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Recent trends in hydrogen and oxygen electrocatalysis for anion exchange membrane technologies

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Keywords: Hydrogen evolution reaction, hydrogen oxidation reaction, oxygen reduction reaction, oxygen evolution reaction, electrocatalysis, alkaline electrolytes

Abstract

This review aims at presenting recent findings in the understanding of oxygen and hydrogen electrocatalysis in alkaline electrolytes that are key processes for the emergence of sustainable energy storage and conversion devices such as anion exchanged membrane fuel cells and electrolyzers. In these systems, the exchange of electrons through electrochemical reactions provides a unique pathway to reversibly convert the electricity vector into chemical one: hydrogen. A concise and critical review of advances made during the last past years in the design of catalysts is provided. Challenges and opportunities for the development of the next catalyst generation are also addressed.

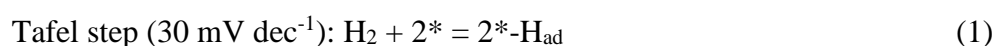
1. Introduction

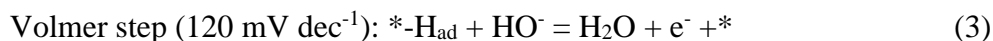
Storing and then using renewable resources are sustainable processes to reduce fossil fuel consumption. The production of clean hydrogen in a water electrolyzer and its further combustion in a fuel cell to deliver heat, electricity and only water as by-product are thereby sustainable perspectives [1] for the implementation of a future energy grid based on a hydrogen economy. Hydrogen as well as oxygen electrocatalysis will govern electrical performances of the above-mentioned applications. The recent development of anion exchange membranes [2] with useful conductivities in the range of 20-40 mS cm⁻¹ [3] paved the way for the design of solid anion exchange membrane technologies, recently reinforcing the interest to design catalysts evolving in alkaline environments. These media allow using catalysts free from PGM and even free from critical raw materials [4]. In this review, recent advances in the design of catalysts and in the understanding of their activity towards key hydrogen evolution (HER), hydrogen oxidation (HOR), oxygen evolution (OER) and oxygen reduction (ORR) reactions in alkaline medium are discussed. In this review, the emphasis will be mainly on recent developments made in the design of non-PGM based catalysts.

2. Hydrogen electrocatalysis in alkaline medium

2.1 Understanding factors affecting hydrogen electrocatalysis in alkaline medium

Hydrogen electrocatalysis has been extensively studied to lay the basis of modern electrocatalysis [5]. Reaction mechanisms generally imply three different elementary steps (Heyrovsky-Volmer or Tafel-Volmer mechanisms) that can be described as follows in alkaline electrolytes (* refers to a catalytic site):





To be more informative, HER/HOR mechanisms have been illustrated in Figure 1.

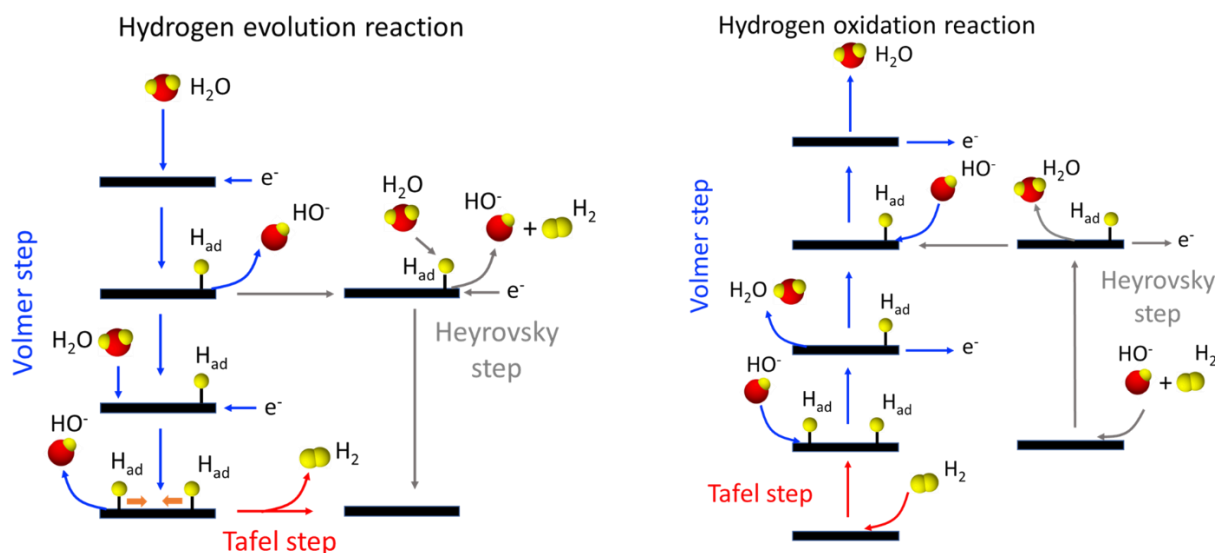


Figure 1: Illustration of HER and HOR mechanisms in alkaline medium

HOR/HER have been largely investigated in acidic electrolytes [6] and reactivity of PGM-based catalysts was shown to be lower by at least two orders of magnitude in alkaline media [7, 8] making it difficult to explain reactivity with a simple descriptor. It was first proposed that metal-hydrogen bond strength increased with pH value in agreement with the position of Hupd peaks [9]. Nevertheless, this quite simple correlation has to be reviewed since Hupd peaks position depends both on Pt surface oxophilicity [10] and the adsorption of cations from the alkaline electrolyte [11]. Recently, Strmcnik et al. [12, 13], showed that three main factors affect HOR and HER kinetics. In addition to H adsorption energy, the nature of the proton source (oxonium ion in acidic medium or water in alkaline medium) as well as the presence of surface species (hydroxides, electrolyte ions) should be considered to explain HOR/HER activity of a material. The two latter phenomena are responsible for modifying both adsorption energy of hydrogen and water molecules, thus particularly affecting kinetics of the Volmer step (3). Furthermore, very recently, the role played by the formation of $\text{OH}_{\text{ad}}\text{-(H}_2\text{O)}_{\text{x}}$ -

AM^+ (with AM^+ = alkali metal cation) adducts in alkaline electrolytes has been brought to light and has been shown to be responsible for destabilizing OH_{ad} , thus limiting the rate of HOR whereas promoting HER kinetics [14]. From the previous discussion, it appears that tuning of OH adsorption energy at a catalyst surface is a promising pathway to improve its catalytic efficiency towards hydrogen electrocatalysis.

