ChemPubSoc Europe

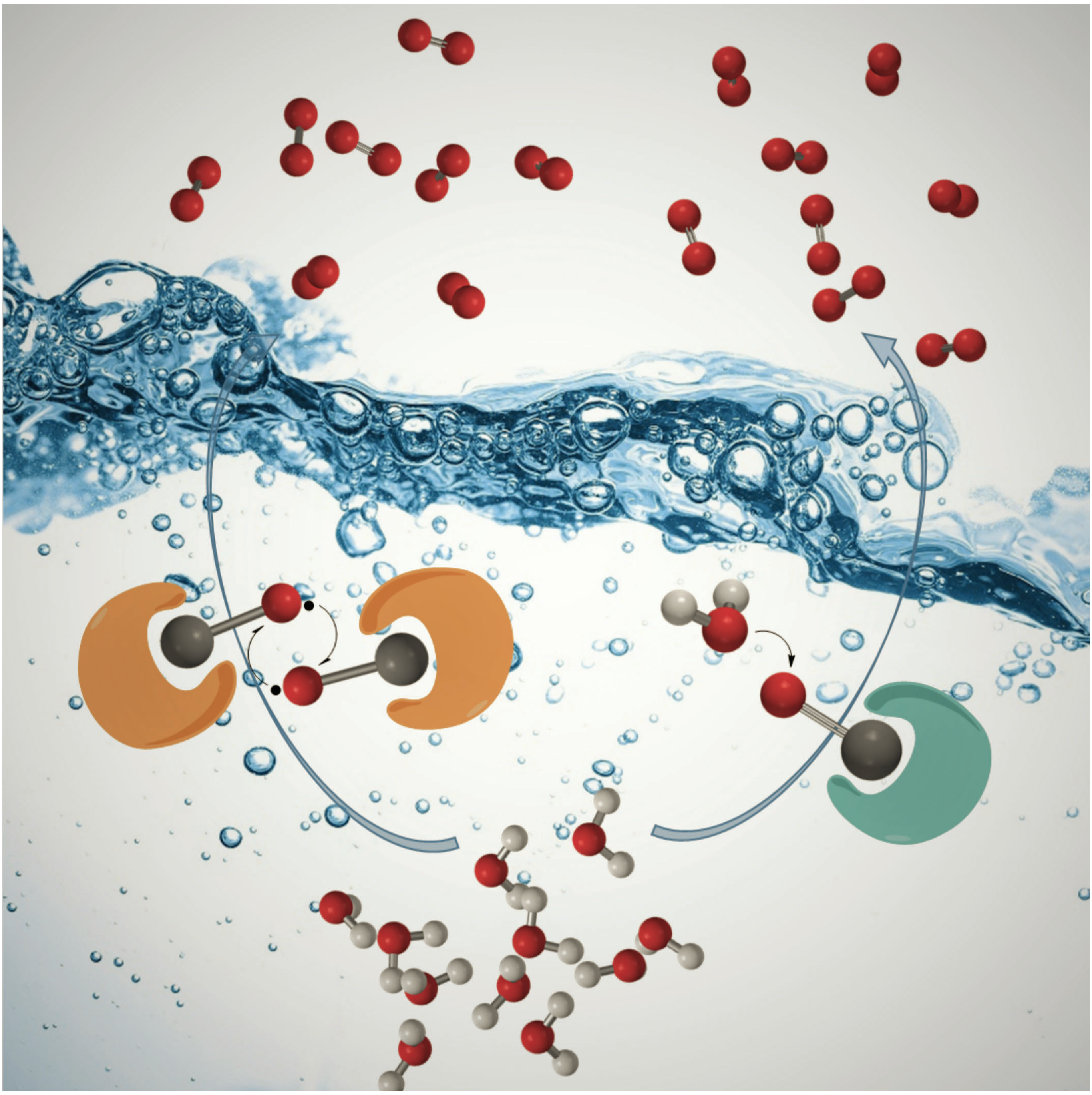
DOI: 10.1002/chem.201702850

CHEMISTRY
A European Journal
Concept

Water Oxidation

Rational Design Rules for Molecular Water Oxidation Catalysts based on Scaling Relationships

