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Review

Performance of Stainless-Steel Bipolar Plates (SS-BPPs) in Polymer Electrolyte Membrane Water Electrolyser (PEMWE): A Comprehensive Review

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Abstract: Bipolar Plates (BPPs) play a critical role in Polymer Electrolyte Membrane Water Electrolysers (PEMWEs) for effective hydrogen generation. The performance and longevity of the system can be considerably impacted by choosing the suitable material for these components. Polymer electrolyte membrane water electrolysis technology relies on cost-effective and corrosion-resistant BPPs. Tantalum, niobium, and titanium are low-cost, easy-to-machine materials that have good electrical and thermal conductivity; however, they exhibit low corrosion resistance. Noble metal and metal nitride coatings are usually investigated to minimize corrosion and interfacial contact resistance. Because of its performance-to-cost ratio, Stainless Steel (SS) based materials are among the most popular materials for BPP development. This study recommends material and operating parameters to improve PEMWE systems for sustainable hydrogen production's efficiency, durability, and economic viability.

Keywords: Polymer Electrolyte Membrane Water Electrolyzer or Proton Exchange Membrane Water Electrolyzer (PEMWE); Stainless-Steel Bipolar Plates (SS-BPPs); Coated Bipolar plates; corrosion testing; corrosion resistance; Interfacial Contact Resistance (ICR)

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1. Introduction

Hydrogen (H_2) is supposed to play a significant role in energy storage from renewable energy sources (RES) [1–3] and is widely regarded as one of the most promising energy carriers for the future [1–4]. Steam reforming of natural gas or gasification of coal and oil are the most common methods used today to create H_2 [1]. Producing H_2 in this manner is inexpensive, but it also results in a lot of carbon dioxide (CO_2), which slows down the shift to renewable and sustainable energy. Due to economic issues, water splitting produces only 4% of the world's commercial hydrogen using water electrolysis [3]. In contrast, it is noteworthy to mention that the process of H_2 production via the electrolysis of water results in H_2 of nearly 100% purity. This method holds the advantage of not relying on fossil fuels, thus circumventing any associated environmental concerns. Furthermore, when coupled with RES, the production of H_2 via electrolysis emits no CO_2, thereby contributing to a more sustainable and environmentally friendly approach (Figure 1). Since its discovery in 1789, Alkaline Water Electrolysis (AWE) has emerged as the prevailing electrolyzer technology that is widely accessible in commercial markets across the globe [1,5,6]. It has a very long lifespan with minimal maintenance costs, is made up of very inexpensive components, and can be integrated into big units. Furthermore, it possesses the capability of being assembled into sizable configurations. However, it has a low partial load range, a low operating pressure, and a low current density.

Polymer Electrolyte Membrane Water Electrolyzers or Proton Exchange Membrane Water Electrolyzers (PEMWEs) are a class of electrochemical devices that adhere to the zero-gap principle (Figure 2). In this design, a solid electrolyte (proton conducting membrane), commonly a humidified perfluoro sulfonated polymer known as Nafion®, is directly integrated with two electrodes, where the electrocatalyst is located. The PEMWE has gained significant attention as a potential alternative to the AWE [1,6]. This is primarily due to its ability to operate at higher current densities and accommodate a wide range of power inputs [1]. The dynamic operation capabilities of PEMWEs, which include a load-following mode, make them ideal for use in energy capture and storage systems for intermittent energy sources such as wind, solar, and wave, which are typically located in remote areas [1]. The membrane in a PEM water electrolyzer offers high proton conductivity, low gas crossover, and a compact design [1]. The PEM water electrolyzer is safer and more reliable than the AWE because no liquid corrosive electrolyte is circulated throughout the cell stack [5].

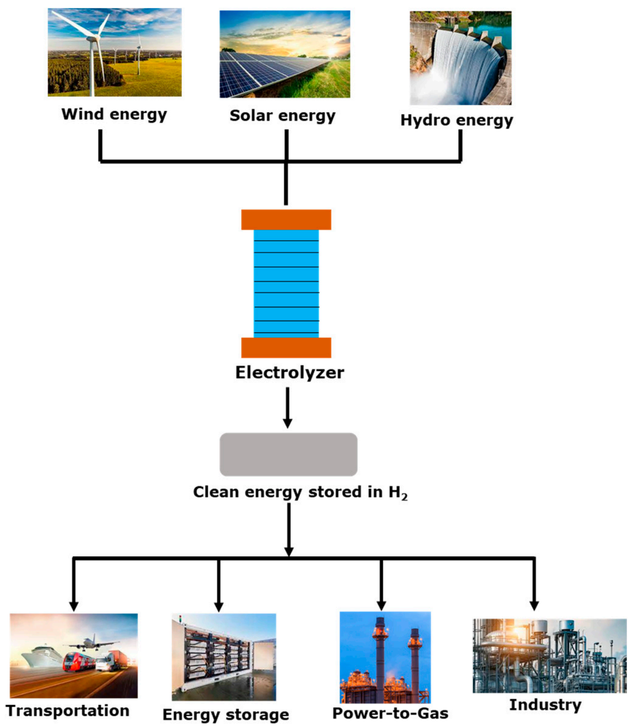

Figure 1. Overview of applications based on water electrolysis process supplied by renewable energy sources.

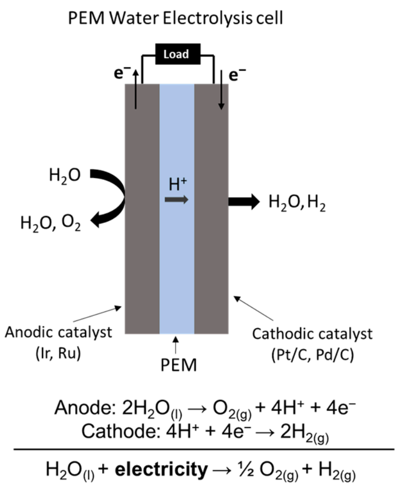

Figure 2. Schematic showing the working principle and the reactions of a PEM water electrolyser and its reactions.

