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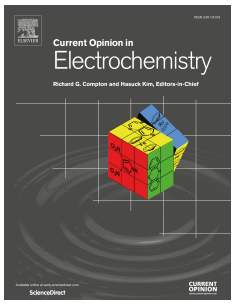

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Advances, Opportunities and Challenges of Hydrogen and Oxygen Production from Seawater Electrolysis: An Electrocatalysis Perspective

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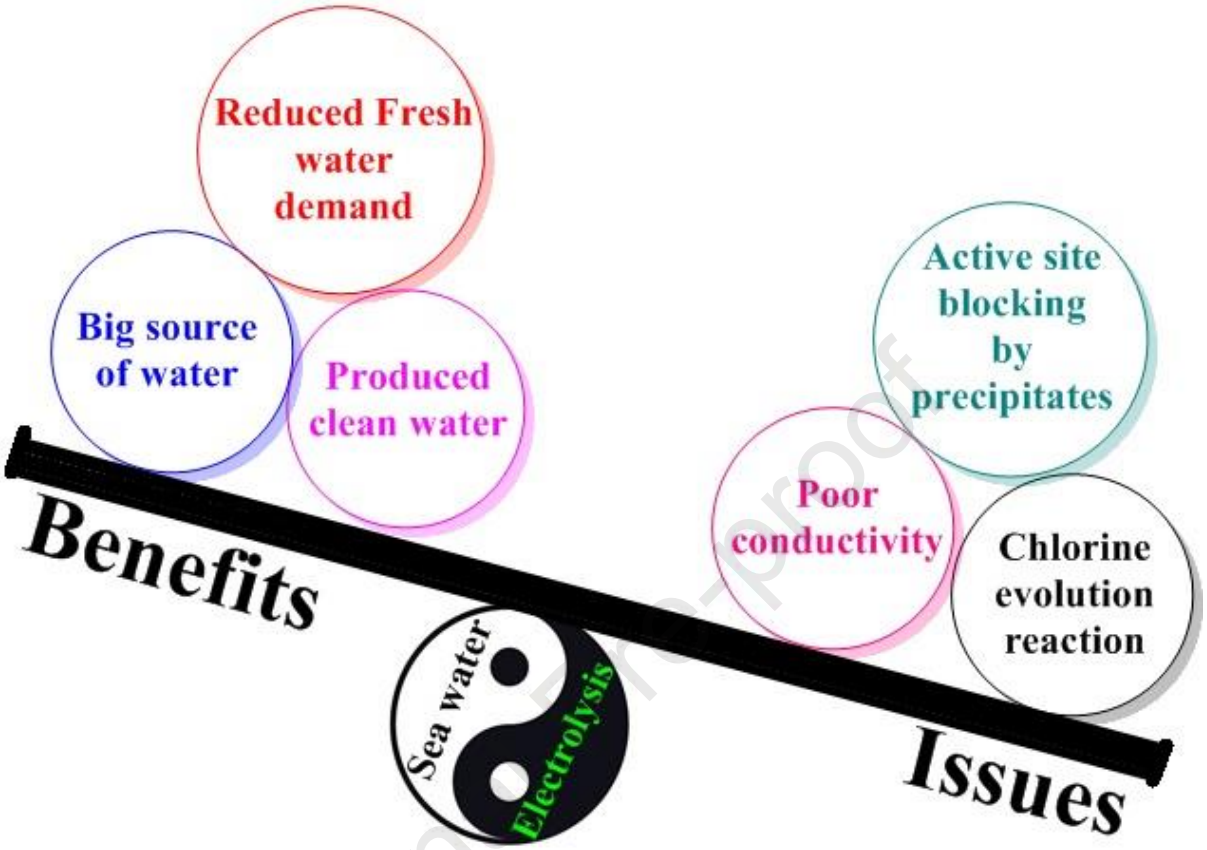
Graphical abstract



Abstract

With increasing energy consumption and greenhouse gas emissions, the importance of developing renewable energy sources to replace fossil fuels has become a vital global task. Hydrogen produced via water electrolysis powered by renewable energy systems at a large scale is an essential measure to reduce greenhouse gas and particulate emissions. Electrolysers use a substantial amount of water (mainly freshwater) to produce hydrogen and oxygen at the cathode, and anode, respectively. However, seawater is preferred because it is the most abundant water resource. Although many R&D efforts on seawater electrolysis have been carried out since the 1970s, the barriers are the undesired chlorine gas evolution reaction at the anode, and corrosion induced by chloride ions. Unlike the available data for electrocatalyst materials based upon platinum group metals in pure solutions, limited data is available for electrocatalysts in seawater. Therefore, there is an urgent need to develop new electrocatalysts for seawater electrolysis.

Keywords: Seawater electrolysis; Electrocatalyst; Hydrogen evolution reaction (HER); Oxygen evolution reaction (OER); Chlorine evolution reaction (CER)

1. Introduction

Electrochemical water splitting for hydrogen generation (currently produces around 1% of global hydrogen) [1] will play a key role in meeting climate change targets. Water electrolysers can provide the foundation of a sustainable hydrogen production network coupled to intermittent renewable energy systems [1]. For example, the European Union (EU) has pledged to reach 2x40 GW of water electrolysers by 2030 (40 GW in Europe and 40GW in EU's neighborhood with export to the EU) corresponding to up to 20million tons of renewable hydrogen, with the industry expecting a dramatic exponential increase in water electrolysers manufacturing. Also, the world's largest seawater hydrogen production plant in Saudi Arabia, powered by 4 GW of wind and solar energies, will produce 650 tons of green hydrogen daily [1,2].

Depending upon the catalysts, electrolytes, separators, working temperatures, and pressures, currently there are five technologies for water electrolysers [1]:

(i) Alkaline Water Electrolyser (AWE),

(ii) Proton Exchange Membrane Water Electrolyser (PEMWE),

(iii) Anion Exchange Membrane Water Electrolyser (AEMWE),

(iv) Solid Oxide Electrolysis Cell (SOEC) , and

(v) Protonic Ceramic Electrolysis Cell (PCEC)

PEMWE and AWE are being used commercially as the technology is fairly mature. In the case of AEMWE, it is now seen as the most promising low-temperature electrolyser technology. For both PEMWE and AEMWE, membrane electrode assemblies (MEA) are used. MEAs are usually made of either catalyst coated substrates (CCS) or catalyst coated membranes (CCM) [1].

Low-temperature water electrolyser technologies use a large amount of freshwater supplies to produce H_2 (i.e., ca. 9litres of pure water per 1kg of H_2; assuming 100% efficiency).

40GW of installed electrolysers in the EU would represent 10million tons of H_2 and 90million liters of freshwater [1]. Thus, producing hydrogen from seawater seems to be a very attractive alternative, especially in regions where freshwater is an issue. Globally, the Middle East, South Africa, the west coast of the Americas, Australia, and the west of China are the main desert coastal lands of the world appropriate for solar-driven seawater electrolysis [2-6].

