition metal WOCs

Challenges

A cheaper alternative for the Ru and Ir-based WOCs is the utilization of first-row transition metal (FRTM) based WOCs, as these metals are earth-abundant. However, FRTMs have different properties than second and third-row transition metals, which lead to additional challenges to overcome. FRTMs have significantly smaller atomic radii, lower electronegativity and are harder Lewis acids than the second and third-row transition metals [17,18]. As a consequence, FRTMs are less stable in the higher oxidation states and suffer from more labile metal–ligand interactions [18,19]. These are disadvantageous physical properties for WOCs and ultimately will lead to catalyst degradation and/or the formation of metal oxide deposits [20]. Consequently, the specific operating conditions are also of more importance, as subtle changes in the reaction conditions have been shown to trigger the instability of the catalyst [21–23].

Homogeneity

A thorough investigation of the homogeneity of the WOC is one of the most important studies that need to be performed when studying FRTM catalysts. In the past, numerous homogeneous catalysts have been postulated, which later turned out to be heterogeneous metal deposits [24–26]. Simple dipping tests by measuring a blank cyclic voltammogram after catalysis may give a first indication but should not be considered evidence for the homogeneity of the catalyst on its own, but rather be an experiment in a series to pinpoint the homogeneity of the active species. The application of additional *ex-situ* surface techniques such as scanning electron microscopy in combination with energy dispersive X-ray or X-ray photoelectron spectroscopy studies, may provide additional evidence. However, the question remains whether the homogeneous species decomposed before, during, or after the catalytic reaction. Combining these *postmortem* techniques with *in operando* techniques such as electrochemical quartz crystal microbalance and a plethora of spectroelectrochemical techniques, would

even be a more trustworthy approach to establishing the homogeneity of the catalyst [27,28]. The use of a combination of *ex-situ* and *in operando* techniques has been shown to be a powerful strategy to solve the homogeneity question for multiple catalysts [24,29–32].

Ligand stability

The ligand employed should be sufficiently stable under the oxidative conditions necessary to oxidize water. The design rules for ligand stability under oxidative conditions have already been summarized by Collins in 1994 as part of their study on the selective oxidation of unactivated C–H bonds using tetra-amido macrocyclic ligands (Figure 2) [33]. These design rules are quoted below:

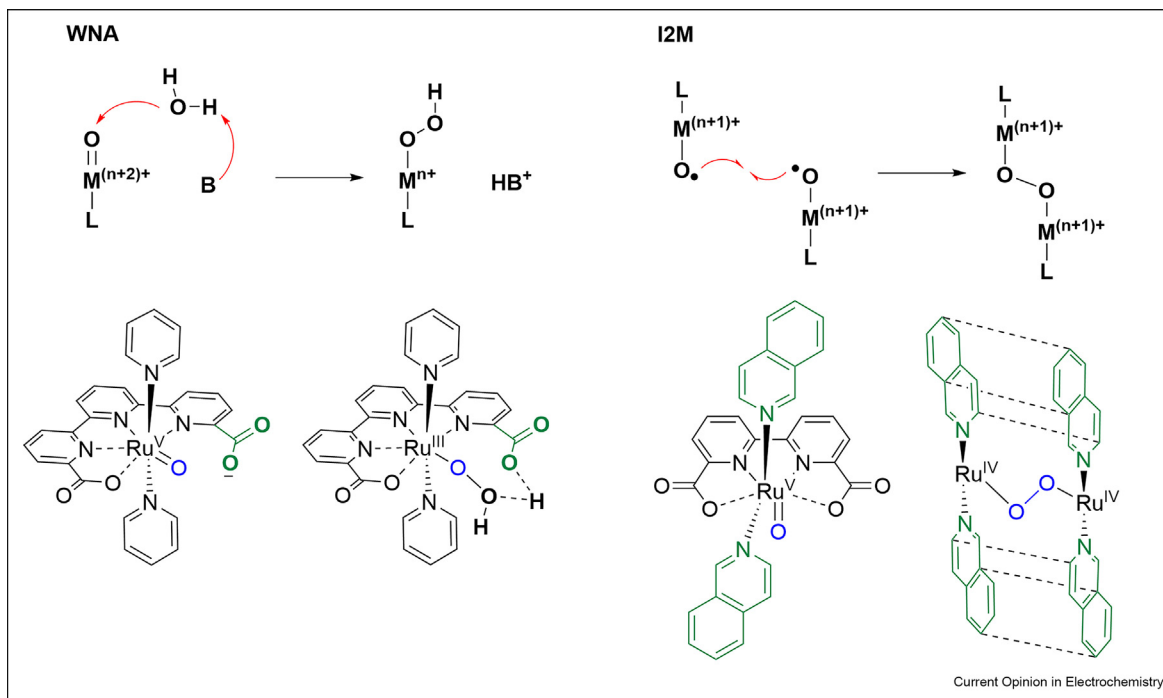
- **Rule 1:** ‘For chelate rings, a hydrogen atom should not be placed on an atom that is β to an oxidizing metal center if the α -atom can support an increase in the bond order with the β -atom’.
- **Rule 2:** ‘A heteroatom should not be attached to a five-membered chelate ring on an atom that is γ to an oxidizing metal center if the heteroatom has an available lone pair to stabilize forming cationic character on the γ -atom as the endocyclic β – γ bond is oxidatively cleaved by the metal’.
- **Rule 3:** ‘A heteroatom should not be employed as an α -donor atom in a five-membered chelate ring if it has an available lone pair to stabilize forming cationic character on the β -atom as the endocyclic β – γ bond is oxidatively cleaved by the metal’.