2.2 Catalysts for HOR/HER in alkaline medium

PGM-based catalysts (based on the use of Pd, Pt, Ir, Ru) are the most efficient ones towards HOR in alkaline medium. Numerous strategies (substrate engineering, alloying effect, particle size effect) have been employed to improve their activity and recently reviewed [15]. During the last years, research efforts were focused on the alloying of noble metals (Pt or Pd) with oxophilic atoms such as Ru and Ni [13, 16, 17]. As an example, resulting Pt/Ru catalyst exhibited a very high HOR activity (see Table 1) in reason of the promotion of OH adsorption. The same kind of effects was observed by depositing Pd nanocrystals onto oxophilic ceria [18]. Non-noble metal-based catalysts presenting a significant HOR activity are exclusively based on the use of Ni. Performances of such catalysts are presented in Table 1. Alloying Ni with Co and Mo allowed obtaining a very active CoNiMo catalyst [19] presenting a hydrogen binding energy close to that of Pt. The synthesis and the use of N-doped carbon nanotubes supported Ni nanoparticles as catalyst allowed achieving a very high HOR kinetics [20], in reason of the electronic modulation of Ni resulting from the interaction between Ni and N-edge atoms grafted onto the carbon substrate. The substrate engineering appears then as a reliable strategy to modulate hydrogen bonding energy at a catalytic surface. More recently, a Ni_3N/C catalyst was synthesized and exhibited a huge activity towards HOR in reason of a downshift of the Ni d-band weakening binding energy of hydrogen as well as oxygenated species [21]. As reviewed in 2015 [1], HER catalysts can be classified into three main subclasses comprising PGM-based catalysts [22], transition-metal carbides [23], oxides

[24], sulfides [25], selenides [26], phosphides [27], nitrides [28], borides [29] and non-metal catalysts based on the use of C, N, S elements [30]. In 2011, Markovic et al. reported a heterostructured catalyst composed of Pt decorated with Ni(OH)₂ clusters. This material exhibited an enhanced HER activity in comparison with the Pt platinum pristine surface. The presence of Ni(OH)₂ favored water dissociation and then faster kinetics for the Volmer step [31]. Based on the same concept a Pt/Ni(HCO₃)₂ catalyst was very recently designed and exhibited a huge HER activity with an overpotential as low as 27 mV to achieve a current density of -10 mA cm⁻² [22]. Recently, numerous nanostructured non-noble metal-based with heterojunctions were developed, some of them being more active than Pt/C catalysts in reason of the lowering of adsorption free energy of H at heterointerfaces [32]. These heterostructured catalysts often combine at least two different efficient catalysts towards HER [25]. This concept was then used to perform the growth of heterostructured catalysts composed of sulfides [33] or phosphides [34] directly onto Ni foam. The established interfaces allow facilitating both chemisorption of hydrogen and oxygen intermediates, thus improving the overall water splitting activity [33]. Another recent trend consists in atomically engineering active sites by doping a poorly active HER catalyst. This allows tuning electron density of active sites, thus modifying H adsorption energy and favoring the cleavage of water molecule [35-37]. HER/HOR activities of previously described materials are reported in Table 1.

Table 1: Non-exhaustive list presenting representative recently developed catalysts for HER/HOR in alkaline medium. j_0 represents the exchange current density. It has been normalized using either platinum active surface area (in that case the unit is denoted as mg cm⁻²_{Pt}) or using geometric surface area. The mass normalized j_0 value is also given for HOR catalysts. η represents the overpotential. For HER, overpotential values at -10 mA cm⁻² (η_{-10}) as well as at -100 mA cm⁻² (η_{-100}) are given. b is the Tafel slope.

Hydrogen oxidation reaction (HOR)	Catalyst	Morphology / structure	Loading ($\text{mg}_{\text{metal}} \text{cm}^{-2}$)	Working electrode	Electrolyte	j_0 ($\text{mA mg}^{-1}_{\text{metal}}$)	j_0 ($\text{mA cm}^{-2}_{\text{metal}}$)	Activity at $\eta = 50 \text{ mV}$	Ref.	
	Pt	Nanowires	0.02	Vulcan XC 72 R coated glassy carbon	0.1 M KOH	$16 \text{ mA mg}^{-1}_{\text{Pt}}$	$0.229 \text{ mA cm}^{-2}_{\text{Pt}}$	$69 \text{ mA mg}^{-1}_{\text{Pt}}$	[17]	
	PtRu	Nanowires	0.02	Vulcan XC 72 R coated glassy carbon	0.1 M KOH	$32 \text{ mA mg}^{-1}_{\text{Pt}}$	$0.493 \text{ mA cm}^{-2}_{\text{Pt}}$	$160 \text{ mA mg}^{-1}_{\text{Pt}}$		
	PtFe	Nanowires	0.02	Vulcan XC 72 R coated glassy carbon	0.1 M KOH	$27 \text{ mA mg}^{-1}_{\text{Pt}}$	$0.459 \text{ mA cm}^{-2}_{\text{Pt}}$	$122 \text{ mA mg}^{-1}_{\text{Pt}}$		
	CoMoNi	Electroplated material	n/a	Au	0.1 M KOH	n/a	0.015	$0.044 \text{ mA cm}^{-2}_{\text{metal}}$	[19]	
	Pt	polycrystalline disk	n/a	Pt	0.1 M KOH	n/a	0.61	$1.4 \text{ mA cm}^{-2}_{\text{metal}}$		
	Ni/N-CNT	Nanoparticles (20 nm)	0.25	Glassy carbon	0.1 M KOH	3.5	0.028	$9.3 \text{ mA mg}^{-1}_{\text{metal}}$	[20]	
	$\text{Ni}_3\text{N/C}$	Nanoparticles (4.6 nm)	0.16	Glassy carbon	0.1 M KOH	12	0.014	$24.4 \text{ mA mg}^{-1}_{\text{metal}}$	[21]	
Hydrogen evolution reaction (HER)	Catalyst	Morphology / structure	Loading (mg cm^{-2})	Working electrode	Electrolyte	η_{-10} (mV)	η_{-100} (mV)	j_0 (mA cm^{-2})	b (mV dec^{-1})	Ref.
	Pt/Ni(HCO_3) ₂	20 wt. % Pt nanoparticles (2-3 nm) on Ni(HCO_3) ₂ nanoplates	0.04	Glassy carbon	1 M KOH	-27	ca. -70 mV	$5.6 \text{ mA cm}^{-2}_{\text{Pt}}$	40	[22]
	Pt	Bare Pt nanoparticles	0.2	Glassy carbon	1 M KOH	-44	ca. -125 mV	$2.8 \text{ mA cm}^{-2}_{\text{Pt}}$	52	
	Pt/C	Commercial 10 wt.% Pt/C (Sigma-Aldrich)	0.02	Glassy carbon	1 M KOH	ca. -50	n/a	n/a	104	
	$\text{Mo}_2\text{C/N-doped carbon microflowers}$	N-doped microflowers consisting of nanoflakes decorated with $\beta\text{-Mo}_2\text{C}$ (particles)	0.28	Glassy carbon	1 M KOH	-100	n/a	n/a	65	[23]
	Pt/C	Commercial 20 wt. % Pt/C	0.28	Glassy carbon	1 M KOH	-50	n/a	n/a	34	
	$\text{Fe}_{1.89}\text{Mo}_{4.11}\text{O}_7$	Microparticles	2.4	Bare carbon paste	1 M KOH	-197	n/a	0.069	79	[24]
	Pt/C	Commercial 20 wt. % Pt/C	n/a	n/a	1 M KOH	-103	n/a	n/a	27	
	$\text{NiS}_2/\text{MoS}_2$	Hybrid porous nanowires composed of MoS_2 nanoplates and NiS_2 particles with heterojunctions	0.2	Glassy carbon	1 M KOH	-204	n/a	n/a	65	[25]
	Pt/C	n/a	0.2	Glassy carbon	1 M KOH	-50	n/a	n/a	35	
	FeNiSe/exfoliated graphene	Mesoporous FeNiSe nanosheets grown onto exfoliated graphene	3.3	Graphite foil	1 M KOH	-187	n/a	0.57	65	[26]
	Pt/C	Commercial catalyst	3.3	n/a	1 M KOH	ca.-75	n/a	n/a	46	