Bipolar Plates (BPPs) are an essential part of the stack that makes up a PEMWE (Figure 3). The main role of bipolar plate components is the separation of single cells within a stack, the distribution of reacting agents inside the electrolyzer, and the conductivity of heat and current through single cells within a stack [1,4]. A BPP is required to have a strong resistance to corrosion, high mechanical strength, high electrical conductivity, and shock endurance. It must also be simple to design and construct so that it can be produced in large quantities. The materials that are normally used for BPP development are graphite and metals (such as titanium, nickel alloys, and stainless steel).

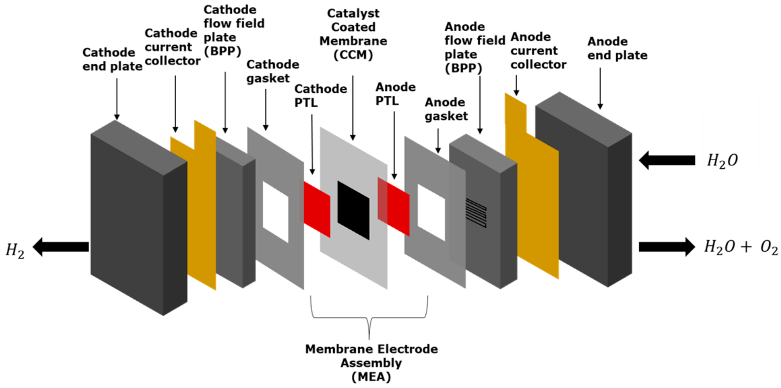

Figure 3. The components of a PEM water electrolyzer stack.

The BPPs represent a significant portion of the stack cost, so a reduction in BPP manufacturing costs could considerably reduce the overall cost of a PEMWE stack [1]. In an operating PEM water electrolyzer, the high single-cell voltage and anode electrode potential, which can exceed 2 V versus RHE (when the device is operating with a high current), considerably restrict the material selection. In general, metal BPPs are simple to mass-produce and exhibit exceptional electrical and thermal properties. However, their propensity to produce less conductive oxides on the surface of the metal can result in high ohmic resistance and poor performance. AISI 316L, molybdenum (Mo), tungsten (W), niobium (Nb), and tantalum (Ta), together with Inconel 625 and 254 SMO, have been the subject of significant research that has been focused on the corrosion properties of various metals. Titanium (Ti) is commonly used as the BPP in PEM water electrolyzers today because of the high anodic potential and acidic operating environment [1,4]. Studies of corrosion do not usually concentrate on putting materials through tests at such high potentials but doing so would be extremely useful in the field of PEM water electrolysis [7–10].

2. Metallic BPPs in PEMWE Devices

The best BPP materials for PEMWE are considered to be metals. Metal flow fields and other characteristics are easier to process or stamp than carbon materials, reducing production costs and time. These materials are strong, chemically stable, and good electrical and thermal conductors [11]. Graphite flow channels, on the other hand, have to be machined or electrochemically etched on the surface, which adds expense and complexity to the manufacturing process. Metallic materials have exceptional mechanical properties that enable the mass production of thinner and lighter plates [12]. Metal BPPs, while effective, have the drawback of eventually corroding in harsh operational conditions. Corrosion is an irreversible chemical reaction that deteriorates metals over time and has a negative impact on the process's profitability and efficiency. Damage caused by corrosion on metal plates manifests as fissures or tiny holes [13]. The area of the PEM water electrolyzer is most susceptible to degradation.

A variety of metal-based BPPs have undergone tests to determine their corrosion characteristics and the development of their Interfacial Contact Resistance (ICR) under conditions relevant to PEM water electrolysis. In comparison to the other materials, tantalum (Ta), niobium (Nb), and titanium (Ti) produced lower current densities in the potentiostatic and potentiodynamic polarisation tests [14]. There was no weight loss during polarisation for either of these materials, indicating that no corrosion occurred. During the one-hour potentiostatic test, Nb and Ta both showed a considerable increase in ICR, but Ti showed a minor increase. Nevertheless, prolonged polarisations at 2 V versus RHE revealed that the ICR of Ti increased with time [5,15]. The increase in ICR for Ti, Ta, and Nb could possibly be attributable to oxide layer formation on the material surface, based on results from the Atomic Emission Spectroscopy (AES) study.

Although metals offer mechanical strength and have the best physical properties and conductivity for BPPs' fabrication, they are susceptible to corrosion in low pH values and extremely oxidative environments, especially during polarization. A coating layer may be used to prevent corrosion of the primary material [16]. However, cladding one metal with another increases the ICR because it introduces two new contact surfaces between the BPP and the Gas Diffusion Layer (GDL) or flow field plate. The ICR of the BPP and GDL should be kept as low as possible, or less than 1 mΩ cm^{-2}, to prevent conductivity degradation. The passivation layer that forms on the surface of the coating material must also be highly conductive. For metallic-based BPPs, noble metals, metal nitrides, or metal carbides are used as coatings. BPPs are also usually coated with gold (Au), silver (Ag), palladium (Pd), platinum (Pt), and carbon (C), as well as with graphite and conductive polymers [17]. Ti-Ag film, (Ti,Zr) N, ruthenium oxide, platinum, and gold are the most frequently employed materials. To prevent the formation of a passive oxide layer on the Ti surface during operation, various precious metal coatings, such as platinum (Pt) and gold (Au), can be utilized. Titanium as a base BPP material in PEMWEs and regenerative fuel cells has been studied to some degree, with coatings being the primary focus [4,18–23].