An original method to reduce the effect of ligand instability by benzylic β -hydrogens has been reported for Fe(mcp)-based (mcp = *N,N'*-dimethyl-*N,N'*-bis(pyridin-2-ylmethyl)-cyclohexane-1,2-diamine) systems, which are studied under electrochemical conditions and upon addition of chemical oxidations (Figure 3) [34–37]. By replacing the oxidation sensitive C–H moieties with C–D (D = deuterium) moieties, a significantly more robust catalyst is obtained, and as a direct result, a fivefold higher TOF was obtained for the water oxidation reaction. However, under electrochemical conditions, no significant differences were observed between the Fe(mcp)-based systems, which also indicates that the nonmodified complex is sufficiently stable under the electrochemical conditions employed. This example shows that catalytic stability can be obtained by small modifications. However, *the operating conditions at which the catalyst is studied may play an even larger role in catalytic stability.*

Oxo-wall and redox-active ligands

In Ru-catalyzed WO, the formation of a metal-oxo intermediate (M=O) with an electrophilic oxo group is crucial for the catalytic WNA and I2M mechanisms. The oxo-wall theory describes an imaginary border between groups 8 and 9 in the periodic table, where M=O

Figure 1



Schematic representation of the WNA and I2M mechanisms and complexes operating via these mechanisms and their transition states.

structures are proposed to only exist before the oxo-wall and not beyond [38]. Therefore, the WNA and I2M mechanisms and the design rules that have been postulated for Ru, may also apply to Mn and Fe-based catalysts [34,36–39]. Beyond the oxo-wall, metal-oxyl ($M-O\bullet$) structures, which contain a more nucleophilic oxyl radical, are considered to be the more likely species formed [40]. Consequently, different design rules must be required for late transition metals, for which high oxidation state $M=O$ species that have a sufficient electrophilic character to undergo a WNA reaction are unlikely to form. To circumvent the formation of a high-oxidation state metal center, redox-active ligands can be utilized to accumulate sufficient redox equivalents on the catalyst to be able to oxidize water. Over the last decade, this strategy has been applied successfully for the late transition metals, Co [41–43], Ni [44,45] and Cu-based [46–54] WOCs.

