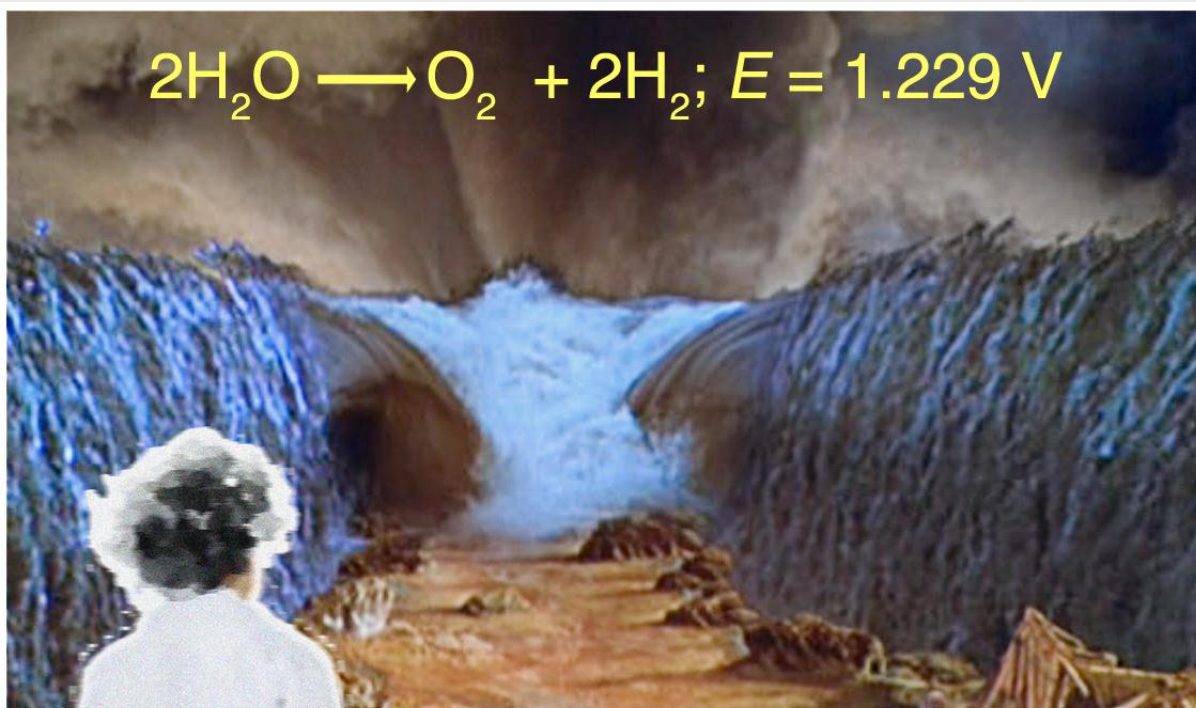


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Water oxidation at electrodes modified with Earth-abundant transition metal catalysts

José Ramón Galán-Mascarós^[a,b]



SPLITTING
WATER IN
MODERN
TIMES

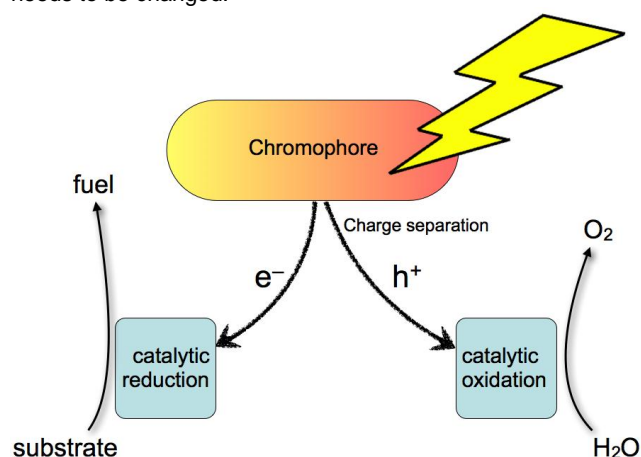
1. Introduction

The development of a real alternative to fossil fuels is one of the most important challenges that scientists are facing at present.^[1] Without a viable renewable energy source able to match global energy consumption, it will not be possible to maintain technological progress and living standards in a viable environment -- at least as we know it. The retrieval and use of fossil fuels has a deleterious impact on the environment that cannot be neglected, and it reaches beyond the controversial climate change. Toxic emissions and greenhouse gases, mainly CO₂, are changing the atmospheric equilibrium where human life has evolved in the last hundred thousand years, with uncertain consequences.

Artificial photosynthesis (Scheme 1),^[2] as a process in which solar energy will be used to reduce a substrate into an energy rich chemical (H⁺ to H₂, or CO₂ to CO or CH₃OH, for example), while oxidizing water to molecular oxygen, is a dream that may come true if the technology becomes robust enough and cost-effective.^[3-11] Solar water splitting is not a strictly scientific problem. Water can be readily split into oxygen and hydrogen using as power source a commercial photovoltaic cell and a pair of electrodes. Indeed, there are several large scale projects working on the combination of renewable energy sources with commercially available water electrolyzers.^[12] Furthermore, the wireless artificial leaf^[13] already exists, and works. The problem is to make the process competitive.^[14] Fossil fuels are so cheap, that the transformational driving-force cannot be exclusively environmental issues and policy-makers. Only a financially attractive green alternative will be able to promote a true societal change.