Nikiforov et al. [24] evaluated the corrosion resistance of several steel and nickel alloys in 85% phosphoric acid at varying temperatures for use in high-temperature steam electrolyzers. Tantalum-coated AISI 316L stainless steel and Inconel 625 are the most suitable materials for BPPs in high-temperature steam electrolyzers with H_3PO_4-doped membranes, according to research conducted by Nikiforov et al. [24]. The superior corrosion resistance of nickel-based alloys over austenitic stainless steels can be attributed to nickel's higher positive standard potential. It has also been discovered that adding a low amount of Ti to alloys increases their corrosion stability in this medium (0.4–0.7% Ti for AISI 321, 0.4% Ti for Inconel 625, and 1% Ti for Incoloy 825). AISI 321 has the lowest corrosion rate among austenitic stainless steels. Tantalum exhibited the highest corrosion resistance, while Ti exhibited the lowest corrosion resistance.

Using a 3D printer, Chisholm et al. [25] produced polypropylene flow plates for water electrolyzers. The printed plates were coated with Ag conductive paint. This study examines the fabrication and performance evaluation of flow plates utilized in electrolyzers. Using a Bits from Bytes 3DTouchTM printer, polypropylene flow plates were 3D printed layer by layer and coated with two layers of Ag paint. 3D-printed plates were considerably lighter than Ti plates, weighing only 13.9 g compared to 59.2 g for Ti. Throughout the coating procedure, the electrical resistance of these plates decreased. Although the Ag-coated plates initially exhibited minimal resistance, they were susceptible to oxidation, which caused irreparable damage to the electrolyzer's Nafion® membrane. To counteract this, a layer of Au was sputter-coated onto the silver, rendering the plates oxidation-resistant without altering their electrical resistance. The onset voltage for water electrolysis decreased marginally as the temperature rose from 30 °C to 70 °C, but there was no improvement in current density above 50 °C. This limitation is believed to be caused by the mismatch in thermal expansion coefficients between polypropylene and silver, influencing the integrity of the coating and increasing its resistance at higher temperatures.

Based on the Jung et al. [20] study, a 1 µm Au coating on Ti-based BPP was studied, while it was found that the Au film acts as a barrier that prevents the formation of an oxide layer on the plate surface and significantly enhances the performance of the BPP over time as a result of the low electrical contact resistance. Although Ti-based BPP coated with Au or Pt exhibits excellent performance, the costly coating will increase fabrication costs, preventing the target from being met [20,21]. Table 1 lists the various materials and coatings applied to BPP to improve its corrosion resistance.

Table 1. The corrosion resistance and interfacial contact resistance of the materials and coatings used in the fabrication of Bipolar Plates (BPPs).

BPP Materials	Electrolytes	Methods	Surface Modification	Icorr ($A\cdot cm^{-2}$)	ICR ($m\Omega\ cm^2$) Compression of 150 $N\cdot cm^{-2}$	Ref.
Ti	0.5 M H_2SO_4 + 5 ppm F^- solution at 70 °C with pressured air purging	Pulsed bias arc ion plating	Ti-Ag film	1×10^{-5}	2	[18]
Ti	0.5 M H_2SO_4 with 2 ppm F^-, 70 °C	Pulsed bias arc ion plating	Honeycomb-like nanocomposite Ti-Ag-N films	1×10^{-5}	2.3	[19]
Ti	30 wt% Pt on Vulcan XC-72, 0.5 $mg\cdot cm^{-2}$ Pt loading	Electrodeposition	Gold	—	—	[20]
SS304 Ti	0.5 M H_2SO_4 3 ppm NaF purging with H_2, 60 °C	Evaporation processes that use cathodes are known as cathodic	(Ti,Zr) N	3.10×10^{-7} 2.12×10^{-7}	2.99 2.90	[26]
446 M ferritic SS	1 M H_2SO_4 + 2 ppm F^- solution, 70 °C	Chemical and thermal treatment	Immersion in the HCl, 50 °C, 5 min	1.8×10^{-5}	8	[27]
446 M ferritic SS	1 M H_2SO_4 + 2 ppm F^- solution at 70 °C	Electrodeposition	Ruthenium oxide	1×10^{-6}	2.5	[28]
446 M ferritic SS	1 M H_2SO_4 + 2 ppm F^- solution at 70 °C	Chemical treatment	Immersion in 5 M NaOH, 1 min	0.15×10^{-6}	15.6	[29]

Titanium, on the other hand, is susceptible to hydrogen embrittlement in the hydrogen chamber (cathode), making it unsuitable for use over an extended period of time. The Ti plate has a propensity to absorb more than 1000 ppm of hydrogen throughout the course of a 500 h operation [30,31]. Titanium's mechanical properties, such as ductility and tensile strength, are susceptible to being degraded by hydrogen embrittlement [31]. The corrosion rate will be considerably reduced if the base material is coated. Gold-coated Ti BPPs have demonstrated excellent stability and resistance to hydrogen absorption [20]. However, because coatings add an extra processing step and require an expensive coating material to the already expensive Ti base, any cost reductions are negated [1]. Another effective coating material is TiN deposited via plasma nitridation with a controlled nitrogen gas flow during electrodeposition. Moreover, AM (metal 3D printing) of nonmetallic plastic lattice material and the integration of BPP and diffusion layer on the printed material can reduce costs and eradicate corrosion concerns.

Stainless steel (SS)-based materials, especially those in austenitic grades like 316L, are preferable options for BPPs' development because of their high mechanical strength, strong electrical conductivity, inherent corrosion resistance, affordable price, and extensive availability. However, as mentioned before, they have some limitations, particularly when used in the PEMWE's acidic environment. These restrictions include corrosivity, surface oxidation that affects electrical conductivity, and chromium (Cr) leaching that can contaminate the catalyst and diminish electrolyzer effectiveness. Coated SS-based materials have been investigated as a way to reduce these problems. SS coated with titanium nitride (TiN) provides improved corrosion resistance and maintains good electrical conductivity, although it can be pricey and may delaminate over time (under extended operation). Although Au-coated SS BPPs offer improved corrosion resistance and maintain electrical conductivity, the high cost of Au makes it commercially unviable on a large scale.