Joeri Hessels,[a] Remko J. Detz,[a] Marc T. M. Koper,[b] and Joost N. H. Reek*[a]



Abstract: Lowering the overpotential required for water oxidation is of paramount importance for the efficient production of carbon-neutral fuels. This article highlights the intrinsic influence of the water oxidation mechanism used by molecular catalysts on the theoretically achievable minimal overpotential, based on scaling relationships typically used for heterogeneous catalysts. Due to such scaling relationships, catalysts that operate through the water nucleophilic attack mechanism have a fundamental minimal overpotential of about 0.3 V, whereas those that follow the dinuclear radical oxo coupling mechanism should in principle be able to operate with a lower overpotential. Therefore, it is recommended to design catalysts operating through the latter mechanism to achieve very efficient water oxidation systems.

Introduction

The extensive use of fossil fuels causes ever increasing CO_2 levels, resulting in global warming. The conversion to a society that runs on sustainable energy is therefore crucial and urgent. In addition to the generation of electricity from sustainable resources, the development of carbon-neutral fuels, possibly using these resources, is of paramount importance. The current most promising approaches are based on water splitting, in which water is oxidized to oxygen, providing electrons and protons for the reduction reaction. Both proton reduction, to produce hydrogen, and CO_2 reduction, to produce carbon-based fuels, provide carbon-neutral fuels if driven by sustainable energy (Figure 1).[1] As these overall reactions are uphill, the net effect is that sustainable energy is stored in the form of fuel, providing a solution for both long-term energy storage and for processes requiring energy-dense fuels. Importantly, water is an attractive resource as reagent to make fuels as it is available in sufficient quantities on a global scale and is formed as a product upon combustion of the fuels, thereby closing the cycle.

However, the water oxidation reaction to form oxygen remains a challenging reaction to catalyze efficiently (Figure 1).[2] Therefore, the development of catalysts for water oxidation received considerable attention in the past decade.[2,3] The approaches followed for the development of homogeneous and heterogeneous catalysts are different; however, considering that the reaction pathways may be the same, the design strategies and conclusions could be mutually inspirational. Here, we show that the energetic scaling relationships between catalytic intermediates that has been derived in the field of heterogeneous catalysis can also be applied to facilitate rational approaches in the field of homogeneous water oxidation catalysis. Catalysts are required for both oxidation and reduction reactions to occur efficiently, which means high reaction rates at low overpotential. The stability and activity of catalysts should be maximized, whereas the potential at which these catalysts operate has to be minimized to reduce losses in the transformation of sustainable energy into fuel. The thermodynamic potential for water oxidation is 1.23 V [vs. standard hydrogen electrode (SHE)] at pH 0, and scales with pH (−0.059 V per pH unit) according to the Nernst equation. However, in practice this thermodynamic potential is never attained because an overpotential is needed to drive the reaction. In heterogeneous electrocatalysis, it has been concluded that this overpotential is due to the fact that the reaction has several catalytic intermediates, and that it is difficult to find a catalyst that binds all these intermediates optimally. By optimal, we mean a thermodynamically flat landscape with no uphill or downhill steps, such that energy losses are minimized. This condition is equivalent to the so-called Sabatier principle, which dictates that intermediates have to bind with optimized strength to the catalyst, that is, not too weak and not too strong.[4] If an intermediate binds too strongly it will poison the catalyst and if it binds too weakly, catalysis is limited by substrate binding. This relation is expressed in a so-called volcano plot, in which typically the catalytic activity is plotted versus the binding energy of the key intermediate, with the best catalyst at the apex of the volcano where the intermediate binds with optimal strength. For the proton reduction reaction, clear volcano plots have been obtained because this reaction proceeds through a single catalytic intermediate.[5] Plotting the activity or the overpotential versus the binding energy of the hydride intermediate results in a volcano plot (Figure 2).[6] Platinum has almost the optimal binding energy for the hydride, that is, half the dissociation energy of H_2, and indeed is known as the best metal catalyst for this reaction. Hydrogenase enzymes also perform this reaction near the thermodynamic potential and have a similar optimal binding affinity towards hydrogen.[7]