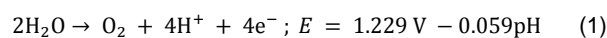
In this regard, the search for a robust, efficient and inexpensive water oxidation catalyst (WOC) appears to be one of the main challenges. This does not mean that the other processes of an artificial photosynthesis scheme cannot be

improved.^[15] Particularly the membrane responsible for fast proton exchange, while efficiently separating products, is another bottleneck.^[16] However, the lack of a stable inexpensive water oxidation catalyst able to work under mild conditions is, arguably, the main reason for the low commercial impact of water electrolysis, which accounts for less than 2% of the total worldwide H₂ production. Some 96 % of the world hydrogen production still comes from fossil fuels reforming. Proton-exchange membrane (PEM) electrolyzers need noble metals as catalysts, and ultra-pure water as feedstock. Noble-metal-free commercial water electrolyzers depend on highly alkaline conditions, and work at low efficiencies. In the absence of these technologies, a photovoltaic plus electrolyzer scheme is far from becoming economically relevant. This needs to be changed.



Scheme 1. An artificial photosynthesis scheme.

This review intends to be a broad and critical description of the state-of-the-art regarding the oxygen evolving reaction (OER) in water oxidation electrocatalysts (Eq. 1) obtained from earth-abundant metals -- in other words, those technologically relevant for energy production. In this direction, it is clear that the OER in a solar to fuels scheme will be required to occur at heterogeneous electrodes. Furthermore, mass production will require abundant material sources. Our analysis of their pros and cons will be complementary to more general recent reviews, focused on another aspects of this crucial challenge.^[17-23]



2. Heterogeneous electrocatalysts

2.1. Metal oxides

[a] Prof. J. R. Galan-Mascaros
Institute of Chemical Research of Catalonia (ICIQ)
Av. Paisos Catalans, 16, E-43007, Tarragona, Spain
E-mail: jrgalan@iciq.es

[b] Prof. J. R. Galan-Mascaros
Catalan Institution for Research and Advanced Studies (ICREA)
Passeig Lluís Companys, 23, E-08010, Barcelona, Spain

“JR” Galán-Mascarós received his PhD from University of Valencia, working with Prof. E. Coronado. After a post-doctoral stay with Prof. Kim R. Dunbar at Texas A&M University, he returned to Valencia as a Research Fellow (Ramon y Cajal program). Currently, he is ICREA Research Professor at the Institute of Chemical Research of Catalonia (ICIQ), where he joined in 2009. His interests are centered in the application of coordination chemistry tools to solve chemical challenges in such fields such as solar fuels, and materials.



Electrocatalytic properties of metal oxides have been studied for decades.^[24-26] Regarding water electrolysis, metal oxides have been heavily investigated since the 1960s and, indeed, they form part of commercially available electrolyzers.^[27] There are two main drawbacks to first-row transition metal oxides as WOCs:

i) Difficult characterization and benchmarking. The activity of metal oxides depends on many parameters such as preparative conditions, aging, thermal treatment, precursors, processing, surface morphology, blending with supports, etc. Experimental conditions need to be carefully controlled to obtain consistent results

ii) Strict working conditions. First row transition metal oxides are excellent WOC in alkali media, but underperform in neutral conditions, and are inactive in acidic media. Higher versatility would be desirable.

The lack of exact structural and electronic information on the active sites make it difficult to model and optimize these WOCs,^[28,29] although some interesting results have been obtained albeit with some uncertainties.^[30-32]

Several reviews have been published from different perspectives,^[33-36] although the literature on the use of first row transition metal oxo/hydroxides for water oxidation is so vast that it is an impossible task to classify and put into context all the results. After decades of research, there are still many open controversies regarding function, stability and performance, with contradictory data available. It is also surprising to find many redundancies, with analogous results published by different groups, in multiple journals.

A comprehensive review of first row transition metal oxide catalysts would be a very useful contribution. Nevertheless, the present article will focus in the main certainties and in some of the open questions about the state-of-the-art in this field.

2.1.1. Cobalt oxides

Co₃O₄ is a typical electrocatalyst with many applications.^[37] Indeed, electrochemical deposition of CoO_x from a buffered solution was first reported over a century ago.^[38,39] Along with other metal oxides, CoO_x was commonly used as a cathode for electrochemical water splitting since the 1970s.^[40,41] Currently, cobalt is the element of choice in WOC research since it has yielded the richest family of WOCs (and also catalysts for the hydrogen evolution reaction, HER).^[42]

The discovery of a self-repairing mechanism operating at neutral pH when the CoO_x cathodes are used in a phosphate (P_i) electrolyte renewed the interest in metal oxides as viable WOCs.^[43,44] To highlight the distinct robustness in this media, these CoO_x catalysts were referred to as "CoP_i", although the role of the P_i anions is exclusively structural, in stabilizing the CoO_x catalytic domains to avoid Co leaching.^[45] This CoP_i catalyst can be better described as layered CoO_x with molecular dimensions, stabilized at neutral pH by the PO₄ groups.^[46] The P_i electrolyte also plays a role by facilitating rapid proton transfer,^[47] and improving the kinetics of the process.^[48]

CoP_i has been extensively studied, including EQCM formation/stability,^[49] electronic structure^[50] and its similarities with the PSII cluster.^[51,52] The growth mechanism of CoP_i films depends on many parameters, including pH, applied voltage and electrolyte. Better performance has been claimed when grown from acetate buffered solution,^[53] or using cobaloximes

as cobalt source.^[54] Self-repair was confirmed to occur at pH values > 6.^[55] Mechanistic studies have also been completed.^[48] The fast kinetics of CoP_i were empirically determined to depend on the catalytic rate constant but also on proton-electron transfer.^[56] Thus, the current density increases with film thickness until reaching saturation as a result of mutual compensation between catalytic rate and proton-electron transfer. An optimal film thickness of 1.44 μm was defined in high buffer concentration solution. When electrodeposited on large surface area electrodes, currents over 100 mA cm⁻² have been reached, working in buffered natural waters.^[57]

Another attractive characteristic of CoP_i is its bi-functionality, since it can be reversibly catalyze OER or the hydrogen evolving reaction (HER) through a self-repairing equilibrium with Co²⁺ species in solution.^[58] In this line, mesoporous Co₃O₄ has proved to be stable achieving high current densities both for OER and for the oxygen reduction reaction (ORR),^[59] showing potential to replace noble metal-based catalysts in air-metal batteries.