Gago et al. [32,33] tested Ti-based coatings and Pt-modified SS-based BPPs for PEMWEs. The purpose of this study was to characterize Pt/Ti coatings and evaluate their corrosion resistance, specifically in a simulated PEM electrolyzer environment. The Pt/Ti/SS samples exhibited no visible corrosion, whereas the Pt/SS samples exhibited severe pitting corrosion, resulting in the formation of small cavities beneath the Pt layer. Morphological behavior on cross-sections of the coated samples before and after corrosion experiments was studied by scanning electron microscopy (SEM). Importantly, no evidence of degradation, such as peeling, pitting, or pinhole formation, was detected in SEM images of Pt/Ti samples (thickness of Ti coating ~120 mm). In contrast, samples lacking the Ti layer (Pt/SS) exhibited severe degradation. In addition, the pitting corrosion enlarged the surface area beneath the Pt layer, which was reflected in the electrochemical measurements. Furthermore, energy-dispersive X-ray spectroscopy (EDX) revealed that this Ti layer was composed of approximately 97 wt% Ti, with the remaining 3 wt% attributable to impurities introduced during the sanding and polishing procedures. The thicknesses of the Pt layer on the Ti coating remain almost the same (~1.1 mm) before and after the corrosion testing. Voltammetry measurements of Ti/SS, high-purity Ti foil, and an uncoated SS plate are performed to assess their electrochemical behavior in O_2-saturated 0.5 M H_2SO_4 at 65 °C. The high-purity Ti foil exhibited potentiodynamic curves very similar to those of the Ti/SS sample, corroborating the EDX analysis indicating that the thermally applied Ti coating is comparable to the bulk material. Compared to the Ti/SS sample, the current density at 2 V versus RHE for the Ti/SS sample was approximately 10,000 times lower, indicating that the thermal spraying of Ti effectively protected the substrate from corrosion.

Rasten et al. [34] recommended that the BPP material for PEMWEs be made out of highly alloyed Stainless Steel (SS). The austenitic steel that was recommended had a composition of 20 wt% Ni, 20 wt% Cr, 3–5 wt% Mo, 0.2 to 2 wt% Cu, 30 to 50 wt% Fe, and a maximum of 9 wt% additional elements. An electrolyzer that consists of a housing and a cell stack that contains at least one electrochemical cell for the electrolysis of water at a temperature between 5 and 100 °C and at a pressure between ambient and 50 bars, characterized in that said housing and other structural components of said electrolyzer are made of a material that is an austenitic SS in accordance with the requirements of the electrolysis process.

In a PEMWE fitted with corrosion-resistant BPPs, Langemann et al. [15] evaluated the pH development over time on both the anode and the cathode side. Over the course of 50 h, they observed that the pH dropped not just on the cathodic side of the electrolyzer but also on the anodic side. The same research group conducted polarization tests on AISI 304L that had been coated with Au and TiN in a 0.50 M H_2SO_4 solution at 2 V versus SHE. The effect of pH value on feeding water has also been investigated throughout the course of these measurements. It was discovered that during normal cell operation, the pH value drops considerably, creating an increasingly acidic environment that jeopardizes the stability of the metallic components already exposed to a high potential (>1.48 V) on the anode side. Gold and titanium nitrite-coated BPPs developed using physical vapor deposition (thickness of the coating on AISI 304L: 0.2 mm Au and 0.5 mm TiN) have been used. After being exposed to the corrosive medium, samples have shown varied levels of corrosion. The samples undergo a more severe corrosion development in high-acidity solutions. During the preliminary surface investigation of untreated samples coated with Au and TiN by scanning electron microscopy (SEM), it was discovered that certain portions of the surface were not completely coated, which led to the formation of pinholes in the coating.

Feng et al. [35] altered the surface and surface properties of SS 316L samples by ion-implanting highly corrosion-resistant niobium. Prior to and after potentiodynamic and potentiostatic polarization experiments, the ICR values of bare and Nb-implanted SS 316L were determined. The results indicated that the material's dissolution rate was significantly reduced.

Niobium (Nb) and Titanium (Ti) coated SS-based BPPs (Nb/SS, Nb/Ti/SS) as well as Nb-coated Ti BPPs (Nb/Ti) have been developed by Lettenmeier et al. [36]. Coatings have been applied on the SS substrate by magnetron sputtering physical vapor deposition (PVD) and vacuum plasma spraying (VPS). Interfacial contact resistance (ICR) measurements have been performed under different compaction forces to evaluate the electrical conductivity of the samples. Nb/Ti/SS and Nb/Ti samples showed almost the same low ICR. According to the electrochemical testing, Nb/Ti/SS and Nb/Ti samples were stable and showed similar behavior during polarization at 2 V (vs. RHE). Furthermore, Ti coating (50 um) protects the SS substrate against corrosion. X-ray photoelectron spectroscopy (XPS) has been carried out before and after the electrochemical tests to determine possible material changes. An analogous behavior (Nb3d and Ti2p spectra) was reported for Nb/Ti/SS samples before and after testing and for Nb/SS and Nb/Ti samples. The Nb/Ti/SS BPPs show high durability (more than 1000 h of operation) under the harsh environment of a PEMWE anode, assuring perspectives for Ti-based material replacement in PEMWE.