Freshwater electrolysis results in the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER) on the cathode and the anode of the electrolyser, respectively. Due to the complex chemical and biological composition of seawater, especially high concentrations of Cl^- (*ca.* 3.5wt%, 0.5M, pH~8), the chlorine evolution reaction (CER) competes with the OER on the anode [7]. Hence, selective, stable, and cost-effective catalysts are required for seawater electrolysers to efficiently drive the HER and the OER only. Table 1 summarizes the standard redox potentials for HER and OER in various pH ranges [5,6]. HER is generally described in two ways: H^+ reduction in acidic media and water reduction in alkaline media with traditionally accepted mechanism composed of well-known *Volmer*, *Heyrovsky*, and *Tafel* steps (the corresponding reactions are presented in Table 1) [1]. The classically accepted 4-electron mechanism of OER in acidic and alkaline media is also given in Table 1 and Figure 1(a).

Herein a short discussion of state-of-the-art precious metal-free catalysts for seawater electrolysis is presented, focusing on advances and challenges with electrocatalysts.

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94 **Table 1**. The hydrogen evolution, the oxygen evolution and the chlorine evolution reaction mechanisms in water, seawater and brine.

Reaction		Half-Reaction	Standard Redox Potential (V) vs. SHE	Mechanism		
HER (low pH's)		$2H^+ + 2e^- \rightarrow H_2$	$E^{\emptyset}$ = 0.000 V, pH 0	HER [1,5,6]	$H^+ + e^- \rightarrow H_{ads}$ $H_2O + e^- \rightarrow H_{ads} + OH^-$	Volmer
HER (neutral pH's)		$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	$E^{\emptyset}$ = -0.827 V, pH 14		$H_{ads} + H_{ads} \rightarrow H_2$	Tafel
HER (high pH's)		$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	$E^{\emptyset}$ = -0.827 V, pH 14		$H_{ads} + H^+ + e^- \rightarrow H_2$ $H_{ads} + H_2O + e^- \rightarrow H_2 + OH^-$	Heyrovsky
OER		$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$	$E^{\emptyset}$ = +1.229 V, pH 0	OER [1,5,6]	In acidic media : $M + H_2O \rightleftharpoons MOH + H^+ + e$ $MOH + OH^- \rightleftharpoons MO + H_2O + e$ $2MO \rightleftharpoons 2M + O_2$ $MO + H_2O \rightleftharpoons MOOH + H^+ + e$ $MOOH + H_2O \rightleftharpoons M + O_2 + 2H^+ + 2e$	
OER (high pH's)		$2OH^- \rightarrow O_2 + H_2O + 2e^-$	$E^{\emptyset}$ = +0.402 V, pH 14			
Clhorine evolution reaction (CER)		$2Cl^- \rightarrow Cl_2 + 2e^-$	$E^{\emptyset}$ = +1.358 V, pH 0			
Hypochlorate formation (Electrochlorination)		$Cl^- + 2OH^- \rightarrow ClO^- + H_2O + 2e^-$	$E^{\emptyset}$ = +0.810 V, pH 14		In alkaline media : $M + OH^- \rightleftharpoons MOH + e$ $MOH + OH^- \rightleftharpoons MO + H_2O + e$ $2MO \rightleftharpoons 2M + O_2$ $MO + OH^- \rightleftharpoons MOOH + e$ $MOOH + OH^- \rightleftharpoons M + O_2 + H_2O + e$	
Chlor-alkali	Cathode	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ $H_2O + 1/2\ O_2 + 2e \rightarrow 2OH^-$ (for ODC technology)	$E^{\emptyset}$ = -0.827 V, pH 14 $E^{\emptyset}$ = +0.402 V, pH 14			
	Anode	$2Cl^- \rightarrow Cl_2 + 2e^-$	$E^{\emptyset}$ = +1.358 V, pH 0			

95 M: Metal

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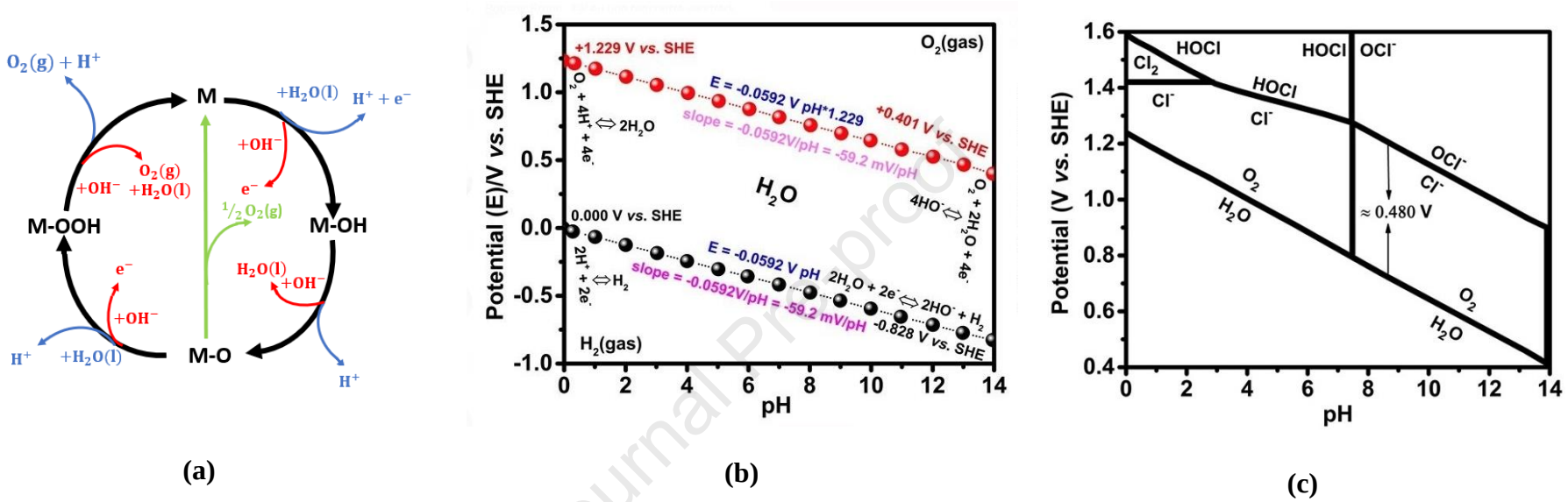

Figure 1. (a) The OER mechanism in acid (blue line) and alkaline (red line) solutions. The black line illustrates the OER involving the formation of a peroxide (M–OOH) intermediate, while another possible route for producing oxygen is the direct reaction of two adjacent oxo (M–O) intermediates (green line); representation modified from [6]. (b) The Pourbaix diagram of aqueous electrolyte at 298.15K. (c) The Pourbaix diagram of saline water at 298.15K. Modified from [5,6].