Bard *et al.* compared Co₃O₄ and CoP_i using dynamic potential-pH diagrams.^[60] The overall higher activity of CoP_i was attributed to higher hydration, leading to an increase in the number of accessible sites.^[61] On the other hand, CoP_i showed a significant decrease of current at high current densities. Although this could be due to oxygen bubble formation, the authors ruled out this explanation. CoP_i did not show any current decrease at pH 14, reaching over 10 mA cm⁻². Thus, current drop, occurring up to pH 12, is probably due to the self-healing process, where cobalt ions need to be re-oxidized from solution to the electrode. This instability, however, was not observed for analogous Co₃O₄ electrodes, probably due to their better mechanical strength and better adhesion to the support. This demonstrates that electrode preparation is key in reaching high current densities that can show significant differences. Substrate support showed no significant influence, and high phosphate concentrations allowed higher currents.

Since CoO_x preparation controls performance, multiple processing techniques have been tested.^[62-65] Aging also has a strong effect on activity.^[66] Inelastic X-ray scattering and absorption support an active CoOOH environment, with significant presence of Co⁴⁺ sites as potential increases in this non-stoichiometric catalyst.^[67] Lithium and lanthanide doping has also been tested.^[68-70]

Nanostructured Co₃O₄ improves catalytic performance, by increasing the surface to volume ratio.^[71,72] Nanoparticles can be prepared by pulsed laser ablation, and drop-casted on pyrolytic graphite,^[73] exhibiting higher turnover frequency (TOF). A single cobalt monolayer has been deposited on gold electrodes to control mass loading and surface area. Under these conditions, phosphate in solution still enhanced the current, four times larger than in the absence of PO₄³⁻ electrolyte.^[74] The activity of nanoparticles of different CoO_x have been shown to be very similar under basic conditions at identical size and shape, independent of stoichiometry.^[75] This indicates that, during water oxidation, the same active species evolve in all cases.

One of the most comprehensive studies on the CoO_x catalysts was carried out by Gerken *et al.*^[76] The activity of the Co²⁺(aq)/CoO_x system was analyzed in terms of pH, preparation and electrolyte. The catalytic activity follows the Pourbaix diagram derived from the thermodynamic properties

of CoO_x structures, assigning the structure of the CoO_x catalysts as prepared in situ on an electrode to that of layered double-hydroxides. This layered structure can support oxidation state change at the cobalt sites, while retaining the same coordination geometry. Proton transfers would compensate charge differences. As a function of pH, the resting state was determined to be Co^{4+} . The authors also argued that the catalytic activity observed in spinel type Co_3O_4 arises from structural remodeling of the latter to generate a layered double-hydroxide surface, the genuine active structure.^[77]

This surface transformation as the origin of the high catalytic activity is also supported by theoretical DFT calculations,^[28] which confer low activity on the regular sites of $\text{CoO}(\text{OH})$ and CoO_2 , the thermodynamically stable CoO_x phases under water oxidation conditions. This is also the case, for example, in the WOC activity found in $\text{Co}(\text{PO}_3)_2$ modified anodes.^[78] Nanocrystals of $\text{Co}(\text{PO}_3)_2$ were grown on Ni foam electrodes by thermal decomposition of the polymeric precursor $\{\text{Co}(\text{O}_2\text{P}(\text{OtBu})_2)_2\}_n$.^[79] These electrodes were claimed to improve the activity of Co_3O_4 , although surface differences and the use of Ni foam make this conclusion difficult to corroborate. Nevertheless, the formation of a CO_x surface species as the active site was confirmed, reducing the role of $\text{Co}(\text{PO}_3)_2$ to that of a catalyst support.

Without a doubt, CoO_x is the WOC that has been more often combined with photoanodes including TiO_2 , $\alpha\text{-Fe}_2\text{O}_3$, BiVO_4 , WO_3 , thallium oxynitride and carbon nitride to promote enhanced photocatalytic water oxidation.^[80-102] The success of CoO_x (or CoPi) has been attributed to its hole-scavenging capabilities,^[103] able to partially suppress surface recombination.^[104,105]

Cobalt oxide activity has also been investigated on semiconducting supports such as silicon,^[106] amorphous carbon,^[107] graphene,^[108] or single-wall carbon nanotubes,^[109] resulting in enhanced OER activity.

2.1.3. Nickel oxides

Although nickel oxides^[110] are used in commercially available alkaline electrolyzers,^[111,112] research wise, their use has been much more limited when compared with CoO_x .^[113] One possible explanation is the need for a highly basic medium,^[114,115] and a complex evolution of the catalyst with aging.^[116] Starting from the stable $\alpha\text{-NiO}(\text{OH})$, it dehydrates into $\beta\text{-NiO}(\text{OH})$. Under an applied oxidation potential in alkali media evolves (at least partially) into a mixture β - and $\gamma\text{-NiO}(\text{OH})$.^[113,117] However, the presence of another unknown phase **cannot be discarded**.^[118] Contradictory reports indicate that NiO_x activity can improve or decrease upon aging.^[113,119] The latter has been more commonly accepted with the high activity assigned to the $\beta\text{-NiO}(\text{OH})$ phase, and its deactivation allegedly due to the formation of Ni^{4+} during OER in alkaline media at high overpotentials.^[113, 120, 121] The only apparent conclusion is that OER NiO_x activity depends heavily on subtle differences in preparation and working conditions.^[110,122-125]

NiO_x Tafel behavior is unique, exhibiting a ca. 60 mV/decade slope at low overpotentials, and a larger 120 mV/decade at high overpotentials, indicating a different mechanism.^[126] This Tafel slope can be reduced through nanostructuring reaching 42 mV/decade, and very high current densities, always in alkaline media.^[127] The different

slope indicates a different mechanism, thus it cannot be due only to nanostructuring. Different active species must be present in these nanostructures.