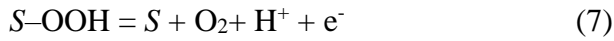
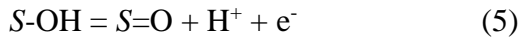
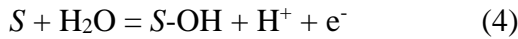
Mn-doped Ni ₂ P	Mn-doped Ni ₂ P Nanosheets array on Ni foam	n/a	Ni foam	1 M KOH	ca. 50	ca. -220	n/a	135	[27]
Pt/C	Commercial 20 wt. % Pt/C (Sigma-Aldrich)	7.0	Ni foam	1 M KOH	ca. 20	ca. -120	n/a	98	
NiCoN/C	Hybrid nanocages composed of nanosheets with a thickness of 2-3 nm	0.2	Glassy carbon	1 M KOH	-103	n/a	n/a	n/a	[28]
Pt/C	Commercial Pt/C	0.05	Glassy carbon	1 M KOH	-91	n/a	n/a	n/a	
Co-Ni-B/carbon cloth	Co-Ni-B nanoparticles (5-10 nm)	0.34	Carbon cloth	1 M KOH	-80	ca. -250	n/a	88	[29]
Pt/C	Commercial Pt/C	0.34	Carbon cloth	1 M KOH	ca. -25	ca. -240	n/a	30	
S-doped C ₃ N ₄ /carbon naotubes/carbon fiber	Fibers decorated with S-doped C ₃ N ₄	0.5	Carbon fiber	1 M KOH	-131	ca. -250	0.28	79	[30]
Mo ₂ C/Mo ₂ N	Mesoporous material	0.38	Glassy carbon	1 M KOH	-145	-222	0.05	55	[32]
Pt/C	20 wt. % Pt/C (Alfa Aesar)	0.38	Glassy carbon	1 M KOH	-60	-263	5.87 mA cm ⁻² _{Pt}	47	
MoS ₂ /Ni ₃ S ₂ /nickel foam	Porous heterostructure grown onto Ni foam	9.7	Ni foam	1 M KOH	ca. -110	n/a	n/a	83	[33]
Pt/C	20 wt. % Pt/C (Fuel Cell store)	0.8	Ni foam	1 M KOH	ca. -25	n/a	n/a	32	
FeP/Ni ₂ P/nickel foam	Porous heterostructures composed of FeP and Ni ₂ P nanoparticles grown onto Ni foam	8	Ni foam	1 M KOH	-14	ca. -130	n/a	24	[34]
Pt	Pt wire	n/a	n/a	1 M KOH	-59	ca. -130	n/a	37	
N-NiCo ₂ S ₄	Nanowires	n/a	Ni foam	1 M KOH	-41	ca. -140	n/a	37	[36]
Pt/C	Commercial 20 wt. % Pt/C	2.3	Ni foam	1 M KOH	-28	ca. -140	n/a	29	
Ni, Zn-doped CoO	Nanorods	0.486	Carbon fiber paper	1 M KOH	-53	ca. -160	n/a	47	[37]
Pt/C	Commercial 20 wt. % Pt/C (Fuel cell store)	0.4	Carbon fiber paper	1 M KOH	ca. -60	ca. -175	n/a	33	

	NiO@1T-MoS ₂ /CFP	Nanosheets	1.02	Carbon fiber paper	1 M KOH	-46	ca. -120	0.44	52	[35]
	Pt/C	Commercial 20 wt. % Pt/C (Johnson Matthey)	1	Carbon fiber paper	1 M KOH	-23	ca. -130	0.69	32	

3. Oxygen electrocatalysis in alkaline medium

3.1 Origin of oxygen electrode overpotentials

OER/ORR kinetic limitations can be described assuming a reaction mechanism composed of four proton coupled electron transfer steps and implying three reaction intermediates ($S=O$, $S-OH$ and $S-OOH$, where S denotes a catalytic site). This reaction mechanism can be described using the following equations (4)-(7):



From these reactions, the different reaction energies can be expressed as follows taking water as the origin of the energy scale:

$$\Delta G_1 = \Delta G_{OH} - \Delta G_{H_2O} = \Delta G_{OH} \quad (8)$$

$$\Delta G_2 = \Delta G_O - \Delta G_{OH} \quad (9)$$

$$\Delta G_3 = \Delta G_{OOH} - \Delta G_O \quad (10)$$

$$\Delta G_4 = \Delta G_{O_2} - \Delta G_{OOH} = 4.92 - \Delta G_{OOH} \quad (11)$$

Considering that total energy required to transform H_2O into O_2 is 4.92 eV (4×1.23 eV) as well as that $S-OH$ and $S=O$ are respectively singly and doubly bonded reaction intermediates, equations (8)-(11) can be written, as follows [38]:

$$\Delta G_1 = \Delta G_2 \quad (12)$$

$$\sum_{i=1 \text{ to } 4} \Delta G_i = 4.92 \text{ eV} \quad (13)$$

$$\Delta G_4 = 4.92 - \Delta G_3 - 2\Delta G_1 \quad (14)$$

Thus ΔG_i can be described using two independent parameters, that is to know ΔG_1 and ΔG_3 . The overpotential required for OER/ORR is obviously governed by the step with highest energy barrier.

Thus, ORR/OER overpotentials can be described with the following equations [38, 39]:

$$\eta_{OER} = \frac{\text{Max}(\Delta G_i)_{i=1 \text{ to } 4}}{e} - 1.23 \quad (15)$$

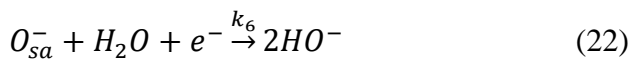
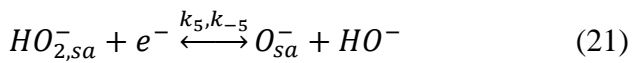
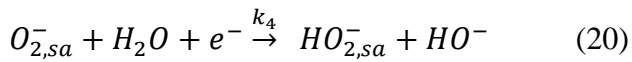
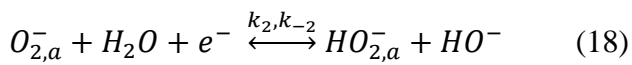
$$\eta_{ORR} = \frac{\text{Min}(\Delta G_i)_{i=1 \text{ to } 4}}{e} - 1.23 \quad (16)$$

where e is the elementary charge.