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2. Electrochlorination and chlor-alkali processes

The electrochlorination and chlor-alkali processes involve electrolysis of seawater and brine, respectively; the former is often used for water disinfection (Cl_2, HOCl, and ClO^- are formed - see Table 1), while the latter producing $Cl_2(g)$, $H_2(g)$, and NaOH(l). Since the 19th century, four technologies have been developed in the chlor-alkali industry [7,8]:

(i) Mercury (Hg) cell: The anodic CER is integrated with sodium amalgam generation reaction ($2Hg + 2Na^+ + 2e^- \rightarrow 2NaHg$) on the liquid Hg cathode. Because of the isolated Cl_2 and NaOH formation, the cell usually generates purer NaOH than later technologies but with higher energy consumption [7].

(ii) Diaphragm cell: A spongy asbestos mat isolates the anode and cathode reactions, and NaOH is generated in the cathode compartment.

(iii) Membrane cell: A polymer ion exchange membrane is used as a separator instead of a diaphragm with the process similar to the diaphragm cell [7].

(iv) Oxygen depolarized cathode (ODC) cells: The formation of hydrogen is prevented by electrochemical reduction of oxygen to OH^- ($H_2O + 1/2O_2 + 2e^- \rightarrow 2OH^-$) with ~30% energy saving. The reaction takes place in the "three-phase zone" of ODC where $O_2(g)$, water (liquid), and electrons (from the solid phase) meet [8]

Consumable graphite-based anodes are being substituted by the so-called dimensionally stable anode (DSA) (also called mixed metal oxide (MMO); a platinum group metal, PGM-based oxide such as PtO_2, IrO_2 or RuO_2 coated onto Ti) [7].

Figure 1(b) shows the *E-pH* (Pourbaix) diagrams of water redox reactions and Figure 1(c) exhibits the Pourbaix diagrams for the seawater redox reactions. The two-electron CER pathway is kinetically favored over the four-electron OER mechanism. To compensate for this, the thermodynamic potential difference of the two reactions must be maximized (~480mV at

pH >7.5) according to Figure 1(c). As observed in the figure, at low pH the CER, and high pH the ClO^- formation compete with the OER. Thus, seawater splitting anodes must be efficient and sufficiently selective for OER in large-scale applications to avoid the CER [5,6].

3. Electrocatalysts for HER in seawater

Pt is the best platinum group metal (PGM) catalyst for the HER due to the medium strength of Pt-H bonds and the fast kinetics of HER; but non-PGM catalysts are considered instead due to the high costs of Pt-based electrodes and stability issues in non-acidic solutions [9-11]. Even traces of Cl^- may lead to a significant dissolution of Pt. The loss of electrochemical active surface area (*ECSA*) in the presence of 500–2,000ppm Cl^- and degradation of electrochemically deposited Pt in the 1-1,000ppm chloride solutions have been reported [12]. Geiger *et al.* [13] also proved that the anodic dissolution occurred via hindering the passive oxide layers formation in chloride solution; in contrast, the cathodic dissolution was influenced by the formation of PtCl complexes.

Two main strategies to minimize the PGM consumption are to: (i) develop alloys/composites on supports that help to diminish the precious metals usage, and (ii) design PGM-free catalysts.

Pt-based hollow structures (Pt@mh-3D MXene[1]) with highly porous structures present large surface areas, enormous adsorption sites, and enhanced diffusion paths; the efficient H-adsorption, moderate H-binding and rapid water dissociation characteristics also give them improved performances but lower costs comparable to bulk Pt electrodes [14].

Binary/ternary metallic nanocomposites such as NiMo nanocomposites are also proposed as efficient HER catalysts due to the synergism between Ni and Mo. Generally, Mo atoms usually are H-adsorption sites and Ni atoms are water dissociation centers [15].

[1] MXene: a 2D category of metallic materials with the general formula of $M_{n+1}X_nT_x$ (n=1-3; M: an early transition metal; X: C or N; T: surface groups like -OH, -O or –F)

Binary RuCo/Ti alloy electrodes with Ru as the primary catalytic component and surface roughness higher than ternary $RuCoMo_x$/Ti alloys indicated better HER performances in filtered seawater. This was due to the effect of surface roughness in enhancing the number of active HER catalytic sites. Partial oxidation of Ru also resulted in reducing the adsorption strength on surface sites [16].

Transition-metal di-chalcogenides (TMDs) such as MoS_2 have been known for many decades, but their catalytic activity remained unknown due to their low conductivity. Their catalytic activity is improved by forming nanostructures, doping metallic atoms like Co and Ni on edge sites and incorporating 2D carbon materials [15].

Intrinsic catalytic activity, porous structure and oxygen vacancies of transition metal oxides (TMOs) make them more appropriate for HER catalysis [15]. For $CoFe_2O_4$ nanoparticles the physical properties were regulated by tuning their oxygen vacancies as a function of particle size and worked under a very low cell voltage of 1.47V at 80^0C in an alkaline seawater electrolyser [17].

Generally, catalysts with adjacent metal oxide (MO_x) or metal (M) sites weaken the H-OH bonds since the MO_x sites tend to adsorb OH^- ions, while the nearby M sites prefer an H-bonding. Recently, Mn-based metal organic frameworks (MOFs), with nickel oxide anchored on nickel foam (NF) (Mn-NiO-Ni/NF), have been introduced as efficient catalysts in seawater. NF was the source of NiO and the pyrolysis of Mn-MOF yielded a MnO/C composite. The carbon matrix facilitated the formation of Mn/Ni composites. The electrodes showed onset potentials lower and current densities higher than commercial Pt/C in seawater. Regardless of scale deposition at long-term electrolysis, Mn-NiO-Ni/NF showed small activity losses at η~140mV with j~7mA/cm^2 for 14h [18].

The close contact of the electrocatalyst with substrate and the synergism between catalytic phases decrease the charge transfer resistances (R_{ct}) and improve efficiency and

durability. Ni-based TMOs mostly composed of α-$Ni(OH)_2$ and Ni sites converted from NF substrates are some examples. With electron transfer from α-$Ni(OH)_2$ sites to the adjacent Ni sites, slightly negative charges on Ni sites are formed that triggers the proton adsorption; the positively-charged $Ni(OH)_2$ sites also weaken the H-OH bonds, promoting water dissociation that improves the catalyst performance and durability [19].

