Towards the Hydrogen Economy—A Review of the Parameters That Influence the Efficiency of Alkaline Water Electrolyzers

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Abstract: Environmental issues make the quest for better and cleaner energy sources a priority. Worldwide, researchers and companies are continuously working on this matter, taking one of two approaches: either finding new energy sources or improving the efficiency of existing ones. Hydrogen is a well-known energy carrier due to its high energy content, but a somewhat elusive one for being a gas with low molecular weight. This review examines the current electrolysis processes for obtaining hydrogen, with an emphasis on alkaline water electrolysis. This process is far from being new, but research shows that there is still plenty of room for improvement. The efficiency of an electrolyzer mainly relates to the overpotential and resistances in the cell. This work shows that the path to better electrolyzer efficiency is through the optimization of the cell components and operating conditions. Following a brief introduction to the thermodynamics and kinetics of water electrolysis, the most recent developments on several parameters (e.g., electrocatalysts, electrolyte composition, separator, interelectrode distance) are highlighted.

Keywords: alkaline water electrolysis; cell components; efficiency; electrocatalysts; overpotential

1. Introduction

Nowadays, energy is at the top of everybody’s needs and concerns. Never before has the consumption of energy been so high, and never before has the impact of the use of that energy been as intense and negative on the planet as a whole.

Growing energy demand due to population increase poses a serious threat to the global economy, environment, and consequent climate change [1]. Currently, fossil fuels are the principal resources used to obtain energy. However, these sources are non-renewable, and they have been exploited on such a large scale for the past 200 years that their reserves are due to run out: in 50 to 60 years for oil and gas, and 150 to 200 years for coal, according to recent forecasts [2]. Furthermore, the pollution resulting from the consumption of fossil fuels is a major issue that must be taken into consideration. Consequently, renewable energy resources, such as solar energy, wind, or wave power, have attracted considerable attention as an alternative response to increasing energy demand, without causing a major environmental impact. Besides cost issues, there are, however, some technical problems, related to energy fluctuations produced by renewable sources that lead to low energy delivery efficiencies and thereby limit their large-scale applications. To take advantage of all the energy produced from these sources, it is crucial to find a solution to storing the energy produced in excess when there is a peak of production, and to make it available to be consumed at a time when consumption exceeds production [3].
Hydrogen is seen as a key component to overcome this issue due to its high energy yield, high gravimetric energy density, relatively high abundance on earth, and zero emissions during consumption. Being an energy carrier, it is as clean as the method employed in its production, so producing hydrogen by splitting water using electricity generated from renewable sources has many advantages. Its use not only benefits from the abundance of water resources but also the zero pollutant emissions generated. In addition, the hydrogen obtained has a high level of purity of 99.99% \([4,5]\). However, only 4% of the total hydrogen currently produced comes from the electrolysis of water. Most hydrogen produced comes from fossil fuels, specifically from the steam reforming of natural gas (48%) followed by oil and coal gasification (30% and 18%, respectively) \([6]\). This is because the hydrogen produced from the electrolysis of water must compete with the relatively low prices of the hydrogen produced from fossil fuel-based techniques. Nevertheless, hydrogen is seen as a promising approach to compete with fossil fuels and to end the planet’s energy dependency on them, so that it has become an item on the political agenda. For instance, the European Commission launched its Clean Hydrogen Alliance in July 2020 to seek the commitment of European Union countries to large-scale hydrogen production. The aim is for this production to be attained via electrolysis but, given that this process is still very expensive, production from natural gas is also allowed. Thus, large efforts are being put towards increasing the efficiency of electrolysis.

2. Water Electrolysis

In the electrolysis of water, a direct current (DC) is applied and electrons flow from the negative terminal of the DC source to the cathode. There, the electrons are consumed by hydrogen ions existing in the water, and hydrogen gas is formed. To keep the charge balance in the cell, the hydroxide ions resulting from the cathodic reaction move towards the anode surface, where they lose electrons (that return to the positive terminal of the DC source) and oxygen is formed \([7,8]\). The overall reaction of water electrolysis is represented by Equation (1).

\[
2\text{H}_2\text{O} + \text{energy} \rightarrow 2\text{H}_2 (g) + \text{O}_2 (g) \tag{1}
\]

The main water electrolysis technologies available are alkaline water electrolysis (AWE), proton exchange membrane (PEM) electrolysis, and the solid oxide electrolyzer cell (SOEC) \([9,10]\). A scheme of these different technologies is presented in Figure 1.

![Figure 1](image-url)

**Figure 1.** Schematic representation of (a) an AWE cell, (b) a PEM electrolysis cell, and (c) a SOEC. Reprinted from \([9]\) with permission from Elsevier.

AWE is the oldest and most well-established technique. The cell consists of an anode and a cathode immersed in an alkaline solution, separated by a diaphragm. The hydrogen
evolution reaction (HER) at the cathode and the oxygen evolution reaction (OER) at the anode are represented by Equations (2) and (3), respectively [7,8].

\[ \text{2H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^- \]  
\[ 4\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \]  

PEM electrolysis is a less mature technique than AWE. PEM electrolysis cells are similar to AWE cells, but instead of an alkaline aqueous electrolyte, they have a solid polymer electrolyte membrane with an acidic nature. The membrane, along with the electrodes, forms what is called the membrane electrode assembly (MEA). In this case, the two characteristic half-reactions for HER and OER are given by Equations (4) and (5), respectively [10,11].

\[ 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2 \]  
\[ 2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \]  

As an alternative to PEM electrolysis, recent studies focused on the use of anion-exchange membranes (AEMs) for the development of a new technology known as AEM water electrolysis. These devices have a structure similar to PEM electrolyzers, but the membrane is selective to the transport of anions, \( \text{OH}^- \), instead of protons, \( \text{H}^+ \). AEM water electrolyzers can either be fed by pure water, concentrated KOH solution, or diluted \( \text{K}_2\text{CO}_3 \) solution. The electrode reactions are the same as those shown for AWE (Equations (2) and (3)) [12].

SOEC is the least developed electrolysis technology, and it is not yet available for commercialization. What distinguishes this technique from the other two, is that it is performed at much higher temperatures, as can be seen in Table 1, where the main features of the three processes are compared. A SOEC performs the electrolysis of water vapor at high temperatures, resulting in higher efficiencies compared to the other techniques. The reactions occurring at the cathode and the anode are given by Equations (6) and (7), respectively [10,13].

\[ \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + \text{O}^{2^-} \]  
\[ 2\text{O}^{2^-} \rightarrow \text{O}_2 + 4\text{e}^- \]  

| Specifications                   | AWE     | PEM     | SOEC    |
|----------------------------------|---------|---------|---------|
| Operating temperature (°C)       | 60–80   | 50–84   | 650–1000|
| Operating pressure (MPa)         | <3      | <3      | <3      |
| Current density (A cm\(^{-2}\)) | 0.2–0.5 | 0.6–2.2 | 0.3–2.0 |
| Cell voltage (V)                 | 1.8–2.4 | 1.8–2.2 | 0.7–1.5 |
| Voltage efficiency (%)           | 62–82   | 67–82   | 81–86   |
| Production rate (m\(^3\)/h)     | <760    | <40     | <40     |
| Specific system energy consumption (kWh Nm\(^{-3}\)) | 4.3–4.8 | 4.4–5.0 | 2.5–3.5 |
| Hydrogen purity (%)              | 99.7–99.9 | 99.999 | 99.9 |
| Cell area (m\(^2\))              | 3–3.6   | <0.13   | <0.06   |
| Minimum partial load (%)         | 10–40   | 0–10    | -       |
| Stack lifetime (kh)              | 55–120  | 60–100  | 8–20    |
| System lifetime (years)          | 20–30   | 10–20   | -       |
| System response                  | s       | ms      | s       |
| Cold-start time (min)             | <60     | <15     | <60     |
| Capital cost * (€ kW\(^{-1}\))    | 620–1170| 1090–1650| >1560   |

* Prices for 2020 [14].

AWE, PEM electrolysis, and SOEC technologies are at different stages of commercialization. As mentioned, the SOEC is still being developed at a laboratory scale, so it will not be the focus of this review. The more mature AWE and PEM technologies have already
reached the commercialization stage. AWE electrolysers, being around the longest, are
sold in greater numbers despite some superior characteristics offered by PEM. As can be
seen in Table 1, PEM electrolysers provide hydrogen with higher purity and can reach
higher current densities than AWE without compromising efficiency [10] due to the tightly
packed structure of the MEA and because the thinner membrane provides higher proton
conductivity [11,15]. They also have a greater operating range [3]. Furthermore, when
compared to AWE, PEM technologies have higher associated costs and have a shorter stack
and system lifetime [8,15]. The polymer electrolyte membrane is made from an expensive
material and has short durability, which implies constant replacement. The short durability
of the PEM is mostly attributed to membrane contamination or chemical self-degradation
and deterioration of the anode materials. While in AWE, non-noble metals, such as nickel
(Ni), are suitable electrocatalysts for HER and OER, in PEM electrolysis, the acidic character
of the electrolyte implies the use of precious metals as electrocatalysts for the reactions to
occur, which increases the investment [16].

Over the years, several authors have compared both technologies. Schalenbach et al. [17]
compared an AWE electrolyzer using Ni-based catalysts and a thinner separator with
a PEM electrolyzer using iridium (Ir) and platinum (Pt)-based catalysts and a Nafion
membrane. They concluded that the AWE with a separator thinner than normally used can
achieve an efficiency greater than PEM electrolysis.

Felgenhauer et al. [18] presented a comparison between sixteen different models
developed by different companies and analyzed AWE and PEM technologies regarding
the economic aspects of scale, production capacity, and all costs related to the production
of H₂. They conclude that, among the 16 electrolysers, PEM had a slight advantage in
terms of efficiency, 57–64% LHV in comparison to AW electrolysers, 52–62% LHV, but suffer
from higher efficiency degradation. They also found an increase in the cost-efficiency of
the systems with the increase in system capacity, which indicates that scale economies are
applied. Therefore, AWE systems are currently mature and cost-efficient solutions. The
lower costs associated with this technology compensate for the slightly better efficiency
of PEM.

3. Thermodynamics

The decomposition of water into hydrogen and oxygen is not thermodynamically
favorable. To accomplish it, a potential difference between the anode and cathode must be
applied, called the equilibrium or reversible cell potential (Eₑ₉). Under standard conditions
(ambient temperature of 25 °C and atmospheric pressure) the ΔHₑ₉ is 286 kJ mol⁻¹ of H₂ and the ΔGₑ₉ is 238 kJ mol⁻¹ of H₂. The difference between the two values arises
because the electrolysis leads to a change from the liquid to the gaseous phase and hence to
a large increase in the entropy of the system. The Eₑ₉ value at these conditions is −1.23 V
(−ΔGₑ₉/nF). At this cell voltage, the water-splitting reaction is endothermic.

When the system is isolated, the entropy increase of the system cannot be achieved by
absorption of heat from the surroundings, so all the energy has to come from an electrical
source, which means that it is necessary to apply a higher potential difference. The total
electrical energy required to maintain an electrochemical reaction without generation or
absorption of heat, at a specific temperature, is called the thermoneutral voltage, E₉, which
is, at standard conditions, 1.48 V (ΔHₑ₉/nF). Although Eₑ₉ is the theoretical minimum
cell voltage required to dissociate water molecules by electrolysis, E₉ corresponds to the
actual minimum voltage for the electrolysis cell to operate in adiabatic conditions, i.e., with
a net zero heat balance between the thermal energy transferred to the cell and produced by
the cell. Above E₉, the reaction becomes exothermic, and heat is generated. This means
that, in practice, all water electrolysers must operate above the E₉ [7,8,19].
When operating at non-standard conditions, the cell potential must be calculated from
the Nernst equation, Equation (8) for the two electrode reactions,

$$E_{\text{cell}} = E_{\text{cell}}^e + \frac{RT}{nF} \ln \frac{a_{\text{H}_2} a_{\text{O}_2} a_{\text{H}_2\text{O}}}{a_{\text{H}_2}}$$

(8)

where $a$ are the activities of the reactant and products and $R$ is the universal gas constant [8,19].

