

# Hydrogen production by PEM water electrolysis – A review

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## ABSTRACT

Hydrogen is the most efficient energy carrier. Hydrogen can be obtained from different sources of raw materials including water. Among many hydrogen production methods, eco-friendly and high purity of hydrogen can be obtained by water electrolysis. However, In terms of sustainability and environmental impact, PEM water electrolysis was considered as most promising techniques for high pure efficient hydrogen production from renewable energy sources and emits only oxygen as byproduct without any carbon emissions. Moreover, the produced hydrogen ( $H_2$ ) and oxygen ( $O_2$ ) directly used for fuel cell and industrial applications. However, overall water splitting resulting in only 4% of global industrial hydrogen being produced by electrolysis of water, mainly due to the economic issues. Nowadays, increased the desire production of green hydrogen has increased the interest on PEM water electrolysis. Thus the considerable research has been completed recently in the development of cost effective electrocatalysts for PEM water electrolysis. In this present review, we discussed about the recent developments in the PEM water electrolysis including high performance low cost HER and OER electrocatalysts and their challenges new and old related to electrocatalysts and PEM cell components also addressed. This review will contribute further research improvements and a road map in order to support in developing the PEM water electrolyser as a commercially feasible hydrogen production purpose.

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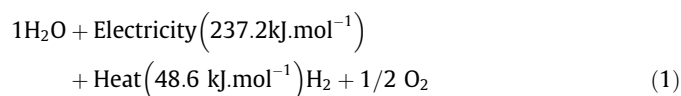
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## 1. Introduction

Nowadays global energy consumption was increased gradually due to the growing the population and standards of living style. Moreover, with increasing the global warming and environmental pollution, the development of renewable energy sources was becoming more essential. Hydrogen is one of the most promising clean and sustainable energy carriers and emits only water as a byproduct without any carbon emissions [1]. Hydrogen having many attractive properties as an energy carriers and high energy density (140 MJ/kg) which is more than two times higher than typical solid fuels (50 MJ/kg) [2]. Presently, the entire worldwide hydrogen production is around 500 billion cubic meter (b m<sup>3</sup>) per year [3,4]. The produced hydrogen is mostly used in many industrial applications, such as fertilizers, petroleum refining processes, petrochemical, fuel cells, and chemical industries [5–8]. Hydrogen has been produced from various renewable and non-renewable energy resources such as fossil fuels, especially steam reforming of methane [9–11], oil/naphtha reforming [12–14], coal gasification [15–17], biomass [18–21], biological sources [22–25] and water electrolysis (WE) [26–28]. The various comprehensive hydrogen production methods (Fig. 1) along with their advantages, disadvantages, efficiency and capital cost are provided in Table 1. Currently ~96% of the global hydrogen production from non-renewable fossil fuels, in particular steam reforming of methane [29,30]. However, the usage of fossil fuels, they produces lower purity of hydrogen with high concentration of harmful greenhouse

gasses [31–33]. Further, the unremittingly growing the global energy needs and the limited reserves of fossil fuels together with sustainability and environmental impact need to be develop new energy approaches without any carbon emissions. Nowadays has taken attention as an environmental friendly energy strategies which possibly to replace the current fossil fuel based energy production [34], this can be achieved by when the hydrogen is produced from the renewable water. Among many hydrogen production methods, eco-friendly and high purity of hydrogen (99.999%) can be obtained from electrolysis of water to produce pure hydrogen and oxygen it is called as water electrolysis. The basic reaction is described in Eq. (1).



However, hydrogen production efficiency through water electrolysis is very low to be economically competitive due to the high energy consumption and low hydrogen evolution rate. Therefore in order to increase the efficiency and reduce the energy consumption, many researchers have been done their work related to development of alternative low cost electrocatalysts, efficiency and energy reduction. In this review, various hydrogen production methods from renewable energy sources along with recent developments on efficiency, durability, cost effective electrocatalysts and its challenges have been discussed and summarized.

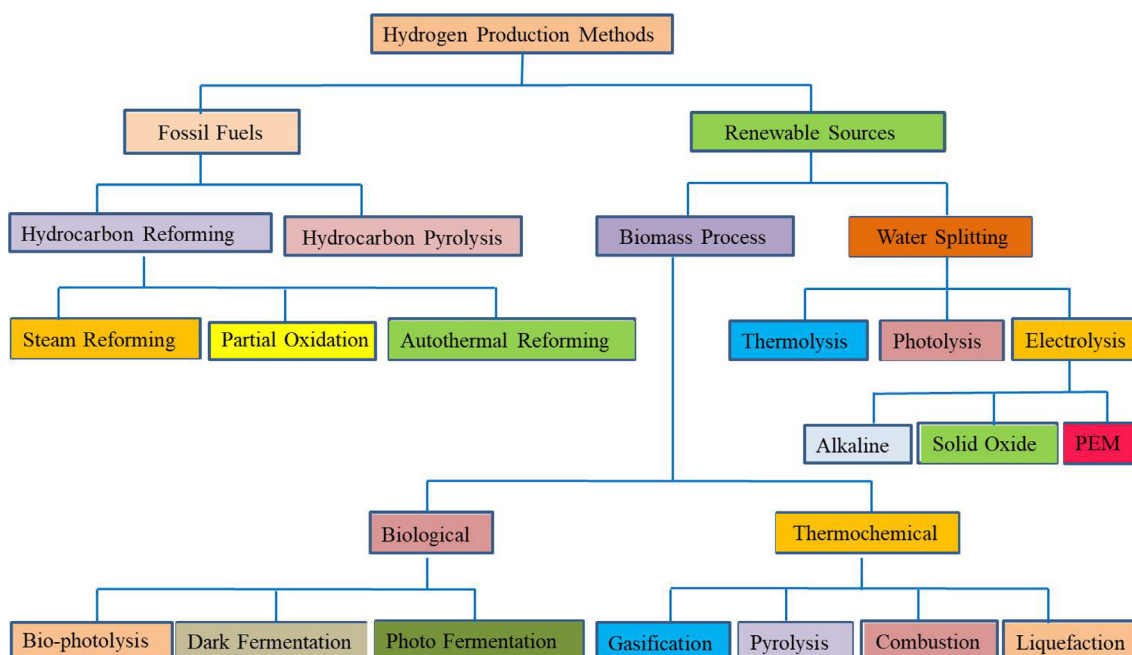


Fig. 1. Various Hydrogen Production Methods.

**Table 1**

Various Hydrogen production methods along with their advantages, disadvantages efficiency and cost [Refs. [2,4,5]].

Hydrogen production Method	Advantages	Disadvantages	Efficiency	Cost [\$/kg]
Steam Reforming	Developed technology & Existing infrastructure	Produced CO, CO <sub>2</sub> Unstable supply	74–85	2.27
Partial Oxidation	Established technology	Along with H <sub>2</sub> Production, produced heavy oils and petroleum coke	60–75	1.48
Auto thermal Reforming	Well established technology & Existing infrastructure	Produced CO <sub>2</sub> as a byproduct, use of fossil fuels.	60–75	1.48
Bio photolysis	Consumed CO <sub>2</sub> , Produced O <sub>2</sub> as a byproduct, working under mild conditions.	Low yields of H <sub>2</sub> , sunlight needed, large reactor required, O <sub>2</sub> sensitivity, high cost of material.	10–11	2.13
Dark Fermentation	Simple method, H <sub>2</sub> produced without light, no limitation O <sub>2</sub> , CO <sub>2</sub> -neutral, involves to waste recycling	Fatty acids elimination, low yields of H <sub>2</sub> , low efficiency, necessity of huge volume of reactor	60–80	2.57
Photo Fermentation	Involves to waste water recycling, used different organic waste waters, CO <sub>2</sub> -neutral.	low efficiency, Low H <sub>2</sub> production rate, sunlight required, necessity of huge volume of reactor, O <sub>2</sub> -sensitivity	0.1	2.83
Gasification	Abundant, cheap feedstock and neutral CO <sub>2</sub> .	Fluctuating H <sub>2</sub> yields because of feedstock impurities, seasonal availability and formation of tar.	30–40	1.77–2.05
Pyrolysis	Abundant, cheap feedstock and CO <sub>2</sub> -neutral.	Tar formation, fluctuating H <sub>2</sub> amount because of feedstock impurities and seasonal availability	35–50	1.59–1.70
Thermolysis	Clean and sustainable, O <sub>2</sub> -byproduct, copious feedstock	High capital costs, Elements toxicity, corrosion problems.	20–45	7.98–8.40
Photolysis	O <sub>2</sub> as byproduct, abundant feedstock, No emissions.	Low efficiency, non-effective photocatalytic material, Requires sunlight.	0.06	8–10
Electrolysis	Established technology Zero emission Existing infrastructure O <sub>2</sub> as byproduct	Storage and Transportation problem.	60–80	10.30