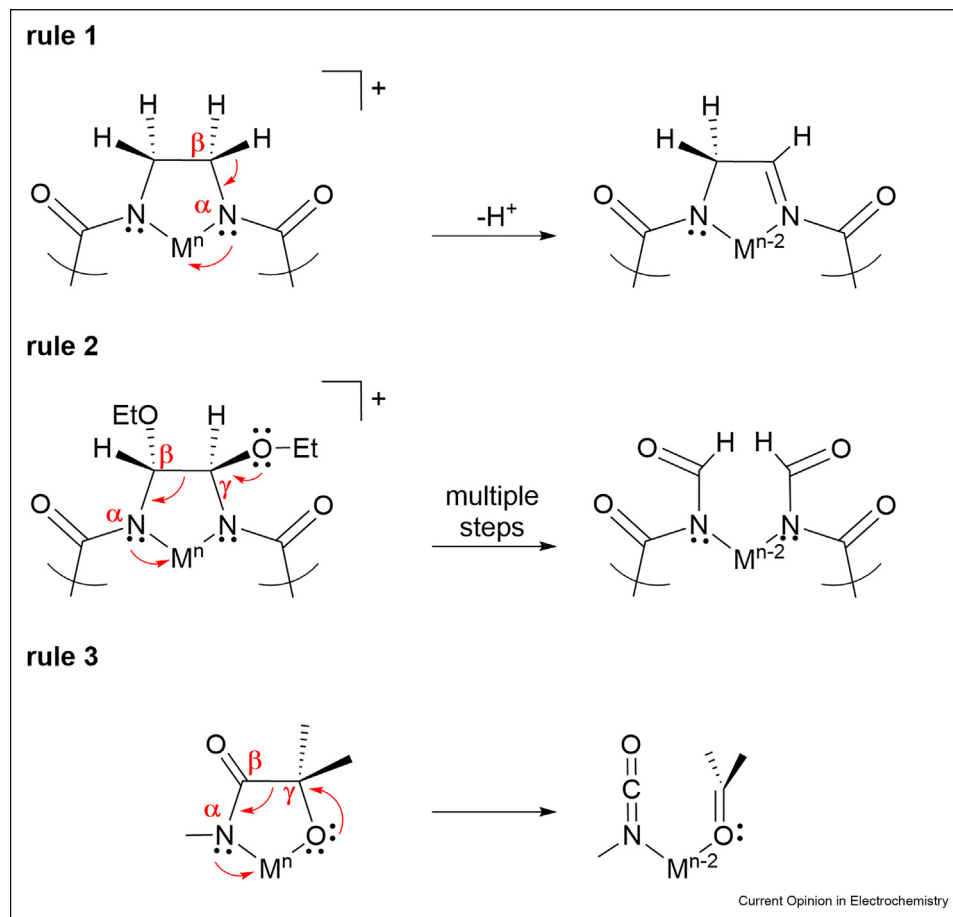
The group of Llobet studied Cu-based WOCs with the redox-active phenyl bisamidate group (Figure 4, highlighted in green). Because of the negative charge of -4 on the ligand, the copper center can be oxidized to the $+III$ oxidation state, while another oxidation reaction is centered on the ligand. By modification of the ligand system with two methoxy groups, the overpotential for the water oxidation reaction could be drastically decreased from 700 to 170 mV. However, as a direct

effect, the turnover frequency also decreased by an order of magnitude. As so often [55], *overpotentials and turnover frequencies are correlated, and to make any meaningful comparisons in electrocatalysis, both should be given*. An alternative O–O bond formation pathway than WNA or I2M was suggested on the basis of an extensive computational study [47,48]. In this alternative mechanism, two consecutive single electron-transfer (SET) steps are proposed to take place during O–O bond formation. The first SET takes place from the incoming hydroxide ion to the oxidized ligand (Figure 4). This results in an intermediate with a two-center three-electron $HO\cdot:OH$ bond ($\cdot$, which symbolizes the two-center three-electron bond) [56]. A second SET from the $HO\cdot:OH$ bond to the Cu^{III} center results in the formation of a $Cu^{II}(HO-OH)$ species. This alternative mechanism is more in line with the nucleophilic character of the $M-OH$ or $M-O\bullet$ species of late FRTM than the WNA-type mechanisms postulated for Ru-catalyzed water oxidation.

Based on these examples and the Co, Ni, and Cu-based systems bearing redox-active ligands, we propose the following design principles for these late FRTM WOCs.

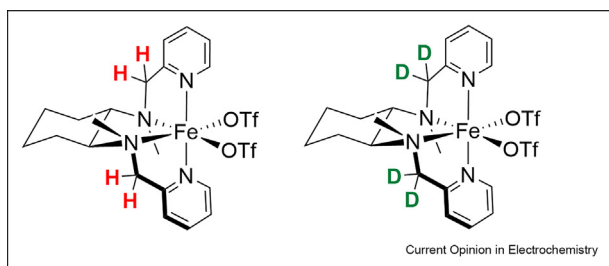
- Water oxidation occurs via different mechanistic pathways than WNA or I2M for late-transition metals, as the electrophilic $M=O$ species that is necessary for WNA cannot be formed easily [47,48,50]. Moreover,

Figure 2



Visualization of Collins rules for the design of oxidatively stable ligands.

Figure 3



Structures of the discussed Fe(mcp) systems.

we are unaware of such late FRTMs reacting via I2M mechanisms.

- In most examples, ligands with a negative charge prevail, as it is easier to remove electrons from these

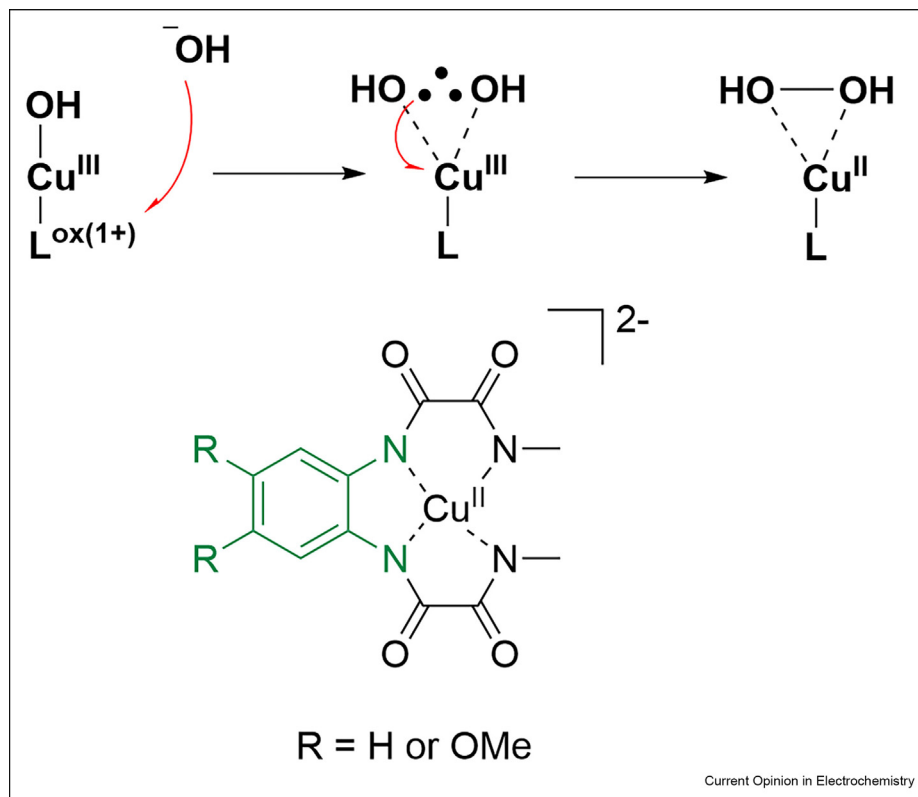
ligands without compromising the stability of the metal-ligand interaction too much [42–47,49,51–54].

- If an oxidation reaction occurs on the ligand rather than on the metal center, the use of ligand substituents may result in large shifts of the oxidation potential. Therefore, the overpotentials and rate constants may be controlled more easily by variations in the electronic structure of catalysts employed with redox-active ligands [42,47,53,54].
- The stability of the oxidized ligand can be further increased through delocalization of the ligand radical over a larger π -system [49,52].

Summary and outlook

In this review, we have stated the most important design principles and lessons learned by the homogeneous catalysis community for the design of WOCs based on FRTMs. Pinpointing these design principles aid in the understanding and development of a new generation of sustainable WOCs that we ultimately need for the energy transition toward renewable fuels.

Figure 4



Alternative pathway for O–O bond formation for Cu-based WOCs and two Cu-based WOCs with redox-active ligands (green).

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Dennis Hetterscheid reports financial support was provided by the European Research Council. Dennis Hetterscheid reports financial support was provided by the Nederlandse Organisatie voor Wetenschappelijk Onderzoek.

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