Analogous to the CoPi work, NiO_x films can also be electrodeposited in a controllable fashion using a borate electrolyte.^[128,129] These films operate at higher pH (9.2) and require a pre-electrolysis treatment in order for their efficiency to increase two orders of magnitude.^[130] This has been initially related to an increase in the oxidation state of Ni centers, from Ni^{3+} to Ni^{4+} , at least on the surface of the films, although Ni^{4+} was thought to be inactive. HER activity has also been reported for these NiBi amorphous films.^[131]

NiO_x have also been used as catalysts on photoanodes.^[132-135] On single-crystal TiO_2 electrodes it has shown good performance through a unique "adaptive" evolution of the catalyst-semiconductor junction.^[136] Thin NiO_x films have shown electrochromic properties, with increased water oxidation currents under solar radiation.^[137] A combined $\text{TiO}_2/\text{NiO}_x$ photocatalyst has been processed on a WO_3 photoelectrode from a single Ti/Ni precursor.^[138]

2.1.4. Iron oxides

Iron oxide films are very attractive as they are the cheapest possible catalyst (rust).^[139] They were studied in detail by Doyle *et al.*^[140] including kinetic and mechanistic data.^[141,142] In addition to their catalytic activity, FeO_x films could also function as photoelectrochemical anodes since the hematite band gap should be good enough to promote water oxidation (2.1 eV).^[143,144] However, the mismatch between hole diffusion, slow interfacial electron transfer, and optical penetration yields very poor efficiency.^[145-147] As a WOC, though, FeO_x is less active than Ni or Co, although Fe content dramatically improves the activity of NiO_x , and maybe CoO_x (vide infra).

In general, photoelectrodes can be improved by nanostructuring.^[148,149] For example, remarkable activities were found by deposition of antimony-doped tin oxide colloids on FTO surfaces, as transparent support for incorporation of nanostructured hematite.^[150-152] Ti-doped Fe_2O_3 films have shown enhanced electrical conductivity, facilitating charge separation,^[153-155] which can be further optimized through design of the heterojunction in contact with the electrolyte.^[156,157] A reduction pretreatment in the dark (1 M NaOH) has also yielded enhanced photocurrent.^[158] As with the rest of the metal oxides, enhanced activity has been reported when FeO_x is combined with solid state supports, such as Nafion, or single-walled carbon nanotube composites, showing a decrease in overpotential up to 50 mV.^[159] Remarkably, when hematite photoanodes are covered with a thin film of amorphous FeOOH , the photocurrent doubles,^[160] exhibiting a catalytic activity and long-term stability comparable to the best CoO_x catalysts.^[161]

2.1.5. Manganese oxides

Manganese is one of the most studied metals in water oxidation catalysis,^[24,162-164] being the element selected by photosynthetic organisms to split water.^[165,166] In addition to the fascination of mimicking life, Mn is earth-abundant, but also non-toxic with in comparison with the other more active catalysts. The identification of the active MnO_x forms is particularly difficult. WOC activity has been attributed to

layered oxides,^[167-169] rutile phases,^[170] spinels^[171-173] and perovskites.^[174,175] In general, MnO_x catalysts exhibit lower activity than CoO_x or NiO_x, which has been attributed to the stable formation of inactive MnO₂ domains.^[176] Dau et al. disclosed a clever solution to avoid this deactivation by potential cycling during electrodeposition of MnO_x films. During reduction potential sweeping the already formed MnO₂ is modified into a mixed-valency Mn^{3+/4+} oxide,^[177] which remains highly active even in mildly acidic solutions. However, stability is still a concern since rapid dissolution cannot be avoided at neutral pH. Evolution of a nanolayered MnO_x structure at neutral pH structure has been related to enhanced activity.^[178]

The presence of Mn³⁺ species has been described as crucial to promote water oxidation.^[179] Since Mn³⁺ is unstable at pH < 9, due to the disproportionation reaction into Mn²⁺ and Mn⁴⁺, additional strategies are needed to improve the long term catalytic activity. One possibility is the use of electrolytes that stabilize the conversion of MnO_x into layered structures, *i.e.* Li⁺.^[178] Layered MnO_x has been interleaved by organic molecules to tune the catalytic activity.^[180] Coordinating amine groups on the surface of MnO₂ stabilize Mn³⁺, shifting electrocatalytic activity by ~500 mV.^[181,182] Oxygen vacancies enhance WOC activity.^[183] Interestingly, photocurrents have been found in birnessite-type MnO₂ nanostructures,^[169,184] with a heavy dependence on the selected precursors.