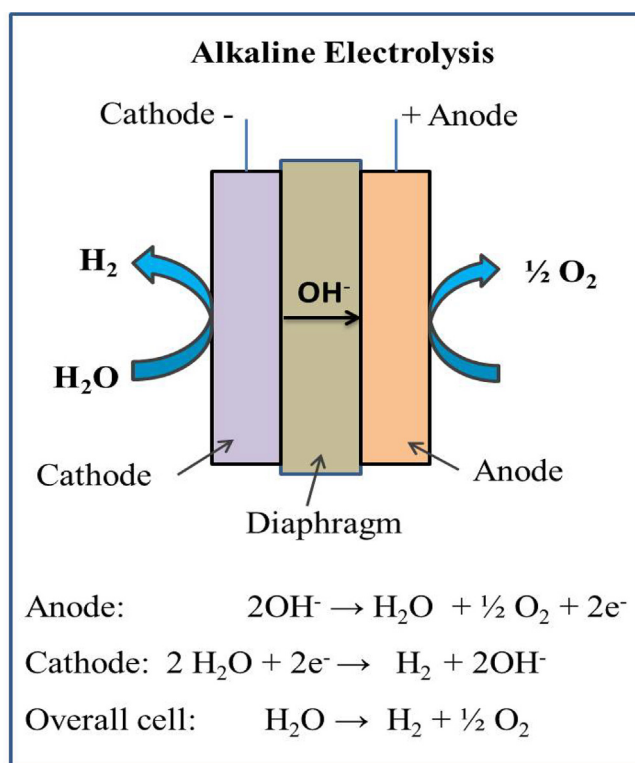
## 2. Water electrolysis technologies

Electrolysis of water is one such most capable method for production of hydrogen because uses renewable H<sub>2</sub>O and produced only pure oxygen as by-product. Additionally, in electrolysis process utilizes the DC power from sustainable energy resources for example solar, wind and biomass. But, at present only  $\Sigma$  4% of hydrogen can be obtained by electrolysis of water mainly due to the economic issues [35,36]. It is expected to this value is increased in the near in future although increase the usage of renewable energy (solar, wind, nuclear), meanwhile the European Energy Directive has been fix the goal to utilize 14% of the energy requirements from renewable energy sources by 2020 [34]. Furthermore, water electrolysis having tough advantages such as high cell efficiency and greater hydrogen production rate with high purity this is more advantage for its further conversion in to electrical energy using low temperature fuel cells [26]. In electrolysis process, water molecule is the reactant it is dissociated into hydrogen (H<sub>2</sub>) and oxygen (O<sub>2</sub>) under the influence of electricity. Water electrolysis can be classified in to the four types based on their electrolyte, operating conditions, and ionic agents (OH<sup>-</sup>, H<sup>+</sup>, O<sup>2-</sup>), however operating principles are both the cases same. The four kinds of electrolysis methods are (i) Alkaline water electrolysis (AWE) [37–39], (ii) Solid oxide electrolysis (SOE) [40,41] (iii) Microbial electrolysis cells (MEC) [170,173]. (iv) PEM water electrolysis [34,42].

## 3. Alkaline water electrolysis (AWE)

Hydrogen production by alkaline water electrolysis is well established technology up to the megawatt range for commercial level in worldwide and the phenomenon first introduced by Troostwijk and Diemann in 1789 [43–46]. Alkaline water electrolysis process initially at the cathode side two molecules of alkaline solution (KOH/NaOH) were reduced to one molecule of hydrogen (H<sub>2</sub>) and two hydroxyl ions (OH<sup>-</sup>) are produced. The produced H<sub>2</sub> eliminate from the cathode surface to recombine in a gaseous form and the hydroxyl ions (OH<sup>-</sup>) transfer under the influence of the electrical circuit between anode and cathode through the porous diaphragm to the anode, here in discharged to  $\frac{1}{2}$  molecule of oxygen (O<sub>2</sub>) and one molecule of water (H<sub>2</sub>O). The O<sub>2</sub> recombined at the surface of electrode and escapes as hydrogen, the following

mechanism as shown in Fig. 2. Alkaline electrolysis operates at lower temperatures such as 30–80 °C with aqueous solution (KOH/NaOH) as the electrolyte, the concentration of the electrolyte is  $\sim$ 20% to 30% [37,47–49]. In alkaline water electrolysis process, asbestos diaphragm and nickel materials are used as the electrodes [39]. The diaphragm having in the middle of the cell and it is separates the cathode and anode also separates the produced gases from their respective electrodes and avoiding the mixing of produced gases electrolysis process. However, in alkaline electrolysis have negative aspects such as limited current densities (below 400 mA/cm<sup>2</sup>), low operating pressure and low energy efficiency

**Fig. 2.** Schematic illustration of alkaline water electrolysis.

[37,50]. Finally, a new approach in the alkaline electrolysis is under development of anion exchange membranes (AEM) made up of polymers with anionic conductivity instead of asbestos diaphragm. This innovative technology appears to be interesting in the field of alkaline water electrolysis [51–56].

#### 4. Solid oxide electrolysis (SOE)

The solid oxide electrolysis (SOE) first introduced by Donitz and Erdle in the 1980s [45,58]. Solid oxide electrolysis has attracted an abundant deal of attention due to the electrical energy converts into the chemical energy along with producing the ultra-pure hydrogen with greater efficiency [57,59]. Solid oxide electrolysis operates at high pressure and high temperatures 500–850 °C and utilizes the water in the form of steam. Solid oxide electrolysis process conventionally uses the  $O^{2-}$  conductors which are mostly from nickel/yttria stabilized zirconia [60], operating principle of SOE has shown Fig. 3. Nowadays, some of the ceramic proton conducting materials have been developed and studied in solid oxide fuel cells. However, increasing the much attention towards ceramic proton conducting materials for SOE electrolysis process, due to these materials demonstrates high efficiency and superior ionic conductivity than  $O^{2-}$  conductors at an operating temperature of 500–700 °C [34]. The main characteristics of solid oxide electrolysis (SOE) technology is higher operating temperature which makes advantageous compared to low temperature electrolysis. Although, the SOE having some issues related to lack of stability and degradation, which have to be solved before going to commercialization on a large scale [41,61–63].

#### 5. Microbial electrolysis

Hydrogen production by Microbial electrolysis cell (MEC) technology can be achieved by organic matter including renewable bio-

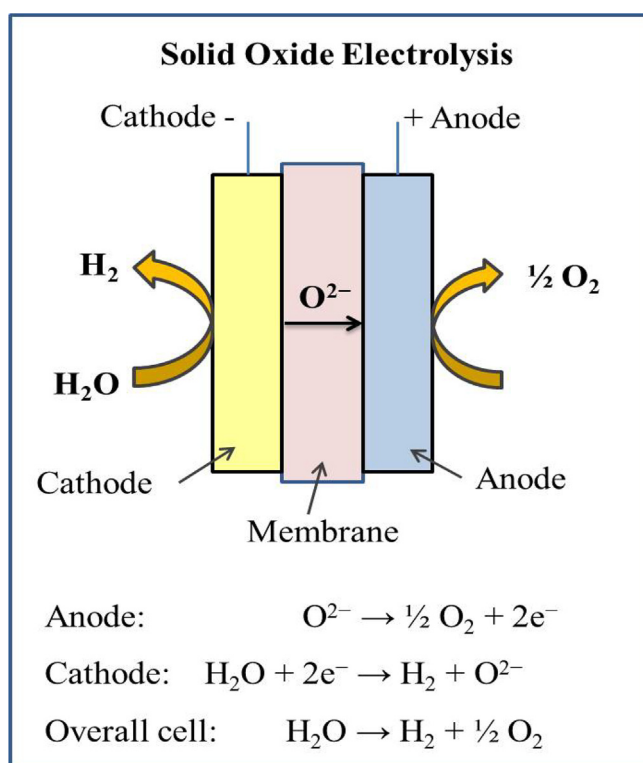


Fig. 3. Schematic illustration of Solid Oxide electrolysis.

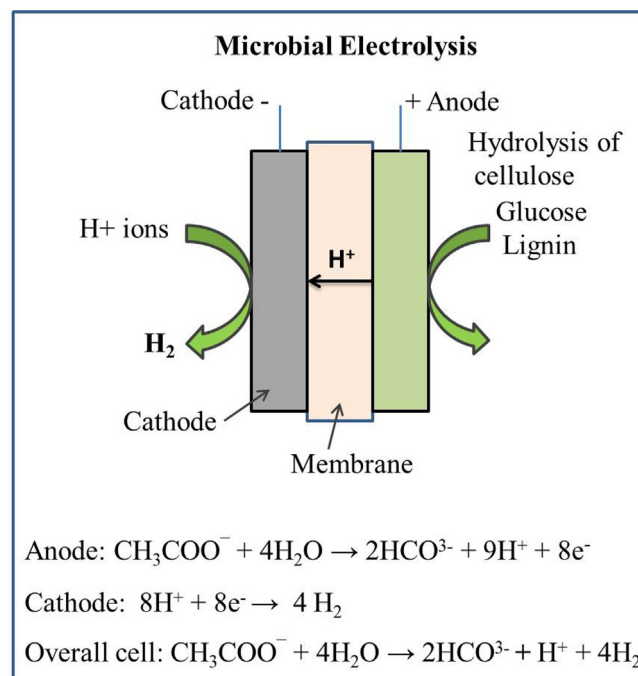


Fig. 4. Schematic illustration of Microbial Electrolysis.

mass and wastewaters and this MEC technology is closely related to microbial fuel cells (MFCs) but operational principle is reverse of MFCs [170].

The first Microbial electrolysis cell (MEC) approach is introduced by two independent research organizations such as Penn state university and Wageningen University, Netherlands in 2005 [170,171]. In microbial electrolysis cells (MECs), electrical energy converted into chemical energy. MECs produced hydrogen from organic materials in the influence of electric current. In microbial electrolysis process, initially in anode side the substrate is oxidized by microbes and then produces  $CO_2$ , protons and electrons. The electrons are moving through the external circuit to cathode side and the protons are travelled to cathode via proton conducting membrane (electrolyte) whereas the protons and electrons combined with produces the hydrogen. Fig. 4 shows the principle of MEC. MEC process some electrochemical potential is produced during the oxidation in the anode side is insufficient to give decreased voltage required for the hydrogen evolution reaction at the cathode side hence it required extra voltage (0.2 V–1.0 V). Therefore MEC process required small amount of external voltage when compared to water electrolysis [172]. However, this MEC technology is still under development and having several challenges towards hydrogen production rate, high internal resistance, electrode materials and complicated design need to be addressed before and commercialization of this technology [173].

#### 6. PEM water electrolysis

The first PEM water electrolysis was idealized by Grubb in the early fifties and General Electric Co. was developed in 1966 to overcome the drawbacks to the alkaline water electrolysis [64–66,68,69]. PEM water electrolysis technology is similar to the PEM fuel cell technology, where solid polysulfonated membranes (Nafion<sup>®</sup>, fupapem<sup>®</sup>) was used as a electrolyte (proton conductor) [57,67,70,71]. These proton exchange membranes having many advantages such as lower gas permeability, high proton conductivity ( $0.1 \pm 0.02 \text{ S cm}^{-1}$ ), lower thickness ( $\Sigma 20\text{--}300 \mu\text{m}$ ) and



high-pressure operations. In terms of sustainability and environmental impact, PEM water electrolysis is one of the favorable methods for conversion of renewable energy to high pure hydrogen. Another promising PEM water electrolysis has great advantages such as compact design, high current density (above  $2 \text{ A cm}^{-2}$ ), high efficiency, fast response, small footprint, operates under lower temperatures ( $20\text{--}80^\circ\text{C}$ ) and produced ultrapure hydrogen and also produced oxygen as a byproduct [70–74], also described in Table 2. Additionally, balancing PEM electrolysis plants is very simple, which is more attractive for industrial applications. The state-of-the-art electrocatalysts for PEM electrolysis are high activity of noble metals such as Pt/Pd as the hydrogen evolution reaction (HER) at the cathode [73–75] and  $\text{IrO}_2/\text{RuO}_2$  as the oxygen evolution reaction (OER) at the anode [76–82], which makes the more expensive than alkaline water electrolysis. Therefore, one of the main challenges in PEM water electrolysis is to reduce the production cost and to maintain the high efficiency. Since then, substantial research has been devoted to improve the PEM water electrolysis components, and as a result, this technology is approaching commercial markets [57].

### 6.1. Principle of PEM water electrolysis

In PEM water electrolysis, water is electrochemically split into hydrogen and oxygen at their respective electrodes such as hydrogen at the cathode and oxygen at the anode. PEM water electrolysis is accrued by pumping of water to the anode where it is split into oxygen ( $\text{O}_2$ ), protons ( $\text{H}^+$ ) and electrons ( $\text{e}^-$ ). These protons are traveled via proton conducting membrane to the cathode side. The electrons exit from the anode through the external power circuit, which provides the driving force (cell voltage) for the reaction. At the cathode side the protons and electrons re-combine to produce the hydrogen, the following mechanism as shown in Fig. 5.

### 6.2. Thermodynamics

Electrolysis process water is split in to hydrogen and oxygen, for this water splitting some energy is required at the same time the equal energy released during the formation of water molecule form gases of hydrogen and oxygen. Therefore the minimum required energy for water splitting can be calculated from Gibbs free ( $\Delta G$ ) energy. Standard conditions, Gibbs free energy for the splitting of water into hydrogen and oxygen can be calculated by following Eq. (2).

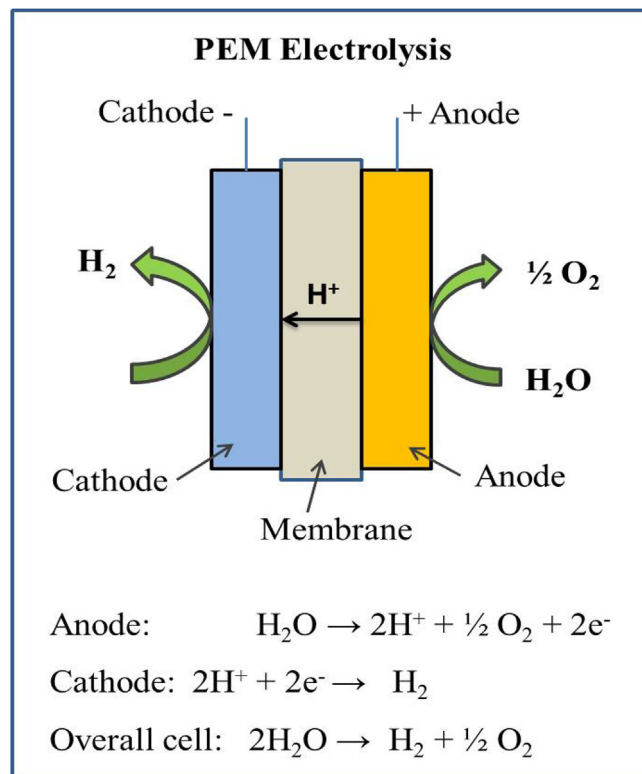
$$\Delta G = nFE_{\text{rev}} \quad (2)$$

Where

$n$  = no. of electrons involved  
 $F$  = 96500 (Faraday's constant)  
 $E_{\text{rev}}$  = Reversible voltage

**Table 2**  
Advantages and Disadvantages of different water electrolysis technologies.

Electrolysis process	Advantages	Disadvantages
Alkaline Electrolysis	Well established technology Non-noble electro catalysts Low cost technology The energy efficiency is (70–80%) Commercialized	Low current densities Formation of carbonates on the electrode decreases the performance of the electrolyser Low purity of gases Low operational pressure (3–30 bar) Low dynamic operation Laboratory stage Large system design Low durability
Solid Oxide Electrolysis	Higher efficiency (90–100%) Non-noble electro catalysts High working Pressure	
Microbial Electrolysis	Used different organic waste waters	Under development Low hydrogen production rate Low purity of hydrogen
PEM Electrolysis	High current densities Compact system design and Quick Response Greater hydrogen production rate with High purity of gases (99.99%) Higher energy efficiency (80–90%) High dynamic operation	New and partially established High cost of components Acidic environment Low durability Commercialization is in near term



**Fig. 5.** Schematic illustration of PEM water electrolysis.

The reversible voltage can be calculated by the following Eq. (3).

$$E_{\text{rev}} = \frac{\Delta G}{nF} = 1.23\text{V} \quad (3)$$

However, at the time of water splitting some entropy generated. Thus, it is more suitable to employ enthalpy ( $\Delta H$ ) in its place of  $\Delta G$  for the potential calculation. Therefore at the standard conditions, the change of enthalpy is  $\Delta H = 285.84 \text{ kJ mol}^{-1}$  and change of Gibbs free enthalpy is  $\Delta G = 237.22 \text{ kJ mol}^{-1}$  [83,84]. Therefore, the minimum required voltage ( $V_{\text{TN}}$ ) for the water electrolysis can be calculated by following Eq. (4).

$$V_{\text{TN}} = \frac{\Delta H}{nF} = \frac{\Delta G}{nF} + \frac{T\Delta S}{nF} = 1.48\text{V} \quad (4)$$

Where

$V_{\text{TN}}$  = thermo-neutral voltage  
 $\Delta S$  = change in entropy  
 $T$  = temperature

According to the first law of thermodynamics energy is conserved. Thus, the conversion efficiency calculated from the yields

of converted electrical energy into chemical energy. Typically, water electrolysis efficiency is calculated by the higher heating value (HHV) of hydrogen. Since the electrolysis process water is supplied to the cell in liquid phase efficiency can be calculated by the following Eq. (5).

$$\eta = \frac{V_{TN}}{V_{cell}} \quad (5)$$

Where

$V_{TN}$  = Thermo-neutral voltage

$V_{cell}$  = Cell voltage

Therefore, the water electrolyser efficiency can be calculated by any current density. Since operating the lower current densities at lower voltages, the electrolyser efficiency becomes higher [85].

### 6.3. Faradaic efficiency

In water electrolysis, faradaic efficiency is a one of the quantitative analysis which is useful for to determine the how many electrons are transported in the external circuit to the surface of electrode for conducting the electrochemical reaction either oxygen evolution reaction (OER) or hydrogen evolution reaction (HER) and other electrochemical reactions in the electrolytes. Therefore, the faradaic efficiency can be defined as the ratio between experimentally evolved volume of gas value (hydrogen or oxygen) and theoretically calculated volume of gas value, as shown in Eq. (6)

$$\eta_{\text{faraday}} = \frac{V_{H_2}(\text{Product})}{V_{H_2}(\text{Calculated})} \quad (6)$$

The theoretical volume of gas can be calculated by the Faraday's second law, based on the current density, electrolysis time and electrode area by assuming a 100% Faradaic efficiency, as shown in Eq. (7). When the practical amount produced in the experiment can be measured by water-gas displacement method or gas chromatography analysis.

$$V_{H_2} = V_M(l) \left( \frac{10^3 \text{ ml}}{1} \right) \left( \frac{t(60s)}{\text{min}} \right) \left( \frac{I(\frac{C}{s})}{2F(C.)} \right) \quad (7)$$

Where  $V_{H_2}$  indicates the yield of theoretical hydrogen,  $V_M$  is the ideal gas expression ( $V_M = \frac{R(273+T)}{P}$ ),  $R$  indicates the ideal gas constant ( $0.082 \text{ l atm K}^{-1} \text{ mol}^{-1}$ ),  $T$  denotes the temperature,  $P$  means presser (atm),  $t$  is time (s),  $I$  is the applied current (A) and  $F$  indicates the Faraday's constant ( $96,485 \text{ C.mol}^{-1}$ ).

### 6.4. PEM water electrolysis cell components

The major PEM water electrolysis cell components are membrane electrode assemblies (MEAs), current collectors (gas diffusion layers), and separator plates. Typical overview of PEM water electrolysis cell assembly was shown in Fig. 6. However, heart of the electrolysis cell is MEA which is separated the cell in to two half cells (anode and cathode).

#### 6.4.1. Membrane electrode assemblies (MEAs)

The membrane electrode assemblies are consisting of membrane, ionomer solution and anode, cathode electrocatalysts which is responsible 24% of overall cell cost (Fig. 7). Membrane is back bone of the PEMWE cell, the most commonly used membranes are Perfluorosulfonic acid polymer membranes such as Nafion<sup>®</sup>,

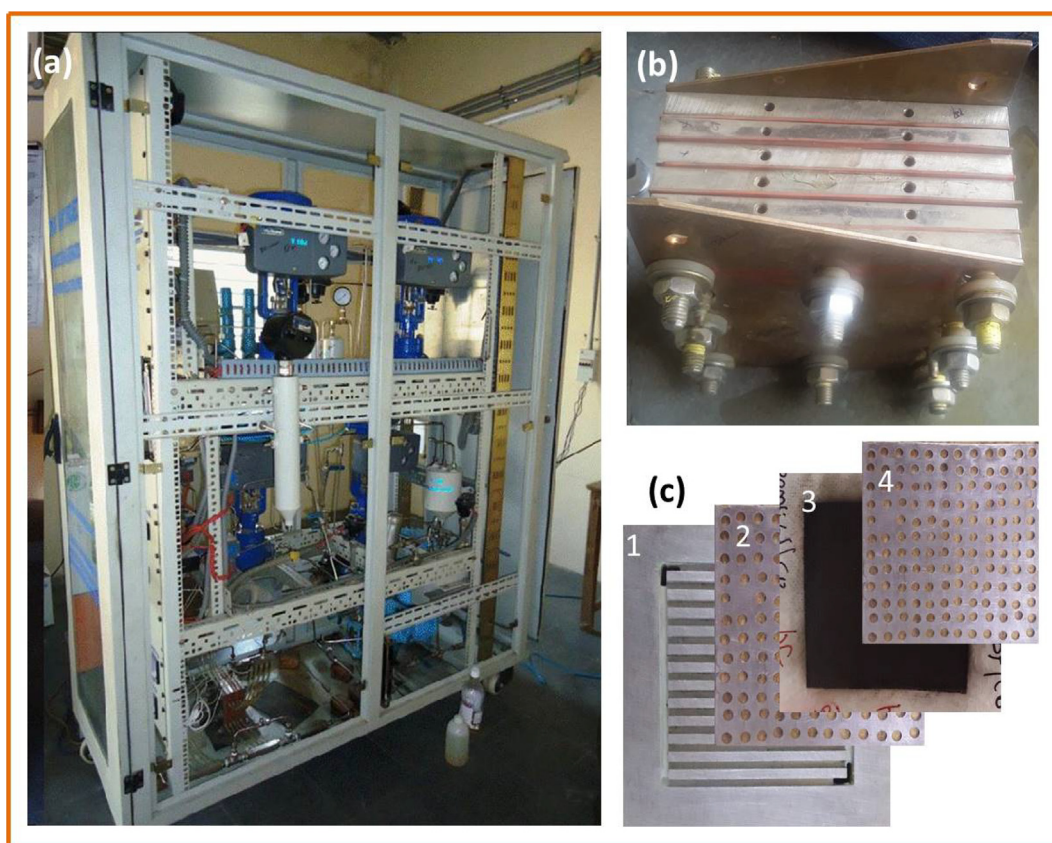


Fig. 6. (a) Overview of typical PEM water electrolyser (b) PEM cell stack (c) Cell components; 1-Bipolar plate, 2-Anode current collector, 3-MEA, 4-Cathode current collector.

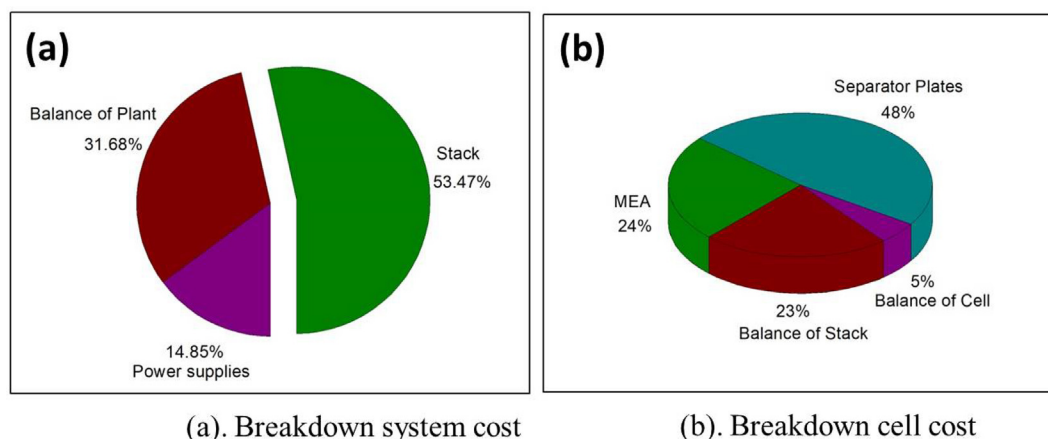


Fig. 7. Breakdown capital cost of PEM water electrolyser ( $13 \text{ kg day}^{-1}$ ), Reprinted from Ref. [2].

Fumapem®, Flemion®, and Aciplex® [83,86]. These membranes have unique properties such as high strength, high efficiency and high oxidative stability, dimensionally stable with change of temperatures, good durability and high proton conductivity. However, currently Nafion® membranes (Nafion® 115, 117, and 212) are mostly used in PEM water electrolyzers because Nafion® membranes have tough advantages such as operating at higher current densities ( $2 \text{ A/cm}^2$ ), high durability, high proton conductivity and good mechanical stability [45]. Typically the membrane electrode assemblies are fabricated by different methods, but most of researchers are followed catalyst coated on membrane (CCM) method, in this method the electrocatalyst slurry is directly coated on the surface of membrane and then hot pressed at  $120^\circ\text{C}$  temperature with  $60 \text{ kg cm}^{-2}$  pressure [166,167]. The electrocatalysts are employed to promote the charge transfer kinetics in order to decrease the activation energy of water electrolysis method.

The homogeneous electrocatalyst slurry was prepared by using appropriate amounts of electrocatalyst along with ionomer solution (eg. Nafion® ionomer), isopropanol and water followed by sonication about 30 min. The addition of ionomer solution with ionic transport properties in the catalytic layers has two different on the electrodes in the PEM water electrolysis. The ionomer is promoting the proton transport from the electrode layers to the membrane thus increasing the cell efficiency by decreasing the cell ohmic loss. Further the ionomer solution act as a binder, which gives the dimensionally stable structure of the catalyst and providing the mechanical stability subsequently durability of the electrodes [57]. On the other hand with increasing the ionomer content, it reduces the electrical conductivity due to the ionomer is electron resistant. Therefore, the optimization of the ionomer content is necessary.

#### 6.4.2. Current collectors

In PEM water electrolysis process water is pumping to the anode side of the PEM cell where oxygen evolution reaction occurs, the feed water travels through the separator plates and diffuses via current collectors. The feed water reaches the electrode surface and the water molecule is decomposed into oxygen, protons and electrons. The oxygen was return to out of the cell through electrode surface, current collectors then separator plates. The protons are moving from the anode electrode surface to cathode side through the proton conducting membrane. The electrons are travelled from the current collectors, separator plates than moving to the cathode side, after reaching the electrode surface recombined with protons to gives the hydrogen. The obtained hydrogen was leaving from the cell via cathode current collector

and separator plates. Therefore current collectors are plays a significant role on overall mechanism of PEM water electrolysis and cell efficiency. The current collectors have must be corrosion resistance, good electrical conductivity due to the acidic environment, high over potential and presence of oxygen. The current collectors also deliver good mechanical strength to the membrane. Moreover, current collectors have an optimized porosity and pore volumes due to the produced gases are effectively expelled and water must be reaching the catalytic sites of electrode surface, therefore optimized current collectors are required, the optimized parameters of current collectors are described in Table 3. Typically in PEM water electrolysis pours titanium plates are using as promising current collectors due to the these materials having unique properties such as good electrical conductivity, mechanical stability and corrosion resistant under acidic medium [168]. The porous titanium plates act as current collectors and gas diffusion layer (GDL) for both sides of the MEA and enclosed by bipolar plates followed by gaskets. The current collectors were used to allow the electrical current to flow between the electrodes and bipolar plates [87–89]. In many studies titanium grids/meshes/felts, carbon current collectors and stainless steel grids are used, but the electrochemical performance is lower than pours titanium plates.

#### 6.4.3. Separator plates

In typical PEM water electrolysis separator plates and current collectors are responsible for the 48% (Fig. 7) of overall cell cost and a linear donor to the required cell voltage. Presently, the PEM water electrolysis separator plates made up titanium, stainless steel and graphite but these materials were high cost and having different operational drawbacks. This is under the drawbacks also essential reduction of cost that the research and development of the separator plates are facing the major challenges. Moreover, the separator plates surface structure was more essential for the PEM water electrolysis cell, they must be provision conduction path of pumping water and produced gases out of the electrolysis cell [90–92]. Many electrolyzers systems, different designs of separator plates are using for better performance however the straight

Table 3  
Parameters of current collector for PEM water electrolysis [Ref. [3]].

Current collector thickness	0.8–2 mm
Electrical Resistance	5–10 mΩ cm
Gas permeability	$1 \times 10^{-13}$ – $1 \times 10^{-11} \text{ m}^2$
Porosity	20–50%
Pore size	5–30 μm
Particle size	25–250 μm



parallel flow field design was shown promising electrochemical activity especially in PEM water electrolysis [169]. Typically titanium materials give outstanding strength, high thermal conductivity, low permeability and low resistivity but anode side (oxygen) titanium material corrodes and grows inert oxide layer. Therefore decrease the performance of the electrolyser. To address these issues and protect the titanium plates precious metal coatings and alloys have been studied. This coating are drastically decreased the corrosion rate but this extra process, precious coating materials and also expensive base titanium. Therefore cost effective separator plates are still under challenges.

### 6.5. Electrocatalysts for PEM water electrolysis

Typically, in PEM water electrolysis noble metal based electrocatalysts are used such as Pt/Pd-based catalysts as cathode towards the hydrogen evolution reaction (HER) and RuO<sub>2</sub>/IrO<sub>2</sub> catalysts as anode for oxygen evolution reaction (OER) [57,93–96]. The first PEM water electrolysis research article published by Russell et al., in the year of 1973 at general electric company using the PEM electrolysis cell. In this study experimental results have shown considerably efficient and the obtained performance of 1.88 V at an operating current of 1 A cm<sup>-2</sup> and 2.24 V at 2 A cm<sup>-2</sup> with cell life of 15,000 h without any degradation performance [57,97]. However, the cost of PEM electrolysis was high due to the use of expensive materials despite these drawbacks PEM electrolysis has numerous advantages for example high operating current densities, high purity of gases and high efficiency. Later on to address these drawbacks several researchers much effort focused on inexpensive PEM electrolysis methods and developed many alternative electrocatalysts based on improving the efficiency and stability of the low cost Ru-based multi-metallic oxides also reducing the usage of the high cost metals (Ir, Pt) using the alternative active carbon supports have been developed and reported, as shown in Fig. 8, which are discussed in the following paragraphs and some of the results have been summarized in Table 3.

#### 6.5.1. Electrocatalysts for hydrogen evolution reaction

The challenges towards hydrogen evolution reaction (HER) in PEM electrolysis were focused on to development of electrocatalysts for the cathode. In most of the previous reports, typically platinum (Pt) based materials have been used as a standard catalyst for the hydrogen evolution reaction [57,98,99] due to the Pt gives the excellent HER activity and exhibits outstanding stability in acidic environment but highly dispersed carbon supported Pt-based materials are currently benchmark catalysts for HER in PEM water electrolysis [57]. However, these platinum based catalysts are more expensive, therefore most of the research has been mainly focused on to decrease the cost of electrocatalysts and operational

costs by increasing the specific performance and durability of the electrocatalysts. Although for economic viability it is necessary to decrease the Pt loading on carbon or to find out the alternative to Pt based electrocatalysts [100,101]. The electrochemical active surface area is generally developed by the dispersed carbon nanoparticles in order to enhance the surface area and thereby decrease the Pt loadings [102,103]. The electrocatalyst was then hosted in gas diffusion electrodes based on large surface area cost effective electronic carriers such as carbon nanotubes/carbons black. Later on many researchers initiated to use of different carbon blacks (CB) as support materials for platinum based catalyst as a standard electrocatalyst towards the HER [57]. Though, the lower Pt loading on carbons are still indicates the significant portion of the overall system value, mainly due to the performance degradation or corrosion of the carbon support. Nowadays, cathode side metal loading were maintained approximately 0.5–1 mg cm<sup>-2</sup> and further decreases will be always needed for the potential values reaching below 0.2 mg cm<sup>-2</sup>. Further, Badwal et al. reported on the development of PEM water electrolyser system for producing high pure oxygen and hydrogen. The electrolyser was operated at 2 bar pressure with 75–85 °C temperature. The Nafion 112 and 115 membranes were used as electrolyte and Pt/C with loading of up to 0.4 mg cm<sup>-2</sup> and various noble metal catalysts with metal loading of 0.2–0.4 mg cm<sup>-2</sup> were maintained for cathode and anode respectively [104]. Giddey et al. studied 20 wt% Pt/C as cathode electrode and Ir, Ru as anode electrocatalysts along with an electrode surface area of 50–150 cm<sup>2</sup> coated on Nafion 115 membrane. The noble metal loading varied between 0.2 and 0.4 mg cm<sup>-2</sup> and operated the electrolyser at 20 bar pressure and at 70–80 °C temperature [105].

Later on, several researchers have been developed various alternative electrocatalysts and studied towards the hydrogen evolution reaction. For example, Hinnemann et al. studied MoS<sub>2</sub> electrocatalyst for the HER [106]. These studies have been carried out by fabricating the MEA with MoS<sub>2</sub>/graphite and standard Pt, the obtained results have demonstrated that MoS<sub>2</sub> has an acceptable catalyst for HER, though potentially lower current densities (10 mA cm<sup>-2</sup> at 175 mV) than conventional Pt cathodes. Corrales-Sánchez et al. reported the performance of three different types of MoS<sub>2</sub>-based electrodes such as bare pristine MoS<sub>2</sub>, MoS<sub>2</sub> mixed with commercial conductive carbon, Vulcan<sup>®</sup> XC72, and MoS<sub>2</sub> on reduced graphene (MoS<sub>2</sub>/rGO) with the anode of IrO<sub>2</sub>. The obtained results of the pristine MoS<sub>2</sub> was shown worst performance the achieved current density of approximately 0.02 A/cm<sup>2</sup> at 1.9 V. Later, their best performing MoS<sub>2</sub>/rGO electrode achieved a current density of 0.1 A cm<sup>-2</sup>, while the best mixture of MoS<sub>2</sub> and Vulcan<sup>®</sup> (47 wt% MoS<sub>2</sub>) reached almost 0.3 A cm<sup>-2</sup> at 1.9 V. The MoS<sub>2</sub> mixed carbon shown superior electrocatalytic performance towards the HER but only comparative to the other MoS<sub>2</sub> electrocatalysts still not comparable to Pt based catalysts [106]. Further in order to increase the hydrogen production rates and current density recently Sarno M et al. synthesized RuS<sub>2</sub>@MoS<sub>2</sub> electrocatalyst and studied experimentally for hydrogen evolution reaction. The synthesized RuS<sub>2</sub>@MoS<sub>2</sub> catalyst revealed outstanding properties such as high exchange current density, acceptable over potential and Volmer-Tafel behavior (36 mV dec<sup>-1</sup>). Because of high contact of RuS<sub>2</sub> boundaries on the MoS<sub>2</sub> with robust d character of RuS<sub>2</sub> and electrical conductivity of these two materials were grown together which lead the responsible for the high production of hydrogen yields (10.2 l/h) at an operated current density of 1.1 A cm<sup>-2</sup> with utilization of 41.8 W power with 3.8 KWh/Nm<sup>3</sup> of energy consumption and 93% efficiency [107].

Nowadays Pd based electrocatalysts have shown increasing the significant interest towards the hydrogen evolution reaction because, palladium which is earth abundant and low cost compared to platinum, also shows remarkable electrocatalytic activity

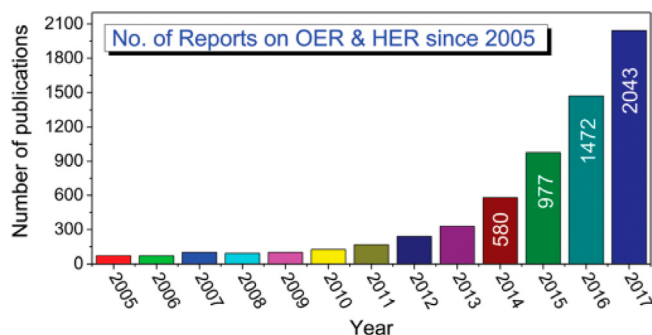


Fig. 8. Number of scientific reports on OER and HER from 2005 to 2017 (Reprinted from Ref. [153]).