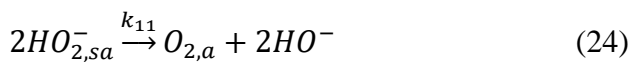
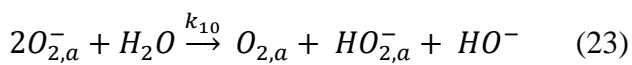
For an ideal catalyst, it is observed that $(\Delta G_i)_{i=1 \text{ to } 4} = \frac{4.92}{4} = 1.23 \text{ eV}$ meaning that ΔG_{OH} , ΔG_O and ΔG_{OOH} are respectively equal to 1.23, 2.46 and 3.69 eV [40]. In such case, the energy difference $\Delta G_{OOH} - \Delta G_{OH}$ is equal to 2.46 eV. The transition from one intermediate to another is thus spontaneous for an electrode potential of 1.23 V vs. RHE. To optimize a real catalyst, it is required to reach a situation where $\Delta G_1 = \Delta G_3 = 1.23 \text{ eV}$. For this purpose, ΔG_{OH} and ΔG_{OOH} have to be tuned independently [38]. Nevertheless, as oxygenated intermediates are chemically bonded to the catalyst surface through O atom, binding energies of S-OH and S-OOH are interdependent [40, 41] and linearly scaled, rendering impossible their separate optimization. Furthermore, the energy difference $\Delta G_{OOH} - \Delta G_{OH}$ is nearly constant whatever the considered materials and is equal to 3.2 eV [39], far from the ideal value of 2.46 eV. For the real catalyst, at 1.23 V vs. RHE, all steps are not downhill processes. Applying an electrode potential away from 1.23 V vs. RHE is thus required. Comparison between different catalysts families using this theoretical framework is nevertheless only possible if catalytic surfaces follow the same reaction mechanism. That is not the case for all catalysts families and OER/ORR mechanisms are still under debate. Some recent studies pointed out that breaking scaling relations are a required but not sufficient condition to optimize the activity of a catalyst and the potential determining step has to be considered through the examination and comparison of the electrochemical-step symmetry index value with overpotential [39, 42].

coordinated to the surface). It is widely accepted that these two adsorption modes lead to a four-electron pathway and a two-electron pathway, respectively [50].

On platinum surfaces the first electron transfer step to adsorbed oxygenated species (O_{sa} resulting from the dissociation of $O_{2,a}$ or O_{2a}) is widely considered as the *rate determining step* [45] and the reaction pathways (Figure 2a) can be described using the following electrochemical equations as already reported [44, 45]:



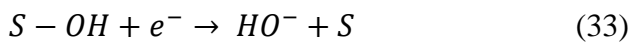
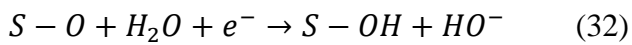
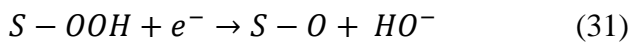
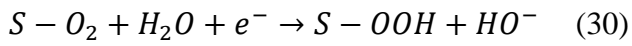
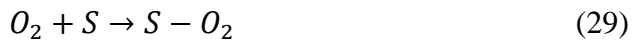
All adsorbed species may be subjected to several chemical transformations, as described by the following equations:



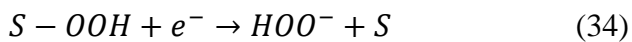
Finally, equilibria exist between weakly adsorbed species (adsorption energy in the range of kT) and strongly adsorbed species. The strength of adsorption greatly affects the rate of chemical and electrochemical steps. These equilibria can be described by the following equations:



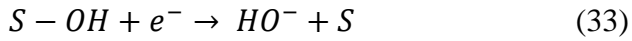
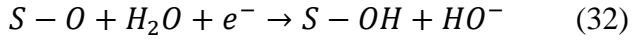
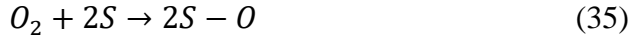
As for platinum-based catalysts, ORR at metal free surfaces can occur through associative or dissociative mechanisms (Figure 2b) [48, 51]. It was nevertheless found that the energy barrier to form adsorbed peroxide from adsorbed O_2 is lower than that corresponding to O_2 dissociation, thus associative mechanism is energetically favored [52]. Associative mechanism first involves the adsorption of molecular oxygen onto the catalyst surface and the overall reaction mechanism proceeds as follows (S represents the active site):



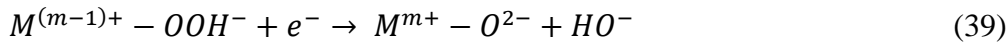
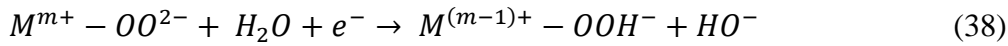
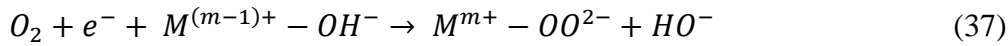
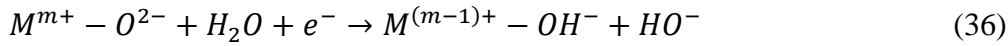
Alternatively, depending on the relative stability of $S-O$ and $S-OOH$ intermediates, $S-OOH$ may accept an electron before the releasing of peroxide anion into the electrolyte according to the following equation:



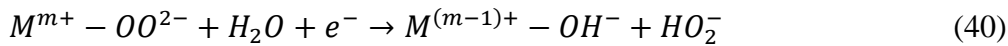
For the dissociative mechanism ORR begins with adsorption of O₂ and its further dissociation into two S-O intermediates. This reaction pathway only leads to the formation of hydroxyl ions as reduction products. This reaction pathway can be described as follows:



ORR at transition metal oxide surfaces has a quite different pathway. First, surface transition metal cations (*M*) of the oxide react with water molecules to form adsorbed OH⁻ species. The charge modification occurring subsequently to protonation of surface oxygen ligand is counterbalanced by the reduction of the metallic cation (*M*). The overall reaction process can be described as follows:



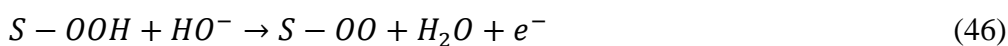
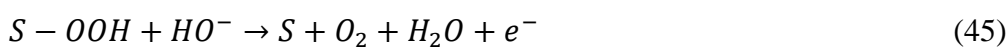
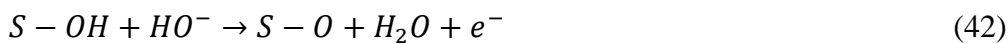
In this reaction pathway, the displacement or the regeneration of surface hydroxide can be considered as the *rate determining step* [53]. The reduction process can also lead to the formation of the two-electron product that is to know peroxide anion according to the following equation:



The uniqueness of double layer structure in alkaline medium allows modifying ORR kinetics independently on the chemical nature of the electrode. This is made possible in reason of H-bond formation between H atom of OH⁻ species at the inner Helmholtz plane and water solvating O₂ molecules located at the outer Helmholtz plane. This facilitates the outer electron transfer towards O₂ molecule leading to the formation of superoxide anions [54]. This latter phenomenon allows

compensating the possible weak interaction between O₂ and a given catalyst and consequently explains the high reduction potentials of O₂ observed for a large number of catalysts in alkaline medium. The promotion of the outer sphere electron transfer may be also responsible for the release of large amounts of peroxide species. Nevertheless, at ORR potentials, the electrostatic interaction between negatively charged peroxide anion and positively charged electrode surface could allow the fast peroxide reduction to hydroxyl ion [54].