Nb-coated SS BPPs (Nb/SS and Nb/Ti/SS) have also been produced using a novel plasma-sprayed technique [37]. During long-term operation in PEMWE, the performance of both samples (Nb/SS, Nb/Ti/SS) was comparable to that of the baseline material from Nel Hydrogen. Coating quality and morphology before and after operation were studied by scanning electrode microcopy. Signs of corrosion of the SS substrate beneath the coatings have not been reported. Atomic force microscopy and X-ray photoelectron spectroscopy show the formation of poorly conductive amorphous Nb oxides, contributing to an increase in interfacial contact resistance. However, the latter did not affect the cell performance. According to the experimental results, Ti-based materials could be substituted by SS-based components as base materials for manufacturing stable, low-cost, and high-performance BPPs.

A comprehensive investigation of low-cost materials for BPPs with applications in PEMWE has been conducted by Nuria Rojas et al. [38] (Table 2). Different coated stainless steels (SS 316L, SS 321, SS 904L) have been evaluated and characterized for corrosion resistance, electrical conductivity, and surface characteristics in the PEMWE environment. Multi-layer coatings (CrN/TiN and Ti/TiN) and two mono-layer coatings (Ti and TiN) were obtained by Physical Vapor Deposition (PVD) and were analyzed. According to Rojas et al. [38], BPP manufactured with PVD techniques could be an effective choice for PEMWE, with SS 321 exhibiting the optimal behavior as a base material for all coatings. Since trans passivation at high positive potential is involved in PEMWE, the presence of Cr has a negative effect as an alloying element in SS 904L and a coating material in CrN/TiN systems. Utilizing Ti/TiN bilayers improved the correlation between corrosion resistance and ICR values.

A PVD coating based on Ti/TiN bi-layers on SS 321 exhibited promising results for cost-effective application as a material for Bipolar Plates in PEMWE. In situ testing of optimized PVD Ti/TiN-coated systems is required to validate the excellent performance demonstrated in this investigation. Especially considering that replacing TiPt with SS such as SS 321 coated with a coating material such as Ti/TiN using the PVD technique employed in this study results in a 90% reduction in the cost of the material used to produce BPPs.

The main challenge of PEMWE Is to inhibit corrosion of the metallic components, like the Bipolar Plates (BPPs) and the porous transport layers (PTLs), which are subjected to acidic and oxidizing conditions at the anode and cathode. Various coatings, including precious metals, metal nitrides, metal carbides, silane, and conductive polymers, have been applied to protect metal surfaces. Yet, these coatings may lack the durability needed to endure the mechanical and thermal loads, as well as the electrochemical processes, that take place during PEMWE operation [39]. Peeling and erosion of surface coatings can adversely affect the performance and longevity of the PEMWE cell. Peeling the coating can expose the metal underneath to corrosion, leading to higher interfacial contact resistance (ICR) and worse electrical conductivity in the BPPs and PTLs. Erosion of the coating may release particles or ions that can contaminate the membrane or electrodes, causing higher ohmic resistance and decreased catalytic performance. The peeling and erosion of the coating can change the surface structure and porosity of the BPPs and PTLs, impacting the movement of water and gas, as well as mass transfer at the electrode interface [40]. Therefore, it is crucial to provide surface coatings that possess corrosion resistance, mechanical and thermal stability, and electrochemical inertness for PEMWE applications. Potential options are conductive polymers and nanoparticle-enhanced polymer hybrid coatings. These materials can create a consistent and strongly attached layer on metal surfaces, offering excellent electrical and mass transfer characteristics. Additional study is required to enhance the coating composition, thickness, and deposition process and to assess the long-term stability and longevity of the coatings in PEMWE settings [41].

Table 2. Corrosion current and corrosion potential of samples evaluated. Data from [38].

Stainless Steel	Samples Tested under Each SS Category	Corrosion Current Density (I_{corr}) mA cm^{-2}	Corrosion Potential (E_{corr})	Current Density at 2 V versus SHE, mA cm^{-2}
SS 321	Bare	9.13	0.06	30,117
	Ti	31.6	0.02	532
	TiN	0.84	−0.18	412
	Ti/TiN	2019.00	−0.22	436
	CrN/TiN	72.92	−0.01	77,985
	$TiGr_2$	0.40	−0.81	145
SS 316L	Bare	1.47	−0.39	27,423
	Ti	3.79	−0.04	882
	TiN	145.30	0.24	549
	Ti/TiN	139.43	0.14	564
	CrN/TiN	15.04	−0.13	69,549
SS 904L	Bare	0.78	−0.16	23,298
	Ti	0.02	−0.11	1713
	TiN	139.70	−0.26	564
	Ti/TiN	124.81	−0.21	721
	CrN/TiN	1.24	−0.35	43,844

As mentioned above, SS-based BPPs are appealing for PEMWE systems due to their ability to lower the cost of PEMWE manufacturing. Even though SS-BPPs might prove more cost-effective compared to the Ti-BPPs option, problems such as corrosion and pollution can impact the efficiency and longevity of the PEMWE. Hence, SS-BPPs must be coated with non-precious metal coatings, like Ti and Nb/Ti, to enhance their conductivity and wettability and protect them from corrosion. Based on Stiber et al. [42], the PEMWE cell utilizing coated SS-BPPs can achieve high performance, durability, and cost-effectiveness similar to a PEMWE cell with Ti-BPPs. The study found that the cost of the SS-BPPs was approximately 0.5 EUR/cm^2, but the cost of the Ti-BPPs was around 1.5 EUR/cm^2. The investigation demonstrated that the PEMWE cell using coated SS-BPPs performed similarly to the PEMWE cell using Ti-BPPs in terms of efficiency and performance. Additionally, no iron contamination was seen after over 1000 h of operation. The study found that SS-BPPs can significantly reduce costs in PEMWE technology and promote the mainstream adoption of green H_2 [42].

The study by Brian D. James et al. [42] revealed that the cost of the BPPs significantly impacted the capital cost of the PEM electrolysis system, representing approximately 30% of the total capital cost. The study calculated that the cost of the BPPs for PEM electrolysis was around 5.35 EUR/kW, exceeding the existing objective of 2.5 EUR/kW by more than double. The study proposed reducing the cost of Bipolar Plates (BPPs) by utilizing low-cost coated metal BPPs like BPP-SS and implementing active area welding in upcoming applications [43].

Michael Götz et al. [43] worked on the creation of low-cost BPPs for PEM fuel cells, which have requirements and challenges similar to those of PEMWE cells. The study found that the cost of BPPs for PEM fuel cells was around 6.5 EUR/kW, which is higher than the existing objective of 2.5 EUR/kW. The study developed a novel manufacturing process for BPP-SS that included stamping, laser welding, and coating. According to the study, this technique might reduce the BPP-SS cost to around 3.5 EUR/kW, bringing it closer to the target [44].

3. Large Scale, Pilot Scale and Industrial Scale PEMWE Systems

3.1. Large Scale PEMWE Systems

In larger-scale production, durability and cost-effectiveness become paramount. Graphite is widely recognized for its exceptional ability to conduct electricity and its remarkable resistance to corrosion. However, it lacks the necessary structural strength for prolonged use. As a result, metals such as SS are frequently selected since they have been treated or coated to prevent corrosion [45]. Expected to surpass 40,000 h of operation. The key hurdles for large-scale systems are constant hydrogen purity, heat control, and durability, especially in the case of probable BPP corrosion. Given the mechanical pressures from processes, the brittleness of graphite BPPs can be a disadvantage [46] (Table 3). Cell counts often range from the hundreds to the thousands in large-scale PEMWE systems, particularly those designed for use in industrial applications. The required rate of hydrogen generation, the design of the system, and a number of other criteria all contribute to the determination of the exact number of cells. For instance, as a data point, the PEM electrolyzers for large-scale operations that are manufactured by ITM Power, a major manufacturer, such as their HGas3SP product that is built for capacities of up to 3 MW, are composed of hundreds of cells.

Table 3. Summary of leading manufacturers of PEM water electrolyzers.

Manufacturer	Power	Electrolyte	Hydrogen Flow Rate ($Nm^3 \cdot h^{-1}$)	Energy Consumption ($kWh \cdot Nm^{-3}H_2$)	Load Range (%)	Series and Operating Pressure
Proton OnSite	No Available	solid polymer electrolyte (SPE)	0.265–1.05	6.7	0–100	S Series 13.8 bar
Proton OnSite	No Available	SPE	2–6	6.8–7.3	0–100	H Series 15—30 bar
H-TEC Systems	1–5 kW	SPE	0.22–1.1	No available	No available	H-TEC Series-S
H-TEC Systems	225 kW–1 mW	SPE	13–210	4.9	No available	ME unpressurized 30 bar
Areva h2 gen	80–1600 kVA	SPE	10–200	4.7–5.3	No available	E series Up to 35 bar
Hydrogenics	No Available	SPE	1–2	6.7	0–100	HyLYZER 0–7.9 bar
ITM Power	2 mW	SPE	0.6–35	4.8–5.0 (system)	No available	HPac, HCore, HBox, HFuel 15 bar
Siemens	1.25 mW	SPE	225	No available	No available	SILYZER 200 35 bar
Green Hydrogen	4.95 kW	SPE	1	No available	25–100	P–series/15–50 bar
NEL	0.5–2 mW	SPE	103–413	4.53	0–100	M Series 30 bar

3.2. Pilot Scale PEMWE Systems

This is an experimental size where different materials may be tried. While graphite remains the most common option, SS and its derivatives may be preferred due to economic reasons [46]. Titanium, however more expensive, might also be investigated for its corrosion resistance [47]. These systems have been running for about 5000 to 20,000 h. They serve as a connection between smaller laboratory systems and larger industrial environments. As a link between research and industry, these systems may degrade quickly if the materials are not optimized. While comparable, the operational circumstances may not fully replicate the demanding needs of industrial-scale systems. Cell counts can exhibit significant variation. Some pilot-scale systems have been reported to have as few as one to 10 cells, while others can have several dozen or even more than 50 cells.

3.3. Industrial Scale PEMWE Systems

Material selection for full-fledged commercial operations favors long-term stability. Stainless steel, particularly when coated with protective layers such as titanium nitride (TiN), emerges as a good option. Titanium, with its natural corrosion resistance, might be explored, although the expense connected with it may restrict its widespread application [48]. Industrial installations aim for a long operational life of 60,000 to 80,000 h or more. At this scale, the main consideration is to guarantee near-continuous operation with little downtime. The problem is keeping efficiency up under heavy loads. The risk of BPP corrosion becomes critical since any degradation might result in pollution and decreased system performance [49].

Nel Hydrogen and ITM power companies use large-scale systems. Titanium or SS coated with Ti or Nb/Ti alloy for BPPs and PTLs (Porous Transport Layers) are used [37]. Nafion-based MEAs contain iridium (Ir) and ruthenium (Ru) based electrocatalysts as anode, and platinum (Pt) based electrocatalysts are used as cathode. German aerospace produces PEMWE on an industrial scale. They use SS coated with Nb/Ti BPPs and PTLs.

4. Corrosion Evaluation of Metallic Components in PEMWE Devices

Corrosion testing on metallic BPPs and PTLs can be performed at various PEMWE system scales, from laboratory to industrial. The corrosion evaluation results and findings can aid in the selection of the best materials and coatings for metallic BPPs and PTLs, as well as in optimizing the design and operation of PEMWE systems. Corrosion evaluation of metallic BPPs and PTLs is a critical stage in the advancement of PEMWE technology and its use for H_2 production.