Apart from the theoretical energy consumption during electrolysis, several additional electrical barriers need to be overcome for the electrolysis process to occur. All these barriers contribute to the required cell voltage of the electrolysis (Figure 2) and constitute the overpotential, which is defined as the difference between the theoretical cell potential (i.e., the equilibrium cell potential, $E_{\text{cell}}^e$) and the actual cell potential that is necessary to drive the reaction at the desired rate, $E_{\text{cell}}$ (Equation (9)) [15,20].

$$\eta = E_{\text{cell}} - E_{\text{cell}}^e$$

(9)

Overpotential can be divided into three major categories: ohmic overpotential, $\eta_o$, activation overpotential, $\eta_a$, and concentration overpotential, $\eta_c$. Therefore, the total overpotential of the electrochemical cell is the sum of these three contributions, Equation (10) [21].

$$\eta = \eta_o + \eta_a + \eta_c$$

(10)

### 3.1. Ohmic Overpotential

Ohmic overpotential is related to the ohmic internal resistance, $R$, of the cell, which combines the resistances of the electrode, the electrolyte solution, the diaphragm, the connection wires, and those induced by hydrogen and oxygen bubbles. This means that the overpotential arises from the ionic resistance of the solution (related to its conductivity) and from the electronic resistances to and from the cell or stack components. Ohmic overpotential, as its name suggests, follows Ohm’s law ($\eta_o = iR$, where $i$ is the applied current). This relation indicates that the ohmic drop varies linearly with the applied current [21,22].

### 3.2. Activation Overpotential

The activation overpotential is the difference above the equilibrium potential required to overcome the activation energy of the cell reaction to produce a specified current. This
overpotential is related to the electron transfer that occurs at the electrode interface. One of the main causes is the accumulation of charge at the electrode surface, producing an energy barrier for the incoming electrons [21,23].

In the absence of mass transfer limitations and at high activation overpotentials, the relationship between the rate of reaction, i.e., the current density, $j$, and the activation overpotential is given by the Tafel equation, Equation (11),

$$|\eta| = a + b \log |j|$$  \hspace{1cm} (11)

being $a$ the intercept, Equation (12), and $b$ the so-called Tafel slope, Equation (13),

$$a = -b \log j_0$$  \hspace{1cm} (12)

$$b = \frac{2.3RT}{\alpha F}$$  \hspace{1cm} (13)

where $\alpha$ is the anodic or cathodic transfer coefficient that represents the fraction of overpotential that lowers the kinetic barrier for the reaction at the electrode/electrolyte interface and $j_0$ is the exchange current density, which is defined as the rate at which the reactants are transformed into products at equilibrium and the products are regenerated as reactants, free of any limitation due to mass transfer [8].

3.3. Concentration Overpotential

Concentration overpotential is caused by the concentration gradient of the reactants or the products in the electrolyte on the electrode surface, due to mass transport limitations as the reactions proceed. It occurs when mass transport cannot accompany the rate of the cell reaction. When the mass transport is relatively low, the reactant molecules cannot reach the reaction sites and/or the product molecules cannot drift from the reaction sites, resulting in a reduction of the reactants or accumulation of the products at the electrode surface. The mass transference step can follow three different mechanisms: diffusion (movement of species conducted by a concentration gradient, from high to low concentration), migration (movement of charged species imposed by an electric field), and convection (movement of species driven by an unstable behavior of forces upon the electrolyte) [21,23].

4. Efficiency-Related Parameters

There are several ways to express the efficiency of an electrolysis cell, depending on how the electrolysis system is assessed and compared. The voltage efficiency is usually calculated following Equation (14), and it gives the proportion of effective voltage used to split water, from the total voltage applied to the cell.

$$\%\text{voltage efficiency} = \frac{(E^e_{\text{anode}} - E^e_{\text{cathode}})}{E_{\text{cell}}} \times 100$$  \hspace{1cm} (14)

The Faradaic efficiency and the thermal efficiency, Equations (15) and (16), respectively, are two different parameters calculated based on the energy changes of the water electrolysis reaction. The energy input is the Gibbs free energy change and the enthalpy change of water decomposition reaction, respectively.

$$\eta_{\text{Faradaic}} = \frac{\Delta G_{\text{cell}}}{(\Delta G_{\text{cell}} + \text{Losses})} = \frac{E^e_{\text{cell}}}{E_{\text{cell}}}$$  \hspace{1cm} (15)

$$\eta_{\text{thermal}} = \frac{\Delta H_{\text{cell}}}{(\Delta G_{\text{cell}} + \text{Losses})} = \frac{E_{\text{in}}}{E_{\text{cell}}}$$  \hspace{1cm} (16)
Another way to evaluate the efficiency of water electrolysis systems is to consider the output of hydrogen production against the total electrical energy, $\Delta W$, applied to the system, Equation (17),

$$\eta_{\text{thermal}} = \frac{r_{\text{H}_2 \text{ production rate}}}{\Delta W} = -\frac{V_{\text{H}_2}}{(i_{\text{cell}} \cdot t)} \tag{17}$$

where $t$ is the time and $V_{\text{H}_2}$ is the hydrogen production rate per unit volume of the cell [7,8].

Based on the above expressions, it can be concluded that to improve the efficiency of AWE, it is necessary to reduce the energy required to split the water molecules. By reducing the total overpotential that needs to be overcome, the cell potential required to drive the reactions decreases [8,9]. As discussed above, overpotentials rise due to some aspects of the electrochemical cell components.

Thus, the loss of efficiency in AWE can be related to several factors. First, the activation energy that has to be overcome for the HER and OER to take place, which is represented by the activation overpotential. Ohmic losses are also a problem that needs to be taken into consideration. The bubble effect is a major contributor to the ohmic drop. During water electrolysis, gas bubbles are formed at the electrodes and cannot disperse rapidly through the electrolyte and be removed from the electrolytic system, so they accumulate at the surface of the cathode and anode, blocking the active sites. When the bubbles’ diameter achieves a critical value, bubbles detach from the electrode surface into the electrolyte [24]. The ionic resistance of the electrolyte, the electrode distance, and the diaphragm resistance are also parameters that have a great influence on ohmic losses [3].

Consequently, properly defining the materials of the electrode and electrocatalysts, electrolyte and separator, the operating conditions and cell configuration is crucial to minimizing the total value of the overpotentials and ohmic losses and achieving maximum efficiency of the electrochemical system [23].

Operating conditions of commercial AWE electrolyzers, concerning electrolyte concentration and separator materials, are already more or less well established. A literature survey shows that the path for improving the efficiency of AWE is now focused on the development of new electrocatalysts to increase the activity of the hydrogen and oxygen evolution reactions.

In the following sections, a review of several characteristics of AWE cell components will be presented, with a focus on the recent developments in electrocatalysts that have shown promising behavior at an industrial level.

### 4.1. Electrocatalysts

To develop a proper electrode for an AW electrolyzer, the materials selected must have high corrosion resistance, high conductivity, high surface area, high catalytic effect, and must have a reasonable price and lifetime [8].

As was already stated, to increase the efficiency of an electrolysis system, it is necessary to reduce the activation overpotentials for the hydrogen and oxygen evolution reactions [9]. This can be achieved by using electrocatalysts deposited on the surface of the electrodes or as the electrodes themselves. Electrocatalysts provide low activation pathways for a specific electrochemical reaction and enable the reactions to occur at high current densities. They work by changing the kinetics of the reaction or even by changing the mechanisms through which the reaction takes place [15,25]. Based on Equation (11), for a material to be a good electrocatalyst, that is, to achieve a low overpotential, the Tafel slope it generates must be low and/or the exchange current density must be high.

The performance of the electrodes depends not only on the composition of the catalyst but also on their surface area and microstructure [19]. When the electrolysis process takes place, hydrogen and oxygen bubbles are formed on the surfaces of the electrodes, detaching themselves from the surface only when they achieve a certain size. This phenomenon decreases the effective active area of the electrodes; the bubbles act as an electric shield, increasing the ohmic loss of the system [8,24]. Consequently, regarding the composition
of the electrodes, in addition to having proper catalytic activity, they must also be porous, allowing multiple pathways for electrolyte penetration [26] and facilitating the detachment of the bubbles [3]; this detachment also depends on the electrode wettability, so that hydrophilic electrode surfaces reduce the surface coverage by gas bubbles [8].

In the following sections, the mechanism for HER and OER will be briefly presented, as well as a review of the most commonly used electrocatalysts for both reactions, with a focus on the ones that can be easily applied to a more industrial environment. To get a more accurate analysis and compare the performance of the electrocatalysts, the overpotentials will be presented at the current density of 10 mA cm\(^{-2}\) and, when possible, within industrial operational conditions.

Unfortunately, reports in the literature can be a poor guide to the performance of the electrocatalysts in operating water electrolyzers, firstly, because many of the electrochemical measurements to evaluate the performance of the catalysts are done at room temperature, whereas water electrolyzers generally operate in the 60–90 °C range and at current densities of 10 mA cm\(^{-2}\), well below that of the state-of-the-art (200–400 mA cm\(^{-2}\)). Secondly, since the structure and effective surface area are as important as the composition of the catalyst layer in determining its activity, there is no fixed criterion to compare these characteristics [19].

4.1.1. HER Mechanism

The hydrogen reaction in alkaline media is widely accepted to be a combination of the Volmer-Tafel and Volmer-Heyrovský mechanisms. The first step, the Volmer step, consists of the reduction of a water molecule, adsorbed on the catalyst surface, to form adsorbed hydrogen (H\(_{\text{ads}}\)), Equation (18). After this initial step, hydrogen can be produced either by chemical desorption, where two adsorbed atoms form a hydrogen molecule, the Tafel step—Equation (19)—or by electrochemical desorption where another water molecule attacks the adsorbed atom of hydrogen forming a hydrogen molecule, the Heyrovský step—Equation (20) [8].

\[
\begin{align*}
\text{H}_2\text{O} + \text{e}^- & \rightarrow \text{H}_{\text{ads}} + \text{OH}^- \quad (18) \\
2\text{H}_{\text{ads}} & \rightarrow \text{H}_2 \quad (19) \\
\text{H}_{\text{ads}} + \text{H}_2\text{O} + \text{e}^- & \rightarrow \text{H}_2 + \text{OH}^- \quad (20)
\end{align*}
\]

The Volmer step in alkaline medium is also related to the adsorption energy of water and desorption energy of the hydroxide anions. Low water adsorption can lead to insufficient reactants, while high hydroxide anion adsorption causes a poisoning effect owing to a loss of catalytically active sites. These multi-step surface reactions make the Volmer step highly complex [27].

To identify the rate-determining step of HER, the Tafel slope represents a diagnostic criterion for the determination of the HER mechanisms on different electrode surfaces. Assuming that Langmuir adsorption isotherm applies, a Tafel slope of 30 mV dec\(^{-1}\) suggests that the mechanism proceeds through a Volmer-Tafel route, and the chemical desorption is rate-limiting, whereas a Tafel slope of 40 mV dec\(^{-1}\) indicates hydrogen production occurs through the Volmer-Heyrovský mechanism and, therefore, that electrochemical desorption is now the rate-determining step (Figure 3). When the Tafel slope registered is 120 mV dec\(^{-1}\), the rate-determining step will depend on the surface coverage of adsorbed hydrogen: at low surface coverages by H\(_{\text{ads}}\), the Volmer step is considered rate-limiting, while at saturation coverage, this slope value can be observed for both Heyrovský and Volmer reactions [28].

Overpotential on the cathode is, thus, directly related to the formation of hydrogen in the surrounding area of the electrode material, which in turn is determined by the bond between hydrogen and the electrode surface. The mechanism for hydrogen adsorption and desorption requires good binding of hydrogen to the reaction site of the metal surface. Therefore, overpotential will depend on the catalytic activity of the electrode and on some of its physical properties.
The overpotential for hydrogen production, $\eta_{H_2}$, is generally measured by the Tafel equation in the form of Equation (21),

$$\eta_{H_2} = \frac{2.3RT}{\alpha c F} \log \left( \frac{j}{j_0} \right)$$  \hspace{1cm} (21)

where $\alpha_c$ is the cathodic charge transfer coefficient [8,9].