One of the advantages of MnO_x electrodes is that they can even be screen-printed.^[185] Additionally, although it shows lower catalytic activity, it exhibits a unique self-repairing mechanism in acidic media, where Mn²⁺ ions from solution are re-oxidized at OER potentials.^[186] The activity of MnO_x WOCs has been enhanced in hybrid nanocomposites on gold or CoSe₂ surfaces,^[187,188] and as Ca²⁺-doped nanostructures.^[189]

2.1.6. Mixed oxides

Metal oxide catalysts have traditionally been prepared by electrodeposition and this makes difficult to obtain and study desirable mixed-metal compositions that can improve catalytic features, as described for the case of NiO_x. Preparation from co-precipitation or alloys does not yield well-defined materials.^[190,191]

Boettcher *et al.* disclosed a clever approach to obtain a variety of nanostructured mixed metal oxides by simple solution casting.^[192] This easy procedure allows for the preparation of a few nanometer thick oxide thin films of controlled composition and good reliability. They found optimized performance in Ni_{0.9}Fe_{0.1}O_x films, exhibiting a 30 mV/decade Tafel slope, and reaching 1 mA cm⁻² at just 300 mV overpotential at pH 14. These thin films have the advantage of being perfectly compatible with photoanodes.^[136,193]

The better performance of films containing Ni was attributed to the in situ structural transformation from oxides to layered double hydroxides, as already proposed by Gerken *et al.*^[76] Fe doping improved the performance of NiO_x, whereas Co doping did not produce any synergic effect, when CoO_x is just second best after NiO_x.

The improved catalytic activity of NiO_x when doped by Fe had already been described by Corrigan,^[194] who observed an enhancement of the OER activity of NiO_x films after several cycles, correlated with the incorporation of Fe impurities from the KOH electrolyte. Tafel slopes down to 25 mV/decade were

found. The positive effect of Fe upon the catalytic features of NiO_x were also corroborated by experiments performed by Bell *et al.*^[195] Kitchin *et al.* identified the presence of a mixed NiO/NiFe₂O₄ phase at low Fe concentrations as a key component for the enhanced activity.^[196] In a complementary study, by doping Fe₃O₄ with Ni, the NiFe₂O₄ was the most active phase, with Tafel slopes of 41 mV/decade.^[197] Low Fe doping also improves the electrocatalytic properties of other oxides, such as Cr₂(MO₄)₃.^[198,199] The lower overpotentials with Fe doping were studied over 20 years ago, relating the better performance to the Fe centers increasing the oxidation potential of the active sites.^[200]

Very recently, experiments in Fe-free KOH solutions demonstrated that NiO_x is not as active as it was supposed,^[201] with a real onset catalytic activity above 400 mV. In the absence of Fe impurities (coming from the electrolyte), the OER activity of NiO_x films actually decreases upon anodization. Thus, the increased activity upon aging, observed even in NiBi films, is suggested to come from Fe incorporation, which occurs even without an applied potential. Ni(OH)₂ uptakes Fe when suspended in KOH solutions of different purity. Structurally, the presence of Fe³⁺ facilitates the formation of a layered double hydroxide structure. Aging of NiFeO_x films did not show significant changes, suggesting that the OER activity is not related to defects, but inherent to the Fe/Ni structure. The lack of OER activity up to very positive potentials in the absence of Fe³⁺ also reveals an electronic contribution. Fe increases the conductivity of the NiO_x films, diminishing the potential drop. More importantly, Fe has an electron withdrawing effect upon Ni centers, giving more oxidizing power to the Ni^{3+/4+} sites. These findings also call into question most studies (if not all) reported with NiO_x (in section 2.1.3) or even those for other oxides in alkali media, regarding the composition of the true catalysts.

In the case of photocatalytic currents, "optocatalytic" efficiency has also been defined taking into account electrocatalytic performance, but also considering photon absorption. An optimal thickness of 0.4 nm (2 monolayers) has been proposed for Ni_{0.9}Fe_{0.1}O_x.^[193]

Berlinguette *et al.* described another technique for the preparation of amorphous mixed-metal oxides, through the photochemical decomposition of metal-organic complexes.^[202,203] Using this strategy the authors completed another systematic study of binary and ternary amorphous metal oxides. They found that amorphous FeNi₄O_x offered the best performance at pH 13 (0.1 M, KOH solution), in very good agreement with the previous work by Boettcher.

Surface modified fluoride-doped tin oxide (FTO) with Co^[204] gave a distinct catalytic activity, with very fast TOF (4 s⁻¹ at pH 7.2 and 800 mV overpotential) although current densities were very low due to the low Co content. This could also maximize experimental TOF if compared with bulk or even nanostructured catalysts.

Layered double hydroxides (LDH), supposed to be the active site of most oxide-based WOCs, are efficient catalysts in base,^[205-207] but also at neutral pH. The latter depends greatly on preparation and electrode architecture. Although good current densities are reached at relatively low overpotential, the very high Tafel slopes observed indicate a kinetic reaction problem that has been assigned to the formation of an insulating layer of anions.^[208] The highest efficiency has been

assigned to derivatives with higher Fe content in the layered structure.^[209]

Double perovskites have been described as highly active WOCs and stable in alkaline solution,^[210-213] although the need to include rare earths precludes their extended use.^[214,215] For example, Ba-Sr-Co-Fe perovskite proved to be 10 times faster than IrO_x .^[216] Some of these perovskites have shown structural changes during the water oxidation reaction, going from crystalline to amorphous, which could be due to conversion of the local structure from corner sharing octahedral to edge sharing octahedral, associated with enhanced activity.^[217,218] Low-temperature annealing optimizes the performance promoting less concentration of charged cations, and increased OH surface coverage.^[219] It is worth mentioning that perovskites are bi-functional catalysts, being active also for ORR.^[220]