In large-scale PEMWE, metallic BPPs are essential components that facilitate efficient H_2 production using water electrolysis. A thorough corrosion assessment is required, however, to guarantee their long-term performance and durability. In order to find corrosion-resistant materials that are appropriate for industrial-scale PEMWE applications, researchers use a variety of electrochemical techniques, material selection, and accelerated aging experiments. For H_2 manufacturing techniques to be economically viable and sustainable, an understanding of corrosion behavior at this scale is essential.

Corrosion behavior evaluation of metallic BPPs becomes crucial for scaling up from lab-scale prototypes to pilot-scale PEMWE. The performance of these plates significantly impacts the feasibility and scalability of the PEMWE technology. Researchers utilize electrochemical characterizations, environmental exposure assessments, and accelerated aging tests to study the corrosion kinetics and identify potential degradation mechanisms. This evaluation aids in the selection of robust materials for pilot-scale PEMWE, ensuring a reliable and efficient H_2 production process.

In industrial-scale PEMWE, the corrosion evaluation of metallic BPPs assumes critical importance. The magnitude of H_2 production demands the utmost reliability and durability of these plates. These methods allow for a detailed study of the effects of corrosion on the surface. This in-depth evaluation ensures the selection of materials that can withstand the rigors of industrial-scale PEMWE, contributing to sustainable and cost-effective H_2 generation.

Metal corrosion in PEMWE is a critical problem that threatens the efficiency, longevity, and economic feasibility of these systems. Promising materials for large-scale PEMWE encompass Ti, SS, and graphite. As mentioned previously, these materials have demonstrated excellent resistance to harsh working conditions. Typically, these conditions involve acidic environments generated by the proton exchange membrane, high current densities, and frequently elevated temperatures. Nevertheless, it is important to acknowledge that these materials possess inherent limitations and encounter operational challenges (Table 4). Even though Ti has excellent resistance to corrosion, it can be extremely costly for commercial purposes. Although SS are less expensive, they are susceptible to localized corrosion or pitting when exposed to highly corrosive conditions close to the membrane. These material limitations are also compounded by operational difficulties. Essential for achieving high rates of H_2 production, high current densities can accelerate corrosion by rapidly triggering redox reactions at electrode interfaces. Moreover, fluctuations in temperature and pressure during operation can induce thermal stresses in metallic components, accelerating material deterioration and introducing mechanical failures in addition to electrochemical corrosion. Occasionally, impurities in the water supply or the membrane itself can function as corrosion catalysts, introducing an additional variable that makes corrosion evaluation even more complex.

Table 4. Promising materials, limitations, and problems during operation in different scales PEMWE systems Data from [50,51].

Scale	Promising Materials	Limitations and Problems during Operation
Large-Scale	Titanium, Stainless steel, Graphite	Titanium and stainless steel both have the potential to corrode over time if exposed to an environment that is either extremely acidic or alkaline. The cost of these materials can be quite high when used in large quantities.
Industrial	Graphite, Coated titanium, Nickel-based alloys	There is some evidence to suggest that graphite degrades after extended use. Coated titanium can corrode more quickly when exposed to high operating temperatures.
Pilot-Scale	Graphite, Carbon composite materials	Restricted Durability: There is a possibility that materials based on graphite will have a restricted ability to withstand long-term use. There is a possibility that the mechanical qualities are insufficient for usage on an industrial scale.

Graphite, coated Ti, and Ni-based alloys are often employed materials in industrial-scale PEMWE systems. Although graphite exhibits favorable conductivity, it is susceptible to deterioration over extended periods of operation. The utilization of coated Ti serves to augment its resistance against corrosion; nonetheless, it should be noted that elevated operating temperatures can potentially expedite the occurrence of corrosion. The utilization of Ni-based alloys exhibits promises, yet it is imperative to address economic considerations and the potential for Ni contamination.

Graphite and carbon composite materials are frequently utilized in pilot-scale PEMWE systems. Nevertheless, certain constraints exist on their utilization. Graphite-based materials exhibit potential limitations in terms of durability during extended periods of operation, particularly when subjected to severe operating conditions.

The overall efficiency of a PEMWE system depends heavily on the materials used for the BPPs and PTLs. Considerations including corrosion resistance, affordability, durability, and scalability must be made. More effective materials for widespread use in high-efficiency PEMWE systems are the focus of ongoing research and development.

5. Materials and Equipment in PEMWE Systems

The electrolyzer unit contains the proton exchange membrane, which is typically composed of Nafion™ or a similar sulfonated polymer. The electrodes typically consist of iridium oxide for the anode and platinum or its alloys for the cathode, both of which are investigated for their corrosion resistance in these harsh conditions. The electrolyzer unit incorporates the metal components that are the subject of the corrosion evaluation, which are typically Ti, Ta, or SS-based plates and connectors. A source of external current provides the high current densities required for electrolysis, thereby simulating the accelerated redox reactions that may cause corrosion. The monitoring and evaluation of corrosion onset and progression are facilitated by specialist electrochemical characterization instruments, such as potentiostats/galvanostats, in conjunction with techniques like cyclic voltammetry, polarization curves, and Electrochemical Impedance Spectroscopy (EIS). Operando techniques may also be used to evaluate corrosion under actual working conditions, yielding invaluable information for studies of long-term durability. All these materials and apparatus work in tandem to enable a comprehensive and multidimensional evaluation of corrosion in PEMWE systems, thereby contributing to the ongoing effort to increase the effectiveness and durability of these vital devices.

At the moment, most BPPs are made of Ti because it is strong and can withstand tough circumstances. However, the material has some problems, like being prone to hydrogen embrittlement and having a higher ICR. These problems have led to a wider search for other materials. The development of SS-based BPPs and PTLs will drastically reduce Ti usage in PEMWE. As Ti is included in the CRM list by the EU, the change from Ti plates to an SS with a thin Ti-based coating represents a big step for the PEMWE community in the EU. Corrosion testing of coated SS-based BPPs and PTLs in PEMWE is ripe for innovations that could drastically improve both efficiency and cost-effectiveness. As mentioned before, scientific research suggests that SS-based BPPs covered with Nb/Ti exhibit favorable corrosion-resistant characteristics. In this work, comprehensive corrosion evaluation methods using electrochemical methods and real-world testing settings are described.