![Figure 3. Schematic diagram of the Volmer-Heyrovsky and Volmer-Tafel processes on a catalyst surface. Reproduced from [29] with permission from The Royal Society of Chemistry.](image)

4.1.2. HER Electro catalysts

Noble metals, in particular Pt group metals, have been regarded as the benchmark electrocatalysts for HER [30]; they are considered the most efficient, with low overpotentials and low Tafel slopes. However, noble metal electrocatalysts are expensive and rare, making it impossible to use them as electrodes to economically produce hydrogen from water splitting on a larger scale. Hence, there is a great interest in using earth-abundant transition metals (TMs) as electrocatalysts for AWE, such as Ni, cobalt (Co), iron (Fe), molybdenum (Mo), or zinc (Zn) [19,27,29–32]. Among these, Ni is the most active non-noble metal. It is stable in strong alkaline solutions, it is abundant and, therefore, it is a cheap material. For these reasons, Ni and Ni-based alloys are currently the preferred choices as electrocatalysts for HER and OER [15,19,27,33].

Bare Ni has been traditionally used as an electrocatalyst by many researchers. However, at the current densities desired for water electrolyzers, the overpotential for HER with Ni electrodes is reported to be about 300 to 400 mV [19,34], which is far too large for modern electrolyzers. Moreover, most studies report an increase of the overpotential over time, due to the deactivation of the cathode material [19,27,35]. Consequently, research has evolved to find new pathways to activate this material and increase its catalytic performance.

One obvious way to improve the electrocatalytic performance of Ni materials is to increase their surface area by developing more porous electrodes [27,34]. The rapid development of nanotechnology has made it possible to build nanostructures with uniform size and even morphology, such as nano-sized Ni powders and porous Ni foams (NF) or meshes [27]. Both Ni foams [36,37] and Ni meshes [28,36,38] present higher catalytic activity than bare Ni, thus lower overpotentials, but they have been mostly used as electrode supports to more active non-noble metal electrocatalysts [28,38–42].

Ni-carbon composites can significantly improve the catalytic activity of electrodes for HER. They take advantage of the intrinsic activity of Ni and the features of carbon materials with good conductivity, large surface area, easy surface functionalization, and high stability [37,43]. Yang et al. [43] have proposed the development of large-scale electrodes with Ni nanoparticles (NPs) partially embedded into carbon fiber cloth (CFC) via a metal-mediated pitting process, a methodology that can easily be adapted for industrial hydrogen production. The Ni NPs embedded into CFC are advantageous for the regulation of the electron density state of carbon, exposing the Ni catalytic sites and improving the
catalytic stability. The electrodes have exhibited remarkably high catalytic activity for HER, as can be observed in the polarization curves obtained and corresponding Tafel plots (Figure 4).

Figure 4. Development of large-scale electrodes with NPs partially embedded into CFC via a metal-mediated pitting process, showing the (a) polarization curves of CFC-600, CFC-900, NF-900, Ni/CFC, Ni₆CFC and 20 wt.% Pt/C and (b) the corresponding Tafel plots, as well as (c) the synthetic procedure of (i) Ni(OH)₂ and CFC, (ii) Ni/CFC, and (iii) Ni₆CFC. Adapted from [43] with permission from Elsevier.

Wang et al. [37] also focused their research on promoting the outstanding performance of Ni-carbon-based composites. They designed co-electrodeposited Ni NPs and reduced graphene oxide (rGO) sheets on Ni foam by supergravity electrodeposition. Electro-catalysts with a carbon content of 3.3 wt.% exhibit outstanding performance for HER, with a small overpotential of 183 mV to drive 100 mA cm⁻², and a small Tafel slope of 77 mV dec⁻¹. In stability and durability tests, the catalyst was submitted to current densities of 250 mA cm⁻² for 10 h, 100 mA cm⁻² for 20 h and again 250 mA cm⁻² for 10 h. The activity of Ni-rGO remained almost stable during the 40 h test, at an overpotential of around 220 mV, which confirms its high stability and its suitability for industrial hydrogen production.

Later, they compared the performance of Ni-rGO, Ni-ONC (oxidized N-enriched carbon), and Ni-OCNT (oxidized carbon nanotube) at different current densities. The results showed that Ni-rGO exhibited the smallest Tafel slope and overpotential. At the highest current density tested, 80 mA cm⁻², the catalyst had an overpotential of 245 mV. The enhancement of the catalytic behavior of Ni-rGO could be a result of the grain refinement effect of the homogeneously distributed rGO layers, which increased the active surface area [44].

Moreover, the properties of Ni can be enhanced by the introduction of other transition metals into metallic Ni to form Ni-based alloys. Arul Raj and Vasu [45,46] studied several Ni-based alloys (binary and ternary) as cathodes for HER. The activity trend of the binary electrocatalysts on a steel substrate followed the order: Ni-Mo > Ni-Zn > Ni-Co > Ni-W > Ni-Fe > Ni-Cr > Ni. The Ni-Mo was found to be the best electrocatalyst of all the alloys tested in terms of stability under open-circuit conditions, corrosion resistance, and long-term stability under the chosen operational condition (6 M KOH at −300 mA cm⁻² and 80 °C) [45]. Regarding the ternary Ni-based alloys, under the same conditions of the previous tests, they obtained the following activity order during HER: Ni-Mo-Fe > Ni-Mo-Cu > Ni-Mo-Zn > Ni-Mo-Co ~ Ni-Mo-W > Ni-Mo-Cr > Ni. Ni-Mo-Fe alloy could deliver a current density of −300 mA cm⁻² at an overpotential of 187 mV and 80 °C [46]. Since then, the combination of Ni with Mo compounds has been proved to be one of the most
effective approaches to creating effective electrocatalysts for HER. While, as already seen, Ni is active for water dissociation, Mo has good adsorption properties toward hydrogen, because of their unique electronic structures.

Raney Ni has been used for almost 50 years as an effective electrocatalyst for HER. It is produced by leaching aluminum (Al) or zinc (Zn) from Ni-Al or Ni-Zn alloys, which results in a more porous structure with a larger surface area when compared to typical Ni electrodes [34,47]. There are several ways to prepare Raney Ni electrodes. For example, Kim et al. [47] proposed an atmospheric plasma spraying coating method. After the coating stage, the electrodes were annealed at 610 °C for 1 h under a hydrogen atmosphere, to increase the adhesion of the coating to the substrate and reduce the NiAl phase. The cathode thus developed presented an overpotential of 108 mV and a Tafel slope of 54 mV dec⁻¹, at a current density of −300 mA cm⁻², in 1 M KOH and room temperature. To examine the durability of the electrodes, a constant current of −400 mA cm⁻² was applied to the electrodes with and without heat treatment. The Raney Ni electrodes after heat treatment showed a quicker deactivation (stable potential for around 48 h) than without heat treatment (stable potential for 144 h).

Coli et al. [34] presented a Raney Ni (Ni-Zn) electrode obtained from electroplating. Under AWE typical operational conditions (−300 mA cm⁻²) the overpotential is around 150 mV, which was around 230 mV lower than the Ni overpotential. They compared the performance of the Raney Ni with other established electrocatalysts. In Figure 5 it is possible to observe the plot of the overpotential against the current density of the studied materials. The Raney Ni electrode showed an outstanding performance, with an overpotential value far inferior when compared to the other electrocatalysts.

![Figure 5. Plot of the overpotential against the current density of several electrocatalysts at 30 °C and 6 M KOH. Reprinted from [34] with permission from MDPI.](image)

Recent research has introduced the NiSn alloy as another interesting electrocatalyst for HER. Jović et al. [28] electrodeposited NiSn onto a Ni mesh substrate and compared the performance of this alloy with pure Ni electrodes, on a 30 wt.% KOH electrolyte, at 80 °C. The NiSn showed superior HER activity at a current density of 250 mA cm⁻², with overpotentials 350 and 377 mV lower than electrodeposited Ni onto Ni mesh and simple Ni mesh, respectively. The Tafel slopes measured were 44, 129, and 132 mV dec⁻¹ for the NiSn, Ni electrodeposited, and Ni mesh, respectively, which indicates a change in the mechanism when adding Sn to Ni compounds. Later, the same authors decided to study the behavior of the NiSn sample over a longer time of HER (5 h) at industrial operating conditions (30 wt.% KOH and current density of 300 mA cm⁻² at 80 °C). The overpotential of the NiSn electrode remained relatively stable, unlike the overpotential of a simple Ni mesh, which only stabilized near the end of the set time. After 5 h, the overpotential for the NiSn sample was 169 mV, significantly lower than the Ni mesh electrode, 787 mV [38].
Transition metal sulfides (TMSs), phosphides (TMPs), selenides (TMSes), nitrides (TMNs), and carbides (TMCs) are being reported as newly discovered families for water electrolysis. The performance of the electrocatalysts of these groups is still being studied at the laboratory scale, mostly at low current densities and outside of the typical industrial electrolyte concentration and temperature. However, they are promising electrocatalysts for both half-reactions and may be implemented in the near future. From the trend presented above, it is clear that Ni-based composites are the most interesting and most commonly reviewed in the literature. However, some Fe, Mo, and Co-based composites show catalytic activity near that of the Ni-based compounds [27,29,31].

TMSs display good electrocatalytic activity because S atoms can withdraw electrons from the transition metals due to their high electronegativity, and sulfur can then act as the active site to stabilize the reaction intermediates. On the other hand, S atoms may also create S-vacancies to tailor the electron density of TMSs or improve water dissociation [29]. At operating conditions closer to the ones that AW electrolyzers perform, the work of Han et al. [48] can be taken as an example. They prepared NiS and NiSCo coatings by electrodeposition on mild steel. The performance of the electrocatalysts was evaluated in 28 wt.% NaOH aqueous electrolyte at 150 mA cm$^{-2}$. The overpotential of NiS was 90 mV, 20 mV higher than the overpotential of NiSCo. Regarding the Tafel slopes for NiS and NiSCo, the values obtained were 80.9 and 61.7 mV dec$^{-1}$, respectively.

TMPs are also being reported as promising electrocatalysts for both half-reactions, but in particular for HER. The reason for the excellent catalytic performance is related to the electronic features of phosphide. The phosphorus and metal sites in phosphide composites act as proton-acceptor sites and hydride-acceptor sites, respectively. Among all TMPs, also extensively reviewed [29,49–51], NiCoP is the most frequently documented one [29,39]. Li et al. [39] designed a NiCoP nanowire array grown on Ni foam as a cost-effective, highly efficient, and stable bifunctional electrocatalyst for overall water splitting. To achieve the current density of 100 mA cm$^{-2}$, the electrocatalyst needs an overpotential of 197 mV. The Tafel slope reported was 54 mV dec$^{-1}$. Both values are indicative that this electrocatalyst exhibits promising activity to be used in an industrial environment. The direct growth of NiCoP on Ni foam accelerates electron transport from the electrocatalyst to the support, which is essential for the enhancement of OER activity. Moreover, the stability test, performed at 10 mA cm$^{-2}$, showed stable HER and OER catalytic performance for 28 h.

On the other hand, interest in the catalytic activity of selenides is increasing due to their metallic nature with low intrinsic electrical resistance. Compared with sulfides, they manifest a faster electron-transfer capacity [52]. Catalysts of the type Ni$_x$Se$_y$ are the most widely studied [29,52,53], but their catalytic activity still needs to be improved to achieve performance comparable to the other electrocatalysts mentioned before, especially from a commercial-stage point of view. Doping the Ni$_x$Se$_y$ selenides with other metals is a procedure normally used to enhance their catalytic activity [29,52]. Using a heat treatment, with and without NH$_3$ atmosphere, Jing et al. [54] developed N-doped NiSe$_2$ and NiSe$_2$, respectively, on Ni foam (Figure 6). The first showed significantly better performance for HER, with an overpotential almost 90 mV lower than the second. The $\Delta G_{H^*}$ value of N-NiSe$_2$ is relatively close to the ideal hydrogen-adsorption free energy and this catalyst has lower water adsorption energy than NiSe$_2$. As in the case of sulfides, the electronegativity difference between Se and H is smaller than that between N and H, so the implanted N promotes the H adsorption, enhancing HER activity.