Reduction reactions:

$$2\,H^+ + 2\,e^- \xrightarrow{PRC} H_2 \qquad E^0 = 0.00\ V\ vs.\ RHE$$

$$CO_2 + X\,H^+ + Y\,e^- \xrightarrow{CO_2RC} CO,\ CHOOH,\ CH_3OH\ or\ C_nH_x$$

Oxidation reaction:

$$2\,H_2O \xrightarrow{WOC} 4\,H^+ + 4\,e^- + O_2 \qquad E^0 = +\,1.23\ V\ vs.\ RHE$$

Figure 1. Redox reactions for sustainable fuel formation (PRC = proton reduction catalyst, $CO_2RC = CO_2$ reduction catalyst and WOC = water oxidation catalyst).

The main reason why water oxidation is so much more challenging is that it involves two water molecules that together undergo four proton and four electron transfer steps (Figure 1) to generate oxygen. This leads to a multitude of intermediates that can form, which as a consequence results in a multidi-

---

[a] *J. Hessels, Dr. R. J. Detz, Prof. Dr. J. N. H. Reek*
Homogeneous, Supramolecular and Bio-Inspired Catalysis
University of Amsterdam, HIMS
Science Park 904, 1098 XH Amsterdam (The Netherlands)
E-mail: j.n.h.reek@uva.nl

[b] *Prof. Dr. M. T. M. Koper*
Leiden Institute of Chemistry, Leiden University
POX 9502, 2300 RA Leiden (The Netherlands)

The ORCID number(s) for the author(s) of this article can be found under: https://doi.org/10.1002/chem.201702850.

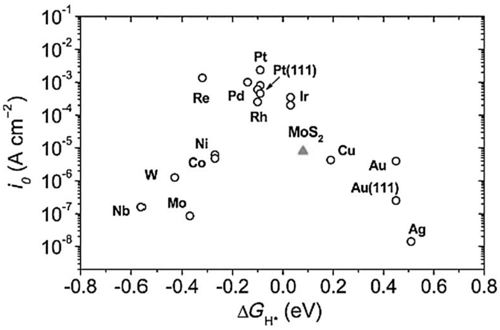


Figure 2. Volcano plot for H_2 evolution.[6b] From [*Science* **2007**, *317*, 100–102]. Reprinted with permission from AAAS.

mensional volcano plot. For water oxidation to occur with low overpotential, these intermediates should differ by 1.23 eV in energy, to generate the flat thermodynamic landscape (Sabatier optimum) mentioned above. However, because these different intermediates bind to the catalyst in a similar way, their binding energies cannot be optimized individually. These energetic relationships between catalytic intermediates are known as scaling relationships.[8] Due to the scaling relationships, the best catalyst has a non-zero thermodynamic overpotential, and is therefore sub-optimal. Interestingly, there are two well-known reaction mechanisms for water oxidation catalysis by which homogeneous catalysts oxidize water and these differ in the type and number of intermediates that are required to complete the catalytic cycle. By using the scaling relationship approach typically used for heterogeneous catalysts, we can rationalize the influence of the mechanism on the minimal overpotential that can be attained.

Mechanisms for Water Oxidation

The two different mechanisms for water oxidation catalysis are known as the water nucleophilic attack (WNA) mechanism and the radical oxo coupling (ROC, Figure 3) mechanism. The WNA mechanism is the dominantly proposed mechanism for metal-oxide surfaces and for most molecular catalysts.[3a] This mechanism has three intermediates. First, H_2O coordinates to a vacant site, where it is converted to a hydroxy group after oxidation and deprotonation (Figure 3, intermediate B). This species undergoes a second proton and electron transfer resulting in an oxo-species (Figure 3, intermediate C). Subsequently, a peroxo-species is formed after nucleophilic attack by a second H_2O molecule, accommodated by a proton-coupled electron transfer (Figure 3, intermediate D). In the final oxidation step, again involving proton-coupled electron transfer, oxygen is released and the catalyst is recovered.[9] DFT calculations have shown that scaling relationships occur between intermediate B and D on metal-oxide surfaces (but also on a variety of other catalysts), because the OH and the OOH groups bind in an identical fashion to the catalyst.[10] There exists a fixed energy difference between OOH and OH of about 3.2 ± 0.2 eV instead of the desired 2.46 eV.[11] This fixed energy difference results into a fundamental thermodynamic overpotential of $(3.2\pm0.2-2.46)/2\approx0.3$ V for the WNA mechanism (Figure 4). This scaling relationship between the M–OOH and M–OH intermediates has been established for heterogeneous catalysts, but molecular complexes should follow the same scaling as long as the ligand environment does not change during catalysis and the water nucleophilic attack is external. Essentially, the high energy difference between M–OOH and M–OH expresses the high energy (instability) of the peroxide intermediate. DFT calculations by Calle-Vallejo et al. have shown that both functionalized graphitic materials and molecular porphyrins display similar trends between O, OH, and OOH binding at metal-oxide surfaces.[12]