for several oxidation and reduction reactions [108–110]. For example, S.A. Grigoriev et al. has been experimentally studied Pd/VulcanXC-72 and Pt/VulcanXC-72 for the HER, the attained results of Pd/VulcanXC-72 has shown slightly less efficient than those obtained with Pt/VulcanXC-72 [111]. Pd activated carbon also tested for the HER with different weight loadings but unfortunately the obtained performance has not compared with the conventional Pt electrodes. The Pd carbon nanotubes (Pd/CNTs) have also been evaluated towards the HER though acceptable difference has not obtained compared to Pt/CNTs [112,113]. Carbon nanotubes are generally used as an electron carrier support material for noble metal catalysts since they are generally known as having superior electron conductivity and corrosion resistance than conventional carbon blacks. Afterward, to better electrocatalytic activity and stability, hetero atom (N, P, S and B) doped carbon nanoparticles have been widely used as an electron carrier support material for noble metal electrodes in oxygen reduction reactions and hydrogen evolution reactions [114–118]. Ramakrishna et al. studied palladium supported on N- doped CNTs electrocatalyst (Pd/N-CNTs) towards the hydrogen evolution reaction and compared with commercial Pt/C. The obtained Pd/N-CNTs results have shown comparable electrocatalytic activity than commercial Pt/C towards the HER [100]. Shiva Kumar et al. reported experimental studies on phosphorus (P) doped graphene (Pd/PG) and P-doped carbon nanoparticles (Pd/P-CNPs) for the HER and compared with the conventional Pt/CB. The attained results have exhibited almost similar electrochemical performance than conventional Pt/CB. Hence, Pd- based electrocatalysts can be used alternative to Pt-based catalysts for the HER [83,120].

In order to further reduce the cost of HER catalysts produced by using the other carbon-supported electrocatalysts, especially those only consist of earth abundant materials and low cost, such as A-Ni-C,  $\text{Mo}_2\text{C}/\text{CNTs}$ ,  $\text{Ni}_2\text{P}/\text{CNTs}$ , Co-doped  $\text{FeS}_2/\text{CNTs}$ ,  $\text{WO}_2/\text{C}$  nanowires and CoFe nanoalloys encapsulated in N-doped graphene etc., have been extensively studied in potential HER electrocatalysts for alternative to Pt [121–126]. However, these carbon-supported Pt free HER catalysts that have actually been tested in PEM water electrolysis are rarely reported. In summary, in PEM water electrolysis alternative to Pt-based catalysts for HER several electrocatalysts have been developed and studied towards the HER. However, most of the catalysts belong to the main family of metals with support of nano carbons have been developed. Among these catalysts  $\text{MoS}_x$  and Pd-based nano carbons appears to be the most capable electrocatalysts in terms of electro catalytic activity and stability.

#### 6.5.2. Electrocatalysts for oxygen evolution reaction

The state-of-the-art, metal oxides are used as an electrocatalysts for oxygen evolution reaction (OER) in PEM water electrolyser. However, among these metal oxides  $\text{IrO}_2$  and  $\text{RuO}_2$  have shown higher metallic conductivity which is of  $10^4 \text{ cm}^{-1} \Omega^{-1}$  also in these oxides metal-metal distance value and the radius of the cations are overlapping of the inner d-orbital is feasible, the electrons of d-orbitals in these d-bands are responsible for the electron conductivity [127]. Therefore  $\text{RuO}_2$  has shown the better OER performance among the other metal oxides [57,76]. Although  $\text{RuO}_2$  more active than  $\text{IrO}_2$  but poor stability due to the corrosion from the strong acidity at the perfluorosulfonic membrane and high anodic potential at OER, other hand  $\text{IrO}_2$  is most resistive material to OER in acidic environment but lower performance [128]. To address these drawbacks with the purpose of to enhance the stability with high efficiency and decreasing the cost, in these directions researchers in the recent years initiated developing the different substitute catalysts for the OER. When it comes to economic feasibility and better stability, need to be addition of  $\text{IrO}_2$  in order to

enhance the stability of  $\text{RuO}_2$  [129–131]. Li, G. et al. prepared and experimentally studied bimetallic oxide of  $\text{Ir}_x\text{Ru}_{1-x}\text{O}_2$  electrocatalyst as the anode in PEM water electrolysis. From the electrochemical results, it was observed that the increased electrochemical performance was achieved with the subsequent addition of  $\text{RuO}_2$ , the cell voltage of 1.676 V at an operating current density of  $1 \text{ A cm}^{-2}$ . Meanwhile, the physicochemical studies demonstrated the increased surface area, pore volume and average pore size of the electrocatalyst also with increasing the Ru concentration in  $\text{Ir}_x\text{Ru}_{1-x}\text{O}_2$  along with increased the rutile crystallinity [132]. Kalliopi M. Papazisi et al. synthesized  $\text{Ir}_x\text{Pt}_{1-x}\text{O}_2$  electrocatalysts by modified Adams fusion method and studied electrochemical performance and stability towards the OER. The attained results of  $\text{Ir}_x\text{Pt}_{1-x}\text{O}_2$  electrocatalysts have been revealed the stable electro chemical activity towards the OER in PEM water electrolysis. The electrochemical performance of  $\text{Ir}_x\text{Pt}_{1-x}\text{O}_2$  along with their durability and large surface area are quite advantageous for the development of low cost electrocatalysts for OER [133]. However, in order to reduce the cost and limited resources of Ir, it is required to reduce or replace the Ir usage in electrocatalysts by using the other non-noble metal oxides. Therefore significant research efforts focused at reducing noble metal content by mixing transition metal oxides with  $\text{IrO}_2$  and/or  $\text{RuO}_2$ , such as  $\text{TiO}_2$  [134–137],  $\text{SnO}_2$  [78,138],  $\text{Ta}_2\text{O}_5$  [119,139],  $\text{Nb}_2\text{O}_5$  [140],  $\text{Sb}_2\text{O}_5$  [141],  $\text{PbO}_2$  [142],  $\text{MnO}_2$  [143,144] and other mixed oxides also studied for OER [81,145–147], some of the experimental results have been discussed following paragraphs and summarized in Table 4.

Vinod Kumar et al. A bimetallic  $\text{Ru}_x\text{Nb}_{1-x}\text{O}_2$  electrocatalyst was synthesized by Adams, and hydrolysis methods also studies towards OER. The Adams method found to be better mixture of  $\text{RuO}_2$  with  $\text{Nb}_2\text{O}_5$  and influenced the electrochemical properties. The attained results have been demonstrated increased stability with the addition of 20%  $\text{Nb}_2\text{O}_5$  to  $\text{RuO}_2$  in Adams method. Further there is no improvement in electrocatalytic activity with increasing the  $\text{Nb}_2\text{O}_5$  content of above 20% owing to the dilution of active material [148]. Ardizzone et al. experimentally studied nanostructured  $\text{SnO}_2\text{-IrO}_2\text{-Ta}_2\text{O}_5$  oxides as a promising electrocatalyst for OER. The  $\text{SnO}_2\text{-IrO}_2\text{-Ta}_2\text{O}_5$  electrocatalyst has shown better electro analytical properties, the main role of tantalum for increasing the surface area with charge storage capacity and enhancing the electrical conductivity. Meanwhile  $\text{SnO}_2\text{-IrO}_2\text{-Ta}_2\text{O}_5$  has shown better electrochemical performance towards the OER in acidic environment [149]. Further, to reduce the noble metal content and improve the stability Thomas Audichon et al. suggested trimetallic  $\text{Ru}_{0.8}\text{Ir}_{(0.2-x)}\text{Ce}_x\text{O}_2$  electrocatalyst towards the OER. In this study, effect of cerium (Ce) content in  $\text{Ru}_{0.8}\text{Ir}_{(0.2-x)}\text{Ce}_x\text{O}_2$  electrocatalyst was studied for determining the electrochemical performance and stability by cyclic voltammetry method in acidic medium. The attained results have shown the addition of cerium is not effected on stability. Therefore, the addition of cerium only permits the reducing the Ir and Ru content without destroying the OER performance. Furthermore, the oxygen mobility in cerium crystallographic nature may participate to enhancing the electrocatalytic activity of active sites [150].

Datta, M.K. et al. experimentally studied F doped Thin film ( $\text{Sn}_{0.8}\text{Ir}_{0.2}$ )  $\text{O}_2$  electrocatalyst as an potential OER electrode in PEM water electrolysis. The electrocatalytic activity of F doped Thin film ( $\text{Sn}_{0.8}\text{Ir}_{0.2}$ )  $\text{O}_2$  increased with increasing the F loading along with increased electrochemical performance such as polarization resistance, Tafel slope, efficiency and stability at an optimum percentage of 10 wt% of F. The prepared ( $\text{Sn}_{0.8}\text{Ir}_{0.2}$ )  $\text{O}_2$ :10F electrocatalyst showing remarkably similar electrochemical performance and improved stability compared to pure  $\text{IrO}_2$  [151].

Furthermore, recent investigations by S.D. Ghadge et al. suggested one dimensional vertically aligned nanotubes of ( $\text{Sn}_{0.8}\text{Ir}_{0.2}$ )

**Table 4**  
Historical Results of Different Electrocatalysts in PEM Water Electrolysis.

anode catalyst	cathode catalyst	anode loading (mg/cm <sup>2</sup> )	cathode loading (mg/cm <sup>2</sup> )	membrane	Temp (°C)	Voltage at 1 A/cm <sup>2</sup>	Ref.
Ir-Black	40% Pt/GNF	2.0	0.8	Nafion-115	90	1.67	[113]
Ir-Black	40% Pt/XC-72	2.0	0.8	Nafion-115	90	1.70	[113]
Ir-Black	Pt40/Vulcan XC-72	2.4	0.7	Nafion-115	90	1.66	[72]
Ir-Black	Pd40/Vulcan XC-72	2.4	0.7	Nafion-115	90	1.70	[72]
Ir-Black	Pt-black	2.0	0.8	Nafion-117	90	1.71	[156]
IrO <sub>2</sub>	Pt-black	2.0	2.5	Nafion-115	80	1.60	[157]
RuO <sub>2</sub>	40% Pt/C	10	0.4	Nafion-115	–	1.88	[158]
RuO <sub>2</sub>	30% Pt/C	3.0	0.5	Nafion-112	80	1.65	[160]
RuO <sub>2</sub>	30% Pt/C	1.5	0.5	Nafion-1035	80	1.63	[159]
IrO <sub>2</sub>	30% Pt/C	1.5	0.5	Nafion-1035	80	1.67	[159]
IrO <sub>2</sub>	60% Pt/C	3.0	0.5	Nafion-115	80	1.58	[161]
IrO <sub>2</sub>	30% Pt/C	2.5	0.5	Nafion-115	80	1.7	[162]
Ir-Black	Pt/CNT	2.4	–	Nafion-115	90	1.72	[112]
Ru <sub>0.7</sub> Ir <sub>0.3</sub> O <sub>2</sub>	40% Pt/C	2.5	0.5	Nafion-117	80	1.70	[154]
IrO <sub>2</sub> /SnO <sub>2</sub>	40% Pt/C	1.5	0.5	Nafion-212	80	1.57	[155]
RuO <sub>2</sub> /SnO <sub>2</sub>	40% Pt/C	30.	0.6	Nafion-115	80	1.723	[155]
RuO <sub>2</sub>	40% Pt/C	3.0	0.6	Nafion-115	80	1.74	[155]
RuO <sub>2</sub>	30%Pd/N-CNT	3.0	0.7	Nafion-115	80	1.84	[100]
RuO <sub>2</sub>	30%Pd/P-CNPs	3.0	0.7	Nafion-115	80	2	[82]
RuO <sub>2</sub>	30%Pd/PG	3.0	0.7	Nafion-115	80	1.95	[120]
RuO <sub>2</sub>	30%Pd/PN-CNPs	3.0	0.7	Nafion-115	80	1.90	[163]
Ru <sub>0.8</sub> Pd <sub>0.2</sub> O <sub>2</sub>	30% Pt/CB	3.0	0.7	Nafion-115	80	2.03	[164]
Ir <sub>0.6</sub> Ru <sub>0.4</sub> O <sub>2</sub>	20% Pt/C	2.04	2.04	Nafion-115	80	1.56	[154]
RuO <sub>2</sub>	46% Pt/C	1.0	0.2	Nafion-117	80	1.68	[165]
Ru <sub>0.9</sub> Ir <sub>0.1</sub> O <sub>2</sub>	46% Pt/C	1.0	0.2	Nafion-117	80	1.75	[165]
Ru <sub>0.7</sub> Ir <sub>0.3</sub> O <sub>2</sub>	46% Pt/C	1.6	0.2	Nafion-117	80	1.80	[165]
Ru <sub>0.3</sub> Ir <sub>0.7</sub> O <sub>2</sub>	46% Pt/C	1.4	0.2	Nafion-117	80	1.74	[165]
IrO <sub>2</sub>	46% Pt/C	1.2	0.2	Nafion-117	80	1.80	[165]

O<sub>2</sub>:10F as a promising OER electrode for PEM water electrolysis. The synthesized Sn<sub>0.8</sub>Ir<sub>0.2</sub>O<sub>2</sub>:10F-NTs electrocatalyst exhibited better electrochemical performance with significantly 2.5 times more electrocatalytic activity compared to IrO<sub>2</sub> and Sn<sub>0.8</sub>Ir<sub>0.2</sub>O<sub>2</sub>:10F – Thin films electrocatalyst. Moreover, the synthesized Sn<sub>0.8</sub>Ir<sub>0.2</sub>O<sub>2</sub>:10F-NTs exhibits outstanding electrochemical stability in the harsh acidic environment. Additionally, Sn<sub>0.8</sub>Ir<sub>0.2</sub>O<sub>2</sub>:10F-NTs electrocatalyst has shown higher mass (21.67 A g<sup>-1</sup>), superior electrochemical surface area (38.46 m<sup>2</sup> g<sup>-1</sup>), specific activity (0.005633 mA cm<sup>-2</sup>), lower charge transfer resistance ( $\Sigma$ 4.2  $\Omega$  cm<sup>2</sup>) and lower Tafel slop (58.8 mV dec<sup>-1</sup>) compared to the as-synthesized IrO<sub>2</sub> and Sn<sub>0.8</sub>Ir<sub>0.2</sub>O<sub>2</sub>:10F-Thin film based electrocatalysts [152]. Finally conclude that, mixed metal oxides are contributes to enhance the efficiency and stability against corrosion and additionally they degreasing the cost of electrocatalysts.

## 7. Conclusion

In this review, we have discussed a short introduction about the various hydrogen production techniques and their advantages and disadvantages. In addition, have mainly focus on the recent development of PEM water electrolysis including their HER, OER electrocatalysts for water splitting and highlighting the most efficient electrocatalysts among similar materials. The present review not only discussed the present state-of-the-art also elaborated the in-depth investigations of historical research, challenges and recent achievements on PEM water electrolysis. In particular attention has also paid to the electrocatalysts that are more efficient and stable at large current densities in HER and OER, which have been remarkably advanced to show outstanding electrocatalytic activity and stability at higher current densities. Therefore in PEM water electrolysis considerable achievements have been made in emerging robust and stable electrocatalysts for commercial criteria. Finally, we outlined our idea for future research direction it should be proceed in order to improve renewable energy based PEM electrolyzers should be more cost effective approach.

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## Conflict of interest

On behalf of all authors, the corresponding author states that there is no conflict of interest.

## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.mset.2019.03.002>.

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