TMNs possess unique physical and chemical properties such as excellent thermal and chemical stability, high electronic conductivity, and high electrocatalytic activity for HER. Moreover, bonding with N atoms alters the d-band structure of the host metal, thereby contracting the d-band of the metal. The active sites of the metal can improve the catalytic activity efficiently because their electronic structure is similar to the noble metal Pt [29,55]. Several Ni-based nitrides have been reviewed [29,42,56]. Xing et al. [41] synthesized a Ni$_3$N film onto NF using a one-step procedure, a thermal treatment at 350 °C for 2 h under an NH$_3$ atmosphere. The electrodes thus developed showed remarkable catalytic
performance, obtaining an extremely low overpotential of 34 mV at −10 mA cm$^{-2}$. Hence, using an NF as a conductive substrate results in a high catalyst loading and a high number of catalytic sites. Furthermore, seamless contact between Ni$_3$N nanosheets and NF ensures high conductivity of electrodes and rapid charge transfer, and the tight integration prevents catalyst shedding. The easy preparation procedure and the high stability and durability of the cathode developed (no significant degradation was found even at 100 mA cm$^{-2}$) suggest the use of this electrocatalyst for large-scale hydrogen production.

![SEM images of fresh NF and N-NF](image)

**Figure 6.** Development of N-doped NiSe$_2$ in Ni foam, using a heat treatment. (a) Low- and (b) high-resolution SEM images of the fresh NF, (c) low- and (d) high-resolution SEM images of the as-prepared N-NiSe$_2$/NF sample, (e) polarization curves of the NF, N-NF, NiSe$_2$/NF and N-NiSe$_2$/NF electrodes and (f) the corresponding Tafel plots. Adapted from [54] with permission from Elsevier.

Last, but not least, regarding carbide-based species, they are characterized for having similar electronic structures to noble metals and structural robustness, allied with an abundance on earth. TMCs require high conductivity substrates to intensify the conductivity of the electrocatalysts. Unlike the other catalyst groups presented, where Ni was the principal metal, in the case of carbide species, Mo$_x$C$_y$ [57–60] is the most commonly used TMC for alkaline HER [57]. Huang et al. [60] have developed an easy two-step preparation method for Mo$_2$C NPs dispersed on carbon microflowers via the self-polymerization of dopamine. The resulting hybrid material exhibits impressive performance with both low overpotential and Tafel slope. Moreover, when submitted to 10,000 cycles, between −0.23 and 0.07 V at 100 mV s$^{-1}$ the electrocatalyst showed great operation stability.

Table 2 presents a summary of the main features of the HER electrocatalysts described.
Table 2. An overview of the overpotentials and Tafel slope of HER for several electrocatalysts suitable for industrial AWE.

| Composition | Support | Preparation Method | Electrolyte | T (°C) | $j$ (mA cm$^{-2}$) | $\eta_{\text{HER}}$ (mV) | $b_{\text{HER}}$ (mV dec$^{-1}$) | Stability | Ref. |
|-------------|---------|-------------------|-------------|--------|----------------|-----------------|----------------------|-----------|-----|
| Ni          | Ni      | Aged              | 6 M KOH     | 30     | −300            | 385             | -                    | -         | [34]|
| NF          | NF      | -                 | 1 M KOH     | RT     | −10             | 217             | 130                  | -         | [36]|
| Ni mesh     | Ni mesh | -                 | 1 M KOH     | RT     | −10             | 275             | 143                  | -         | [36]|
| Ni mesh     | Ni mesh | -                 | 6 M KOH     | 80     | −250            | -               | 132                  | -         | [28]|
| Ni mesh     | Ni mesh | -                 | 6 M KOH     | 80     | −300            | 787             | -                    | -         | [38]|
| NF          | AISI SS | Electrodeposition | 1 M KOH     | RT     | −10             | 130             | 160                  | -         | [37]|
| Ni          | Ni mesh | Electrodeposition | 6 M KOH     | 80     | −250            | -               | 129                  | -         | [28]|
| Ni          | AISI SS | Electrodeposition | 6 M KOH     | 80     | −100            | 229             | 111                  | -         | [61]|
| Ni          | CFC     | Pitting process   | 1 M KOH     | RT     | −10             | 131             | 123                  | -         | [43]|
| Ni-rGO      | NF      | Supergravity      | 1 M NaOH    | RT     | −100            | 183             | 77                   | -         | [37]|
| Ni-rGO      | Cu      | Supergravity      | 1 M NaOH    | T      | −80             | 245             | 93                   | -         | [44]|
| Ni-ONC      | Cu      | Supergravity      | 1 M NaOH    | RT     | −80             | 286             | 134                  | -         | [44]|
| Ni-OCNT     | Cu      | Supergravity      | 1 M NaOH    | RT     | −80             | 330             | 135                  | -         | [44]|
| Ni-Zn       | Mild steel | Electrodeposition | 6 M KOH     | 80     | −300            | 225             | 175                  | -         | [45]|
| Ni-Mo       | Mild steel | Electrodeposition | 6 M KOH     | 80     | −300            | 185             | 175                  | -         | [45]|
| Ni-Mo-Fe    | Mild steel | Electrodeposition | 6 M KOH     | 80     | −300            | 187             | 165                  | -         | [46]|
| NiCuCo      | Cu      | Electroplating    | 6 M KOH     | 30     | −10             | 160             | -                    | -         | [34]|
| Ra-Ni (Ni-Al) | Ni   | Atmospheric plasma spraying and heat treatment | 1 M KOH | RT | −300 | 108 | 54 | Stable potential for 48 h at −400 mA cm$^{-2}$ | [47]|
| Ra-Ni (Ni-Zn) | Cu | Electroplating    | 6 M KOH | 30 | −10 | 20 | - | - | [34]|
| Ra-Ni (Ni-Zn) | Cu | Electroplating    | 6 M KOH | 30 | −300 | 150 | - | - | [34]|
| NiSn        | Ni mesh | Electrodeposition | 6 M KOH | 80 | −250 | - | 44 | - | [28]|
| NiSn        | Ni mesh | Electrodeposition | 6 M KOH | 80 | −300 | 169 | - | - | [38]|
| NiSe2       | NF      | Hydro(solvo) thermal treatment | 1 M KOH | RT | −10 | 170 | 95 | Stable current density at -1.25 V for 2.8 h | [62]|

Stable potential for ca. −400 mV at −50 mA cm$^{-2}$ for 20 h
Large current density (no decay) of −147 mA cm$^{-2}$ for 114 h at an overpotential of 515 mV
Stable potential of −220 mV for 40 h (10 h at −250 mA cm$^{-2}$, 20 h at −100 mA cm$^{-2}$ and 10 h at −250 mA cm$^{-2}$)
Almost steady potential of −1.40 V at 100 mA cm$^{-2}$ for 5.6 h
Almost steady potential of −1.45 V at −100 mA cm$^{-2}$ for 5.6 h
Almost steady potential of −1.53 V at −100 mA cm$^{-2}$ for 5.6 h
Stable potential of ca. −400 mV at −50 mA cm$^{-2}$ for 20 h
| Composition | Support | Preparation Method | Electrolyte | T (°C) | $j$ (mA cm$^{-2}$) | $\eta_{\text{HER}}$ (mV) | $b_{\text{HER}}$ (mV dec$^{-1}$) | Stability | Ref. |
|-------------|---------|-------------------|-------------|--------|-------------------|-------------------|--------------------------|-----------|------|
| Ni$_3$Se$_2$ | NF | Solvothermal treatment | 1 M KOH | RT | $-100$ | $279$ | $79$ | Stable current of $-5$ mA cm$^{-2}$ at $-200$ mV for 200 h. Negligible degradation after 2000 CV cycles | [63] |
| N-NiSe$_2$ | NF | Heat treatment (in NH$_3$ atmosphere) | 1 M KOH | RT | $-10$ | $86$ | $69$ | Stable potential of ca. $-100$ mV at $-10$ mA cm$^{-2}$ for 20 h. Negligible degradation after 5000 CV cycles (between $-250$ mV and $150$ mV at $50$ mV s$^{-1}$) | [54] |
| NiS | Mild steel | Electrodeposition | 28 wt.% NaOH | $80$ | $-150$ | $90$ | $80.9$ | Stable current density of ca. $-95$ mA cm$^{-2}$ at $-1.2$ V for 2.2 h | [48] |
| NiS-Co | Mild steel | Electrodeposition | 28 wt.% NaOH | $80$ | $-150$ | $70$ | $61.7$ | Stable current density of ca. $-95$ mA cm$^{-2}$ at $-1.2$ V for 2.2 h | [48] |
| NiCoP | NF | Hydrothermal treatment and phosphorization | 1 M KOH | RT | $-10$ | $98$ | $68$ | Stable after 300 CV cycles and no current density degradation ($-10$ mA cm$^{-2}$) at $98$ mV for 24 h | [40] |
| NiCoP | NF | Solvothermal and heat treatment | 1 M KOH | RT | $-100$ | $197$ | $54$ | Electrochemical stability for 28 h at $10$ mA cm$^{-2}$ | [39] |
| Ni$_3$N NS | NF | Thermal treatment (in NH$_3$ atmosphere) | 1 M KOH | RT | $-10$ | $34$ | $54$ | Stable current density of ca. $-12$ mA cm$^{-2}$ at an overpotential of $174$ mV for 8 h | [56] |
| NiMoN | CFC | Hydrothermal treatment (in NH$_3$ atmosphere) | 1 M KOH | RT | $-10$ | $40$ | $70$ | Stable potential around $-50$ mV, at $10$ mA cm$^{-2}$ for 12 h | [64] |
| FeNi$_3$N | NF | Heat treatment and calcination | 1 M KOH | RT | $-10$ | $75$ | $98$ | Stable potential and no degradation after $30$ h at $-50$ mA cm$^{-2}$ | [42] |
| MoC | GS | Carburization process | 1 M KOH | RT | $-10$ | $77$ | $50$ | Stable current density of ca. $15$ mA cm$^{-2}$ at $150$ mV for $10$ h | [58] |
| Mo$_2$C | NCF | Polymerization process | 1 M KOH | RT | $-10$ | $100$ | $55$ | Electrochemical stability at $105$ mV for $8$ h and after $10,000$ CV cycles (between $-230$ and $70$ mV at $100$ mV s$^{-1}$) | [60] |
| Mo$_2$C | HNCPs | Chemical vapor deposition and heat treatments | 1 M KOH | RT | $-10$ | $87$ | $49$ | Suitable stability: drop of $3.7\%$ of the current density over $10$ h | [59] |
4.1.3. OER Mechanism

The mechanism of the oxygen evolution reaction is more complex compared to that suggested for the hydrogen evolution reaction. Several pathways have been suggested, with the most widely accepted for AWE being given by Equations (22)–(24).

\[
\begin{align*}
\text{OH}^- & \rightarrow \text{OH}_{\text{ads}} + e^- \quad (22) \\
\text{OH}^- + \text{OH}_{\text{ads}} & \rightarrow \text{O}_{\text{ads}} + \text{H}_2\text{O} + e^- \quad (23) \\
\text{O}_{\text{ads}} + \text{O}_{\text{ads}} & \rightarrow \text{O}_2 \quad (24)
\end{align*}
\]

At low temperatures, the rate-determining step is one of the charge-transfer steps, Equations (22) and (23). On the other hand, a slow recombination step, Equation (24) controls the reaction at high temperatures.

The overpotential of oxygen evolution reaction is generally measured by the Tafel equation in the form of Equation (25),

\[
\eta_{\text{O}_2} = \frac{2.3RT}{\alpha_a F} \log\left(\frac{j}{j_0}\right) = \frac{2.3RT}{(1-\alpha_c) F} \log\left(\frac{j}{j_0}\right)
\]

where \(\alpha_a\) is the anodic charge transfer coefficient. The overpotential associated with OER is more difficult to reduce than that of the HER, due to its complex mechanism, since OER involves four electron transfers. As in the HER mechanism, the rate of the OER, and thus, the efficiency, is related to the catalytic activity of the electrocatalysts [8,9].

4.1.4. OER Electrocatalysts

As already mentioned, the mechanism for the OER is more complex than the one for the HER, which means that the overpotential will be higher at the anodes, in comparison to the overpotential at the cathodes. Until now, no electrocatalysts developed for this half-reaction can be considered entirely satisfactory and, as a consequence, intensive efforts are still being made to developing lower overpotentials and more stable electrocatalysts for the oxygen evolution.