6. Ex Situ Testing: Procedures and Methods

Interfacial contact resistance (ICR) versus compaction force measurements are performed before the ex situ corrosion test to evaluate the conductivity of the coatings. The BPP is polished with abrasive paper. For the measurement, the BPP is placed between two pieces of carbon paper (simulate real conditions operation) and two copper plates. This sandwich-like assembly is placed between two insulating plastic plates and introduced into a hydraulic press. A hydraulic press is used to apply the required pressure, while the direct current is applied between the two copper plates using a power supply. The potential response is recorded using a multimeter.

Electrochemical measurements are carried out in a three-electrode assembly corrosion cell using a potentiostat. The electrode sample holder in which BPP samples are mounted exposes only a specific area of the coated surface to the electrolyte solution. A Pt plate and a reversible hydrogen electrode are usually used as counter and reference electrodes, respectively. The reference electrode is placed in the close vicinity of the working electrode via a Luggin capillary. Corrosion tests are carried out in acidic pH (usually in O_2-saturated H_2SO_4 electrolyte solution at 60–90 °C) to simulate the anode side of PEMWE environment under operating conditions and in the presence of fluoride ions to simulate conditions due to the proton exchange membrane degradation by fluoride release. Corrosion parameters (corrosion potential E_{corr}, corrosion current j_{corr}) are determined for the samples before and after an accelerated stress test achieved by polarizing the samples at a constant potential of 2 V versus RHE.

7. Discussion

This article summarizes several studies on the complicated trade-offs between material qualities and operational demands and emphasizes the necessity for a holistic approach to selecting and designing SS-based BPPs for PEMWE applications. When metallic BPPs are employed, the majority of the electrical resistance is due to the surface contact resistance between the BPP and the component in direct contact, such as the flow field plate or GDL. In an electrolyzer, the actual contact resistance is determined using the BPP material and the structure of the component in direct contact with the BPP. This value differs between stacks based on their construction and intended applications. By employing strategies such as surface roughness optimization and carefully selecting manufacturing processes, it is possible to minimize ICR and enhance the overall system's performance and efficiency.

The study also looked at SS-based BPPs that are treated with coatings and found ways that their real-world performance could be improved. Corrosion is a prevalent issue with metallic-based BPPs. The metallic plate's corrosion increases the ICR of the material. Therefore, a corrosion-resistant coating is applied to the material surface to create a barrier between the plate and the surrounding environment. Nonetheless, this process decreases the ICR, which impacts the efficacy and longevity of the PEM water electrolyzer. To prevent corrosion, the coating material applied to the plate base material must possess certain properties, including excellent adhesion to the plate base material, conductivity, stability, and inertness.

8. Conclusions and Future Directions

Polymer Electrolyte Membrane Water Electrolyzers or Proton Exchange Membrane Water Electrolyzers, also known as PEMWEs, are devices that have emerged as potential and environmentally benign systems for producing high-purity hydrogen. This technology is a response to the worldwide endeavor to find sustainable and renewable energy options. On the other hand, the fact that PEMWE devices are dependent on crucial raw materials (CRMs), including platinum, iridium, ruthenium, and titanium, that are used as electrocatalysts and to manufacture BPPs and PTLs presents economic issues due to the high cost of these elements and their limited availability. In order to ensure that PEMWE can be economically viable, it is important that rapid improvements be made to low-cost components that have high performance and durability.

Both the efficiency and cost-effectiveness of PEMWEs are heavily dependent on the presence of BPPs and PTLs, which play crucial roles in the process. Despite the fact that titanium (Ti) is widely used for BPPs because of its remarkable resistance to anodic potentials and acidic environments, it is not without limits. These limitations include the fact that titanium is susceptible to hydrogen embrittlement and that its interfacial contact resistance (ICR) gradually increases over time. Tantalum (Ta), niobium (Nb), and titanium (Ti) with coatings, such as gold (Au) and titanium nitride (TiN), are some of the alternative materials that have been suggested by research to have the potential to alleviate these difficulties. In order to mitigate the utilization of Ti, a designated critical raw material as identified by the European Union, the development of SS-based BPPs that incorporate thin-film Ti-based coatings is a promising approach.

In the future, BPPs made of stainless steel (SS) offer an appealing alternative for PEMWE applications. These BPPs offer cost-effectiveness in comparison to materials such as titanium or graphite. In addition to having strong mechanical qualities and great electrical conductivity, stainless steel is also ideal for the rigorous conditions that are present in PEMWE. Stainless steel's ease of fabrication enables cost-effective production techniques such as stamping, forming, and welding. In addition, corrosion-resistant coatings or treatments can be applied to stainless steel to increase its suitability for electrolysis environments. The material's extensive availability and recyclability also contribute to its desirability, providing both supply chain stability and a more environmentally friendly option for long-term use. Further investigation is required to examine the corrosion rates at elevated anodic potentials, as this particular aspect has received less attention.

According to the literature, corrosion-resistant and highly conductive coatings called CRMs, SS-based BPPs, and PTLs can be used as viable replacements for Ti-based equivalents in coating processes. Furthermore, investigating therapies using non-CRMs has demonstrated promise in enhancing practical outcomes. The resilience of these coatings in acidic settings has been confirmed using electrochemical accelerated stress testing, effectively safeguarding SS from corrosion. Nevertheless, a thorough investigation is required to evaluate the long-lasting performance of these coatings under real-world operating conditions of a PEMWE.

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