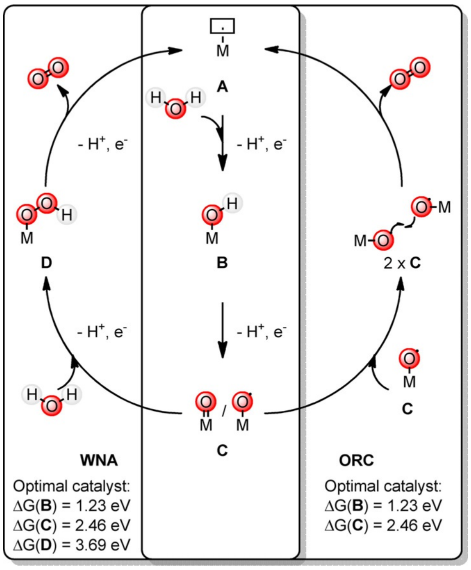


Figure 3. The two possible mechanisms for water oxidation, water nucleophilic attack (WNA) and radical oxo coupling (ROC) and the optimal energy levels of their intermediates.[9]

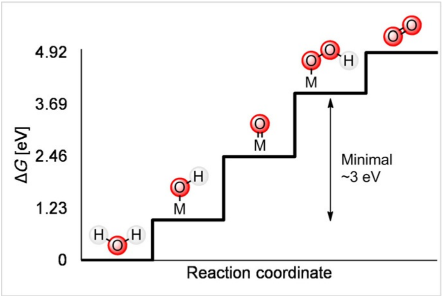


Figure 4. Potential levels for an optimized water oxidation catalyst operating through the water nucleophilic attack mechanism.

Interestingly, certain molecular catalysts have been claimed to operate through an ROC mechanism (Figure 3).[3a, 13] In this mechanism, two metals with a vacant site go through the first two proton and electron transfers resulting in two metal-oxo species, identical to the first two steps of WNA (Figure 3, intermediate C). Instead of a nucleophilic attack by water, these two oxo-species couple in a bimolecular reaction, and release oxygen and the two catalytic metal centers. The essential difference between ROC and WNA is that the peroxo intermediate D (Figure 3) is not part of the catalytic cycle for ROC, thus the scaling relationship between M–OOH and M–OH will be irrelevant. As a consequence, water oxidation following the ROC mechanism does not suffer from the fundamental minimal overpotential of about 0.3 V. DFT calculations on metal oxides and porphyrinic materials have shown that there still is a scaling relation between the binding energies of M–OH and M=O, expressed in Equation (1):