Mixed spinels are also active WOCs,^[210,221-225] including molybdates^[226-229] and Cr-doped ferrites.^[230,231] Zinc-doping in the Co_3O_4 spinel led to the preparation of nanostructured hierarchical arrays exhibiting better performance due to their high porosity.^[232] After a detailed combinatorial survey of thousands of trimetallic oxides, Stahl *et al.* have discovered that the inverse spinel NiFeAlO_4 shows activity exceeding all other Ni/Fe mixed oxides.^[233] NiCo_2O_4 improved its electrocatalytic behavior when prepared on a graphene- MnO_2 3D framework.^[234] Lithiated Li_xCoO_2 spinels ($x \approx 0.5$) have been proposed as bifunctional catalysts able to promote oxygen reduction and oxygen evolution reaction.^[235]

2.1.7. Comparison and benchmarking

The lack of a standardized method to evaluate and compare the activity and stability of WOCs makes it difficult to derive final conclusions from the available data. This is particularly relevant for metal oxides. Table 1 summarizes some representative catalytic parameters reported for oxides and other heterogeneous WOCs. In general, most experimental data indicate that catalytic performance decreases in the order $\text{Ni} > \text{Co} > \text{Fe} > \text{Mn}$ in the MO_x family.^[236] For this reason, most alkali electrolyzers work with Ni alloys, and its superior activity has been rationalized on the basis of the HO-M bond strength.^[237] Indeed, the experimental data available shows a good relationship between activity and the binding energy of HOO^* and HO^* .^[238]

A detailed comparison of the electrocatalytic activity of multiple metal oxides, taking into account their preparation, has recently been reported by Doyle and co-workers.^[33] The Tafel slope decreases down to 40 mV/decade with increasing charge capacity in the case of FeO_x suggesting that hydrated oxide formation is proportional to charge capacity.^[239] Dehydration of FeO_x , which has a characteristic 40 mV/decade Tafel slope, results in higher slopes above 60 mV/decade.^[140,240] The opposite has been found in NiO_x films. However, catalysts transformation due to impurities could be crucial and has not been studied in detail until very recently,^[241] casting doubt on common belief. Novel in operando characterization techniques will be very valuable in determining the genuine performance of metal oxides.^[242]

Peters *et al.* developed a strategy for comparing WOC activity of all metal oxides under strictly identical conditions, concluding that all of them exhibit similar activity, reaching comparable current densities within a very short potential

window (~ 80 mV).^[243] So it is apparent that neither kinetics nor stability makes one candidate significantly better in alkali media. None of them is active at low pH, though. Beyond the presence of impurities in the electrolyte, other interesting trends have been found, for example that smaller alkali cations lead to lower activity.^[244]

Metal-oxide WOCs have also shown enhanced performance when coupled with conducting substrates, such as nanocarbon,^[108,245-247] or gold.^[188] Copper nanowires are a particularly attractive support because they are transparent to visible light, exhibiting promising features.^[248]

Table 1. Comparison of some catalytic parameters for heterogeneous WOCs

compound	η^a (mV)	η^b (mV)	η^c (mV)	Tafel slope (mV/decade)	pH	ref.
NiFeO_x	-	-	297	30	14	192
NiO_x	-	-	-	67	14	110
NiO_x	>400	-	>1000	-	14	201
NiO_x	-	-	300	29	14	192
CoO_x	-	-	381	42	14	192
NiCoO_x	-	-	312	33	14	192
FeO_x	345	-	445	40	14	140
FeO_x	-	-	405	51	14	192
Fe_2O_3	<350	-	430	64	14	151
MnO_x	320	-	514	49	14	192
$\text{Fe}_3\text{Ni}_2\text{O}_x$	270	-	-	41	13	233
FeNiO_x	211	-	-	24	13	202
$\text{Fe}_2\text{Ni}_3\text{O}_x$	190	230	250	34	13	203
NiO_x	191	250	280	73	13	203
NiO_x	295	-	-	54	13	233
CoFeO_x^d	397	-	-	-	13	207
CoO_x	<200	-	<250	54	13	76
FeO_x	320	380	410	40	13	203
CoO_x	210	260	270	42	13	203
CoO_x	295	-	-	75	13	233
FeCoO_x	181	-	-	33	13	202
FeCoNiO_x	191	-	-	31	13	202
$\text{Ni}_2\text{FeAlO}_x$	270	-	-	30	13	233
$\text{NiFeMo}_3\text{O}_x$	250	-	-	36	13	233
$\text{Ni}_2\text{FeCr}_2\text{O}_x$	240	-	-	38	13	233
$\text{NiFeGa}_3\text{O}_x$	240	-	-	35	13	233
CoSe_2	373	-	380	66	13	249
NG-CoSe_2	294	-	320	40	13	249
MnO_x	<300	-	>1000	60	>11.5	186
FeOOH	300	-	420	-	11	161
NiBi	300	-	425	59	9.2	128

MnO _x	<300	-	>1000	127	8.5-5.5	186
CoO _x	<200	-	<300	65	7	76
MnO _x	390	-	590	60-80	7	177
MnO _x	441	-	600	120	7	250
CoFePBA	291	-	> 600	88	7	303
MnO _x	150	-	>1000	-	7	184
CoP _i	281	-	410	60	7	43
MnO _x	>700	-	>1000	109	7	176
Li _x MnP ₂ O ₇	500	-	-	120	7	251
Co(PO ₃) ₂	313	-	320	74	6.4	78
MnO _x	<300	-	>1000	653	3.5	186
Co ²⁺ (1M)	<580	-	600	118	1	76

[a] onset overpotential. [b] @ 0.5 mA cm⁻². [c] @ 1 mA cm⁻². [d] LDH.

2.2. Prussian blue derivatives

The catalytic activity of Prussian blue analogs (PBAs) in redox chemistry has been well documented for many years.^[252] PBs have been used for the preparation of modified electrodes^[253-262] for multiple applications: from electrochemical sensors^[263-271] to electrochromic displays.^[272 - 274] In the field of electrocatalysis, different derivatives have been used for the oxidation or reduction of organic materials.^[275,276] In oxidation catalysis,^[277,278] PB-modified electrodes have been developed to detect and quantify a variety of substrates, such as hydrazine,^[279 - 283] vitamins,^[284 - 287] amino acids,^[288 - 291] nucleobases,^[292] glucose^[293] and other biologically relevant molecules.^[294 - 299] They have also been postulated for electrocontrolled drug delivery.^[300]

In the field of energy applications, Prussian white was reported as an efficient proton reduction catalyst for hydrogen evolution, exhibiting higher activity than noble metals, such as Pt.^[301] Ruthenium purple also showed HER activity.^[302] Despite being heavily used as oxidation catalysts, the activity of PBAs for the OER was not disclosed until 2013, when we reported the electrocatalytic activity of K_{2x}Co_(3-x)[Fe(CN)₆]₂ (CoFePB)^[303] At neutral pH this PBA exhibits kinetics comparable (if not superior) to those of metal oxides, with unparalleled long term stability. Electrodes coated with CoFePB maintain a persistent catalytic activity for weeks at neutral pH and ambient conditions. At high overpotentials current densities deviate from Tafel behavior, which has been attributed to poor connectivity between PBA crystallites and the electrode surface.

Although kinetics and poisoning studies are still needed to be completely definitive about the nature of the active sites in these PBAs, we were able to gather experimental evidences of several types, which permit us to rule out the participation of metal oxide nanostructures evolved during the catalysis. Detailed structural characterization, including surface-sensitive techniques such as Raman spectroscopy or XPS, confirmed the absence of any trace of a transition metal oxide in the "as used" PBAs.^[304] In addition, they remain active in acid media, where CoO_x participation cannot be claimed.

PBAs appear to be a viable WOC alternative to metal oxides for promoting water oxidation in artificial photosynthesis devices. They present competitive kinetics, have better stability in neutral and acidic media, are obtained from Earth-abundant metals, and can easily be processed as powders, thin-films or nanoparticles, with classic coordination chemistry tools. Furthermore, they are active at neutral or acidic pH, without the need for additional electrolytes, since their stability resides in the strong cyanide bridge in the solid state, with no participation of oxo or hydroxo groups in their skeleton.

2.3. Other heterogeneous catalysts

Apart from oxides and cyanides, no other type of heterogeneous WOC has been systematically studied, although there are some promising examples.

Manganese pyrophosphate exhibits superior catalytic performance to that of the corresponding Mn oxides at neutral pH,^[251] opening novel future perspectives for Mn-based WOCs, active and robust under mild conditions.

Cobalt MOFs with carboxylate or polypyridyl ligands have also been claimed to promote electrocatalytic oxygen evolution from water,^[305] where high surface area could be an additional advantage.

Amorphous cobalt potassium phosphate has been reported to exhibit slightly lower activity than CoO_x in the dark, but also with a unique photocurrent, which could have further interest.^[306]

CoWO₄ has also shown WOC activity in neutral electrolytes.^[307] Amorphous phases resemble CoP_i activity, whereas crystalline phases, annealed at high temperatures, show different behavior, with significantly higher Tafel slopes (-110 mV/decade), indicating a different mechanism and a different active catalyst.

One of the most interesting candidates is CoSe₂. This material has been used as co-catalyst or promoter for classic oxide WOCs. Very recently, its genuine activity has been revealed,^[249] offering very promising performance in alkaline media. When supported on nitrogen-doped graphene, Tafel slopes as low as 40 mV/decade, and very high current densities at low overpotentials (10 mA cm⁻² @ η = 366 mV) have been achieved.

3. Supported homogeneous electrocatalysts

Homogeneous and heterogeneous catalysts have their respective intrinsic advantages.^[308,309] For an electrocatalytic cycle, heterogeneous conditions are clearly preferred in order to maximize the efficiency of electron transfer. However, homogeneous catalysts offer superior processability, optimization and kinetics.^[310-312] Therefore, immobilization of homogeneous catalysts onto (high surface area) solid state supports appears to offer the best of both worlds. At the nanoscale, multiple strategies are available to process homogeneous catalysts on electrodes.^[313-315]

Stability, though, is a main issue for homogeneous catalysts, since they are typically not as robust as their heterogeneous counterparts. Under water oxidation conditions this is even more crucial, because of the easy evolution of metal oxides in situ from decomposition of molecular precursors.^[308,316-318] As metal oxides are highly efficient WOCs,

some homogeneous WOCs have been mistakenly reported, when the activity of minor oxide impurities has been wrongfully assigned to the homogeneous species. The determination of the true active site in catalytic reactions is a clear challenge, particularly in water oxidation due to the extreme working conditions. Actually, great effort is needed to obtain experimental evidence to identify the genuine catalyst, beyond any reasonable doubt -- if indeed this is feasible.^[308,309,319,320,321,322,323,324,325]

Genuine homogeneous WOCs have been fixed into a polymeric matrix or onto surfaces to produce modified electrodes, although in most cases with noble-metal catalysts.^[326-332] In the case of Earth-abundant WOCs, few examples have been reported.

A plausible strategy to immobilized homogeneous WOC onto electrodes is the use a Nafion-containing solution to be drop casted on the electrode surface. This approach has been used successfully with cobalt cubanes.^[333] The incorporation of these pyridine-based WOCs improves the current and photocurrent of hematite electrodes, while maintaining the molecular structure. The same strategy with $[\text{Mn}_4\text{O}_4\text{L}_6]^+$ (L = diaryl-phosphinate) cubanes^[334,335] was not equally reliable. Although solar-to-hydrogen conversions of up to 1% were reported,^[336] it was later found that the cluster was only a pre-catalyst for the formation of high surface area MnO_x .^[167]

Iron complexes of tetra-amido macrocyclic ligands (TAML) have been mixed with carbon black and immobilized with Nafion to prepare electrocatalytic anodes.^[337] These electrodes are robust, although with limited selectivity for O_2 evolution.