Transition metal phosphides (TMPs) are also considered as one of the most promising categories of non-PGM HER catalysts, especially in acidic solutions [15]. Despite the high electrical conductivity, stability, and catalytic performance of TMPs in pure aqueous solutions, limited data are available in seawater. Recently, porous 3D feather-like NiCoP nanoarrays on NF (PF-NiCoP/NF) indicated high HER activity in seawater, showing an onset potential of -287mV with a FE of 96.5%. The NiCo nanoarrays were synthesized on NF via a hydrothermal method followed by a phosphorization step at 300^{o}C under an N_2 atmosphere. Synergism between Ni and Co phosphides, 3D network and high porosity of the NiCoP perpendicularly grown on NF, facilitate the diffusion of produced gases and mass transport of H^+/H_2O, increase the *ECSA* and provide many adsorption sites. The overpotential of PF-NiCoP/NF has been compared with other NiP-based electrodes in Figure 2(a). As observed, the reduced HER overpotential on PF-NiCoP/NF electrodes signifies the effect of morphology on electrode performance. In natural seawater, these structures indicated the HER performance even better than Pt/C electrodes. Under cathodic overpotential of 290mV, the electrode response remained unchanged after 20h of electrolysis. Despite this, white scales precipitated on the electrode, which were entirely removed with dilute acid washing, and the electrode worked again for 12h without significant degradation [20].

Generally, in TMPs, higher electronegativity with high P-content increase the number of negatively charged sites (for H-adsorption). Elevated P-content can also improve the

corrosion resistance and stabilities; however, its further enhancement has adverse effects on electrocatalytic performance because of the conductivity reduction [15].

It was found that doping nitrogen in the carbon shell of CoMoP@C core-shells made them more appropriate for seawater electrolysis. The N-doped carbon shell protected the CoMoP core from poisoning and corrosion with no significant current loss in artificial seawater and just slight decline in real seawater. Gibbs free energy of H-adsorption for N-doped samples was much lower than un-doped CoMoP@C. The electron-donating tendency of CoMoP, electron-withdrawing nature of N and high conductivity of C made a facilitated electron transfer path CoMoP→C→N; carbon shell also acts as an active HER catalytic site due to its high electron density [21].

Nanocomposites of transition metal carbides (TMCs) like WC and W_2C with high mechanical robustness and corrosion resistance also improve the stability of the catalysts. For example, Pt monolayers (MLs) or nanoparticles revealed low adhesion to the commonly used carbonaceous supports, causing low integrities that were improved significantly using WC and W_2C due to the strong binding energies between Pt and WC/W_2C. Carbon supports with high porosities but low intrinsic HER catalysis properties show gradual degradation. TMCs provide better intrinsic catalytic properties, higher stabilities, and strong binding to the upper layer [22]. Bimetallic TMCs of Co_3Mo_3C with carbon nanotubes (CNT) on NF (Co_3Mo_3C/CNT/NF) showed a Tafel slope and j_o of 249mV/dec and 415μA/cm^2, respectively (j_o ~13 times larger than bare NF) due to larger active surface area and higher catalytic activity of Co_3Mo_3C/CNT [9].

We have summarized a list of recently studied PGM-free electrocatalysts for HER and OER in seawater in Table 2.

218 **Table 2**: A summary of PGM-free electrocatalysts for HER and OER in different electrolytes

HER					
HER Catalyst	**Performance**	**Electrolyte**	**Tafel slope (mV/dec)**	**Highlights**	**Ref.**
Ni_2P-Fe_2P	η~41 mV at 10 mA/cm^2	1 M KOH 1 M KOH + seawater	86	Bi-functional HER/OER catalyst with almost similar efficiencies in both KOH and KOH + seawater	[23]
Co_3Mo_3C/CNT/Ni-F*	η_{onset} = 42 mV j_0 = 0.415 mA/cm^2	Seawater	249	Persistent operation over 26 h	[9]
Nanosheets, Mo_5N_6	η = 257 mV at 10 mA/cm^2	Natural seawater	-	Extremely stable H_2 production for 100 h at an overpotential of 300 mV	[24]
(Ni, Ru, Ir)-G**	-	Real seawater	48	A low overpotential of 0.08 V for 250 cycles; constant current density for 200 h; almost a 100% H_2 production efficiency.	[11]
ReS_2-T/Td	j_0 = 54.7 μA/cm^2	Saline water	69.5	Stable HER performance for over 12 h	[10]
NiCoP@Ni-F	η = 287 mV at 10 mA/cm^2	Seawater	54	Increased active surface area and adsorption sites; efficient electron-transfer due to 3*D* structure	[20]
N-doped CoMoP@C	η_{onset} not as good as Pt/C	Simulated and real seawater	49.73	N-doped carbon shell protected the CoMoP core from poisoning and corrosion	[21]
Binary RuCo and ternary $RuCoMo_x$ on Ti foils	η_{onset} =370 mV for RuCo	Seawater	>107 (RuCo)	Higher Ru amount and the rougher surface yield higher activity; stable for over 12 h	[16]
OER					
OER Catalyst	**Performance**	**Electrolyte**	**Tafel slope (mV/dec)**	**Highlights**	**Ref.**
NiO/FTO*** coated glass	η = 340 mV at 10mA/cm^2	1.0 M KOH 0.5 M NaCl	-	Dimensional stability increased due to the lack of metallic phase,	[25]
Fe-$Ni(OH)_2$/Ni_3S_2	η = 269 mV to at 10 mA/cm^2	Alkaline artificial seawater	46	Heterogeneous lamellar-edged. 27 h work at 100 mA/cm^2	[26]
Bimetallic oxy-boride (Co−Fe−O−B)	η = 294 mV at 10 mA/cm^2	1.0 M KOH + 0.5 M NaCl	52.6	Lowering the charge-transfer resistance. 100% O_2 selectivity	[27]
Ni borates and Co phosphates	-	0.5 M NaCl and seawater	-	CoPi and NiBi selectively generated O_2 suppressing the oxidation of Cl^- and Br^-	[28]
Se-NiFe-LDH****	-	Seawater-like electrolyte	26.3	250 h operation with a Se incorporated phase; large SeO_x^- ions suppressed the corrosion via Cl^- repulsion	[29]

NiFeN decorated on NiMoN nanorods on the Ni-F NiMoN@NiFeN	η = 277 mV for 100 mA/cm^2	Alkaline seawater	58.6	High conductivity of nanorods; large active surface area; formation of thin amorphous layers → corrosion resistance 3D structure → facilitates the diffusion of reactants and products	[30]
3D bifunctional CoSe (Co_9Se_8)	η = 280 mV at 100 mA/cm^2	Seawater	40.4	High activity and stability over both HER and OER; stable for 2,000 cycles in 1.0 M KOH	[31]
*CNT: carbon nanotube; Ni-F: Nickel Foam; **G: Graphene; *** FTO: fluorinated titanium oxide; ****LDH: layered double hydroxide					