As in HER, earth-abundant TMs are being used as substitutes for the traditional noble metals, like Ru and Ir [19,30,32]. Co, Fe, Mo, Mn, and especially Ni have drawn great attention and have been extensively reviewed [65–69]. These transition metals, in OER, are mostly used in the form of oxides and (oxy)hydroxides, which can be explained by reporting to the Pourbaix diagrams of the elements. A Pourbaix diagram is a bidimensional chart of the electrochemical potential versus pH, at a specific temperature, pressure, and ion concentration, and maps the different phases of the elements [69,70]. Taking the example of Ni at typical electrolyte concentrations used in AWE, in the OER (where the applied potential is positive), it can be seen from Figure 7 that Ni is stable (hence it does not corrode) when it is in oxide and (oxy)hydroxide form. From Figure 7, it can also be concluded that Ni in oxide and (oxy)hydroxide form is not that stable for HER, which is why Ni is normally used in its metallic form.

Miles et al. [65] prepared various metal oxide electrodes by a thermal decomposition method and observed that the catalytic behavior of Ni was similar to that of noble metals such as Ir, Pt, Rh, and Pd, and was only surpassed by Ru. Subbaraman et al. [66] have proved the higher electrocatalytic activity of Ni, in comparison to other transition metals, by developing several metal hydroxide electrocatalysts through electrodeposition. They established the following activity trend: Ni > Co > Fe > Mn.

Plata-Torres et al. [67] studied the electrochemical performance of single (Ni, Co, Mo), binary (Co_{30}Ni_{70}, Ni_{30}Mo_{70}, Co_{30}Mo_{70}), and ternary (Co_{10}Ni_{20}Mo_{70}, Fe_{10}Co_{30}Ni_{60}, Co_{10}Fe_{30}Ni_{60}) alloys, developed by a process of mechanical alloying. The alloys were deposited on graphite substrates, and their behavior was analyzed in 30 wt.% KOH at 70 °C. The performance of the electrocatalysts was compared by their Tafel slopes, at low (150–300 mV) and high (450–600 mV) overpotentials, and the current density required for
them to achieve different values of overpotential. Concerning single transition metals, as already seen from other work, Ni exhibited the best electrochemical performance. From the polarization curves presented for 1 cycle and 50 cycles, it was possible to identify that the surface of the milled metallic powders appeared to be dominated by different forms of the metals: at low potential cycles, the predominant species were Ni, Co, and Mo oxides, and at high potential cycles, some hydroxide compounds, such as Ni(OH)$_2$, NiOOH, Co(OH)$_2$, and CoOOH, or some oxides, less conductors, like MoO$_4^{2-}$, were formed.

![Pourbaix Diagram of Ni](image)

**Figure 7.** Pourbaix diagram of Ni at 25 °C and atmospheric pressure. Reprinted from [71].

Concerning the binary and ternary alloys developed, it was possible to identify that their catalytic activity was directly influenced by the ratio of Ni, Co, Mo, or Fe in each species: the activity of the alloys increased with the increase of Ni and/or Mo content, so the electrocatalysts that showed the best electrochemical performance were Co$_{10}$Ni$_{20}$Mo$_{70}$ and Ni$_{30}$Mo$_{70}$. These results highlight the fact, already mentioned in Section 4.1.2, relating to the electrocatalysts for HER, that alloying Ni with other transition metals improves the catalytic performance of the electrocatalysts. As with the single transition metals, for the binary and ternary species, it was also possible to observe a change in the polarization curves at 1 and 50 cycles. In Table 3, the Tafel slopes and current densities at different overpotentials of all the alloys mentioned are presented. Further research has been reported on the performance of these electrocatalysts (NiMo [72,73], CoNi [74,75], CoNiMo [76] and FeCoNi [77,78]).

Even though the NiFe-based alloys did not show the best electrocatalytic performance for OER in the studies mentioned above, they are a successful approach to reducing the OER overpotential and are therefore intensively studied for that aspect. The affinity of Ni and Fe facilitates the formation of a NiFe alloy in the earth’s core [79].

A significant number of studies report on the performance of NiFe oxides [80] and (oxy)hydroxides [34,81,82]. As an example, Jin et al. [81] reported the electrodeposition of highly efficient NiFe alloy onto NF. During the OER, the species Ni and Fe are oxidized in the air, resulting in the formation of Ni hydroxides and ferric hydroxides. In consequence, the electrocatalyst exhibited a higher OER efficiency, with low overpotential, 191 mV to reach 10 mA cm$^{-2}$ and low Tafel slope, 44 mV dec$^{-1}$. It also showed remarkable long-time
stability, where the potential increased less than 10 mV after more than 8 h at 100 mA cm$^{-2}$, confirming the potential to use the electrocatalyst at an industrial level.

Table 3. Tafel slopes for OER at high and low overpotentials and current densities at different overpotentials after 50 potential cycles in 30 wt.% KOH at 70 °C. Adapted from [67] with permission from Elsevier.

| Alloy                  | $b_{\text{low } \eta}$ (mV dec$^{-1}$) | $b_{\text{high } \eta}$ (mV dec$^{-1}$) | $i_{\eta=200\text{mV}}$ (mA cm$^{-2}$) | $i_{\eta=400\text{mV}}$ (mA cm$^{-2}$) | $i_{\eta=600\text{mV}}$ (mA cm$^{-2}$) |
|------------------------|----------------------------------------|----------------------------------------|----------------------------------------|----------------------------------------|----------------------------------------|
| Ni                     | 125                                    | 120                                    | 0.03                                   | 21.3                                   | 38.9                                   |
| Co                     | 190                                    | 198                                    | 1.23                                   | 3.46                                   | 30.9                                   |
| Mo                     | 178                                    | 273                                    | 6.30                                   | 4.36                                   | 36.2                                   |
| Co$_{30}$Ni$_{70}$      | 130                                    | 206                                    | 1.58                                   | 5.24                                   | 58.9                                   |
| Ni$_{30}$Mo$_{70}$      | 75                                     | 112                                    | 7.24                                   | 138                                   | 708                                     |
| Co$_{30}$Mo$_{70}$      | 150                                    | 165                                    | 12.0                                   | 32.4                                   | 195                                     |
| Co$_{10}$Ni$_{20}$Mo$_{70}$ | 130                                   | 221                                    | 60.2                                   | 234                                   | 577                                     |
| Fe$_{10}$Co$_{30}$Ni$_{60}$ | 119                                   | 180                                    | 10.4                                   | 40.7                                   | 70.8                                     |
| Co$_{10}$Fe$_{30}$Ni$_{60}$ | 102                                   | 180                                    | 9.77                                   | 32.4                                   | 77.6                                     |

Layered double hydroxides (LDHs) are two-dimensional materials that have attracted increased attention for OER in the last decade [32,83], because of their large surface-to-bulk ratios; efficient exposure of catalytic active sites in comparison to 0D and 1D materials; easy adjustment of the structure of the layers; hierarchical porosity, which improves the diffusion of the water molecules and release of the gases; and strong electrostatic interactions between layers and interlayer anions, which offer, among several advantages, more structural stability [83]. They consist of positively charged layers and charge-balancing interlayer anions. The positively charged layers are constructed by partially substituting monovalent cations (Li$^+$), divalent cations (Ni$^{2+}$, Mg$^{2+}$, Ca$^{2+}$, Mn$^{2+}$, Co$^{2+}$, Cu$^{2+}$, Zn$^{2+}$) or trivalent cations (Al$^{3+}$, Fe$^{3+}$, Cr$^{3+}$). The intercalated anions are typically carbonate (CO$_{3}^{2-}$), which can easily be substituted by other anions (SO$_{4}^{2-}$, NO$_{3}^{−}$, Cl$^{−}$, Br$^{−}$) [32,79].

Following the previous trend, NiFe LDH is the most reviewed [32,79,84]. One of the major advantages of NiFe LDHs is that metal atoms can regularly be located on the LDHs flakes to provide abundant exposed active sites. However, the low conductivity of LDHs has hindered their practical applications as OER catalysts. To overcome this problem, some researchers use LDHs hybridized with conductive materials [32]. As an example, Youn et al. [85] developed a NiFe LDH/rGO composite by a solvothermal method that was later electrodeposited in glassy carbon. This electrocatalyst showed superior OER performance when compared with bare NiFe LDH. The NiFe LDH/rGO exhibited a synergistic effect between active NiFe nanoplates and rGO layers, possessing high electrical conductivity and a large surface area. The rGO layers played an important role in enhancing the activity of the catalyst by providing a good electrical pathway and high surface area.

TMss, TMs, TMSe, and TMNs also show interesting catalytic activity towards OER. Similar to other transition metal groups, Ni compounds [30,42,76] are the most active for OER, and it has already been well established that incorporating Fe can boost the OER performance [42,54,86,87].

The introduction of other transition metals enhances the electrocatalytic activity of NiFe alloys. Chai et al. [88] prepared an efficient electrode for water oxidation through the electrodeposition of NiFeCo onto NF before solvothermal sulfurization. The NiFeCoS electrode achieved an overpotential of 180 mC at 100 mA cm$^{-2}$ and a low Tafel slope of 50.4 mV dec$^{-1}$. Later a Fe hydroxide film was electrodeposited on the surface of the NiFeCoS. This procedure lowers the catalytic activity of the electrode but ensures stability and durability of the electrode (since the Fe protects the catalyst from the severe alkaline medium). Combining more than one metal from these groups also enhances the behavior of the catalysts. For instance, Liu et al. [89] developed a phosphorus-doped Fe-Ni sulfide, P-doped (Ni,Fe)$_{3}$S$_{2}$ bifunctional electrocatalyst in Ni foam by a simple one-step simultaneous phosphorization and sulfuration route. They observed that the introduction of Fe into
the \( \text{Ni}_3\text{S}_2 \) improved the OER activity. Further introduction of P into \((\text{Ni,Fe})_3\text{S}_2\) enhanced the performance even more, with an overpotential of 246 mV, to drive the current density of 100 mA cm\(^{-2}\), less 30 mV and 150 mV than the overpotential of \((\text{Ni,Fe})_3\text{S}_2\) and \(\text{Ni}_3\text{S}_2\), respectively. The introduction of P anion increased the ratio of \(\text{Ni}^{3+}/\text{Ni}^{2+}\) in the \((\text{Ni,Fe})_3\text{S}_2\), resulting in stronger OH\(^{-}\) absorption, which efficiently enhanced OER activity. In addition, during OER the surface of the catalyst was converted to \((\text{Ni,Fe})\text{OOH}\) and \((\text{Ni,Fe})\text{-(OH)}_2\). The electrocatalyst also shows high durability, 15 h, at high current densities of 100 mA cm\(^{-2}\).

Despite major advances in this field, stainless steel (SS) is still the most commonly used material as an electrode for the OER in commercial AWE. In addition to being an inexpensive and corrosion-resistant material, it has excellent mechanical strength \[90\] and it contains different kinds of elements, like Fe, Ni, and Mo, that have already been presented as active centers in the electrochemical reactions \[91,92\].

Yu et al. \[90\] directly used commercially available 316L SS as an anode material. The electrode presented a Tafel slope of 30 mV dec\(^{-1}\) and an overpotential of 370 mV to achieve a current density of 10 mA cm\(^{-2}\) in a 1 M KOH solution. This behavior is comparable and can even surpass the performance of some electrocatalysts already presented, at the same conditions. The AISI 316L SS electrode also exhibited high durability, since the overpotential was maintained constant for 20 h (under the same current density). After 50 h of electrolysis at 10 mA cm\(^{-2}\), the durability and stability was tested again and the performance was consistent with the first test.

Hu et al. \[36\] compared a 316L SS mesh electrode with other usual electrocatalysts used at the OER and recorded its polarization curves and respective Tafel plots (Figure 8). The SS mesh showed remarkable catalytic activity, even surpassing one of the benchmark catalysts, RuO\(_2\).