Modified cobalt hangman corroles have been tailored to optimized oxidation catalysis, conveniently supported on Nafion films.^[338] Reasonably good activity and remarkable stability at any pH were achieved through chemical modification of the corrole framework, demonstrating how subtle differences can greatly affect performance. This was analyzed through theoretical modeling.^[339]

Insoluble Cs^+ salts of high nuclearity Co-containing POMs are able to promote catalytic water oxidation reaching high currents at low overpotentials when incorporated into a carbon paste blend.^[340] Remarkably, catalytic activity of these POM-carbon blends is maintained at any pH range, since the insolubility of these ionic salts is not affected by OH^- concentration. If these insoluble POM salts can be incorporated into large surface area electrodes, they would constitute a unique opportunity to prepare anodes able to work at any pH conditions. $[\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]^{10-}$ ^[341,342] has also been immobilized into a mesoporous carbon nitride matrix, resulting in improved catalytic activity and durability.^[343]

Cobalt porphyrins can be processed in organic solvents to prepare water-insoluble thin films on FTO working electrodes. These films have shown very fast catalytic cycles although only at high pH.^[344] When combined with a perylene derivative, visible-light-induced dioxygen evolution has been detected.^[345]

Water-insoluble cobalt corroles have also been processed as thin films by simple drop casting of organic solutions.^[346] Bifunctional action has been observed in these films, promoting water oxidation at neutral or basic pH, and proton reduction in acidic media. The dynamics of these molecular species at the water interface are not completely understood yet, since ligand substitution from the solution-organic film equilibrium needs to occur.

4. Summary and Outlook

Although many problems remain to solve, in our opinion, one may derive some reasonable conclusions from the presently available data.

At this moment, metal oxides are the only WOC solution in alkaline media. Some of them can also be used in neutral and/or acidic media, with the help of electrolytes (phosphate) or favorable disproportionation (as with Mn). However, the selection of the best performers is still difficult due to the contradictory data available. This is probably a result of the different experimental environments in which experiments have been carried out. Comparison of catalytic parameters (Table 1) is only meaningful under exact identical working conditions. It is surprising that better performance is claimed in some relevant recent publications comparing parameters obtained even under different conditions of pH. It is well known that the water oxidation mechanism changes with pH, along with the thermodynamic potential.^[43,76] Thus, such claims should be put into context.

Careful processing and optimization of mixed metal oxides has been very valuable, although it is not easy to determine if the benefit is worth the extra cost. Alkali media electrolyzers are a very mature technology, and Ni alloys already seem to perform well enough, when evolving into the highly active mixed Fe/Ni LDHs under working conditions, through Fe-uptake from the alkali media.

Cyanides are a promising solution in neutral and acidic media. Compared with the oxide WOCs, PBs have already proved to be competitive, with many possibilities still open for improvement in processing. The main difference between these two WOC types is their stability under working conditions. Oxides are greatly affected by pH in water, changing structure, activity and solubility. PBs remain identical in structure and function through the entire pH range at which they are stable (pH < 9), being inert to most electrolytes. Their stability in acid media could also be exploited.

In acid media the most appealing alternative to noble-metal oxides appear to be modified electrodes with homogeneous catalysts. Cobalt seems the element of choice in this approach, and several promising examples with organic and inorganic ligands stabilizing the active sites are available.

Although outside the scope of this review, it is worth mentioning here that metal-free doped-carbon nanostructures could also become important players in oxygen evolution electrocatalysis.^[347]

With so many examples of available of WOCs, with excellent Tafel slopes, and more-than-acceptable current densities, one wonders if the challenge is still of a chemical nature. In our opinion, the next most crucial step is electrode design and engineering. Many efforts are being made to find the newest, fastest, most rugged, precisely designed WOC. However, how will this be technologically relevant? In any introduction to a WOC manuscript, including this one, one encounters a discussion of the future of the energy challenge, often with a reverie of green chemistry and fuels production. Unfortunately, later on, what we read about is often a discussion about a remarkably good WOC, available only in milligrams, after a huge investment, and with a relatively short lifetime. Such a WOC is of great interest, to us and to a wide audience. Fundamental chemistry is not only useful but key in pushing the limits of knowledge. Nevertheless, we may be in

danger of oversell when the results do not match all the initial promises from the so-called "introduction section". If technologically relevant requirements are not taken into account, seems appropriate not to claim technological relevance. A closer, honest and open-minded collaboration between electrochemists, chemists and engineers will be needed to define viable solutions to the solar fuels production challenge as society demands.

Another subject that remains open for discussion is the incorporation of WOCs onto photoanodes.^[103,348] This is again a very interesting chemical and photophysical problem from a fundamental perspective. Great efforts are being made, and the scientific challenge is clearly worthy. Nevertheless, on the technological road to solar fuels production, why would this approach be preferred to one of using photovoltaics plus an electrolyzer? The latter should be considered, also from a basic science perspective. Sometimes, the easier approach can also be the most effective and convenient.

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Entry for the Table of Contents

REVIEWS



*J. R. Galan-Mascaros**

Page No. – Page No.

**Water oxidation at electrodes
modified with earth-abundant
transition metal catalysts**

A critical description of the state-of-the art in water oxidation electrocatalysts in heterogeneous conditions, highlighting their technological relevance towards a solar fuels production scheme.