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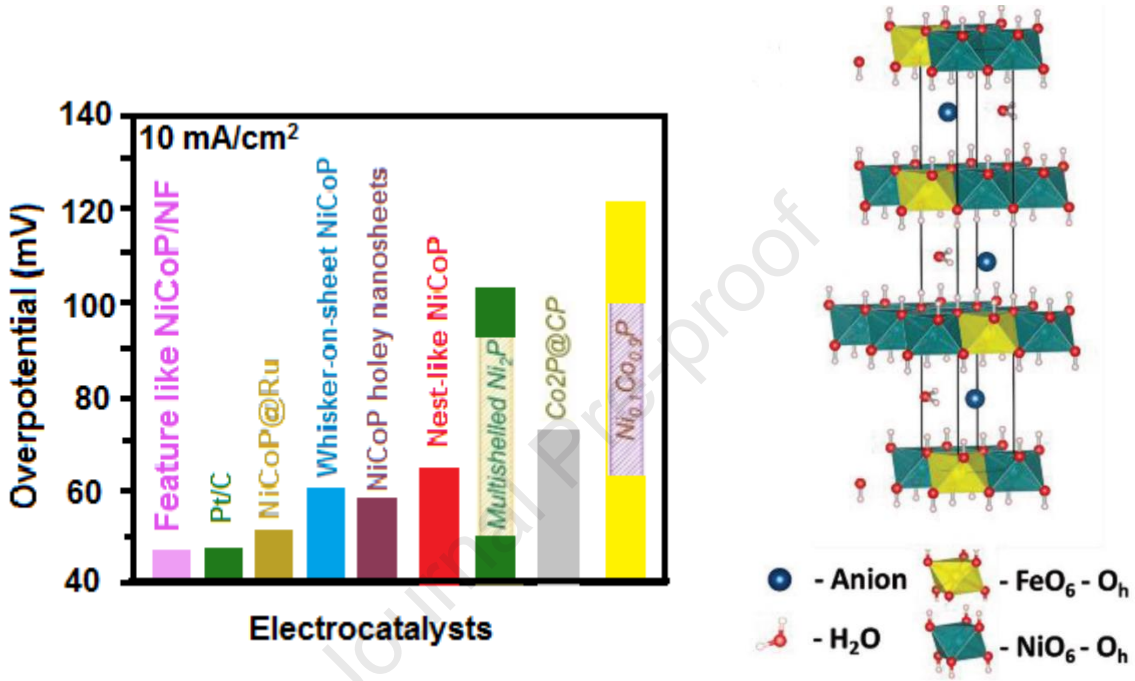


(a) **(b)**

Figure 2: **(a)** Comparison of the HER overpotential[2] for different nanostructured electrocatalysts [*reproduced from ref.* 20] **(b)** Crystal structure of NiFe-LDH with H_2O and CO_3^{2-} ions in the interlayer. The nickel and iron are octahedrally (Oh) surrounded by oxygen atoms [*reported from ref.* 40]

[2]Overpotential was considered as the potential with respect to the equilibrium potential

4. Electrocatalysts for the OER in seawater

Iridium and ruthenium oxides (such as IrO_2/Ti) are highly efficient OER catalysts in non-chloride solutions but not selective in seawater [32]. Although, γ-MnO_2 layers on IrO_2 can suppress CER blocking the Cl^- diffusion to the active catalyst layer [33,34].

Nickel oxide [25], layered double hydroxides (LDHs) [29,35,36], lamellar-edged Fe-$Ni(OH)_2$/Ni_3S_2 nanoarrays [26], oxy-borides (Co−Fe−O−B) [27,29,25,36] and Ni/Co oxidic metallates [28] have been reported as selective OER catalysts for seawater electrolysis.

A corrosion-resistant 3*D* core-shell of NiFeN with NiMoN nanorods on NF exhibited very high current densities at low cell voltages in alkaline seawater. High conductivity of the inner NiMoN nanorods, large surface area, and 3D structure yielded highly active stable electrodes. The high current densities observed even after normalization to *ECSA* confirmed that their improved catalytic performance was not only due to surface area enhancement but also because of their high conductivity, facilitated charge transfer in the catalyst/electrolyte interface, and robust contact between components [30].

Layered double hydroxides (LDHs) are a family of ionic materials composed of brucite-like layers. Counter ions and solvent molecules may enter in their interlayer spacing. The interlayer spacing in these materials can be engineered by doping various metallic atoms (see the crystal structure of the Ni-Fe LDH in Figure 2(b)). Regardless of their great potential as promising non-PGM OER electrocatalysts in freshwater, few of them have been studied in seawater [29,35-38]. Ni-Fe LDH catalysts with a Ni/Fe ratio of 3.6 were reported for seawater OER catalysis by Dresp *et al.* [39]. Ni-Fe LDH deposited on a Se-covered NiFe foam proved decreased overpotential and Tafel slope and enhanced lifetime (~250h) in artificial seawater due to enhanced conductivity, protective properties of Se against corrosion, and the synergism between different layers [29]. Dresp *et al.* [40] extensively fabricated an AEMWE using the

NiFe-LDH and proved their great potential as promising low-cost selective anodes for real electrolysers [35,40,41].

Heterogeneous bimetallic phosphides of Ni and Fe (Ni_2P-Fe_2P) on NF with high intrinsic catalytic activity, micro-sheet structure, enhanced active sites, and a hydrophile surface were also reported as selective OER catalysts in seawater [23].

Lamellar-edged Fe-$Ni(OH)_2$/Ni_3S_2@NF nanoarrays showed decreased overpotentials and R_{ct} values compared with bare Ni_3S_2@NF. They also worked with a negligible activity decay for 27h at 100mA/cm^2. Fe sites on lamellar edges were responsible for their raised activity and selectivity. The 2D structure made high exposed area, more active sites, facile electron/mass transfer and better gas movement; the Ni_3S_2 was responsible for corrosion resistance [26].

For anodes made from MnO_2/Mn_2O_3 composites with Co_3O_4 nanoparticles the intrinsic catalytic activity of Co_3O_4, high oxygen defect content, and the oxide/oxide heterojunctions even in real seawater yielded a FE% ~100% showing their selectivity. They were more durable in simulated seawater because in real seawater, higher ionic strength decreased the number of available water molecules at the electrode/electrolyte interface [34].

5. Challenges with seawater electrolysis from an electrocatalytic perspective

Even the most durable electrodes for seawater electrolysers have not shown significant durability at high current densities (j > 500mA/cm^2). Thus, the development of robust catalysts is crucial for future seawater electrolysers [15]. Seawater components also affect the membrane in PEMWE and AEMWE, as well as the electrolyser performance [36].

5.1.Chlorine chemistry interference with OER

For the anode, competition between chlorine chemistry and OER is a challenge and the main strategies to suppress the chlorine evolution reaction (CER) can be summarized as [5,34,41,42]:

(i) Electrolysis at current densities lower than 1mA/cm^2:

The OER is thermodynamically preferred at j < 1mA/cm^2; however, it is not practical for large H_2 production [33,42].

