# A Perspective on Increasing the Efficiency of Proton Exchange Membrane Water Electrolyzers– A Review

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# ABSTRACT

Decarbonized hydrogen production using renewable energy sources and water electrolysis is perceived as a promising solution for a sustainable future. The efficiency of PEMWEs relies on several multiphysical aspects and even a slight increase in their efficiency may change the future of sustainable energy routes. Hence, this paper reviews the most compelling research on increasing PEMWE efficiency, which is one of the main pillars for the advancement of this technology. Various publications, including chemical engineering, materials, mass transfer, energy transfer, electrical control, power generation, and hybrid systems, are considered. From the electrolyzer power sources (renewable energy, hybrid, power to gas), inputs (power regulation, water temperature, pressure, ambient temperature), and stack, to components design, control strategy, and new hybrid designs have come under scrutiny in this manuscript. Finally, five essential recommendations are given as the pathways for future studies on PEMWE efficiency.

Keywords: PEMWE; HyPro; Electrolyzer Efficiency; Membrane electrolyzer; Hydrogen

# Nomenclature

<b>Renewable Energy Source</b>	RES	Transport Layer	TL
Hydrogen Production	HyPro	Gas Diffusion Layer	GDL
Proton Exchange Membrane	PEM	Membrane Electrode Assembly	MEA
Water Electrolyzer	WE	<b>Temperature Swing Adsorption</b>	TSA
Fuel Cell	FC	Porous Transport Layer	PTL
Photovoltaic	PV	Catalyst Coated Membrane	CCM
Power-to-Gas	PtG	Mass Transport Limitation	MTL
Catalyst Layer	CL	Charge Transfer Coefficient	CTC
Computational fluid dynamics	CFD	Maximum Power Point Tracking	MPPT
Fuzzy Logic Control	FLC	Dual Organic Rankine Cycle	DORC
<b>Oxygen Evolution Reaction</b>	OER	Ground Source Heat Pump	GSHP
Platinum Group Metal	PGM	Balance of Plant	BOP
Stainless Steel	SS	Fuzzy Logic Control	FLC

# 1. INTRODUCTION

One of the most practical alternatives to traditional energy, which mainly depends on fossil fuel, is renewable energy sources (RESs) [1]. They are much less detrimental to the environment. The key downsides of renewable energy are its reliance on the weather, its incapacity to store, and its availability when needed. In this regard, power-to-gas (PtG) is undoubtedly one of the best environmentally friendly solutions for storing renewable energy [2, 3], which is dominating the market [4]. In the literature, PtG is reviewed from various points of view, such as technology [5], economics [6], market and portfolio effects [7], electrolysis and methanation status [8], thermochemical water splitting cycles [9], and solar energy [10]. In recent years, hydrogen production (HyPro) has drawn the attention of policymakers, industries, and individuals. The production and use of hydrogen are also on the rise worldwide [11, 12], with technologies such as hydrogen vehicles, hybrid cars, and other green systems [13]. Researchers predict that HyPro from RESs will be critical in transforming the global energy system into a sustainable energy system by 2050 [14-16].

Electrolysis is now a crucial technology for HyPro, forming the basis of future energy systems as an energy carrier. Most PtG systems use the electrolysis process to produce hydrogen. Electrolyzers are rapidly expanding in the market to meet the world's clean energy demand, although they need additional durability, efficiency, and performance improvement [17]. Brynolf *et al.* studied the production costs of modern fuel (electrofuels or PtG) for transportation systems. Based on a review of more than 130 articles, they concluded that HyPro with electrolysis could be reliable in both small and large-scale applications if capital costs and stack life are considered [18]. This study reviews all of the struggles in increasing the PEMWE's efficiency. After this short introduction, in the second section, the PEMWE's importance, advantages, industrial status,

literature review, drawbacks, and possible solutions are reviewed. Section 3 discusses; operational conditions and the stack component's role in increasing efficiency, system configuration, models, and energy control. Finally, in the third section the combined systems and hybrid sources are discussed. Section four explores future perspectives, and section five gives a conclusion.

# 2. Polymer Electrolyte Membrane Water Electrolyzer (PEMWE)

PEMWE is an efficient and clean method for generating H<sub>2</sub> from water by electrolysis. Proton conduction, separation of the produced gases, and electrical insulation of the electrodes occur in a zero-gap cell equipped with a solid polymer electrolyte in a stack section. From this reaction among cathode and anode sides and catalyst layers, H<sub>2</sub> and O<sub>2</sub> are generated [19]. PEMWE has a considerable potential of HyPro from RES by its privileges to play an essential role in reducing greenhouse gas emissions in the hydrogen sector. Studies show that PEMWE may eliminate conventional steam methane reforming from the field of HyPro by 2050 [20].

# 2.1. Popularity of PEMWE

PEMWE has been attracting significant attention in recent years due to its superiority over other green HyPro methods, and its excellent potential to connect to RESs. These clean and free sources, such as solar and wind, are tremendously dynamic. This challenging operational condition makes the HyPro complicated and inefficient because the energy intensity is intermittent. However, unlike alkaline water electrolyzers, PEMWE quickly reacts to the fluctuations of RESs, withstand high-temperature ranges, performs well in variable power input modes, operates at higher current densities, and has high energy conversion efficiencies [21, 22]. PEMWE can either be directly coupled with other sources in proper circumstances or use maximum power point tracking (MPPT) tools by a regulator (DC/DC).

Moreover, PEMWE is more straightforward than the alkaline type since it delivers high-quality gas and has lower maintenance requirements. Therefore, the operational, maintenance, and repair costs of HyPro are reduced, and energy efficiency is increased using PEMWE [23]. Mohammadi and Mehrpooya reviewed several studies on the performance of various electrolyzers linked with a variety of RESs. The positive aspect of such research is to optimize the electrolyzer's connection with RESs [24].

It is also shown in [25] that PEM electrolyzers can generate hydrogen and oxygen as a byproduct at up to 350 bar pressures with small additional power consumption, which is attractive for hydrogen storage usage or applications that use pressurized hydrogen. In addition, depending on the material used, PEMWE can maintain high efficiency while operating at high pressures [26]. A PEMWE can produce ultrapure hydrogen with higher than 99.999% purity, and even a fuel cell can be fed by it [27].

The benefits of the PEMWEs, such as less corrosivity [28], flexibility, high proton conductivity [29], thin proton exchange membranes [30], relatively low operating temperature [31], and low computational complexity [32], are explained in numerous articles. In this regard, decarbonization [33], fast response [34], and fast cold start [35] are also noticeable.

PEMWE modules require less space than alkaline ones (about 20%) [31]. Hence, they have a higher density (smaller footprint) than their rivals. On a small scale, it is efficient, clean, and has good compactness. Increasing the electrolyzer's scale to enormous sizes [32]. The produced hydrogen in the output can also be compressed to reduce transport storage costs [36].

In a nutshell, fast response to the power source, high differential operating pressure, high current densities, high power densities, hydrogen purity, high production rates, compact design, and the capability of working in variable operating conditions are the upper hands of PEMWE in its

industrial success [59]. Currently, PEMWEs are in a state of development with various limitations. A complete list of these limitations and disadvantages is discussed in section 1.4.

# 2.2. The embracement of PEMWE by industry

As mentioned in the previous section, due to the ability to connect to new energy sources, PEMWEs are becoming more popular year by year. The first commercial version was sold in 1978 [37]. However, the competition among companies and even countries is in progress to set a new record for HyPro nowadays [38]. Mittelsteadt expressed, "today at least five companies are at or near the launch of MW electrolyzers systems" in 2015 [39], and now, every forward-looking company knows the only path for the future is RES." The capability of PEM electrolyzers to rapidly change the power consumption has a desirable feature for frequency stability," said Alshehri *et al.* [44]. Figure 1 illustrates these concepts and the industrialization process of PEMWEs. Several key events have occurred along the path to PEMWE improvements, including obstacles, critical successes, and significant advances. According to this Figure, the modern design of PEMWE has caused models and control strategies to become more sophisticated after the 19th century. The flowchart shows that efficiency is among the highest importance for future scenarios, same as durability and cost.



Figure 1 Improvements, turning points, and challenges of PEMWEs

Table 1 illustrates the size, output pressure, energy demand, and model of nearly all PEMWE providers. From this table, the United States of America, France, Germany and China are the greatest PEMWE providers. It is also noticeable that there are of course other laboratory and industrial manufacturers, however only the census of prominent companies has been conducted. Furthermore, The largest operating unit of PEMWE using 20 MW RES is implemented in Bécancour, Canada (Quebec) by the Air Liquide company and Cummins technology. This unit ensures the low-carbon hydrogen supply for industrial use and mobility in North America by up to 8.2 tons of HyPro per day [40]. Cummins Inc. also claims that they have constructed the largest PEMWE in the USA at the Douglas County Public Utility District in Washington [41]. Thus, it is the beginning of the competition for manufacturing more outstanding PEMWEs. Shortly after, Linde announced that the worlds largest PEMWE (24-megawatt) will be established at the Leuna chemical complex in Germany and then some months later a 35-megawatt in Niagara Falls, New York [42, 43], and Air liquid unveiled a 30-MW project by 2023 [44].

Table 1 Origin, model, sze and energy requirement of PEMWE providers

power consumption Output pressure	Brand (Company)	Model	HyPro	Required power	Average power consumption	Maximum Output pressure	Country
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		200-250	1.4-1.7	55		
	-	(Nm³/h)	(MVA)	(kWh/kg)	_	
		400-500	3.2	54		
Cummins	HyLYZER	(Nm³/h)	(MVA)	(kWh/kg)	- 435	
		1000	7	51	(P	
	-	(Nm³/h)	(MVA)	(kWh/kg)	JIS	
		4000	23	51		
	М	$\frac{(Nm^3/h)}{104.417}$	(MVA)	(KWh/Kg)	_	
	IVI	104-41/ (Nm <sup>3</sup> /h)	(MVA)	$\frac{39}{(kWh/kg)}$		-
	G	200-600	120-230	(9.17-6.94)	116	JSA
Proton on site	U	(cc/min)	(VAC)	(Vh/L)	(PSIG)	-
i i oton on site	G4800	4 7	205 - 240	617	(1510)	
	01000	(L/min)	(VAC)	(Wh/L)	200	
	S	9.4-18.8	205-240	6.7	(PSIG)	
		(L/min)	(VAC)	(kWh/Nm <sup>3</sup> )		
Plug Power	EX-425D	200	1	49.9		
0		(Nm³/h)	MVA	(kWh/kg)	_	
	EX-2125D	1000	5	49.9	580	
		(Nm³/h)	MVA	(kWh/kg)	(PSIG)	
	S	027-1.05	NA	6.1	200	
		(Nm <sup>3</sup> /h)		(kWh/Nm <sup>3</sup> )	(PSIG)	No
	С	10-30	85-236	68.9 - 64.5		rwa
	<u></u>	(Nm³/h)	(kVA)	(kWh/Nm <sup>3</sup> )	_	ıy/
	М	1,698-4,920	NA	4.5		De
	MC	$(Nm^{3}/n)$	NI A	<u>KWN/NM<sup>3</sup></u>	-	nm
Nel	MC	$(Nm^{3}/h)$	INA	4.3 (kWh/Nm <sup>3</sup> )	<del>4</del>	ark
	н	2-6	22-55	7 3-6 8	- 35	SD/
	11	$(Nm^{3}/h)$	(kVA)	(kWh/Nm <sup>3</sup> )	(PS	01
	ELYTE	10-260	100-1680	4.9	- <u>I</u> G –	
		(Nm <sup>3</sup> /h)	kVA (AC)	(kWh/Nm <sup>3</sup> )	<u> </u>	
Elogen	Open Power	Min. 500	Min. 3.2	5	-	
		(Nm³/h)	MVA (AC)	(kWh/Nm <sup>3</sup> )	_	Fra
	Multi MW	Min. 2000	Min. 13	4.8		nce
	Systems	(Nm³/h)	(MVA) (AC)	(kWh/Nm <sup>3</sup> )		
AREVA H2Gen	Е	5-120	40-960	5.7 -4.8	507.6	
		(Nm <sup>3</sup> /h)	(kVA) (AC)	(kWh/Nm <sup>3</sup> )	(PSIG)	
	PURIFIER	1.2	7.3			
	CUSTOMIZE	<u>(Nm<sup>3</sup>/n)</u>	$\frac{(KVA)(DC)}{17.5}$			
	D	$2.\delta$ (Nm <sup>3</sup> /h)	1/.5			
	SUPPI IFR	7.6	$\frac{KVA(DC)}{47.3}$			
	SOLLER	$(Nm^{3}/h)$	(kVA) (DC)		58	
	STORAGER	19.4	120.6		30 (	
	STORATOLIC	$(Nm^{3}/h)$	(kVA) (DC)	7	PS	
	PURIFIER 100	0.8	4.6	VA	IG	
		(Nm <sup>3</sup> /h)	(kVA) (DC)		C	G
HIAT	CUSTOMIZE	1.9	11.1			iem
	R 100	(Nm³/h)	(kVA) (DC)			nar
	SUPPLIER	4.8	30.1			ıу
	100	(Nm³/h)	(kVA) (DC)			
	HYP	5-20	35-102		1450 - 580	
		(Nm <sup>3</sup> /h)	(kVA) (DC)		(PSIG)	
	HCS	420-2100	2-10	4.8	125	
		(Nm <sup>3</sup> /h)	(MVA)	$(kWh/Nm^3)$	435	
U TEC SVETEME	ME450	210		4.8 (1-W/h/NT3)	(PSIG)	
II-LEC STSLEMS		$(1 \times 10^{-7} / 1)$	(IVI V A) 1 5	(K W II/INM <sup>2</sup> )		
	3	$(Nm^{3/h})$	$(kV\Delta)(\Lambda C)$	N۸	ΝA	
		(1111/11)		11/1	11/1	

	ME	46.3-210	500-1.707			
		(Nm <sup>3</sup> /h)	(kVA) (AC)			_
		10	75	5.4 (kWh/Nm <sup>3</sup> )		
		(Nm <sup>3</sup> /h)	(kVA)(DC)		_	
		30	205	5.2 (kWh/Nm <sup>3</sup> )		
		(Nm <sup>3</sup> /h)	(kVA) (DC)		_	
	gEl	60	400	5.2 (kWh/Nm <sup>3</sup> )	580	
	PEM	(Nm³/h)	(kVA) (DC)		D (I	
Igas	MD	100	660	5.4 (kWh/Nm <sup>3</sup> )	[Sol	
		(Nm <sup>3</sup> /h)	(kVA)(DC)		G	
		160	1050 (kVA)	5.4 (kWh/Nm <sup>3</sup> )		
		(Nm³/h)	(DC)			
		320	2070 (kVA)	5.3 (kWh/Nm <sup>3</sup> )	-	
		(Nm <sup>3</sup> /h)	(DC)			
		100 up to	70		NA	_
Siemens	Silyzer	2000 (kg/h)	(MVA)			
		21 (kg/h)	1.25 (MVA)		507.6 (PSIG)	_
ALIKEWEL /ANDO	APS VO 06	200 (m1/min)	190			
AUKEWEL/ANDU S	ADS-AQ-00	500 (mi/mii)	(VA)(AC)			
DELINC CEL	UCDM	200 1500	(VA)(AC)			
DEIJING CEI TECHNOLOCV	порм	(m1/min)	INA			
TECHNOLOGI 7hongwui	70 4 2	$\frac{(111/1111)}{50.(m1/min)}$	20(VA)(DC)			
Znongrui	ZKAS	50 (mi/min)	50 (VA) (DC)			
	QLSC-H4	4	22			
Saikesaisi		(Nm <sup>3</sup> /h)	(kVA) (DC)			
	QLC	60-1000	(45-540)			
		(ml/min)	(VA) (DC)			$\sim$
Cawolo	150-600	150-600	70 - 300			É.
		(ml/min)	(VA) (DC)		Ň	na
Eason Industrial	GH	2-100	(12.88-469.2)			
Engineering Co.,		(Nm³/h)	(kVA) (DC)			
Ltd						
	ZDQ-12	12	90	NA		
PERIC		(Nm³/h)	(kVA)(DC)	r		
	CNDQ-(5-12)	5-12	40-120			
		$(Nm^{3}/h)$	(kVA) (DC)			
SENZA	SZPE	300-1200	80-260			
		(ml/min)	(kVA)(DC)			
ITM Linde	N/A	N/A	N/A			Germany
Electrolysis						-
Swiss hydrogen	PEM	1	6		435 PSIG	Switzerland
	electrolyser	(Nm³/h)	(kVA) (AC)			
Hydrogenics Corp	HyLYZER	1-5000	6.7-25000			Canada
		(Nm³/h)	(kVA) (AC)			
ITM Power	Hgas	0-2000	0-10			UK
	-	(Nm³/h)	(MVA)			
GreenHydrogen.dk	А	30-90	135-418.5		NA	Denmark
ApS		(Nm³/h)	(kVA) (AC)		r'	
McPhy Energy S.A.	NA	NA	NA			France
Giner Inc	NA	NA	NA			USA
Giner, Inc		11/1				USA

# 2.3. State of the art, obstacles and possible solutions regarding PEMWEs

Carmo *et al.* examine the new and old challenges relating to electrocatalysts, solid electrolytes, current collectors, separator plates, and modeling efforts. The structure of PEMWE is analyzed, materials are discussed, and the challenges are noted [23]. Shiva Kumar and Himabindu's paper

contains new studies, graphical comparisons, and PEMWE models [23]. Ayers's publication in "Current opinion in electrochemistry" is about the potential of PEMWEs and their associated components. A description of the performance of a typical electrolyzer can also be found in this paper [45].

HyPro using PEMWE can be tracked in review papers from 2004 when Zoulias et al. published a review article on WE with a deep insight into various techniques of that time and its history from 1789 [46]. Almost all review articles on electrolyzers are included in this section; most of these publications discuss PtG [47, 48], different methods of HyPro [49-55], and HyPro by RES [56-58]. For instance, Berstad et al. [59] review liquid hydrogen as a prospective energy carrier. They studied the impact of battery limits on hydrogen value chain studies and identified the knowledge gaps that need to be addressed. They also mentioned that it needs a comprehensively bottom-up approach to understand better the pros and cons of different hydrogen energy carriers. Shan et al. [60] have reviewed long-duration energy storage technologies. They mainly focused on projects that were commercially mature or industrialized. This work also compares modularity, long-term energy storage capability, and average capital cost with varying durations. Insights gained from this study can assist the development of long-duration energy storage projects, inspire use cases for different long-duration energy storage technologies, and be used to create a foundation for future relevant modeling and decision-making studies. Some highlight chemical and fundamental topics, which are the basis of PEMWE [61, 62]. HyPro in a particular country is also the subject of two publications [63, 64]. Some authors propose increasing the efficiency approach in a particular component or process, intensification [65], the definition of energy efficiency coefficient [66], verification of existing HyPro systems, and PEMWE models [67-69]. Other articles consider varying points of view, such as exergy attention [49], techno-economics [70, 71], economics [72],

transportation [73], special applications in space [74, 75], and specific supplements (geothermal [76], wastewater [77]). The number of all review papers that PEMWE is the main or part of their concerns is presented in Figure 2. From 2014-2018 and 2010-2014, the number of reviews has increased by over twofold and fivefold compared to 2018-2022, respectively, which illustrates that PEMWEs are becoming more popular. The main concern of all these publications is demonstrated in Figure 3, as no publication has not directly reviewed all possible ways of enhancing PEMWE efficiency.



Figure 2 Number of review papers on PEMWE and its associated components



Figure 3 The main concern of review papers

Based on the studies conducted on PEMWEs, their development challenges are mainly attributed to production costs, component durability, and high efficiency. Decreasing electrolysis costs is expected to make PEMWE technology more welcome [78]. Most publications point out the cost of platinum group metal (PGM) materials, such as iridium (Ir) and platinum (Pt), as the major

disadvantage, and researchers explore solutions [79, 80]. The PEMWE cost has experienced a dramatic reduction in recent years due to mass production and scaling up. Additional savings will be feasible based on technology advancements and manufacturing developments, similar to the PEM fuel cells pathway [81]. In addition, Young et al. prove that existing fuel cell materials and hardware can also be applied to PEMWEs, in particular cases adhering to the associated limitations [82]. Therefore, the existing fuel cell pathway can be tracked and transferred to the younger and rapidly growing PEMWEs. The evolution of PEMWE technology involves both process and material advancement, which are currently under investigation by scientists and engineers worldwide. Two significant system costs are manufacturing the PEMWE stack and the balance of plant (BOP). BOP expenses would account for about two-thirds of the total system cost. The share of these costs can be different for various electrolysis scales [83-85]. The final price of the stack mainly depends on cell power density, manufacturing process, membrane and its catalyst, the thickness of the transport layers. Figure 4 shows the general range of prices mentioned in the explored references. From this figure, the costliest part is the heart of the electrolyzer. Catalysts and membranes have an integrated design in new generations of PEMWE (Catalyst Coated Membrane (CCM)). However, if they were designed separately, they would be even more expensive. Secondly, various layers designed for mass and gas transfer are called Porous Transport layers (PTL). Finally, BPs are other costly parts of a stack.



Figure 4 Approximate shares of Influential components on a stack price

PEMWE materials and constructions are expensive, and their prices also fluctuate drastically. As illustrated in Figure 5, the PGM cost, a primary catalyst in PEMWE, fluctuates wildly. HyPro's large-scale by PEMWE faces severe obstacles because of the iridium demand and potential bottlenecks [86].



Figure 5 PEMWE catalysts (PGM)prices [87]

In addition to the cost, another criticism of the PEMWE is its acidic environment, which is responsible for corrosion, degradation, and reduced lifespan. [71]. The mechanisms of the individual component degradation are investigated by Feng *et al.* They showed significant failure in the PEMWE components (the catalyst/catalyst layer, membrane, current collector, and bipolar plate) [88]. The strategies to mitigate the degradation are also presented. Some methods to increase electrocatalyst stability are as follows: adding inert oxides, forming or single-phase alloy of binary or ternary catalysts, catalyst morphology tailored to the application, and increasing the adhesion between the catalyst layer and membrane via unique methods. They divided the membrane degradation into mechanical, chemical, and thermal degradation. Some solutions, such as reducing the creep characteristics of PFSA membranes, membrane reinforcement, or modification by incorporating reinforcement materials in polymer chemistry, are advised to be adopted. Current collectors and bipolar plates are susceptible to degradation mechanisms, such as corrosion,

embrittlement, and passivation. Furthermore, current collectors may be damaged by improper clamping force. BPs are coated by stainless steel (ss), advanced materials and compounds (e.g., metal nitride), and a new deposition to minimize the coating defects and decrease the component's expenses significantly. Furthermore, Stiber *et al.* [89] index that BPs and ss meshes can be used instead of the expensive porous structure of PTLs. Tajuddin *et al.* have shown how recycling can tackle specific acidic electrolyte problems with remarkable stability and relatively cheap prices [90]. In addition, Khatib *et al.* completely covered the material degradation of PEMWE components in a review paper and strategies for improving cells' durability and efficiency [91].

Shirvanian & van Berkel have published an exciting mini-review on the PEMWE limitations. The study is mainly about the performance and durability of different components. They considered long-term implementation and short-term strategies for decreasing costs and significantly improving lifetime [92]. Another problem listed for PEMWE is the water inlet. It must be purified for the current membranes, which can be detrimental to its reputation. Since desalination and water treatment are necessary before the initial process, more cost, technology, and time will apply consequently [51]. However, ongoing studies show efforts to make electrolyzers available to consume a more comprehensive range of H<sub>2</sub>O [93]. The main concern of papers that studied PEMWE problems are listed in Table 2, and the possible solutions suggested by the authors are also mentioned.

	Obstacle					
Perspective	Cost	Durability	Operating	manufacturing	Solutions and suggestions	Ref.
	~				Catalyst	[79]
					separation, recovery, and recycling	
PGM materials	~		~		replacement of conventional PGM	[90]
					metal catalysts with non-noble	
					metal catalysts	
					material reduction, substitution,	[80]
Techno-	~	~	~		scale-up, and learning by doing	
economic	~				large-scale, high-temperature	[71]
analysis (TEA)					technologies	
					source availability and	
					uninterrupted energy supply	
	~			~	material and process development	[81]
	~		~		Carbon paper as anode PTLs	[82]
					Avoid Contact between membrane	
					and graphite	
Technology		~		~	Mitigation and alleviating strategies	[88]
and					catalyst, membrane, current	
performance					collector, bipolar plate	

Table 2 summarizes the main indicated obstacles and their solutions in the discussed papers

	~	~	~	Adding inert oxides and forming a	
				solid solution	[91]
				reinforcing materials such	
				as polymer fibers	
				Coating the bipolar plate,	
				improving materials	
	~	~	~	reinforced membranes,	[92]
				overpotential operation,	
				stable support and coating	
				materials	
	~		~	chlorine evolving reaction,	[51]
Input water				utilization of ion-selective	
				membrane	
	~	~	~	ion crossover in direct saltwater	
				electrolysis, preventing cathode	[93]
				fouling and considering HER-	
				catalyst crystal structure,	
				morphology, and loading effects	

All in all, any efficiency increase in the electrolyzer will help raise the HyPro and reduce the cost of the process. Consequently, a lower cost, higher capacity, and more durable PEMWE system would be a technological leap that can lead to the higher application of the zero-carbon hydrogen for various applications. In this regard, no review article has explicitly looked at increasing PEMWE efficiency.

In this paper, several articles are reviewed to comprehensively define methods for improving the electrolyzer's efficiency. Numerous efforts have been made to enhance the PEMWE efficiency, durability, and affordability. The roots of most of these methods offer material science or chemistry solutions to study and improve electrolyzer fundamentals. However, some suggest energy management or integration with other systems. Furthermore, some studies work on the flow system with a fluid mechanic approach (Figure 6).

## 3. Increasing PEMWE energy efficiency

Considerable efforts have been made to enhance the efficiency of PEMWEs. The roots of these studies for increasing PEMWE efficiency are represented in Figure 6. From this figure, It is evident that the four main science branches that can increase PEMWE efficiency are; Chemistry, Material science, Electrical engineering, and Fluid mechanics. It also illustrates that the studies on PEMWE are in three main areas: in-situ, ex-situ, and as a black box. First, in the in-situ research, a part of PEMWE or an action is studied in its original place. Second, ex-situ is the investigation of a section, component, or phenomenon out of the PEMWE and separately from the other parts. Finally, from the black box point of view, the researcher studies the PEMWE as a whole system and analyzes it with inputs and outputs. Lamy and Millet have studied the rate of energy efficiency by collecting various coefficients. Their work focuses on the most common electrolyzers near ambient temperature [66]. Other authors also employ process investigation, exergy calculation, and alternative methods to increase efficiency. Burton *et al.* have reviewed various methods, including hybrid coupling technology, magnetic fields, light energy, ultrasonic fields, and pulsating electric fields, to realize their effect on the efficiency of HyPro using RESs [94].



Figure 6 Various science branches that can increase different parts of PEMWE efficiency

# 3.1. Operation conditions

The main electrolysis process in a PEMWE takes place in its stack, where operation occurs by gas interaction and mass transfer. [95, 96]. The influence of different operating conditions on the performance of PEMWEs has been investigated in different papers and is shown in Table 3. According to this table, several studies have focused on the effect of operational conditions and input currents on the PEMWE efficiency. Moreover, other factors have been influential, including temperature, pressure, flow rate, and current density. In this regard, Fritz *et al.* [97] focused on the

simulation of capturing the performance of a PEMWE model operating at high current densities. Their study entailed predicting membrane proton transport and accurately studying the mass transport and ohmic losses under electrolyzing conditions. Marangio et al. analyzed different new objectives for PEMWE performance. First, a break-even value of the operating pressure in the range of 30-45 bar was considered. Second, a new design with a metal foam layer as the support at the anode side of MEA was successfully tested and validated [98]. Toghyani et al. studied different design parameters and operating conditions to analyze the performance of PEMWE at the steady-state condition with a three-dimensional numerical model. They have done one of the most comprehensive research by surveying temperature, pressure, gas diffusion layer (GDL) thickness, and membrane thickness. At a voltage of 1.65 V, temperature varies from 373 K to 403 K, the maximum HyPro from  $1.9 \times 10^{-4}$  to  $2.2 \times 10^{-4}$  mol/m<sup>3</sup>. GDL change from 0.2 mm to 0.5 mm decreased current density from 0.426 A/cm<sup>2</sup> to 0.40 A/cm<sup>2</sup>. Thickening membrane from 50 to 200 µm caused a drop of current density from 0.32 to 0.16 A/cm<sup>2</sup>. Operating pressure variation from 5 bar to 20 bar led to higher open-circuit voltage and the partial pressure of different species responsible for reducing the charge transfer rate and, consequently, the inferior performance of the PEMWE [99].

In [100], the influence of temperature, pressure, and flow rate in two different cell designs (with and without flow channels on the anodic side) was presented. Five different PTL structures were also investigated by analyzing the polarization curves. Lickert *et al.* observed significant differences in the performance between the two cell configurations. The electrolyzer performance without a flow field was with lower pressure and temperature, and consequently, the flow rate increased. However, they observed significant losses for incomplete removal of oxygen gas induced by anodic PTL. Finally, they announced that the transport properties related to porosities and particle/fiber diameters as PTL characterization and the in-plane and through-plane permeabilities should be measured to characterize PTL structures for PEMWE properly. A uniformly distributed heat, mass, and charge system is explained by Olesen *et al.* [101]. They studied a high pressure and high current density operation of PEM electrolysis cells using a dynamic flow approach. The effect of gravity has been examined by Choi *et al.* [102]. They studied different parameters by the orientation of the cell, and the gravity impact on the electrolyzer performance was explored. It was concluded that the single serpentine channel affected the performance at high current density (about 8.3% more than the quintuple serpentine channel). Moreover, the two-phase flow regime of water and oxygen in this channel and the PTL varied with the cell orientation. It was also noticed that it did not affect the performance of the PEMWE cell with the quintuple serpentine channel because its active areas did not vary with the cell orientation.

	Op	oerating	conditio	ons		
Main study	Pressure	Temperatu	Current	Transport	<b>Result/Suggestion</b>	Ref.
Water transport		~	~		Calculation of electro-osmotic drag	[95]
					coefficient, mass flow rate equation	
					of discharged water with hydrogen	
					in a cathode	
Bubble				~	Observation with Synchrotron	[96]
formation and					radiography	
					new transport pathways	

Table 3 operating conditions and their influence over the performance of the PEMEW

porous						
structures						
Zero	~	~		~	prediction of the ohmic losses,	[97]
dimensional					maximizing the conductive contact	
simulation					areas	
Manufacturing	~	~			new activity should aim at a	[98]
					pressure of about 30–45 bar and	
					higher temperatures	
Thermal and	~	~	~		Best size of membrane, GDL,	[99]
electrochemical					catalyst for highest performance in	
performance					the sample	
			~	~	the in-plane and through-plane	[100]
Anodic PTL					permeabilities should be measured	
					in order to properly characterise	
					PTL structures	
Heat and	~	~	~	~	electrochemical performance	[101]
charge					parameters for obtaining the highest	
transport in the					accuracy	
anode and						
membrane						
The pattern of		~	~		high operating temperature and low	[102]
anode channel					flow rate reduce the activation and	

and effect of		ohmic losses, and bubble coverage	
gravity		on the catalyst should be reduced	

Two influential operating parameters of PEMWEs are pressure and temperature because they affect various components [103, 104]. It has always been a question for designers and researchers about the relationship between temperature, pressure, and maximum efficiency in different systems. Should the operating pressure or temperature be higher, or an external process is necessary for compaction? Tjarks *et al.* tried to find the answer about PtG systems with electrolyzer pressure levels up to 20 bar. They studied the overall PtG plant's energy demand optimization, considering compression and temperature swing adsorption (TSA). They concluded that a particular optimum pressure exists for various operating conditions in the electrolyzer, which depends on the stack's current density and the hydrogen storage pressure [105]. Some authors expressed how the high-pressure PEMWE operation eliminates the need for external compression in the HyPro process. Saebea *et al.* showed the advantage of delivering hydrogen at high pressure with a more negligible effect on performance and low power requirement by simulating the PEMWE based on an electrochemical model [106]. Scheepers *et al.* investigate the capability of PEMWE membrane for efficiency improvement [107].

A mini-review of the high-pressure PEMWE system until 2014 can be found in the introduction of Bensmann *et al.*'s paper [108]. Then, three possible thermodynamic models are energetically evaluated in this work. The models are named pathways and are compared by balances for energy, entropy, and mass. Finally, they mentioned the importance of this evaluation in decreasing the costs and lessening the process, especially compacting the gas, as they studied PEMWEs up to 40 bar. Kim *et al.* predicted high-pressure PEMWE behaviour for gaining the advantage of a new generation of large-scale electrolyzers by developing a one-dimensional dynamic model. They studied voltage-current relations, overvoltages, water and gas permeation through the membrane, 1-D profiles of two-phase flow, temperature, concentration in the anode and cathode channels, and profile over the MEA [109]. In 2021, Afshari *et al.* worked on a mathematical model of PEMWE (a combination of electrochemical, and fundamental thermodynamic relations) [110]. They studied the crossover phenomenon, water transferring mechanisms, and diffusion concentration. Their final goal was to improve electrolyzer efficiency by controlling voltage loss, so the contribution of electrodes, BP, and membrane resistance to electrolyzer performance was examined. They have also investigated the influence of membrane thickness, cathode pressure, and temperature on the anodic hydrogen content. So, they showed a significant reduction in hydrogen crossover from cathode to anode due to a thicker membrane, whereas a larger cathode pressure will result in an increased rate of crossover as the pressure difference between anode and cathode channels increases, at a current density of 10,000 A/m2 results in 85% and 3% contribution of concentration and activation over potentials, respectively.

#### **3.2. Stack components**

A stack primarily consists of the membrane, electrodes, catalyst, TLs, and BPs. A general view of a cell from a PEMWE stack is shown in Figure 7. However, thanks to new research and cuttingedge technology in unique modern designs, some components can be added, and some can be changed or removed.

# A. Membrane

The membrane is one of the stack components in the heart of the PEMWE cell. Its superior performance will increase system efficiency. This part can be developed by replacing more appropriate materials [111, 112] or using new electrochemical and physicochemical techniques

[113]. The coated membrane with catalysts, such as Iron(Fe) and Nickel (Ni) [114] porous titanium[115], decreases the level of corrosion and increases the efficiency and durability [116].



Figure 7 PEMWE stack components

# B. Catalyst

The Catalyst Layer (CL) in CCMs is another important PEMWE cell component. Currently, almost all PEM electrolyzers use expensive PGM catalysts. They are expensive, and their degradations are costly [117]. So, replacing them with low-cost [118], earth-abundant [119] non-precious catalysts, such as molecular catalysts [120], metal cobalt phosphide (CoP) [121], MoS<sub>2</sub> based materials [122] and [Mo<sub>3</sub>S<sub>13</sub>] clusters anchored to N-doped carbon nanotubes [123], seems reasonable. Iridium, Titanium, and Platinum compounds, as well as new versions of these compounds, offer substantial improvements through the use of cutting-edge technology. For example, iridium core/shell catalysts via galvanic exchange [124], nano-size IrOx catalyst with high activity and stability [125], N–TiO<sub>2</sub> nanofibres [126], or simply applying aerogel supports to them [127].

Performance and durability at the cell level are not only affected by individual components but also by fabrication methods. In addition, the parameters during fabrication also matter, impacting the CL morphology [128, 129]. Alia et al. examined the effects of ink and ultrasonic spray variables on CL properties, PEMWE performance, and durability. These parameters include the ionomer content, solid concentration, solvent ratio, pump rate, and drying temperature. It was found that kinetic performance was greatly affected by changes in ionomer quantity or dispersion. As a result of increased ionomer concentrations and poor ionomer incorporation (catalyst-ionomer segregation), the kinetics have been slowed, likely because the ionomer limits access to the Ir sites. Besides, inconsistencies in catalyst layer thickness adversely affected ohmic loss, possibly by reducing catalyst layer-PTL contact and increasing contact resistance [130]. For enhancing the CL engaging and optimizing catalyst service even at high current density, transport resistance should fall, and as a result, protonic and electronic conductivities rise [131]. It applies to electrolytes, and their concentration will help their conductivity and increase their performance [132].

# C. Gas Diffusion Layers

The next layer in PEMWE is the GDL. There is a lengthy research background [133] about it, a vast improvement potential [134, 135], and studies on reducing its costs [136]. Accumulating oxygen gas in PEMWE transition layers is a severe obstacle to achieving higher efficiencies. For facilitating mass transport and increasing electrical conductance, a porous layer is ingrained in the design of PEMWE, which is named PTL [137]. Research is still ongoing in this area to raise the

benefits of PTL [138]. Lee *et al.* have collected these studies and focused on PTL mass transport losses in PEMWE to improve efficiency [139]. PTL development can diminish mass transport losses, increase catalyst utilization and minimize the ohmic and kinetics losses of the PEMWE [140].

A common problem in the flow of the PEMWE cell potential in high current density is called the mass transport limitation (MTL). It decreases PEMWE efficiency by crippling transport in the PTL. Panchenko et al. studied this effect on mass transfer processes comprehensively with neutron-based imaging (neutron visualization techniques). They observed different in-situ stoichiometries during the absorption of polarization curves. The importance of their study lies in the optimized and efficient cell design [141]. In their publication introduction, Kim et al. have brought a valuable review of PTL and CL techniques and materials until 2022. They presented a new method of PTL and CL combination. They described it as tailoring the CL interfacial contact in a PEMWE with bilayer titanium mesh PTL [142]. Ojong et al. have a compelling discussion about predicting the PEMWE cell operation without a flow channel in PTL. They developed this subject by studying coupled momentum, heat, and mass transport phenomena on a semiempirical non-isothermal model [143]. Parra-Restrepo et al. studied the effect of the PTL and CL properties on the mass and charge transfer in a PEMWE. They demonstrated that the PTL optimal outlet depends not only on the operational condition of the PEMWE but also on the thickness and the electrical conductivity of the CL. Based on this fact, they proposed a new model for the constriction resistance between the CL and the PTL. [144].

## **D.** Bipolar Plate

The last key element of the PEMWE is the BP (Bipolar Plate). This multi-functional component uniformly distributes air and liquid, manages electrical current from cell to cell, controls heat, and prevents gases and coolant leakage [145, 146]. They must have the least interfacial contact resistance and high resistance counter corrosion to withstand the operational conditions within the stack. Furthermore, a coating layer may also be necessary for BPs [147]. These detailed considerations have made a relatively expensive part out of BP [148].

On the other hand, cost reduction of stack components in PEMWEs is a priority nowadays. So, inexpensive materials coated with anti-corrosive layers can be desired to replace conventional BPs, reduce cost, and hopefully increase performance [149-152]. Taner *et al.* (2019) performed a prototype HyPro study using PEMWE, and the result shows that this system can produce H<sub>2</sub> about 4.5 times more efficiently than the other systems. PEMWE with a magnet (Cr-C Coated SS304 BP) shows higher efficiency than the bare one [153]. As a result of advances in manufacturing technology and 3D printing, electrolyzers, BP, and some integrated components are now being produced [154].

#### E. Charge transfer in cell components

Investigating the Charge Transfer Coefficient (CTC) is essential in anticipating electrolyzers' current-voltage characteristics. Furthermore, this estimation provides insight into the electrode properties. Biaku *et al.* studied the temperature dependency of the oxygen electrode CTC of a commercial PEMWE stack [155]. Tijani *et al.* evaluated the operating temperature effects on the CTC and its consequences on the operating voltage of PEMWE. Their study is essential in PtG systems where activation overpotential plays a crucial role in the operating voltage. Their study results show that CTC's value increases at higher operating temperatures. However, it enhances the anode more significantly than cathode electrodes. In addition, it was observed that pressure does not significantly affect CTC at each electrode [156]. In the next step, they investigated the effect of exchange current density and CTC on PEMWE performance and its polarization. They

demonstrated that CTC needs are lower in higher exchange current density, so less activation overvoltage and, subsequently, lesser operating voltage systems are required. In simpler terms, using overvoltage in PEMWE will be more efficient, and all the excess energy capacity can be used in this design. They also completed studies on the relation between temperature and CTC, primarily effective on the oxygen electrode [157]. Table 4 demonstrates different solutions for improving PEMWE performance, and the viewpoints of different studies are also explained.

Component				Ref.		
membra	CL	TL	BP	Focus	Results or Effects	
~				Solid acid	high proton conductivity at temperatures above 130 °C	[111]
~				Nafion properties (Review)	high-pressure operating	[112]
~				Degradation issues Hot pressing treatment	Mitigation/ Better performance and stability	[113]
~	~			catalyst-coated membranes	increaseperformance and durability	[114- 116]
	~			ultra-low catalyst loading	Insights on the degradation mechanism	[117]
	~			IrO <sub>2</sub> /TNO anode catalyst	low cost and efficient	[118]

Table 4 different ways for efficiency enhancement by each of the stack components

			Earth-Abundant	efficient and stable	[119]
	~		Electrocatalysts		
	~		Molecular catalysts	tolerate high acidity	[120]
			Cobalt phosphide	potential pathway for	[121]
	~		(CoP)	commercial applications	
			low-cost, non-precious		
	~		MoS <sub>2</sub> -based catalyst	reasonable and promising	[122]
			[Mo <sub>3</sub> S <sub>13</sub> ] <sub>2</sub> clusters	Cost reduction	[123]
	~		anchored to N-doped	high-performing and stable	
			carbon nanotubes		
			Iridium Core/Shell	emphasize the	[124]
	~			manufacturing feasibility	
			Nano-size IrOx	cost-effective,	[125]
				outstanding activity for	
	~			oxygen evolution reaction	
				(OER) and stability	
	~		N-TiO <sub>2</sub> Nanofibres	High Efficient HyPro	[126]
	~		SnO <sub>2</sub> :Sb aerogel OER	Better activity and stability	[127]
			Reducing anode	maximizing catalyst	[131]
			catalyst layer proton-	utilization at the high	
~	~		and electron-transport	current density	
			resistances		

				Electrolyte	increasing electrolyzer	[132]
~	~			Concentration	efficiency	
				GDL review	improving process	[133,
		~			efficiency	134,
						137]
				modified titanium	calculate the porosity	[135]
		~		porous matrix		
				Transport perspective	visualize the morphology	[138]
	~	~		Radiography, CT	and oxygen transport	
				Mass Transport Losses	minimize small capillary	[139]
					effects	
		~			and reduce large slug	
					formation	
		~		Neutron spectroscopy	cell visualized in-situ	[141]
				Tailoring catalyst with	Maximize interfacial	[142]
	~	~		titanium mesh	contact area	
				Channel-less PEMWE	costs advantage, mass	[143]
~	~	~		cell	transport constitutes	
				Mass and charge	Optimal performance	[144]
		<ul> <li>✓</li> </ul>		transfer		
				Pressure and velocity	pressure drops diagonally,	[145]
			~	distributions		

			Design, material, cost	the coating layer is	[146]
		~		necessary to protect the	
				substrate	
			pH value, titanium	Improve the adhesion of the	[147,
		~	coatings, plasma	coating, Stable	148]
			processing		
			Electrochemical	the formation of a very	[149]
			Evaluation, Niobium	stable, low	
		~	Corrosion Resistance	porosity, the protective	
				oxide layer	
			Additive manufacturing	possibility to design new	[150]
		~		and more complex flow	
				distribution channels	
		~	Coated stainless steels	Corrosion resistance	[151]
			Carbon-coated stainless	solution for the large-scale	[152]
		~	steel	application	
			Cr-C Coated SS304	more efficiently and	[153]
		<ul> <li>✓</li> </ul>		economically	
			all-in-one bipolar	compact and efficient	[154]
~	~	~	electrode		

# 3.3. System function, configuration, control, and energy management

PEMWE has also been studied from other perspectives, considering system control, energy, and configuration efficiency analyses. Preliminary studies on PEMWE efficiency have encountered severe obstacles such as electrode pressure increase, electrode destruction, membrane melting, membrane drying, overheating, or membrane rupture [158]. Zhang *et al.*'s design with a thermodynamic and electrochemical outlook improves the system's overall performance, avoiding irreversible losses. Interestingly, they expressed how the efficiency of their developed configuration was higher than the conventional system, which directly released redundant heat into the environment. PEMWE efficiency increases by surging the impact of the heat exchanger and working temperature. In contrast, the efficiency is reduced by the increase in the electrolyte membrane's thickness and the inlet water flow rate [159].

Koponen *et al.* studied control and energy efficiency in a commercial PEMWE system powered by PV. They proved that wise pressure selection and control of PEMWE operation could minimize consumption and maximize the real HyPro. They doubled the hydrogen outlet pressure and observed that the electrical energy consumption did not significantly increase. However, the specific energy consumption of the stack has increased significantly. In addition, they concluded that attention to the PEMWE system's dynamic control would prevent accelerated cell degradation [160]. A standard evaluation method for the performance of electrolyzers is to focus on fluid flow. The fluidic phenomena that occur continuously in an electrolyzer can be modeled with Energetic Macroscopic Representation (EMR) viewpoint [161]. Computational Fluid Dynamics (CFD) is a known branch of fluid mechanics that equips researchers with numerical analysis and algorithms to simulate the whole or part of PEMWE. For instance, using CFD, Upadhyay et al. provided a deep insight into the flow pattern factors by assessing the anode flow field hydrodynamic behavior. They considered the velocity value of the inlet and outlet port configuration in a new circular PEMWE design. Furthermore, their findings helped the understanding of a uniform velocity outline, maintenance of the desired temperature, reduced pressure drop, and active removal of oxygen bubbles effectively. [162].

Olivier *et al.* developed a new model using the bond graph tool for improving PEMWE entire system design for green HyPro, considering its exposure to intermittent electrical sources [163]. Martinson *et al.* also focused on RES nature and the current interrupt method on the electrochemical characterization of PEMWE. They announced that increasing the working current density and temperature decreases concentration losses [164].

Another solution proposed to increase system efficiency is using control strategies to protect the electrolyzer against overvoltage, ensure input capacitors in dynamic operations, manage ripples current and voltages, and increase reliability, durability, and efficiency [165, 166]. For instance, Parache et al. observed a rise in ohmic resistance, titanium mesh corrosion and passivation, and mass transport limitations. These effects seem to increase by triangular current ripples[167]. Various parameters can be determined by accurately modeling the PEMWE [168-177]. Dang et al. [178] have represented a high-differential pressure PEMWE zero-dimensional steady and dynamic model with high accuracy by calibrating a 0-700 bar pressure electrolyzer at different cathode pressures and temperatures. Some unclear parts of previous models, such as the concentration overpotential in the voltage composition, the cathode water flow problem, the double-layer, and mass transfer lag effects, are also considered in their study.

Load modeling is essential for control goals, increasing system efficiency, and improving performance [179-182]. Yodwon *et al.* reviewed PEMWE various load modeling with a control approach and their comparison [183]. Keow and Chen used an automated adjustment approach to establish an online proportional-integral control. In simple terms, they achieved the desired current

output by automatically adjusting the voltage applied to the PEMWE. The PEMWE inlet is a nonlinear voltage and current, so its properties need to be investigated and controlled. They evaluated and compared two tuning methods, Ziegler–Nichols and phase margin [184]. Other authors, such as Fuzzy Logic Control (FLC), relied on water temperature to control and optimize the PEMWE system, such as Fuzzy Logic Control (FLC) [185]. Wirkert *et al.* mainly focused on heat management and how it affects PEMWE efficiency. They developed a high-performance modular PEMWE system operation, dynamic high-pressure HyPro.

Moreover, the process water was experimentally validated regardless of heat management. They claimed that future industrial-scale PEMWE stacks with optimized media flow homogeneous operation conditions over a wide dynamic pressure range can be constructed using their presented design approach. At the same time, a high degree of modularity provided complete flexibility for individual system design [186].

Caparros Mancera *et al.* proposed a logic control design to maximize efficiency by evaluating operational factors, observing the environment, and quality testing. The BoP is also considered in power engineering. They tried to find a meaningful relation between performance and minimal BoP in PEMWE [187].

## **3.4. Different Sources and Hybrid Systems**

The efficiency of systems can sometimes be increased by integrating multiple electrical sources to ensure a non-stop operation or by combining two or more configurations for maximum effect. This section presents publications that meet these criteria. One of the advantages of PEMWE is production despite intermittent electrical sources and accepting RES as the power source. However, increasing the system's capability to connect this type of electrical current can significantly raise its efficiency [188, 189]. Since most designs of PEMWEs operate with low voltage and high current, converters using strategies such as LLC resonant can play a vital role in integrating electrolyzer with a power source [190].

PEMWEs are the most well-known sources of HyPro power supply from RES. If they are assumed as the primary power source, as shown in Figure 8, power network and individual batteries are overcharged in some terms. Hence, the overpower of powerline, standalone batteries, and even active consumers can turn into green hydrogen. PVs most often supply PEMWEs and therefore electrolyzers' performance in this arrangement is consistently attractive [191]. Optimal coupling approaches have been proposed by Yang *et al.* to improve the HyPro efficiency using a strategy called direct coupling and increasing leakage resistance [192]. Some authors researched particular combinations with PEMWE, such as concentrating solar plants [193], Photovoltaic Thermal (PVT) [194], and PV directly coupled with PEMWE [195].



Figure 8 Different sources and systems that can be combined with PEMWE

In recent years, hybrid RESs are becoming prominent in the energy sector for achieving more sustainability, especially in standalone systems. So their integration with PEMWE is the subject of new research [196]. As RES's capacity factor is usually low, combining different sources will be helpful. One of the successful scenarios of hybrid sources for PEMWEs is the combination of wind turbines and PV arrays [197]. Zaik & Werle [198] have published an experimental methodology review about PEMWE HyPro with RES. However, the main body of their paper is about a PEMWE running with wind and solar in Poland. Their system produces 158.1 (cc/min) hydrogen with an average efficiency of 69.87%. So, wind energy is another renewable source of power for PEMWE [199]. This continuous energy source will increase the efficiency of HyPro. Seyam *et al.* worked on optimizing a multi-objective hybrid RES supplied by solar panels, wind turbines, and an absorption cooling system. They expressed that they achieved more than 65% of

energy and exergy efficiency [200]. Geothermal is another renewable source that can be combined with PEMWE [201]. This technology brings both fresh water and hydrogen simultaneously. These systems usually use a flash-binary geothermal and Organic Rankine Cycle (ORC) [202]. Alirahmi et al. [203] have equipped ORC-PEMWE system with a lithium/bromide absorption refrigeration cycle. The most influential parameters in their multi-generation system outputs are: geothermal fluid mass flow rate, geothermal fluid temperature, ORC turbines inlet temperature, and evaporator pinch-point. In some studies on power optimization of the geothermal flash systems with Dualpressure Organic Rankine Cycle (DORC), hydrogen generation performance in the PEMWE is also investigated [204, 205]. Mehrenjani *et al.* [206] used liquefied nature gas (LNG) for the stream as a heat sink. Using this method configuration combined with a PEMWE leads to HyPro and liquefied it through a Claude cycle. Their introduced system produces up to 106.8 kg/h of hydrogen, which can be raised to 154.95 (kg/h) due to optimizations.

According to some research, the overall efficiency of systems can be increased by merging them. Furthermore, hydrogen is often generated along with other products in these systems [207]. For instance, Marefati & Mehrpooya polygeneration system based on PV, PEMWE, PEMFC, and thermoelectric device electrical efficiency is 53.3%, it provides the electrical, thermal and cooling demand [208]. A combination of PEMWE and PEM Fuel Cell (PEMFC) seems to provide sustainability of energy and temperature [209, 210]. Pirom & Srisiriwat [211] used this combination and Photovoltaic for a residential house with a compelling overall system efficiency between 1.75% and 7.66%. Freshwater as a byproduct of PEMFC was also available for the netzero emission residential house. Several proposed system produce fresh water, cooling or heating along side with hydrogen using solar heliostat [212], parabolic solar collectors [213, 214], geothermal power [215, 216], solar plus geothermal [217], solar plus wind plus geothermal [218], biomass [219] for renewable electricity generation. Moltames *et al.* expressed that the results of this system optimization were a 22.32% and 8.61% increase in energy and exergy efficiency, respectively. Moreover, the cost rate of the entire system was decreased by 6.65% [220]. Armas-Calderón et al. introduced a hybrid system consisting of a PEMWE, a thermoelectric generator, and a dual-fuel engine. They showed that the overall system would have better exergetic efficiency by integrating this hybrid system. After obtaining positive results, the optimal operating conditions of each subsystem and their behavior were analyzed by varying the effective parameters on their performance [221]. Some systems are more complex and need multi-criteria analysis [222-225]. Zoghi et al. designed a novel biomass-driven multi-generation system to simultaneously produce power, heating, cooling, and hydrogen. They employed a thermoelectric generator, PEMWE, a modified Kalina cycle for power and cooling production. Then they investigated their system from energy, exergy, exergoeconomic, and environmental approaches, which sounds better than other systems. However, there was no clear result to compare original subsystems without this combination, which is necessary for professional conclusions [226]. Table 5 shows various systems integrated with PEMWE, and the total performance, efficiency, cost, or function has been changed. These inventions will give modern energy systems a higher level of flexibility, especially in zero-carbon or low-carbon systems.



Table 5 Hybrid PEMWE systems with their properties







# 4. Future perspectives

The previous chapter mentioned that increasing PEMWE energy efficiency depends upon different scientific disciplines, so improvements in any of these areas will improve PEMWE efficiency. However, multidisciplinary studies also made significant impacts. According to Figure 9 and the PEMWE trajectory, efficiency, durability, and cost are three main domains that should be considered in future studies.

- Although there has been some progress, further study of the new chemical compounds for catalysts remains essential.
- Material science is expected to make the most remarkable contributions to increasing the efficiency of electrolyzers, meaning new designs of the electrolyzer and its components interfaces can be made with modern materials, such as nanomaterials. The studies of membranes, electrodes, TLs, PTLs, and BPs, are highly recommended.
- The study of independent cases with unique circumstances, as demonstrated in several articles, is strongly suggested in control and the studies on PEMWE operational conditions, since each situation has its formula to thrive and be most effective.
- PEMWE technology in renewable energy storage is in its infancy and has much potential. So it is a valuable recommendation for future scientific investigations and environmentally sustainable energy systems. Another practical recommendation is to study hybrid renewable sources for continuous HyPro in further details.
- Some systems can be integrated to boost efficiency and reduce waste, as was discussed in the last chapter. Therefore, future studies should utilize all available capacities to maximize the entire system's efficiency.



Figure 9 Future trends of PEMWE for increasing the efficiency

# 5. Conclusions

Hydrogen will undoubtedly play an essential role in the zero-emission energy system of the future. Electrolysis is a valuable technology used as an energy carrier generator, forming future energy systems to cross the age of fossil fuels and take advantage of the zero-carbon energy system. The PEMWE is considered one of the best instruments for HyPro from RESs due to its reliability. Although the technology is still in its infancy, many improvements are needed to increase durability, performance, and efficiency. Therefore, it seems necessary to give experts in various branches of knowledge a general idea of the situation to determine their capabilities for increasing PEMWE efficiency. In this regard, different concepts of boosting PEMWE efficiencies, such as chemistry, materials, mass and energy transfer, electrical control, power sources, and hybrid systems, are reviewed in this manuscript. Each mentioned concept is explained by summarizing the performed studies in this line of research and development and interpreting their results and discussion. Lastly, five research axes are introduced as the guidelines for future endeavors to enhance the efficiency of PEMWEs.

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