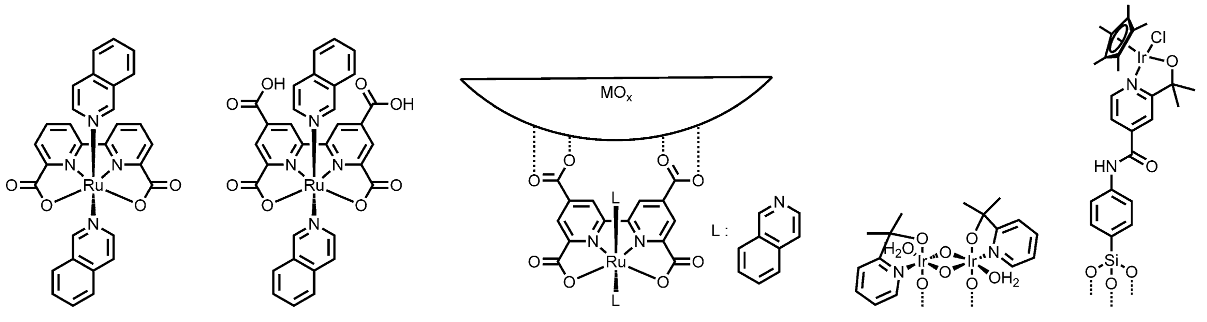
$$\Delta G(\mathrm{OH}) \approx 0.5{*}\Delta G(\mathrm{O}) + \mathrm{K(O,OH)} \qquad (1)$$

in which K(O,OH) is a constant depending on the class of materials to which the scaling relationship applies. The factor 0.5 expresses the fact that O typically binds through a double bond and OH through a single bond, although for real oxo-radical species, the double bond character is lower.[11a] This scaling relationship is also much less detrimental to the overall water oxidation activity than the scaling between M–OOH and M–OH in the WNA mechanism. Within a suitable class of catalysts, it is possible to have binding energies of OH and O that are close to optimal, with $\Delta G(\mathrm{O}) - \Delta G(\mathrm{OH}) \approx 1.23$ eV. In the DFT calculations of Calle-Vallejo et al. on porphyrinic materials, iridium and iron based porphyrins appear to be close to this optimum, but we stress that the optimal metal center should be very sensitive to the ligand environment.[12] In addition, important prerequisites for the ROC mechanism are that the metal-oxo species has considerable spin density residing on the oxygen atom, to allow for feasible coupling, and that the metallo-oxo radicals can easily reach each other in the coupling step.[14] The radical character of these metal-oxo species is highly sensitive to the ligand environment.[15] Calculations indicate that nature's water oxidation catalyst, the Mn_4Ca cluster in photosystem II, also avoids the water nucleophilic attack mechanism; preventing the formation of a high energy peroxide intermediate.[16]

Experimental Examples

In recent literature, several examples of molecular complexes have been reported that appear to catalyze the water oxidation reaction with a lower overpotential than that predicted for a WNA pathway.[17] For instance, several ruthenium complexes show extremely low overpotential, as reported by the group of Sun. Complex **1** starts to oxidize water very close to the equilibrium potential, and according to mechanistic studies operates through the ROC mechanism (Figure 5).[18] The overpotential at the onset of water oxidation of the closely related complex **2** is 0.17 V.[19] Interestingly, when complex **2** is anchored to an ITO surface, the overpotential at the onset of water oxidation increases to 0.3 V. This higher overpotential is presumably caused by a change in mechanism to WNA; the ROC mechanism may be prohibited because the ruthenium centers are not in close proximity due to the fixation on the electrode surface (Figure 5, **2@MO$_x$**). Therefore, the WNA mechanism dominates, resulting in a higher overpotential. Another class of molecular catalysts with a very low overpotential are the iridium catalysts reported by Brudvig, Crabtree and co-workers.[20] Recently, they showed that when molecular iridium dimer catalyst **3** was anchored to an ITO surface, a very low onset potential was found of only 14 mV as reported by the authors (Figure 5, **3@MO$_x$**).[21] This dimeric complex presumably operates through the ROC mechanism.[20] The dimeric nature of this type of iridium catalysts is also supported by kinetic analysis of the reaction progress.[22] When mononuclear iridium catalyst **4** was anchored to an ITO surface, with no freedom to come in close proximity to a second iridium center, preventing ROC, indeed a much higher overpotential of 462 mV was found at the onset of water oxidation (Figure 5, **4@MO$_x$**).[23]

These examples show that the ROC mechanism can indeed lead to powerful catalysts for water oxidation that are active at low overpotential. To design new transition-metal catalysts that operate through this mechanism, two prerequisites need to be fulfilled: 1) the metallo-oxo species should have sufficient spin density at the oxygen atom (Figure 3, intermediate C) and 2) two metal-oxo species should be able to react to form the oxygen–oxygen bond.[24] To allow this final step, the complexes should at least have sufficient space around the oxygen radical to allow this reaction, and one may also facilitate this step by