(ii) CER can be inhibited at an elevated pH:

Using a Ni-FeLDH anode, Dionigi *et al.* [35] established a selectivity criterion presented as the dashed area in Figure 3(a), based on the maximum allowed overpotential of OER as a function of pH. Operation outside the criterion resulted in severe loss of selectivity and electrode degradation. In comparison, highly alkaline conditions impose high costs and triggers the scale deposition on the cathode.

(iii) Covering the catalyst with a Cl^- blocking layer:

MnO_x coatings were shown to repel chloride ions and prevent its adsorption or diffusion. MnO_x is not involved in the OER mechanism but instead acts as a barrier against Cl^- diffusion, while remaining permeable to water [33,34].

(iv) Coating the anode with a cation exchange membrane (CEM) to hinder the adsorption of Cl can block the Cl^- penetration to the electrode/electrolyte interface; however, it might be practically challenging because of the high costs of CEMs [43].

5.2. Recent strategies for increased selectivity of OER electroctalysts

Dresp *et al.* [41] performed a study for understanding the structural transformations and details of Cl^- ion interactions with different phases in Ni-Fe LDH anodes. Unlike Ni hydroxide the Ni-Fe LDH has no β-phases and only include α-$Ni(OH)_2$ ↔ γ-NiOOH transformations. They used a grazing incidence (GID) cell with *operando* wide-angle X-ray scattering (WAXS)

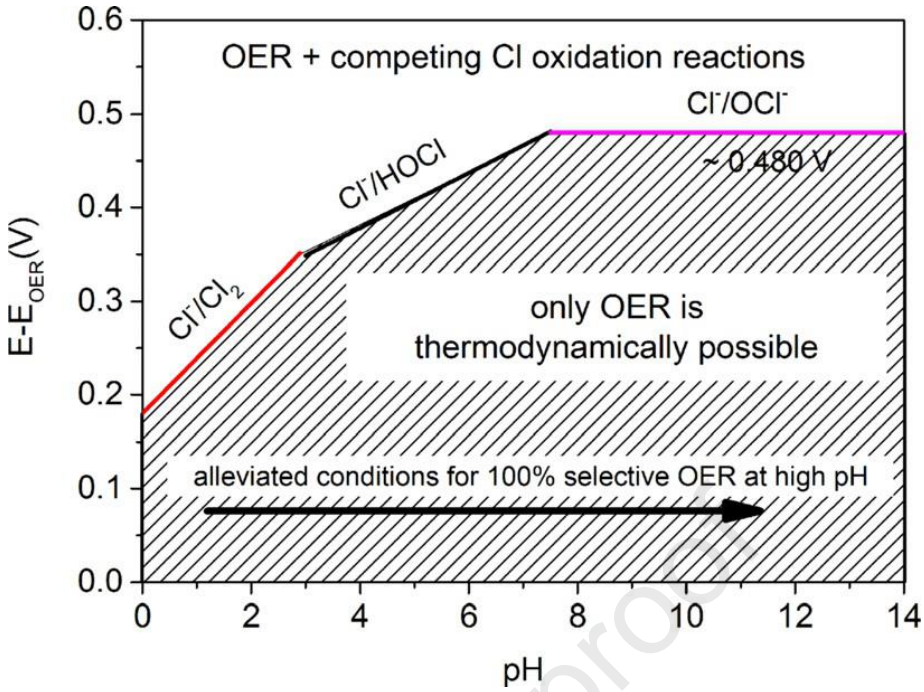
and recorded CV plots in a KOH solution with and without 0.5M NaCl in various pH conditions. The presence of NaCl improved the catalytic performance of Ni-Fe LDH and based upon their previous work, it was not due to the chlorine-related oxidation reactions [36,40]. The increase in OER activity was also observed at an elevated pH. Analysis of the interlayer spacing (Figure 3(b)) revealed that the incorporated Cl^- ions stabilize the α-phase, slowing down the structural α→γ transformations. They also proved that raising pH to 14 enhances the number of the catalytically active γ-NiFe LDH sites and off-sets the negative effects of chloride ions on their performance [41]. Despite this, several strategies have been proposed to diminish the requirement for these anodes for highly alkaline conditions. Lu *et al.* [37] optimized the alkali treatment amount required for the optimal performance of Ni-Fe LDH on carbon cloth (CC). They found that alkali treatment of the seawater before electrolysis helps to remove Ca^{2+} and Mg^{2+} from seawater. Thereafter, no additional alkali is required to have an OER selectivity of over 94%. With their suggested method, Tafel slopes of 51 and 52mV/dec were obtained in treated seawater and pure KOH, respectively, confirming similar mechanisms of OER [37].

Currently, most seawater electrolysers work with symmetric electrolytes at a high pH and current densities lower than 200mA/cm^2. Future electrolysers must work with current densities of at least 1A/cm^2. Recently, Dresp *et al.* [36] proposed an asymmetric AEMWE with direct seawater feed in the cathode compartment (pH ~7-8) and circulating 0.5M KOH in the anode and a CCM configuration (Figure3(c)) The Ni-Fe LDH anode worked better than Ir-based anodes up to a cell voltage of 4.0V. Regardless of Cl^- penetration in trace amounts from the membrane, no chlorine-related oxidation was observed.

Dresp *et al.* [40] also reported an AEMWE with alkaline NaCl electrolyte using an anode based upon highly crystalline Ni-Fe LDH. In the practical large-scale applications, the cell may expose successive stop/restart cycles; thus, they investigated their model electrolyser under similar conditions. Founding a recovery effect after stopping/restarting, they verified that

a programmed stop/start cycle could improve the cell performance, perhaps due to removing gas bubbles and partial "chemical resetting" of the metal oxide electrode. The recovery was less effective with chloride-containing electrolytes. The anode was very selective because a similar FE% was obtained in NaCl-free and 0.5M NaCl-containing KOH solutions without traces of chlorine-related species. Long-term stability tests in two protocols (i) 5 days electrolysis (20h electrolysis at +1.6V and 4h shutdown); and, (ii) 100h continuous electrolysis, exhibited almost similar results. It opened a way for Ni-Fe LDH based anodes to be introduced as promising materials for direct seawater electrolysers.

Amikam *et al.* [42] proposed another innovative water electrolysis system based upon the salting-out effect for NaCl in NaOH solutions (Figure 3(d)). They removed Ca^{2+} and Mg^{2+} from seawater feeds using nanofiltration. A settling tank containing 20-40*wt*% NaOH (~20-30^{0}C) was used for NaCl precipitation. The effluent was injected into an electrolyser with a Ti/IrO_2-RuO_2-TiO_2 anode (temperature > 50^{0}C). The high concentrations of OH^- significantly suppressed CER. The system was successfully operated at 467mA/cm^2 using NaCl-saturated NaOH solution for 12days producing ~ 1.2m^3 H_2 and ~150g of precipitated NaCl(s) [42].