Many research groups have proposed OER mechanisms in alkaline conditions. Some similarities and discrepancies appear in the reported studies. Most of the proposed mechanisms involve –OH as well as –O reaction intermediates and some differences are encountered in what concerns the reaction of formation of molecular O₂. These different reaction mechanisms have been proposed in Figure 2d and can be described using the following equations, where *S* denotes a general catalytic site:



As already mentioned for ORR, HER and HOR, the structure and properties of the double layer strongly influence OER kinetics. In particular, specific interactions developed between cations of the electrolyte and reaction intermediates may affect the strength of hydrogen bonds with interfacial

water. As a result, the energy required for the formation of oxygenated intermediates governing the *rate determining step* (i.e. the formation of O-O bond) is modified [55].

3.2 Catalysts for ORR/OER in alkaline medium

Numerous efficient non-noble transition metal-based hydroxides (especially Co-Fe, Ni-Fe and Ni-Co-based layered double hydroxides [47] and oxides (perovskites [56],...) with performances overcoming those of Pt-based catalysts for ORR and those of Ir- or Ru-based oxides for OER have been reported during the past few years. The ABO_3 (where A is a lanthanide or an alkaline metal and B is a transition metal) structure of perovskites is of large interest for ORR and OER since their lattice can accommodate a wide range of cations substitution both on A and B sites as well as oxygen deficiencies. Varying their composition can adjust their electronic properties and crystal structure and consequently being responsible for modifying their catalytic activity. In these structures B site is considered to be the active site for ORR/OER and their activity can be correlated with the e_g orbital filling [57]. As a result of these lattice modifications, effective materials have been designed for ORR and OER [56] (Table 2). Layered double hydroxide is also a material family which has been largely investigated in the past few years, especially for the design of efficient catalyst towards OER. These materials are composed of hexa-coordinated transition metals. Octahedrons form a two-dimensional layer by edge-sharing. The general chemical formula of layered double hydroxides is $[M_{1-x}^{2+}M_x^{3+}OH_2]^{x+}(A^{n-})_{\frac{x}{n}}.mH_2O$, where M^{2+} cations can be substituted by M^{3+} cations. The interlayer spacings are filled with anions to counterbalance the positive charge of two-dimensional layers. By exfoliating these two-dimensional materials, modifying their chemical composition or adjusting their morphology, very active OER catalysts have been designed. As an example, the high OER activity of NiFe layered double hydroxide hollow microspheres were recently reported [58]. An overpotential of only 239 mV was indeed required to reach a current density of 10 mA cm^{-2} (Table 2).

Additionally, since the amazing catalytic behavior of $\text{Co}_3\text{O}_4/\text{N-rGO}$ composites towards OER/ORR was reported in 2011 [59], studies have highlighted the design of highly efficient heterostructured catalysts for ORR/OER mainly resulting from the coupling of heteroatom-doped carbon-based materials and 3d transition metal (Co, Ni, Fe, Mn) (hydr)oxides (perovskites [60], spinels [59], layered double hydroxides [47] as recently reviewed by Chen et al. [61]. The activity and high stability of these heterostructures result from a higher dispersion degree of the oxide phase, synergistic effects as well as in some cases from the formation of a covalent heterointerface between phases notably favoring charge transfer during OER/ORR [62]. The presence of a highly active and stable oxide phase is responsible for mitigating carbon corrosion rate [61] but it is not sure it is sufficiently stable to be used in real cells. To improve stability and possibly activity of such catalysts the use of oxygen deficient oxides like TiO_{2-x} or WO_{3-x} presenting conductivities in the range of several S cm^{-1} could be of major interest [63]. In the same way, recently developed 2-D carbonitrides known as MXene could lead to very efficient heterostructures in reason of their very high electronic conductivity [64].

Oxygen vacancies at oxide surfaces can be also responsible for modifying adsorption energies of intermediates especially by tuning density of states on metal cations [65]. Another way to tune electronic properties of active sites and the to enhance ORR and/or OER electroactivity of metal oxides consists in substituting oxygen for another or several other anions resulting in the formation of very active chalcogenides [66], nitrides [67], phosphides [68] and borides [69]. These materials can be obviously coupled to an electron conductive and/or active matrix to obtain heterostructured catalysts with improved efficiency [63]. As mentioned in section 2.2, the growth of heterostructured catalysts composed of sulfides [33] or phosphides [34] directly onto Ni foam lead to the design of very efficient catalyst for overall water splitting and thus towards OER. The established interfaces with Ni oxides at OER potentials allow modifying adsorption energies of oxygenated intermediates, thus improving OER kinetics [33].

Another trend consists in developing carbon-based metal free materials in which defects and/or heteroatom are introduced to modulate electronic properties of carbon [70]. As an example, in N doped carbon-based catalysts, electronic structure of carbon atoms adjacent to N atoms (which are believed to be active sites for ORR/OER) are subject to a strong electron density modification. Pyridinic and graphitic nitrogen speciation are mainly responsible for the activity [71]. Based on these results, C₃N₄-based materials containing high amounts of nitrogen were recently investigated [72]. Other heteroatoms (S, P, B) [73] are also efficient to improve catalytic properties of carbonaceous materials. Electronic properties of doped carbon are related to the number of electrons in the external shell of the heteroatom, its electronegativity, chemical hardness and size [73]. Synthesizing multiple-doped materials is furthermore recognized as an efficient way to get an active catalyst. As an example, for nitrogen and phosphorous dual-doped carbon-based materials it was shown from DFT calculations that formation of P-N bonds and the presence of N dopants were respectively at the origin of the OER and ORR activity [74]. These theoretical considerations led to the synthesis of a highly active P/N doped graphene framework exhibiting an ORR half wave potential of 0.85 V vs. RHE and a potential of 1.55 V vs. RHE to drive a current density of 10 mA cm⁻² during OER. Another strategy consists in introducing structural defects in graphitic materials to tune carbon electronic structure. Especially, DFT calculations shown that a five-carbon ring adjacent to a seven-carbon ring leads to an optimal adsorption energy for oxygenated intermediates [75]. Based on this work, numerous catalysts were designed for OER and ORR [76]. Nevertheless, stability of carbon-based catalysts at electrode potentials, required for the OER and under harsh conditions, remains questionable. OER/ORR activities of materials described in this section are reported in Table 2

Table 2: Representative recently developed catalysts for OER/ORR in alkaline medium. Performances of reported catalysts can be systematically compared with those of reference catalysts tested under the same operating conditions. E_{1/2} represents the half-wave potential measured from

ORR polarization curves. n is the number of electrons exchanged per oxygen molecule. E_{j10} and E_{j50} corresponds to the electrode potential required to drive respective current densities of 10 and 50 mA cm^{-2} . b is the Tafel slope.

Oxygen reduction reaction	Catalyst	Morphology	Loading (mg cm ⁻²)	Working electrode	Electrolyte	E _{1/2} (V vs. RHE)	n	Ref.
	La _{0.8} Sr _{0.2} Mn _{0.6} Ni _{0.4} O ₃	Nanoparticles (14 nm)	0.14	Glassy carbon	1 M KOH	0.66 (ca. -0.4 V/ SCE)	3.92	[56]
	Pt/C	Commercial 20 wt.% Pt/C	0.028	Glassy carbon	1 M KOH	0.83 (ca. -0.24 V/ SCE)	4	
	Ba _{0.5} Sr _{0.5} Co _{0.5} Fe _{0.2} O _{3-δ} /acetylene black	Microparticles	ca. 0.4	Glassy carbon	0.1 M KOH	ca. 0.65	n/a	[60]
	MnCo ₂ O ₄ /N-rGO	Particles (5 nm) deposited onto N-rGO	0.1	Glassy carbon	1 M KOH	0.87	3.90	[62]
	Pt/C	Commercial 20 wt.% Pt/C	0.1	Glassy carbon	1 M KOH	0.89	n/a	
	ZrN	Nanoparticles (45 nm)	0.024	Glassy carbon	0.1 M KOH	0.8	3.9 - 4.0	[67]
	Pt/C	Commercial 20 wt.% Pt/C (Johnson Matthey)	0.024	Glassy carbon	0.1 M KOH	0.8	3.80	
	CoS _x @P-C ₃ N ₄ /rGO	Porous C ₃ N ₄ matrix supported onto rGO and containing CoS _x nanoparticles	0.4	Glassy carbon	0.1 M KOH	0.78	3.90	[72]
	Pt/C	Commercial 20 wt.% Pt/C	0.2	Glassy carbon	0.1 M KOH	0.81	3.90	
	P,N-doped graphene	Graphene framework	0.1	Glassy carbon	0.1 M KOH	0.85	3.99	[74]
	Pt/C	Commercial 20 wt.% Pt/C (Alfa Aesar)	0.1	Glassy carbon	0.1 M KOH	0.82	n/a	
	N,P-doped graphene/carbon fiber	P,N dual doped defective graphene interacting with carbon fibers	N/A	Glassy carbon	0.1 M KOH	0.79	3.8	[76]

	Pt/C	Commercial 20 wt.% Pt/C (Johnson Matthey)	0.2	Glassy carbon	0.1 M KOH	0.83	N/A		
Oxygen evolution reaction	Catalyst	Morphology	Loading (mg cm⁻²)	Working electrode	Electrolyte	E_{j10} (V vs. RHE)	E_{j50} (V vs. RHE)	b (mV dec⁻¹)	Ref.
	MoS ₂ /Ni ₃ S ₂ /nickel foam	Porous heterostructure grown onto Ni foam	9.7	Ni foam	1 M KOH	1.45	ca. 1.51	88	
	IrO ₂	Commercial powder (Fuel cell store)	3	Ni foam	1 M KOH	1.56	ca. 1.58	76	
	FeP/Ni ₂ P/nickel foam	Porous heterostructures composed of FeP and Ni ₂ P nanoparticles grown onto Ni foam	8	Ni foam	1 M KOH	1.39	n/a	23	
	IrO ₂	Commercial powder (Alfa Aesar)	n/a	n/a	1 M KOH	1.52	n/a	72	
	La _{0.5} Sr _{0.2} Mn _{0.6} Ni _{0.4} O ₃	Nanoparticles (14 nm)	0.14	Glassy carbon	0.1 M KOH	1.86 (0.85 V/SCE)	n/a	n/a	[56]
	Ni-Fe-layered double hydroxide	Hollow microsphere (350 nm)	0.25	Glassy carbon	1 M KOH	1.47	ca. 1.50	53	[58]
Ir/C	Commercial 20 wt.% Ir/C	0.25	Glassy carbon	1 M KOH	1.52	ca. 1.57	75		

Co ₃ O ₄ /N-rGO	Particles supported onto N-rGO (4-8 nm)	1	Ni foam	1 M KOH	1.54	1.58	67	[59]
Ba _{0.5} Sr _{0.5} Co _{0.5} Fe _{0.2} O _{3-δ} /acetylene black	Microparticles	ca. 0.4	Glassy carbon	0.1 M KOH	1.58	n/a	59	[60]
Co layered double hydroxide/Ti ₃ C ₂ T _x	Mxene covered with layered double hydroxide nanosheets	0.35	Glassy carbon	1 M KOH	1.53	n/a	82	[64]
IrO ₂	Commercial powder (Alfa Aesar)	0.35	Glassy carbon	1 M KOH	1.64	n/a	n/a	
FeCo oxide nanosheets	Nanosheets (width 400 nm - thickness 1.2 nm)	0.36	Glassy carbon	0.1 M KOH	ca. 1.54	n/a	37	[65]
RuO ₂	Commercial powder	0.36	Glassy carbon	0.1 M KOH	ca. 1.65	n/a	80	
Ni _{0.75} Fe _{0.25} -P/PO ₃ @functionnalized CNT	Ni-Fe phosphide nanoparticles (10 nm) anchored onto functionnalized carbon nanotubes	0.5	Glassy carbon	1 M KOH	ca. 1.49	1.52	45	[68]
RuO ₂	Commercial powder (Shangai Hansi chemical industry)	0.5	Glassy carbon	1 M KOH	1.55	ca. 1.65	48	
Fe-Ni-B/NF	Nanosheets (length 100 nm - a few nanometers width)	1	Ni foam	1 M KOH	1.47	ca. 1.49	38	[69]
RuO ₂ /NF	Commercial RuO ₂ powder	1	Ni foam	1 M KOH	1.52	ca. 1.57	78	
P,N dual doped graphene	Graphene frameworks	0.1	Glassy carbon	0.1 M KOH	1.55	N/A	N/A	[74]
Ir/C	Commercial 20 Wt. % Ir/C catalyst (Fuel cell store)	0.1	Glassy carbon	0.1 M KOH	ca. 1.58	N/A	N/A	

4. Conclusions and perspectives

This short review provides a full understanding of HER, HOR, OER and ORR mechanisms in alkaline electrolyte and gives an overview of state-of-the-art catalysts designed for these reactions. Even if very efficient materials have been reported during the past few years, the design of catalysts remains based on a trial and error approach. A general guideline to design efficient catalysts can be summarized in the following points: 1) engineering the porosity of the structure (microporosity, mesoporosity, macroporosity) to increase the number and density of exposed active sites as well as to improve diffusion of reactants and electrolyte 2) using a stable electron conductive substrate improving dispersion of catalysts and active sites activity by accelerating charge transfer and tuning electronic properties of active sites 3) engineering heterostructured catalysts with exposed heterointerfaces leading to the optimization of adsorption energies of reaction intermediates 4) modulating electronic properties of active sites by using a suitable heteroatom doping strategy or by inducing the formation of structural vacancies. Additionally, the better understanding of electrode/electrolyte interface in alkaline media and particularly the interaction between species (water, alkali cations,...) in the double layer and the inner-sphere HO^- adsorption is required to improve our understanding of phenomena and then to extract better rational design principles. The stability of designed catalysts should be evaluated under conditions mimicking the working environment encountered in real cells. Finally, measurements of catalysts activity should be rationalized by following already reported guidelines in order to establish unbiased comparisons between different studies.

Conflict of interest

Nothing declared

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Table 1: Non-exhaustive list presenting representative recently developed catalysts for HER/HOR in alkaline medium. j_0 represents the exchange current density. It has been normalized using either platinum active surface area (in that case the unit is denoted as $\text{mg cm}^{-2}_{\text{Pt}}$) or using geometric surface area. The mass normalized j_0 value is also given for HOR catalysts. η represents the overpotential. For HER, overpotential values at -10 mA cm^{-2} (η_{-10}) as well as at -100 mA cm^{-2} (η_{-100}) are given. b is the Tafel slope

Hydrogen oxidation reaction (HOR)	Catalyst	Morphology / structure	Loading (mg _{metal} cm ⁻²)	Working electrode	Electrolyte	j ₀ (mA mg ⁻¹ _{metal})	j ₀ (mA cm ⁻²)
	Pt	Nanowires	0.02	Vulcan XC 72 R coated glassy carbon	0.1 M KOH	16 mA mg ⁻¹ _{Pt}	0.229 mA cm ⁻²
	PtRu	Nanowires	0.02	Vulcan XC 72 R coated glassy carbon	0.1 M KOH	32 mA mg ⁻¹ _{Pt}	0.493 mA cm ⁻²
	PtFe	Nanowires	0.02	Vulcan XC 72 R coated glassy carbon	0.1 M KOH	27 mA mg ⁻¹ _{Pt}	0.459 mA cm ⁻²
	CoMoNi	Electroplated material	n/a	Au	0.1 M KOH	n/a	0.015
	Pt	polycrystalline disk	n/a	Pt	0.1 M KOH	n/a	0.61
	Ni/N-CNT	Nanoparticles (20 nm)	0.25	Glassy carbon	0.1 M KOH	3.5	0.028
	Ni ₃ N/C	Nanoparticles (4.6 nm)	0.16	Glassy carbon	0.1 M KOH	12	0.014
Hydrogen evolution reaction (HER)	Catalyst	Morphology / structure	Loading (mg cm ⁻²)	Working electrode	Electrolyte	η ₋₁₀ (mV)	η ₋₁₀₀ (mV)
	Pt/Ni(HCO ₃) ₂	20 wt. % Pt nanoparticles (2-3 nm) on Ni(HCO ₃) ₂ nanoplates	0.04	Glassy carbon	1 M KOH	-27	ca. -70
	Pt	Bare Pt nanoparticles	0.2	Glassy carbon	1 M KOH	-44	ca. -125
	Pt/C	Commercial 10 wt.% Pt/C (Sigma-Aldrich)	0.02	Glassy carbon	1 M KOH	ca. -50	n/a
	Mo ₂ C/N-doped carbon microflowers	N-doped microflowers consisting of nanoflakes decorated with β-Mo ₂ C (particles)	0.28	Glassy carbon	1 M KOH	-100	n/a
	Pt/C	Commercial 20 wt. % Pt/C	0.28	Glassy carbon	1 M KOH	-50	n/a
	Fe _{1.89} Mo _{4.11} O ₇	Microparticles	2.4	Bare carbon paste	1 M KOH	-197	n/a
	Pt/C	Commercial 20 wt. % Pt/C	n/a	n/a	1 M KOH	-103	n/a
	NiS ₂ /MoS ₂	Hybrid porous nanowires composed of MoS ₂ nanoplates and NiS ₂ particles with heterojunctions	0.2	Glassy carbon	1 M KOH	-204	n/a
	Pt/C	n/a	0.2	Glassy carbon	1 M KOH	-50	n/a
	FeNiSe/exfoliated graphene	Mesoporous FeNiSe nanosheets grown onto exfoliated graphene	3.3	Graphite foil	1 M KOH	-187	n/a
	Pt/C	Commercial catalyst	3.3	n/a	1 M KOH	ca.-75	n/a
	Mn-doped Ni ₂ P	Mn-doped Ni ₂ P Nanosheets array on Ni foam	n/a	Ni foam	1 M KOH	ca. 50	ca. -22
	Pt/C	Commercial 20 wt. % Pt/C (Sigma-Aldrich)	7.0	Ni foam	1 M KOH	ca. 20	ca. -12
	NiCoN/C	Hybrid nanocages composed of nanosheets with a thickness of 2-3 nm	0.2	Glassy carbon	1 M KOH	-103	n/a
	Pt/C	Commercial Pt/C	0.05	Glassy carbon	1 M KOH	-91	n/a
	Co-Ni-B/carbon cloth	Co-Ni-B nanoparticles (5-10 nm)	0.34	Carbon cloth	1 M KOH	-80	ca. -25
	Pt/C	Commercial Pt/C	0.34	Carbon cloth	1 M KOH	ca. -25	ca. -24
S-doped C ₃ N ₄ /carbon naotubes/carbon	Fibers decorated with S-doped C ₃ N ₄	0.5	Carbon fiber	1 M KOH	-131	ca. -25	

fiber						
Mo ₂ C/Mo ₂ N	Mesoporous material	0.38	Glassy carbon	1 M KOH	-145	-222
Pt/C	20 wt. % Pt/C (Alfa Aesar)	0.38	Glassy carbon	1 M KOH	-60	-263
MoS ₂ /Ni ₃ S ₂ /nickel foam	Porous heterostructure grown onto Ni foam	9.7	Ni foam	1 M KOH	ca. -110	n/a
Pt/C	20 wt. % Pt/C (Fuel Cell store)	0.8	Ni foam	1 M KOH	ca. -25	n/a
FeP/Ni ₂ P/nickel foam	Porous heterostructures composed of FeP and Ni ₂ P nanoparticles grown onto Ni foam	8	Ni foam	1 M KOH	-14	ca. -132
Pt	Pt wire	n/a	n/a	1 M KOH	-59	ca. -132
N-NiCo ₂ S ₄	Nanowires	n/a	Ni foam	1 M KOH	-41	ca. -142
Pt/C	Commercial 20 wt. % Pt/C	2.3	Ni foam	1 M KOH	-28	ca. -142
Ni, Zn-doped CoO	Nanorods	0.486	Carbon fiber paper	1 M KOH	-53	ca. -162
Pt/C	Commercial 20 wt. % Pt/C (Fuel cell store)	0.4	Carbon fiber paper	1 M KOH	ca. -60	ca. -172
NiO@1T-MoS ₂ /CFP	Nanosheets	1.02	Carbon fiber paper	1 M KOH	-46	ca. -122
Pt/C	Commercial 20 wt. % Pt/C (Johnson Matthey)	1	Carbon fiber paper	1 M KOH	-23	ca. -132