1 **2** **2@MO$_x$** **3@MO$_x$** **4@MO$_x$**

Figure 5. Ruthenium and iridium WOCs discussed in this paper.

preorganizing the two metal sites. Along these lines, many dinuclear complexes have been prepared to bring the two metal centers in close proximity, but oftentimes these perform worse than their mononuclear analogues.[25] It is likely that these dinuclear complexes are too rigid because the M–OH_2, M–OH, and M=O intermediates should all be accommodated and require different optimal metal–metal distances. In addition, the M-*O*-O-M dihedral angle during the O–O bond formation is important because the *cis*-like structure (M-*O*-O-M $\approx 0^\circ$) is anticipated to be much higher in energy then the *trans* (M-*O*-O-M $\approx 180^\circ$), in analogy to that reported for hydrogen peroxide.[26] In the design of dinuclear systems, flexibility is therefore considered to be very important. In that respect, the generation of dinuclear systems using weak supramolecular interactions might be key because it allows pre-organization of the two metal-oxo species and at the same time, it provides the required flexibility. As an interesting example, ruthenium complexes **1** and **2** in Figure 5 are excellent catalysts and have been proposed to dimerize based on relatively weak π-π stacking interactions.[18a,27] Providing ligand design rules to increase spin density on the metal-oxo species is less straight forward, however, several general strategies can be employed. Pushkar and co-workers showed that destabilization of the π-bond in metal-oxo species can induce high-spin density on the oxygen atom.[28] In addition, overcoordination of a metal center can also lead to increased spin density on the oxygen atom.[15] Importantly, this means that a small variation in the ligand backbone can already change the coordination number during catalysis, and thus the mechanism, which has been demonstrated for ruthenium WOCs.[15,29] Calculations by Chen and co-workers also indicated that the mechanism in ruthenium WOCs is very sensitive to the structure of the backbone.[30] These examples show that it is possible to increase spin density on the metal-oxo species by rational approaches, but more detailed mechanistic investigations are required to allow a priori predictions on which mechanism a catalyst will follow. Inspiration from nature may be helpful, for example hemoproteins can control the radical character by axial ligand coordination; heme groups in p450 enzymes with an axial cysteine ligand have metallo-oxo species with radical character, whereas the heme in myoglobin with an axial histidine facilitates oxygen binding where there is no radical character.

Conclusions and Outlook

The overpotential of homogeneous water oxidation catalysts can be understood in qualitative terms using the scaling relations derived in heterogeneous electrocatalysis. Catalysts that operate through the ROC mechanism can have an intrinsic lower overpotential for water oxidation than those that go through WNA. Specifically, water oxidation catalysts operating with the external WNA mechanism have a fundamental minimal overpotential of about 0.3 V, due to the scaling relationship between M–OOH and M–OH intermediates. In contrast, water oxidation catalysts that undergo the ROC mechanism do not feature the M–OOH intermediate, and the scaling relationship between M=O and M–OH in the ROC mechanism does not in principle impose a fundamental minimal overpotential. Several examples of molecular catalysts that perform water oxidation at very low overpotential operate through the ROC mechanism. This shows that when designing and optimizing WOCs, there should be focus on the mechanism of action of the catalyst. In addition, in the design of electrodes based on molecular catalysts, the mechanism should be taken into consideration such that for the ROC mechanism, two metal-oxo species should be able to react in a bi-molecular fashion. The insight provided in this article should inspire the development of new (first row) transition-metal catalysts with a low overpotential, ultimately leading to more efficient water oxidation, a prerequisite for sustainable fuel production.

Acknowledgements

This work is part of the research programme of the Foundation for Fundamental Research on Matter (FOM), which is part of the Netherlands Organisation for Scientific Research (NWO). R.J.D. and J.N.H.R. kindly acknowledge the University of Amsterdam for funding through the SOLARDAM program.

Conflict of interest

The authors declare no conflict of interest.

Keywords: electrochemistry · nucleophilic attack · radical-oxo coupling · scaling relationships · water splitting

[1] a) V. S. Thoi, Y. Sun, J. R. Long, C. J. Chang, *Chem. Soc. Rev.* **2013**, *42*, 2388 – 2400; b) J. Schneider, H. Jia, J. T. Muckerman, E. Fujita, *Chem. Soc. Rev.* **2012**, *41*, 2036 – 2051; c) H. Takeda, C. Cometto, O. Ishitani, M. Robert, *ACS Catal.* **2017**, *7*, 70 – 88.
[2] J. D. Blakemore, R. H. Crabtree, G. W. Brudvig, *Chem. Rev.* **2015**, *115*, 12974 – 13005.
[3] a) X. Sala, S. Maji, R. Bofill, J. Garcia-Antón, L. Eschriche, A. Llobet, *Acc. Chem. Res.* **2014**, *47*, 504 – 516; b) M. D. Kärkäs, O. Verho, E. V. Johnston, B. Åkermark, *Chem. Rev.* **2014**, *114*, 11863 – 12001; c) N.-T. Suen, S.-F. Hung, Q. Quan, N. Zhang, Y.-J. Xu, H. M. Chen, *Chem. Soc. Rev.* **2017**, *46*, 337 – 365.
[4] a) G. Rothenberg in *Catalysis: Concepts and Green Applications*, Wiley-VCH, Weinheim, **2008**, p. 65; b) B. Hinnemann, P. G. Moses, J. Bonde, K. P. Jørgensen, J. H. Nielsen, S. Horch, I. Chorkendorff, J. K. Nørskov, *J. Am. Chem. Soc.* **2005**, *127*, 5308 – 5309.
[5] N. M. Marković, P. N. Ross, *Surf. Sci. Rep.* **2002**, *45*, 117 – 229.
[6] a) A. B. Laursen, A. S. Varela, F. Dionigi, H. Fanchiu, C. Miller, O. L. Trinhammer, J. Rossmeisl, S. Dahl, *J. Chem. Educ.* **2012**, *89*, 1595 – 1599; b) T. F. Jaramillo, K. P. Jørgensen, J. Bonde, J. H. Nielsen, S. Horch, I. Chorkendorff, *Science* **2007**, *317*, 100 – 102.
[7] F. A. Armstrong, J. Hirst, *Proc. Natl. Acad. Sci. USA* **2011**, *108*, 14049 – 14054.
[8] J. Greeley, *Annu. Rev. Chem. Biomol. Eng.* **2016**, *7*, 605 – 635.
[9] The mechanisms depicted here are a simplification of reality because the assumption of proton-coupled electron transfer is probably not valid for every step in the mechanism. Many WOCs exhibit a pH-dependent reactivity that is more complex than the mechanisms depicted in Figure 3.
[10] I. C. Man, H.-Y. Su, F. Calle-Vallejo, H. A. Hansen, J. I. Martínez, N. G. Inoglu, J. Kitchin, T. F. Jaramillo, J. K. Nørskov, J. Rossmeisl, *ChemCatChem* **2011**, *3*, 1159 – 1165.
[11] a) M. T. M. Koper, *J. Electroanal. Chem.* **2011**, *660*, 254 – 260; b) M. T. M. Koper, *Chem. Sci.* **2013**, *4*, 2710 – 2723.

[12] F. Calle-Vallejo, J. I. Martínez, J. M. García-Lastra, E. Abad, M. T. M. Koper, *Surf. Sci.* **2013**, *607*, 47 – 53.

[13] T. Kikuchi, K. Tanaka, *Eur. J. Inorg. Chem.* **2014**, 607 – 618.

[14] T. Fan, S. Zhan, M. S. G. Ahlquist, *ACS Catal.* **2016**, *6*, 8308 – 8312.

[15] T. Fan, L. Duan, P. Huang, H. Chen, Q. Daniel, M. S. G. Ahlquist, L. Sun, *ACS Catal.* **2017**, *7*, 2956 – 2966.

[16] P. E. M. Siegbahn, *Proc. Natl. Acad. Sci. USA* **2017**, *114*, 4966 – 4968.

[17] The concept of “overpotential” is poorly defined experimentally. Comparison of “overpotentials”, especially between homogeneous and heterogeneous catalysts, should therefore be performed carefully, keeping in mind that such a comparison is only meaningful if the catalytic rates for oxygen evolution per active site are equal at the given overpotentials. Even then, rates may vary with potential differently for two different catalysts.

[18] a) L. Duan, F. Bozoglian, S. Mandal, B. Stewart, T. Privalov, A. Llobet, L. Sun, *Nat. Chem.* **2012**, *4*, 418 – 423; b) L. Duan, A. Fischer, Y. Xu, L. Sun, *J. Am. Chem. Soc.* **2009**, *131*, 10397 – 10399; c) L. Duan, C. M. Araujo, M. S. G. Ahlquist, L. Sun, *Proc. Natl. Acad. Sci. USA* **2012**, *109*, 15584 – 15588.

[19] T.-T. Li, W.-L. Zhao, Y. Chen, F.-M. Li, C.-J. Wang, Y.-H. Tian, W.-F. Fu, *Chem. Eur. J.* **2014**, *20*, 13957 – 13964.

[20] J. M. Thomsen, D. L. Huang, R. H. Crabtree, G. W. Brudvig, *Dalton Trans.* **2015**, *44*, 12452 – 12472.

[21] S. W. Sheehan, J. M. Thomsen, U. Hintermair, R. H. Crabtree, G. W. Brudvig, C. A. Schmuttenmaer, *Nat. Commun.* **2015**, *6*, 6469 – 6477.

[22] J. M. Koelewijn, M. Lutz, W. I. Dzik, R. J. Detz, J. N. H. Reek, *ACS Catal.* **2016**, *6*, 3418 – 3427.

[23] K. L. Materna, B. Rudshteyn, B. J. Brennan, M. H. Kane, A. J. Bloomfield, D. L. Huang, D. Y. Shopov, V. S. Batista, R. H. Crabtree, G. W. Brudvig, *ACS Catal.* **2016**, *6*, 5371 – 5377.

[24] We focus on catalyst design enabling the ROC mechanism. However, this is not the only parameter to arrive at efficient WOCs because a complex needs to be able to access high oxidation states and must be stable under highly oxidative conditions. For a recent review see, P. Garrido-Barros, C. Gimbert-Suriñach, R. Matheu, X. Sala, A. Loblet, *Chem. Soc. Rev.* **2017**, *46*, 6088 – 6098.

[25] J. Graeupner, U. Hintermair, D. L. Huang, J. M. Thomsen, M. Takase, J. Campos, S. M. Hashmi, M. Elimelech, G. W. Brudvig, R. H. Crabtree, *Organometallics* **2013**, *32*, 5384 – 5390.

[26] a) R. H. Hunt, R. A. Leacock, C. W. Peters, K. T. Hecht, *J. Chem. Phys.* **1965**, *42*, 1931 – 1946; b) O. Ferchichi, N. Derbel, N.-E. Jaidane, T. Cours, A. Alijah, *Phys. Chem. Chem. Phys.* **2017**, *19*, 21500 – 21506.

[27] S. Zhan, D. Mårtensson, M. Purg, S. C. L. Kamerlin, M. S. G. Ahlquist, *Angew. Chem. Int. Ed.* **2017**, *56*, 6962 – 6965; *Angew. Chem.* **2017**, *129*, 7066 – 7069.

[28] D. Moonshiram, I. Alperovich, J. J. Concepcion, T. J. Meyer, Y. Pushkar, *Proc. Natl. Acad. Sci. USA* **2013**, *110*, 3765 – 3770.

[29] L. Tong, L. Duan, Y. Xu, T. Privalov, L. Sun, *Angew. Chem. Int. Ed.* **2011**, *50*, 445 – 449; *Angew. Chem.* **2011**, *123*, 465 – 469.

[30] R. Kang, K. Chen, J. Yao, S. Shaik, H. Chen, *Inorg. Chem.* **2014**, *53*, 7130 – 7136.

Manuscript received: June 21, 2017
Accepted manuscript online: August 24, 2017
Version of record online: November 6, 2017