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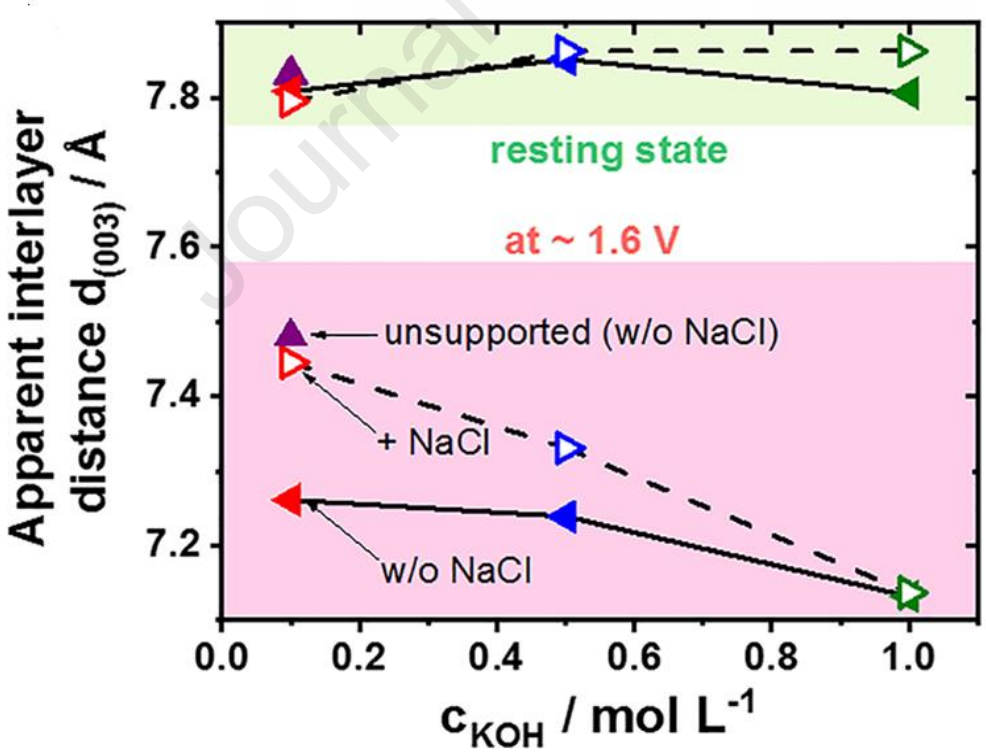
344 **(a)**

345



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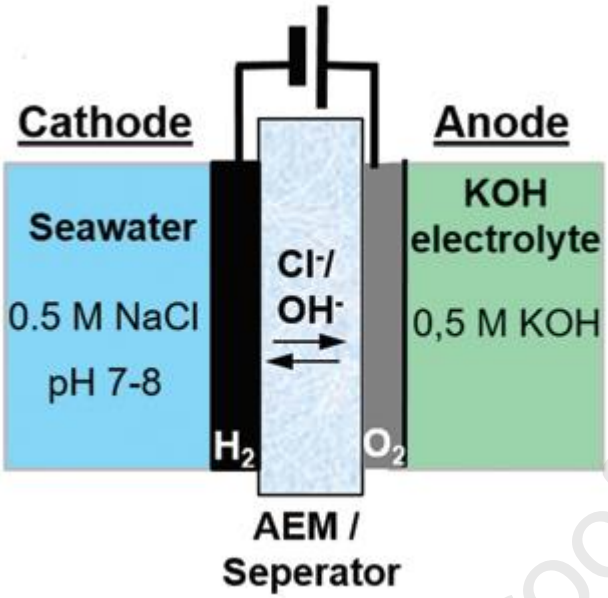
347 **(b)**



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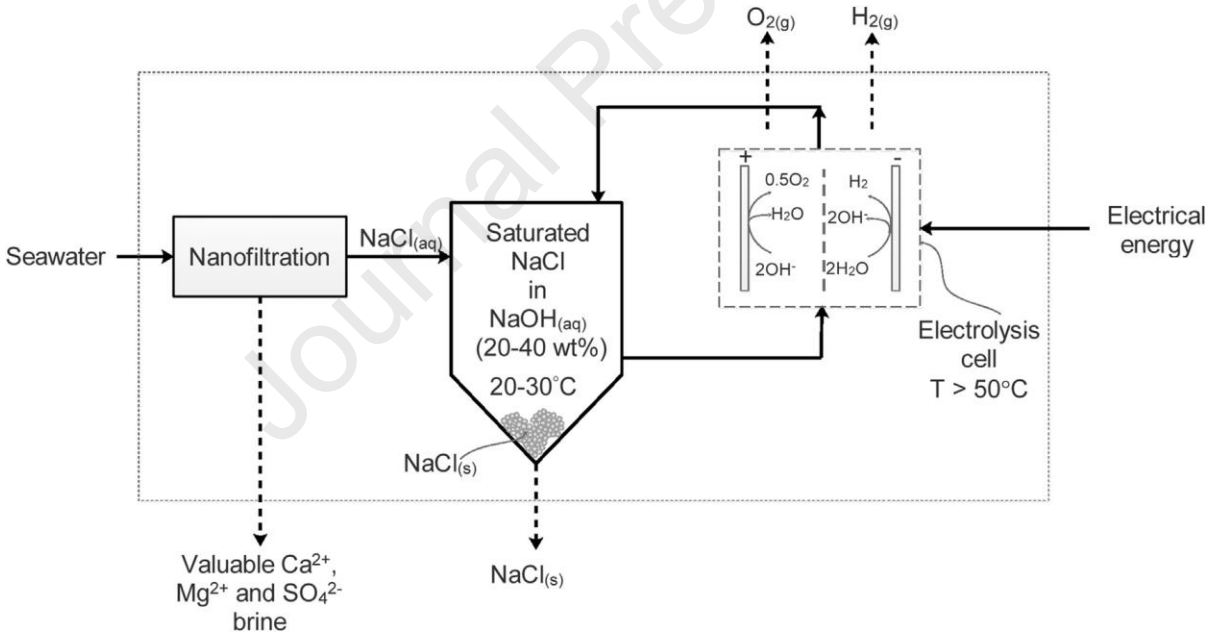
349 **(c)**



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351

352 **(d)**

353 Figure3: **(a)** Maximum allowed overpotential of OER electrolyser catalysts to ensure 100%

354 selective water splitting [*Reported from ref. 35*], **(b)** overview of the estimated interlayer

355 distance of Ni-Fe LDH with NaCl and KOH concentrations [*Reported from ref.41*], **(c)**

356 asymmetric 0.5M NaCl feed at the cathode and 0.5M KOH feed at the anode [*Reported from*

ref. 36], **(d)** Process for chlorine-free seawater electrolysis for H_2 (and O_2) production proposed by Amikam *et al.* [*Reported from ref.42*].