Table 2: Representative recently developed catalysts for OER/ORR in alkaline medium. Performances of reported catalysts can be systematically compared with those of reference catalysts tested under the same operating conditions. $E_{1/2}$ represents the half-wave potential measured from ORR polarization curves. n is the number of electrons exchanged per oxygen molecule. E_{j10} and E_{j50} corresponds to the electrode potential required to drive respective current densities of 10 and 50 mA cm^{-2} . b is the Tafel slope

Oxygen reduction reaction	Catalyst	Morphology	Loadin g (mg cm ⁻²)	Workin g electrod e	Electrolyt e	E _{1/2} (V vs. RHE)	n	Ref .
	La _{0.8} Sr _{0.2} Mn _{0.6} Ni _{0.4} O ₃	Nanoparticles (14 nm)	0.14	Glassy carbon	1 M KOH	0.66 (ca. - 0.4 V/ SCE)	3.92	[56]
	Pt/C	Commercial 20 wt.% Pt/C	0.028	Glassy carbon	1 M KOH	0.83 (ca. - 0.24 V/ SCE)	4	
	Ba _{0.5} Sr _{0.5} Co _{0.5} Fe _{0.2} O _{3-δ} /acetylene black	Microparticles	ca. 0.4	Glassy carbon	0.1 M KOH	ca. 0.65	n/a	[60]
	MnCo ₂ O ₄ /N-rGO	Particles (5 nm) deposited onto N-rGO	0.1	Glassy carbon	1 M KOH	0.87	3.90	[62]
	Pt/C	Commercial 20 wt.% Pt/C	0.1	Glassy carbon	1 M KOH	0.89	n/a	
	ZrN	Nanoparticles (45 nm)	0.024	Glassy carbon	0.1 M KOH	0.8	3.9 - 4.0	[67]
	Pt/C	Commercial 20 wt.% Pt/C (Johnson Matthey)	0.024	Glassy carbon	0.1 M KOH	0.8	3.80	
	CoS _x @P-C ₃ N ₄ /rGO	Porous C ₃ N ₄ matrix supported onto rGO and containing CoS _x nanoparticles	0.4	Glassy carbon	0.1 M KOH	0.78	3.90	[72]
	Pt/C	Commercial 20 wt.% Pt/C	0.2	Glassy carbon	0.1 M KOH	0.81	3.90	[74]
	P,N-doped graphene	Graphene framework	0.1	Glassy carbon	0.1 M KOH	0.85	3.99	
	Pt/C	Commercial 20 wt.% Pt/C (Alfa Aesar)	0.1	Glassy carbon	0.1 M KOH	0.82	n/a	

	N,P-doped graphene/carbon fiber	P,N dual doped defective graphene interacting with carbon fibers	N/A	Glassy carbon	0.1 M KOH	0.79	3.8	[76]	
	Pt/C	Commercial 20 wt.% Pt/C (Johnson Matthey)	0.2	Glassy carbon	0.1 M KOH	0.83	N/A		
Oxygen evolution reaction	Catalyst	Morphology	Loadin g (mg cm⁻²)	Workin g electrod e	Electrolyt e	E_{j10} (V vs. RHE)	E_{j50} (V vs. RHE)	b (m V dec⁻¹)	Ref .
	MoS ₂ /Ni ₃ S ₂ /nickel foam	Porous heterostructure grown onto Ni foam	9.7	Ni foam	1 M KOH	1.45	ca. 1.51	88	
	IrO ₂	Commercial powder (Fuel cell store)	3	Ni foam	1 M KOH	1.56	ca. 1.58	76	
	FeP/Ni ₂ P/nickel foam	Porous heterostructure composed of FeP and Ni ₂ P nanoparticles grown onto Ni foam	8	Ni foam	1 M KOH	1.39	n/a	23	
	IrO ₂	Commercial powder (Alfa	n/a	n/a	1 M KOH	1.52	n/a	72	

		Aesar)							
	$\text{La}_{0.5}\text{Sr}_{0.2}\text{Mn}_{0.6}\text{Ni}_{0.4}\text{O}_3$	Nanoparticles (14 nm)	0.14	Glassy carbon	0.1 M KOH	1.86 (0.85 V/SCE)	n/a	n/a	[56]
	Ni-Fe-layered double hydroxide	Hollow microsphere (350 nm)	0.25	Glassy carbon	1 M KOH	1.47	ca. 1.50	53	[58]
	Ir/C	Commercial 20 wt.% Ir/C	0.25	Glassy carbon	1 M KOH	1.52	ca. 1.57	75	
	$\text{Co}_3\text{O}_4/\text{N-rGO}$	Particles supported onto N-rGO (4-8 nm)	1	Ni foam	1 M KOH	1.54	1.58	67	[59]
	$\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.5}\text{Fe}_{0.2}\text{O}_{3-6}$ /acetylene black	Microparticles	ca. 0.4	Glassy carbon	0.1 M KOH	1.58	n/a	59	[60]
	Co layered double hydroxide/ $\text{Ti}_3\text{C}_2\text{T}_x$	Mxene covered with layered double hydroxide nanosheets	0.35	Glassy carbon	1 M KOH	1.53	n/a	82	[64]
	IrO_2	Commercial powder (Alfa Aesar)	0.35	Glassy carbon	1 M KOH	1.64	n/a	n/a	
	FeCo oxide nanosheets	Nanosheets (width 400 nm - thickness 1.2 nm)	0.36	Glassy carbon	0.1 M KOH	ca. 1.54	n/a	37	[65]
	RuO_2	Commercial powder	0.36	Glassy carbon	0.1 M KOH	ca. 1.65	n/a	80	
	$\text{Ni}_{0.75}\text{Fe}_{0.25}$ - P/ PO_3 @functionalize d CNT	Ni-Fe phosphide nanoparticles (10 nm) anchored onto	0.5	Glassy carbon	1 M KOH	ca. 1.49	1.52	45	[68]

		functionalized carbon nanotubes							
	RuO ₂	Commercial powder (Shanghai Hansi chemical industry)	0.5	Glassy carbon	1 M KOH	1.55	ca. 1.65	48	
	Fe-Ni-B/NF	Nanosheets (length 100 nm - a few nanometers width)	1	Ni foam	1 M KOH	1.47	ca. 1.49	38	[69]
	RuO ₂ /NF	Commercial RuO ₂ powder	1	Ni foam	1 M KOH	1.52	ca. 1.57	78	
	P,N dual doped graphene	Graphene frameworks	0.1	Glassy carbon	0.1 M KOH	1.55	N/A	N/A	
	Ir/C	Commercial 20 Wt. % Ir/C catalyst (Fuel cell store)	0.1	Glassy carbon	0.1 M KOH	ca. 1.58	N/A	N/A	[74]