![Figure 8. Comparison of the performance of several electrodes towards the OER. (a) Polarization curves for OER in 1 M KOH electrolyte and (b) the corresponding Tafel plots. Adapted from \[36\]—published by The Royal Society of Chemistry.](image-url)

The performance of SS electrodes can usually be further improved with surface modifications, like polishing \[34\], cathodic activation \[91\], anodic activation \[93\], and pulsed laser rusting \[92\]. As an example, Zhang et al. \[91\] activated an SS mesh material by cathodization treatment that consisted of applying repetitive potential cycling, in the potential region of \(-1.5\) to 0.4 V at a scan rate of 10 mV s\(^{-1}\) in 0.1 M KOH electrolyte for 10 cycles. In a 1 M KOH electrolyte, the electrode exhibits an overpotential of 275 mV and 319 mV to achieve current densities of 10 and 100 mA cm\(^{-2}\), respectively. This superior OER activity is due to the surface enrichment of Ni hydroxide/(oxy)hydroxide species and due to the facilitated removal of O\(_2\) gas bubbles during the OER. Furthermore, although minor degradation was observed after long-term water electrolysis tests, its initial performance can be easily regained by repeating the cathodization treatment.

Table 4 summarizes some of the main features of the mentioned OER electrocatalysts.


Table 4. Overview of the overpotentials and Tafel slope of OER for the main electrocatalysts suitable for industrial AWE.

| Composition  | Support       | Preparation Method           | Electrolyte | T (°C) | \( j \) (mA cm\(^{-2} \)) | \( \eta_{OER} \) (mV) | \( b_{OER} \) (mV dec\(^{-1} \)) | Stability                                                                 | Ref.   |
|--------------|---------------|-----------------------------|-------------|--------|-----------------------------|------------------------|-----------------------------|----------------------------------------------------------------------------|--------|
| Ni           | Ni            |                             | 1 M KOH     | RT     | 10                          | 403                    | 72                          | Poor stability, with current density decreasing from 7 to 3 mA cm\(^{-2} \), at 1.8 V for 25 h | [94]   |
| Ni           | Porous Ni     | Laser ablation              | 1 M KOH     | RT     | 10                          | 294                    | 41                          | Stable current density of around 7.5 mA cm\(^{-2} \), at 1.65 V for 25 h | [94]   |
| NiO/Ni       | Ni            | Laser ablation              | 1 M KOH     | RT     | 10                          | 420                    | 62.4                        | -                                                                          | -      |
| NiO          | GC            | Drop-cast method            | 1 M NaOH    | RT     | 10                          | 580                    | 39.8                        | -                                                                          | [95]   |
| CoO          | GC            | Drop-cast method            | 1 M NaOH    | RT     | 10                          | 100                    | 137                         | -                                                                          | -      |
| MnO          | GC            | Laser ablation              | 1 M KOH     | RT     | 10                          | 100                    | 203                         | -                                                                          | [94]   |
| MnO\(_2\)    | GC            | Laser ablation              | 1 M KOH     | RT     | 10                          | 100                    | 203                         | -                                                                          | [94]   |
| Co          | NiO            | Laser ablation              | 1 M KOH     | RT     | 10                          | 100                    | 203                         | -                                                                          | [94]   |
| Ni(OH)\(_2\) | NF            | Activation process          | 1 M KOH     | RT     | 10                          | 288                    | 40                          | Stable overpotential of 1.57 V, at 100 mA cm\(^{-2} \) for 240 h          | [68]   |
| Ni(OH)\(_2\) | NF            | Activation process          | 1 M KOH     | RT     | 500                         | 370                    | -                           | Stable overpotential of 1.57 V, at 100 mA cm\(^{-2} \) for 240 h          | [68]   |
| Ni\(_{0.4}\)Mo\(_{0.6}\)O | CC          | Thermal treatments          | 1 M KOH     | RT     | 10                          | 320                    | 63                          | Stable current density of 10 mA cm\(^{-2} \) at 1.57 V for 10 h. Slight shift to smaller current densities after 2000 CV cycles (between 0.40 and 0.84 V at 100 mV s\(^{-1} \)) Stable overpotential (only an increase of 15 mV) at 10 mA cm\(^{-2} \) for 8.3 h | [73]   |
| Co\(_{1.4}\)Ni\(_{0.6}\)O\(_2\) | -            | Co-precipitation and calcination | 1 M KOH     | RT     | 10                          | 366                    | 114                         | Stable overpotential at 100 mA cm\(^{-2} \) for 8.3 h. No significant deactivation detected | [74]   |
| NiFe\(_2\)O\(_4\) | GC          | Dealloying and annealing    | 1 M KOH     | RT     | 10                          | 412                    | 57                          | -                                                                          | [80]   |
| NiFe/NiFe(OH)\(_2\) | NF          | Electrodeposition and oxidation | 1 M KOH     | RT     | 10                          | 191                    | 44.1                        | Stable overpotential at 100 mA cm\(^{-2} \) for 8.3 h. No significant deactivation detected | [81]   |
| NiFe(OH)\(_2\) | Ni            | Electrodeposition           | 6 M KOH     | 30     | 300                         | 365                    | -                           | Constant current density of 50 mA cm\(^{-2} \) for 100 h                 | [34]   |
| Ni(OH)\(_2\) | CP            | Electrodeposition and direct dropping | 1 M KOH     | RT     | 10                          | 223                    | 32.5                        | Stable potential of ca. 1.48 V at 10 mA cm\(^{-2} \) for 20 h. At high current densities (250 and 500 mA cm\(^{-2} \)), the overpotential increases 160 mV after 10 h | [77]   |
| 0.1-FeCoNiO | NF            | Wet chemical method         | 1 M KOH     | RT     | 10                          | 240                    | 36.8                        | Electrochemical stability for 1000 CV cycles (between 0 and 0.8 V at 10 mV s\(^{-1} \)) | [76]   |
| CoMoO\(_4\) | NF            | Hydrothermal treatment, electrodeposition, sonication | 1 M KOH     | RT     | 100                         | 349                    | 67.6                        | Electrochemical stability for 1000 CV cycles (between 0 and 0.8 V at 10 mV s\(^{-1} \)) | [76]   |
| Composition       | Support | Preparation Method                                                                 | Electrolyte | T (°C) | \( j \) (mA cm\(^{-2}\)) | \( \eta_{\text{OER}} \) (mV) | \( b_{\text{OER}} \) (mV dec\(^{-1}\)) | Stability                                                                                                                                  | Ref.     |
|-------------------|---------|------------------------------------------------------------------------------------|-------------|--------|-----------------|-----------------|-----------------|-------------------------------------------------------------------------------|---------|
| NiFe LDH/rGO      | GC      | Solvothermal method and electrodeposition                                             | 1 M KOH     | RT     | 10              | 245             | -               | Electrochemical stability for 1000 CV cycles (between 1.10 and 1.85 V)        | [85]    |
| Ni-doped FeS      | NF      | Electrodeposition                                                                  | 1 M KOH     | RT     | 100             | 255             | 58.3            | Electrochemical stability after 1000 CV cycles (between 0 and -0.35 V)        | [87]    |
| NiFeCoS           | NF      | Electrodeposition and solvothermal sulfurization                                    | 1 M KOH     | RT     | 100             | 180             | 50.4            | Increase in the overpotential to 260 mV to attain 100 mA cm\(^{-2}\) after 500 CV cycles (between 0.1 and 0.5 V at 100 mV s\(^{-1}\)) Decrease in the overpotential to 220 mV to deliver 100 mA cm\(^{-2}\) after 500 CV cycles (between 0.1 and 0.5 V at 100 mV s\(^{-1}\)) | [88]    |
| Fe-NiFeCoS        | NF      | Electrodeposition and solvothermal sulfurization                                    | 1 M KOH     | RT     | 100             | 230             | 113             | Electrochemical stability after 3000 CV cycles (between 1.2 and 1.6 V at 100 mV s\(^{-1}\)). Stable current of 100 mA cm\(^{-2}\) at an overpotential of 295 mV for 15 h | [88]    |
| P-doped (NiFe)\(_3\)S\(_2\) | NF      | Hydrothermal treatment, phosphidation and sulfuration                              | 1 M KOH     | RT     | 10              | 196             | 30              | Stable current density after 1000 CV cycles. Stable potential of around 1.7 V, at 10 mA cm\(^{-2}\) for 140 h | [54]    |
| NiFe\(_x\)P       | NF      | Dip coating and phosphidation                                                       | 1 M KOH     | RT     | 200             | 282             | 37              | Electrochemical stability for 28 h at 20 mA cm\(^{-2}\) | [39]    |
| NiCoP             | NF      | Solvothermal and heat treatment                                                     | 1 M KOH     | RT     | 100             | 370             | 116             | Electrochemical stability for 22 h at 10 mA cm\(^{-2}\) (minor increase of 12 mV in the overpotential) | [96]    |
| Fe-doped NiCoP    | CC      | Electrodeposition and phosphidation                                                | 1 M KOH     | RT     | 50              | 293             | 37.8            | Electrochemical stability after 3000 CV cycles (between 1.2 and 1.6 V at 100 mV s\(^{-1}\)) | [88]    |
| Ni\(_{0.75}\)Fe\(_{0.25}\)Se\(_2\) | CFC     | Hydrothermal treatment and selenization Hydrothermal treatment and calcination      | 1 M KOH     | RT     | 35              | 255             | 47.2            | Stable potential of ca. 1.55 V, at 35 mA cm\(^{-2}\) for 28 h                  | [86]    |
| FeNi\(_3\)N       | NF      |                                                                                   | 1 M KOH     | RT     | 10              | 202             | 40              | Stable potential of ca. 1.55 V, at 50 mA cm\(^{-2}\) for 30 h                  | [42]    |
| 316L SS           | 316L SS | -                                                                                  | 1 M KOH     | RT     | 10              | 340             | 30              | Stable overpotential at 10 mA cm\(^{-2}\) for 20 h                           | [90]    |
| 316L SS           | 316L SS | Polished                                                                          | 6 M KOH     | RT     | 30              | 300             | 385             | Almost stable potential (<10 mV increase), at 10 mA cm\(^{-2}\) for 15 h     | [34]    |
| SSM               | SSM     | Cathodization treatment                                                           | 1 M KOH     | RT     | 10              | 275             | 70              |                                                                                 | [91]    |
| SSM               | SSM     | Cathodization treatment                                                           | 1 M KOH     | RT     | 100             | 319             | 70              |                                                                                 | [91]    |
| 316L SS           | 316L SS | -                                                                                  | 1 M KOH     | RT     | 10              | 431             | 68              | Potential drop at 10 mA cm\(^{-2}\) after 5 h                               | [92]    |
| 316L SS           | 316L SS | Pulsed laser rusting                                                              | 1 M KOH     | RT     | 10              | 382             | 52              |                                                                                 | [92]    |
4.1.5. Preparation Methods

From the review of the main electrocatalysts used for HER and OER presented in Sections 4.1.2 and 4.1.4, respectively, it can be seen that a variety of materials are used by different authors to produce different electrocatalytic layers on electrode supports. This chapter addresses the different methods whereby the catalyst can be applied to the electrodes. Several reviews have been published over the years that collect information about different aspects of the deposition of catalysts on structured surfaces used in several areas of research [97–101]. Here, we focus on the most commonly used methods to coat different substrates with metal elements to be used as electrodes in AWE.

Different preparation methods can produce catalytic coatings with different surface areas and sometimes different structures, resulting in different electrocatalytic behavior [102]. However, they must allow a homogeneous coating with the desired catalyst loading [101].

The first point that has to be addressed is that, in the case of metallic supports, prior to the deposition, whatever the method, the substrates are usually treated. The pre-treatment of the substrates is performed to modify their surface and improve the adhesion of the catalytic layer and thus the lifetime of the structured catalyst. All the treatments are suitable for different substrate metals and, irrespective of the method, they have the same goal: the creation of a thin oxide layer chemically compatible with the catalytic coating and the formation of roughness to help bond the catalyst to the substrate surface. The most relevant pre-treatments of the electrodes are anodic oxidation, thermal oxidation, also called thermal treatment, and chemical treatment. In anodic oxidation, the electrode surface is modified by applying a current density to the electrode placed as the anode. In thermal treatments, as the name suggests, the modifying agent is the temperature. In addition to improving the adhesion of the catalytic layer to the substrate, it also protects the metallic substrate against corrosion. The treatment conditions to achieve a continuous and homogeneous oxide layer (temperature, heating rate, processing time) must be optimized for each alloy. Thermal treatments can be used as pre- or finishing treatment, as will be seen further on. Chemical treatments of the substrate can be also carried out, using alkaline and acidic media. They are usually performed one after the other [98,101].

After the pre-treatment of the electrodes, the deposition of the catalyst can then be carried out. The deposition methods have been classified into two categories, depending on the physical state of the coating medium: vapor-phase methods and liquid-phase methods. Based on the work of several authors, the most well-known vapor-phase methods are chemical vapor deposition and physical vapor deposition; and the most common liquid-phase synthesis methods include wash-coating methods, spray coating, direct synthesis, hydrothermal and solvothermal treatments, electrodeposition, electrophoretic deposition, and electroless plating [97–101]. From both categories, suitable catalyst layers can be obtained. However, the majority of the authors tend to choose liquid-phase methods more often, due to their various advantages: simpler experimental set-ups with conventional reagents and equipment, easier control of the deposition layer (size and shape) because of the lower work temperatures, and shorter operational time to achieve higher mass yield [100].

From the review of the principal electrocatalysts currently used for HER and OER in Tables 2 and 4, respectively, it is easy to see that most of them are prepared by electrodeposition, wash-coating methods, and hydrothermal/solvothermal treatments.

Electrodeposition, also referred to as electrochemical deposition or electroplating, is a process employed to form a dense metallic coating. In this process, the substrate to be coated is negatively charged, working as a cathode, and immersed into an ionic solution of the metal that will be deposited. When a potential difference is applied between the anode and the cathode, metallic ions move from the anode to the electrolyte and from there to the substrate [99,101].

Electrodeposition is a cost-effective and well-established technique that offers several advantages, such as precise control of film thickness, morphology, stoichiometry, doping, and others, by regulating the current density or applied voltage; it allows the growing
of uniform films on different types of substrates, in the laboratory or industrial scale; it occurs closer to equilibrium conditions and, at the same time, allows the deposition of compositionally nonequilibrium materials or modulated structures [103]. In the case of electrodeposition of metal oxides, heat treatment after the process is usually considered necessary to consolidate their microstructure and obtains robust electrodes with well-connect particles [104].

Siwek et al. [105] prepared 3D NF electrodeposited onto SS from different electrolyte solutions and studied the effect of the electrolyte composition on both surface micro size pores and deposit morphology, and consequently the activity of the foams towards HER. The foams were deposited by applying a current density of \(-1\ \text{A cm}^{-2}\) for 150 s. The high current density applied resulted in intense hydrogen evolution, thus a large formation of hydrogen bubbles. The catalytic layer started to form around the hydrogen bubbles, which allowed the formation of micro-size pores, as observed in Figure 9, as they detach from the electrode surface to the electrolyte. This phenomenon, called the dynamic hydrogen bubble template, explains the foam-like morphology of the deposited layer. The high surface area of the films developed greatly contributed to the electrocatalytic activity of the electrodes.

Figure 9. Development of 3D NF electrodeposited onto SS from different electrolyte solutions. (a–c) Optical micrographs of foams’ surfaces taken at a magnification of \(20\times\) and SEM images of the top view of the corresponding foam surface at different magnifications, (d–f) \(1000\times\) and (g–i) \(10,000\times\). Reprinted from [105] with permission from Elsevier.

Wash coating is the more versatile coating method: it is a simple technique, it requires low-cost raw materials and equipment, it is easy to reproduce, and results in a good quality deposit [106]. This method includes sol-gel deposition, suspension methods, and impregnation. After coating, the removal of the excess liquid, drying, and control of the deposited catalyst charge must be carried out, so the process is repeated as many times as necessary to achieve the desired catalytic loading on the metal support. Frequently, after drying, the films need to go through a hardening transformation by heat treatment [101]. The main disadvantages of the process are the non-uniformity of the coating thickness
and the need to be followed by a heat treatment, which can deteriorate the mechanical properties of the metal coat and can lead to low bond strength [106].

Kong et al. [77] developed a FeCoNi spinel oxide nanosheets array directly supported on NF by a wash-coating method followed by an annealing treatment at 300 °C for 3 h (Figure 10). The NF was uniformly covered by the catalyst layer, which presented a large electrochemical surface area, contributing to the positive performance of the electrocatalyst.

![Figure 10. Development of FeCoNi spinel oxide nanosheets array directly supported on NF by wash-coating, followed by annealing. SEM images of (a,b) CoNiO/NF and (c,d) Fe-CoNiO/NF. (e,f) TEM images of Fe-CoNiO/NF. The inset in (a) shows the optical image of the as-prepared samples. Reprinted from [77] with permission from John Wiley & Sons, Inc.](image)

In hydrothermal and solvothermal methods, the reaction is heated over the boiling points of the solvent used. In hydrothermal synthesis, water is taken as the solvent, whereas in solvothermal synthesis, the solvent is something other than water, generally an organic liquid. The reaction for the formation of the electrocatalytic layer is generally performed in a closed steel autoclave, so temperature, pressure, and volume are the variables that must be considered. The microstructure of the layer depends on these conditions [100,107].

From Tables 2 and 4, it can be observed that these two methods are suitable to produce transition metal-based selenides, sulfides, nitrides, and phosphides, since the atmosphere can be controlled and enriched with these elements. As an example, Chai et al. [88] prepared NiFeCoS, an efficient electrocatalyst for water oxidation through a solvothermal treatment, at 140 °C for 12 h, where the precursor was NiFeCo electrodeposited onto NF (Figure 11a,b). The resulting electrocatalyst (Figure 11c,d) showed interwoven nanosheets uniformly covering the surface, and its sulfides were converted to ripple-like morphology, which had many pores and distortions, contributing to a large surface area, abundant exposure of active sites, and improved electron transfer rate. These characteristics contributed to enhancing the catalytic behavior of NiFeCoS.

4.2. Electrolyte Concentration

The electrolyte on an AWE system is usually an aqueous solution of NaOH or KOH. An alkaline medium avoids the corrosion problems caused by acid electrolytes [8], making possible the use of non-precious metal materials as an electrode or as an electrocatalyst, of a cheaper cell component, which, overall, lowers the cost of hydrogen production [34]. KOH is preferred over NaOH because, for the same concentration, its solutions have higher conductivities [108]. To minimize the electrolyte resistance, and hence increase the
efficiency of the AWE, it is essential to enhance the ion conductivity of the electrolyte. The concentration and temperature of the electrolyte solutions are the key variables that impact the ionic conductivity [22,109].

Figure 11. Development of NiFeCoS through solvothermal treatment, by electrodepositing NiFeCo onto NF. SEM images of (a,b) NiFeCo/NF and (c,d) NiFeCoS/NF. Reprinted from [88] with permission from Elsevier.

The established working temperatures for industrial AWE electrolyzers are between 60–90 °C [3,11], as already seen in Table 1 and, therefore, it is necessary to find the concentration to achieve the highest ion conductivity at this operating temperature. Gilliam et al. [110] used the available conductivity data for KOH to develop an equation for calculating the conductivity of KOH in the range of 0–12 M and 0–100 °C. Using such results, Allebrod et al. [108] redrew a 3D plot of the conductivity of aqueous KOH as a function of temperature and concentration (Figure 12). They noted that in the range of the recommended temperature for AWE electrolyzers, the maximum conductivity value was in the concentration range of 30–34 wt.% (7–8.2 M).

Figure 12. 3D plot of the conductivity of aqueous solutions of KOH as a function of temperature and concentration. Reprinted from [108] with permission from Elsevier.

Amores et al. [109] presented a mathematical model that describes the behavior of an alkaline electrolysis cell. Regarding the parameter of ion conductivity, the model showed that, at the normal operating temperature range of AWE electrolyzers, the maximum value was found around 34–38 wt.% (8.2–9.4 M) of KOH. This is in agreement with the data
reported by Gilliam et al. The model also shows that as the temperature increases, the required potential at a given current progressively decreases. This behavior is because the required energy diminishes when the operating temperature is increased as this leads to a reduction of the reversible voltage and, consequently, to the improvement of reaction kinetics. This model also presents 3D plots of the variation of voltage and current density relative to three different variables: temperature, KOH concentration, and the distance between the electrodes and the diaphragm.

The model designed by Zouhri and Lee [22] illustrates that up to a concentration of 8 M KOH (ca. 33 wt.%), irrespective of the temperature, the ionic conductivity increases with the increase in the concentration of the KOH solution. From that point on, ionic conductivity starts to decrease. It also shows that increasing the temperature enhances the ionic conductivity.

Based on the work of these authors it can be said that, at the operating temperature already established, the optimal concentration of the electrolyte is in the range of 30 to 40 wt.% (7–10.1 M). These operating conditions are the best to produce hydrogen from AWE, not only because of the conductivity of the electrolyte, but also because of the corrosion rate. Increasing the amount of KOH leads to a more aggressive alkaline environment for the components of the electrolyte, contributing to an increase in corrosion. Higher temperatures have the same effect. So, operating with less aggressive conditions, despite the slight corrosive effect, increases the lifetime of the electrolysis components, which in turn has a positive effect on the total cost of hydrogen production [15]. These temperatures also prevent greater water loss due to evaporation [9,15,111].

Loss of the efficiency of the electrolytic process due to gas bubbles in the electrolyte is another concern that determines certain operating conditions of the electrolyte. Research indicates that setting an electrolyte flow helps the bubble separation from the electrode surfaces during operation [35]. Moreover, the current state-of-the-art electrolyzers work at pressures up to 3 MPa [3,10], which reduces the volume of the bubbles, minimizing the ohmic loss of the system. However, pressurized operating environments require a more durable separator [9]. This topic is discussed in Section 4.3.

**Electrolyte Additives**

The typical solutions used as electrolytes have several problems associated, such as the low stability of the electrode materials (exposed to corrosive electrolytes) and the low conductivity under cell operating conditions when the formation of gas bubbles is pronounced [112].

Recently, adding ionic activators to the electrolyte attracted much attention. It is a simple, low cost and efficient operation that can significantly reduce energy consumption during water electrolysis. Ionic activators work by electrodepositing metal composites, in situ, on the cathode surface, increasing the catalytic activity towards HER and the stability of the electrodes. They can also enhance electrolyte ionic conductivity and improve resistance to electrode corrosion. Most of the ionic activators for HER are composed of ethylenediamine or trimethylendiamine-based metal chloride complex ((M(en))₃Clₓ or (M(tn))₃Clₓ, M = Co, Ni, and others) and Na₂MoO₄ or Na₂WO₄ [11,24].

In the work of Stojić et al. [113], the ionic activators (Co(en)₃)Cl₃, (Co(tn)₃)Cl₃ were added in situ, solely or in combination with Na₂MoO₄, to a standard electrolyte, in an attempt to reduce energy consumption in the production of electrolytic hydrogen. The authors pointed to energy-saving beyond 10% compared to those of non-activated electrolytes. Nikolic et al. [114] used (Co(en)₃)Cl₃ and Na₂WO₄ as ionic activators, which reduced the energy requirements per mass unit of hydrogen produced by about 15% compared to the standard electrolyte. Amini Horri et al. [115] presented a different approach. They used ZnO as an ionic activator precursor in a conventional AWE system. The hydrogen evolution rate was 1.5 and 2.7 times higher, when using NaOH and KOH, respectively, compared to conventional AWE electrolyzers.
Using ionic liquids (ILs) as an electrolyte or a mixture of them with traditional alkaline solutions are also viable alternatives to improve the cell efficiency, since they have the potential to positively affect the affinity between the electrolyte and the electrodes [8,112]. ILs at room temperature are semi-organic compounds, composed of organic cations and organic or inorganic anions. They possess high ionic conductivity, stability, heat capacity and they are chemically inert to metal electrodes [24,112]. Among them, 3-butyl, methyl imidazolium cations associated with weakly coordinating anion such as tetrafluoroborate ((Bmim)(BF$_4$)) and hexafluorophosphate ((Bmim)(PF$_6$)) have been the subject of an enormous amount of research [116,117]. Souza et al. reported hydrogen production efficiencies between 82% and 98% (at lower operation costs) when using different electroactive materials, such as Pt, Ni, AISI 304 SS, and low carbon steel (LCS) in a 10 vol.% solution of BMI.BF$_4$ in water [116].

More recently, Amaral et al. tested three different 1-ethyl-3-methylimidazolium (Emim)-based room temperature ILs, namely (Emim)(Ac) (acetate), (Emim)(EtSO$_4$) (ethyl-sulfate) and (Emim)(MeSO$_3$) (methanesulfonate), as additives in alkaline solutions of 8 M KOH [112]. When adding these ILs, the determined exchange current density values were significantly increased. Furthermore, higher HER currents were recorded, particularly for (Emim)(MeSO$_3$)-added electrolyte solutions.

### 4.3. Separator Material

The main purpose of the diaphragm is to keep the cathode separated from the anode. It prevents (i) the gases produced at the electrodes from mixing, maintaining chemical stability and safety, (ii) possible side redox reactions (involving reduction of a species at the cathode followed by its reoxidation at the anode), improving the efficiency of the desired reactions, and (iii) possible physical contact between the anode and the cathode if they are closely spaced. Using a diaphragm not only increases the cost and complexity of the cell construction, but also the cell potential required for a given current density, because of the higher cell resistance [8].

To enhance the efficiency of the AWE, the diaphragm material must be: chemically and mechanically stable for the electrolysis media, must have high selectivity for a single type of ion, high ionic conductivity (and low electrical conductivity), and low gas permeability; it must have the ability to operate efficiently at high current densities; it must be resistant to the pressure caused by the formation of gas bubbles; and it should also be easy to handle, be relatively low cost and have a long lifetime [8,118].

The first separators used in commercial AWE electrolyzers were made from asbestos. This type of diaphragm had low corrosion resistance to alkaline medium at high temperatures and because of its toxicity could cause serious, adverse health effects, so there was the need to replace it with other materials [8,119]. Using asbestos as a diaphragm material was prohibited and composite materials based on microporous polymers or ceramics, such as polyphenylene sulfide (PPS) and polysulphone (PSF), were found to be a good alternative [11,119]. The current state-of-the-art material used as a separator is a PSF matrix with zirconium oxide as a filter, also known as Zirfon® [118].

AEMs are seen as the next major advancement for high-performance alkaline water electrolyzers [12]. These membranes consist of non-porous hydroxide-conducting polymers that contain immobilized, positively charged functional groups on their backbone or pendant side chains. AEMs offer several advantages: they do not present precipitation of carbonates due to lack of metallic cations; are thinner than currently used separators, resulting in lower ohmic losses; are less expensive than PEMs; offer improved gas separation and the ability to apply differential pressure; and do not require the use of a concentrated alkaline solution, making their installation less critical and the system easier to operate [3,120].

Nevertheless, AEM water electrolyzers are still at an experimental stage and further improvements are required for this technology to contribute to a future hydrogen-based economy. AEMs durability and degradation are reported to be the most critical problems
to be tackled. While the stack lifetime of commercial AWE is between 55 and 120 kh, the durability of alkaline systems using AEMs has been reported to be less than 3 kh. Additionally, there are still few studies on the use of AEMs in water electrolysis, with its current focus being the application in fuel cells [12,120,121].

4.4. Interelectrode Distance

In general, the ohmic resistance decreases with the reduction in the distance between the electrodes and the diaphragm [22,109].

However, Divisek et al. [122] observed that, when using sheet electrodes, it is necessary to find the optimum value of this distance. When the gap between electrodes is greater than the optimum value, a reduction in the distance results in a decrease in the voltage. Once the optimum distance is achieved, reducing the distance results in a voltage increase because when the distance between electrodes and diaphragm is very low. In this case, the percentage of bubbles becomes so high that the electrolyte resistance increases significantly, thus increasing the required voltage for electrolysis.

Nagai et al. [123] confirmed the findings by the previous authors. They also showed that the optimum distance and the velocity of the bubbles are inversely related; the faster the gas leaves the electrolysis cell, the fewer bubbles accumulate inside, and thus the optimum distance can be reduced and the electrolyte resistance decreases (the efficiency of water electrolysis increases).

The zero-gap cell configuration (Figure 13) was designed to respond to the need to reduce the distance between electrodes and diaphragm to increase the efficiency of the electrolysis [3]. In AWE, the zero-gap cell design works by compressing two porous electrodes on either side of the gas separator, forming the so-called MEA. This allows the inter-electrode gap to be as small as the thickness of the diaphragm, thus significantly reducing the ohmic resistance contribution from the electrolyte between the two electrodes. The main difference between the traditional setups and the zero-gap configuration is the use of porous electrodes rather than solid metal plates, which forces the bubbles to be released from the back of the electrodes, instead of migrating towards the top of the cell, reducing their contribution to the cell voltage. Overall, the zero-gap cell design allows a very small interelectrode gap, compact design, and a high degree of efficiency with a higher degree of safety [124]. Most of the current AWE systems employ this configuration [34,125,126].

![Figure 13. AWE cell configuration. (a) Standard cell configuration and (b) zero-gap cell configuration. Adapted from [124] with permission from The Royal Society of Chemistry.](image-url)
4.5. High Temperature and Pressure Electrolysis

Although AWE operating conditions are already well defined for industrial AWE systems, the present industry trend is to develop high-temperature and high-pressure electrolyzers [33,111,127,128]. As already seen, an increase in the temperature of the electrolyte brings advantages to the efficiency of the system. Ionic conductivity and surface reaction rates increase, while the cell potential is known to thermodynamically decrease. On the other hand, it compromises the durability of the cell components and lowers the water activity in the solution [111]. To overcome this disadvantage, Ganley [111] proposed to accompany the increase in temperature with an increase in pressure, as a means to force water into the solution at high temperature, ensuring the high activity of water within the solution. He tested the alkaline electrolysis cell at temperatures between 35 and 400 °C, and pressures ranging from atmospheric to 8.7 MPa, with current density up to 200 mA cm$^{-2}$ and different electrode materials. The best cell performance was achieved using a Co-plated Ni anode at a temperature of 400 °C and pressure of 8.7 MPa.

In addition, when operational pressure is increased, there is no need to have compressed stages after the production of hydrogen, since the hydrogen is already in the right conditions to be stored [3,127]. Generally, less power is required to compress liquid water than to compress gaseous hydrogen, so it is reasonable to conclude that high-pressure electrolysis systems require less power than using a compressor after the production of hydrogen from water electrolysis at atmospheric temperatures [128]. However, opinions are divided between those who believe that this fact has a positive impact on the efficiency of AWE systems [127,129] and those who assure that this is a loss of efficiency [33].

Kuleshov et al. [129] developed and tested a high-pressure AWE cell stack that could work at a temperature of 95 °C, a pressure of 10 MPa, and current densities up to 1000 mA cm$^{-2}$, without the use of additional compressors. Their data show that up to 3 MPa, the cell stack voltage reduces with the increase in the pressure. However, above that value, an increase in the pressure leads to an increase in the voltage. Despite the increase in the voltage, they still concluded that the 10 MPa electrolysis made it possible to reduce energy costs to produce hydrogen and to accumulate energy.

The Brandenburg University of Technology Cottbus [127] is involved in a project that consists of developing two pressurized AWE electrolyzer prototypes, one working at 6 MPa and another at 10 MPa. They predict that the voltage efficiency of the electrolyzers will increase up to 70–82% (for the 6 MPa prototype) and up to 74–87% (for the 10 MPa prototype) in the short-term and middle-term, respectively [30].

Opposite conclusions were reached by Roy et al. [33]. They presented an analysis that considers the energy consumption in the auxiliary equipment and the loss of gas during the operation in electrolyzers working at 70 MPa. In comparison to atmospheric electrolyzers, they proved to be less efficient: the energy consumption in 70 MPa electrolyzers is about 16% higher than the combined energy consumption of atmospheric electrolyzers and compressors. They have also considered several other problems like corrosion, operation complexity, and costs. So, in theory, it is possible to increase the efficiency of systems by increasing temperature and pressure, but there are still many technical issues to be resolved.

5. Economic Aspects

Schmidt et al. [9] performed an expert elicitation study in 2017, comparing the current characteristics of AWE, PEM, and SOEC technologies, and presented an expert point of view on future capital cost, lifetime, and efficiency. According to them, 2017 figures put capital costs for AWE at around 1000 € kW$^{-1}$, 2000 € kW$^{-1}$ for PEM, both for a 1 MW system, and at above 2000 € kW$^{-1}$ for SOEC. They report that most experts believe that for now, and taking into account the three parameters studied, AWE seems to be the strongest technology. PEM exhibits superior characteristics but requires more manufacturing and operating experience. Nevertheless, they expect that soon, sometime around 2030, PEM technology will surpass AWE technology. They conclude that the decade from 2020 to 2030 will see a shift from AEW to PEM technology with the latter attaining commercial advantage.
in 2030 through competitive cost and higher operational flexibility. Furthermore, 2030 might see the SOEC technology reach the cost and lifetime of AWE and PEM electrolysis.

A recent study by Yates et al. [130] reports a comparison between the AWE and PEM technologies through a Monte Carlo analysis. The results show that, in the vast majority of the iterations, AWE returned lower hydrogen costs, though, in a minority of iterations, PEM comes out cheaper. They then went on to determine which parameters most affected the cost difference between the technologies. They found out that these were the capital cost difference and the energy consumption difference. They also quantified the cost improvement necessary for the PEM technology to become competitive with AWE.

In conclusion, for large-scale industrial water electrolysis, AWE electrolyzers seem to be more suitable: the system shows more durability and has lower capital costs associated. However, there are still issues to be worked out to improve the efficiency of the method.

6. Conclusions

Hydrogen produced by water electrolysis coupled with renewable energy—the so-called green hydrogen—is a promising alternative to fossil fuels. It does not emit CO₂ and almost no air pollution when used, thus offering a solution to decarbonize industrial processes and economic sectors. A comparative survey of the main water electrolysis technologies was carried out. Different points of view regarding the advantages and disadvantages of the two commercially available methods have been pointed out. AWE was established as the current best technology to be used for producing hydrogen in large-scale industrial environment, since it is the most eco-friendly water electrolysis technology with the highest maturity. Nevertheless, it is crucial to improve the efficiency of AWE systems, in terms of energy consumption and cost, so that this electrochemical technology can compete with the conventional energy production from fossil fuels.

In this review, the kinetics and thermodynamics of water electrolysis were analyzed, and it was pointed that the activation overpotential and the ohmic losses, caused by resistances of the electrode, electrolyte, diaphragm connection wires, and gas bubbles, are the main origins of high energy consumption. As discussed, these variables rise due to some aspects of the electrochemical cell components, so a review of these was presented. This focused on the best characteristics of an electrode, as well as the most suitable electrocatalysts for HER and OER. An analysis of electrolyte concentration and possible additives to be used was carried out, followed by an evaluation of the current diaphragm materials used and a study on the interelectrode distance. Finally, high temperature and pressure electrolysis systems were examined.

By presenting options to optimize the cell components and the cell configuration, this study provides an opportunity for industrial systems to minimize the energy input, especially at high current densities, improving their efficiency, and encouraging investment in the implementation of modern electrolysis systems. Even so, it is important to keep in mind that, despite the latest advances highlighted, further research efforts are still needed to build a future based on a hydrogen economy and renewable energy.

Author Contributions: Conceptualization, M.-J.C. and D.M.F.S.; methodology, A.L.S., M.-J.C. and D.M.F.S.; validation, M.-J.C. and D.M.F.S.; investigation, A.L.S.; resources, D.M.F.S.; writing—original draft preparation, A.L.S.; writing—review and editing, A.L.S., M.-J.C. and D.M.F.S.; supervision, M.-J.C. and D.M.F.S. All authors have read and agreed to the published version of the manuscript.

Funding: The support of the Foundation for Science and Technology (FCT, Portugal) is gratefully acknowledged for funding a contract in the scope of programmatic funding UIDP/04540/2020 (D.M.F. Santos).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: No new data were created or analyzed in this study. Data sharing is not applicable to this article.
Acknowledgments: The authors gratefully acknowledge Tecnoveritas (https://www.tecnoveritas.net, accessed on 25 May 2021) for providing the facilities and helping in the supervision of A. L. dos Santos.

Conflicts of Interest: The authors declare no conflict of interest.

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