5.3.Side reactions due to the seawater composition

Based upon a comprehensive table gathered by Dresp *et al.* [5], chloride and bromide are the most important ions in seawater electrolysis. Although the redox potential of Br_2/Br^- (1.331V *vs.* SHE) is very close to that of Cl_2/Cl^- (1.358V *vs.* SHE) due to the low bromide concentration, its competition with OER is neglected [38,44].

Deposition of insoluble compounds such as the $Ca(OH)_2$ and $Mg(OH)_2$ on the cathode with a high pH blocks the active catalytic sites of the electrocatalyst [18,30,42]:

$$Ca^{2+} + 2OH^- \rightarrow Ca(OH)_2 \quad (1)$$

$$Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2 \quad (2)$$

Although the adsorption of small amounts of Mg^{2+} and Na^+ on the electrodes such as Co-Fe LDH may enhance the number of strong basic sites and suppress the necessity of buffering. Cl^- adsorption may also be beneficial for stabilizing the high oxidation forms of Co in the catalyst that positively affects their OER activity [45].

Corrosion in the aggressive chloride medium also causes electrode degradation. The corrosive environment and the shear stresses of the fluid flow make the anodes very susceptible to erosion-corrosion [46]. During electrolysis, the cathode is protected against corrosion; however, under stop conditions, it is vulnerable to corrosion [47]. The dual-layered anode and subsequent activation can improve the resistance against chloride-induced pitting corrosion [38].

5.4. Degradation of electrocatalysts

Metallic substrates such as Ti passivate through the growth of an insulating oxide layer. An intermediate layer of IrO_2 or Sn-doped IrO_2 on Ti substrates primarily prevents the oxide growth on the substrate [33]. With the intimate contact between substrate and catalyst, not only R_{ct} decreases but also the durability improves; thus, Ni-based structures grown directly from a nickel foam are preferred in the design of integrated catalysts [19].

Ledendecker *et al.* [47] studied the stability and corrosion of several PGM-free cathodes, including metal carbides (WC), sulfides (MoS_2), phosphides (Ni_5P_4, Co_2P), their base metals (W, Ni, Mo, Co), as well as Pt in an acidic medium. Under zero current density, the dissolution of phosphides, carbides and sulfides was drastically reduced compared to their base metal samples. Under operation, their dissolution rate was similar to the pure metals. Successive start-stop cycles and the electrode/electrolyte contact before electrolysis resulted in more severe corrosion. They proposed that the pretreatment of the catalyst can remove dangling bonds, defects and surface oxides and increase the durability of the electrodes.

Claudel *et al.* [48] reported that nanostructured IrO_x anodes change during OER process. They verified several morphological changes like migration, agglomeration, coalesce and detaching. Gradual oxidation of Ir(0) and Ir(III) to Ir(IV) and Ir(V) and enhanced local accumulation of hydroxyl/water species on IrO_x nanocatalysts were the main influencing factors. In contrast, for the micro-sized IrO_x anodes, no water/hydroxyl coverage was observed [48].

Accelerated degradation tests for thin $SrIrO_3$ films showed that anodic OER potentials result in the partial dissolution of the flat surface of $SrIrO_3$ to a rough IrO_x-rich one. The IrO_3 dissolution rate is potential-dependent and Sr dissolves with a stoichiometric rate, resulting in an IrO_x-rich layer. Despite this, their bulk remains in its original perovskite structure [49].

406 For Co_2P HER electrocatalysts, Zhang *et al.* [50] indicated that the dissolution mechanism
407 was strongly dependent upon the pH; in acidic solution, the components dissolved
408 stoichiometrically but in alkaline pH, the degradation proceeded through hydroxide formation
409 with preferential dissolution of P over Co.

410

411 **6. Techno-economic insights**

412 Regardless of developments in non-PGM electrocatalysts, practical applications require a
413 pretreatment (such as reverse osmosis or alkali treatment) that imposes high costs equal to
414 those of currently used PGM-based fresh-water electrolysers. Commercial PEMWEs currently
415 use PGM-based electrodes; however, the emerging AEMWEs are promising candidates for
416 future applications, because they can operate with low-cost electrocatalysts. Generally, for H_2
417 production, two economic insights can be suggested [51]:

418 (a) A one-step strategy in which seawater is directly used without any pretreatment, the
419 research is then focused on the design of low-cost, selective and stable materials.

420 (b) A two-step path that uses desalination plants (mostly reverse osmosis). With this
421 strategy, the research efforts and costs are focused on the decrease of desalination costs.

422 Recently, Farràs *et al*. [51] revealed that from an energy and economic point-of-view, the
423 two-step strategy is currently more practical. However, regarding the emerging technologies
424 that are introduced in developing low-cost, stable electrocatalysts and new cell configurations,
425 energy/economic analysis and revisiting the strategies must be regularly performed.

426

427 **7. Closing remarks**

428 Seawater is potentially an infinite resource for hydrogen (and oxygen) production, but
429 complicated composition is a big challenge for its direct electrolysis. The most promising non-
430 PGM cathodic catalysts are based upon transition metal oxides, carbides, chalcogenides, and

especially phosphides and nitrides. TMPs and TMNs with high intrinsic conductivity and corrosion resistances are highly efficiency and stable in seawater; thus, they can be considered as the most promising non-PGM materials for HER. Negatively charged surface sites trigger the H-adsorption, while positively charged sites prefer interaction with hydroxide and weaken H-OH bonds in water molecules. Doping electronegative/electron-withdrawing species facilitates the formation of these separated adsorption sites and promotes HER. For OER, highly selective Ni-Fe LDH based catalysts are the most promising non-PGM anodes as candidates for future commercialization purposes.

Generally, for both HER and OER electrodes, a holey nanostructure and high conductivity of electrocatalysts are vital for enhancing the electrode efficiency. Intimate contact between catalyst and substrate, and integrated electrodes results in facilitated charge transfer with increased stability. The use of carbonaceous nanomaterials can also provide an electron transfer path between catalyst components.

Ni-Fe LDH anodes have been used in a model AEMWE and showed their potential for future applications. However, even the best-studied catalysts have not shown stabilities over 1,000h of electrolysis at current densities not much higher than 200mA/cm^2; while future seawater electrolysers must work with current densities of at least 1A/cm^2 to fulfill the economic expectations.

Another unsolved challenge is the need for seawater purification before electrolysis. The use of an asymmetric feed with direct seawater in the cathode and circulating KOH in anode compartments, or the use of the NaCl salting-out effect in highly concentrated NaOH have been reported; however, there is an urgent need for developing the studies in this regard.

Conflict of interest statement

Nothing declared.

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Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: