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Chapter 4

# Production of Hydrogen and their Use in Proton Exchange Membrane Fuel Cells

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## Abstract

This work will show an overview of the hydrogen production from ethanol by steam reforming method, using distinct catalysts, resulting in low carbon monoxide content in H2 produced; a thermodynamic analysis of reforming employing entropy maximization, the ideal condition for ethanol, and other steam reforming reactions, the state of the art of steam reforming catalysts for H2 production with low CO content. Moreover, in the second part, there will be an overview of the use of hydrogen in a proton exchange membrane fuel cell (PEMFC), the fuel cell operational conditions, a thermodynamic analysis of PEMFC, the catalysts used in the electrodes of the fuel cell, consequences of the CO presence in the hydrogen fuel feed in PEMFC, and the operation conditions for maximum output power density.

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**Keywords:** production of hydrogen, ethanol steam reforming, PEMFC, electrochemical energy, electrocatalysts

## 1. Introduction

This chapter shows the hydrogen production from ethanol-steam reformation and from photocatalysis and photoelectrochemical processes and the use of the hydrogen in a proton exchange membrane fuel cell (PEMFC) to convert chemical energy into electrical energy. The photocatalysis and photoelectrochemical processes use the solar energy for direct conversion of solar energy into renewable hydrogen fuel; moreover, solar energy is the unique renewable source that can fulfill the world's needs for the future to produce hydrogen fuel and generate the electricity. Hydrogen production can feed a PEMFC which converts chemical energy into electric energy by an electrochemical reaction. $H_2$ is oxidized at the anode and $O_2$ (often in the form of air) is reduced at the cathode, which results in electrical work. This system presents the advantage that it can be used in remote place to convert electrical energy without ambient degradation.

## 2. Hydrogen production from ethanol-steam reformation

The development of efficient technologies for the production and use of hydrogen, an alternative source for clean energy generation from the conversion of renewable biomass, has been presented as one of the most attractive possibilities for the gradual adaptation of the energy matrix to the global management policies of air pollutant emissions and to the sustainable use of natural resources.

The use of hydrogen in fuel cells, a clean and energy-efficient technology, has been promoted throughout the twenty-first century for the improvement of hydrogen production processes with low levels of carbon monoxide (CO). In particular, the ethanol-steam reforming reaction, a biomass-derived renewable product, has been considered extremely important for the advancement of PEM non-stationary fuel cell technology. The coupling of an ethanol reformer system to PEMFC results in a significant environmental advantage since it promotes a cycle of zero carbon emission when considering the fixation of $CO_2$ in the growth and development of sugarcane crops, feedstock for ethanol production [1].

The ethanol-steam reforming reaction is ideally characterized by the stoichiometric vapor-phase feed of 1 mole of ethanol and 3 moles of water in a catalytic reactor. The reaction produces 6 moles of $H_2$ and 2 moles of $CO_2$. This reaction is fundamentally endothermic and thus requires a source of energy external to the system for its realization. In addition, the process hardly occurs without the formation of byproducts and intermediates by the means of parallel reactions on the catalytic surface.

In a thermodynamic study via the minimization of Gibbs free energy using a non-stoichiometric method, Rossi et al. [2] verified that temperatures lower than 700 K do not favor the formation of CO; however, the maximum production of hydrogen notably occurs at higher temperatures. This result exposes the complexity of the process and the necessity to develop new highly selective catalysts to $H_2$ and $CO_2$ leading to the minimization of CO concentration via shift reaction. In general, according to Furtado et al. [3], the ethanol-steam reforming reaction involves numerous steps and usually competes with various reactions, which generate byproducts resulting in a lower $H_2$ yield. The breakdown of the carbon-carbon bond of ethanol multiplies the possible paths in the reaction network represented in **Table 1**, which requires higher temperatures, typically in the range from 623 to 923 K [4]. Although thermodynamic predictions indicate that it is possible to carry out the steam reforming reaction of ethanol at temperatures in the order of 523 K, the development of catalysts for the technological establishment of the process involves the understanding of many variables that can influence directly or indirectly in its viability. According to these studies, the temperature, pressure, composition and flow of reagents are variables that have a direct influence on the catalytic performance of the process. On the other hand, the use of different catalysts leads to different reaction paths so that the catalyst is a direct process variable and its composition (active phase, support), precursors and method of preparation are considered indirect variables but essentially important.

| | |
|---|---|
| $C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 6H_2$ | Ethanol steam reforming |
| $C_2H_5OH + H_2O \rightarrow 2CO + 4H_2$ | Incomplete steam reforming |
| $C_2H_5OH \rightarrow CH_3CHO + H_2$ | Ethanol dehydrogenation |
| $C_2H_4O \rightarrow CO + CH_4$ | Acetaldehyde decomposition |
| $2C_2H_4O + H_2O \rightarrow CH_3COCH_3 + CO_2 + 2H_2$ | Aldol condensation |
| $C_2H_5OH \rightarrow CO + CH_4 + H_2$ | Ethanol decomposition |
| $C_2H_5OH \rightarrow C + CO + 3H_2$ | Ethanol decomposition |
| $2C_2H_5OH \rightarrow (C_2H_5)_2 + H_2O$ | Ethanol dehydration |
| $C_2H_5OH \rightarrow C_2H_4 + H_2O$ | Ethanol dehydration to ethylene |
| $C_2H_4 \rightarrow 2C + 2H_2$ | Ethylene decomposition |
| $C_2H_4 + H_2 \rightarrow C_2H_6$ | Ethylene hydrogenation |
| $C_2H_6 + H_2 \rightarrow 2CH_4$ | Cracking reaction |
| $CH_4 + H_2O \rightarrow CO + 3H_2$ | Methane steam reforming |
| $2CO \rightarrow CO_2 + C$ | Boudouard reaction |
| $C + H_2O \rightarrow CO + H_2$ | Gasification |
| $CO + H_2O \rightarrow CO_2 + H_2$ | Water-gas shift reaction |

**Table 1.** Thermodynamically possible reactions in the steam reforming process.

Alternatives for purification of the reformate for the removal of CO and feed in PEMFC have been proposed by several researchers [3–10]. According to Rosseti et al. [5, 6], there are well-established routes, such as high- and low-temperature water-gas shift (WGS) and methanation, which can be integrated into the hydrogen production unit. Chen et al. [8] experimentally investigated a reaction system composed of two stages, an ethanol vapor reforming reactor ($Ni/Al_2O_3$ catalyst) followed by a water-gas shift reactor ($Fe/Cr_2O_3$ catalyst) to purify the hydrogen stream. In this study, four operational parameters including liquid flow, $H_2O/C$ molar ratio, reactor temperature and water-gas shift (WGS) reactor temperature were evaluated. The results indicated that the molar ratio $H_2O/C$ is the factor that most influences the performance of the system, which can be optimized to minimize CO formation.

Another alternative widely evaluated in the available literature [9, 10] considers the use of reactive systems of hydrogen-permeable catalytic membranes, which can lead to the production of highly pure hydrogen and therefore enable direct integration between the reformer unit and PEMFC. Koch et al. [11] studied the ethanol-steam reforming process aiming to feed a PEM fuel cell to produce clean energy. The process consists of two stages as shown in **Figure 1**; the first stage produces a high hydrogen content gas via ethanol steam reformation. The second stage, a palladium-based membrane, separates the hydrogen from the rest of the reformed gas, producing high-purity hydrogen (>99.9999%), which prevents poisoning produced by impurities or fuel shortage. Koch et al. concluded that ethanol-steam reformer process was able to generate a pure hydrogen stream of up to 100 mm/min to feed the PEM fuel cell [11].

Based on the feasibility of energy cogeneration through fuel cells from biomasses such as ethanol, Rossetti et al. [6] performed the simulation and optimization of the $H_2$ production process from the ethanol reformation with water vapor. The layout of the system was inspired by an existing unit in combined heat and power generation, with the purpose of evaluating the

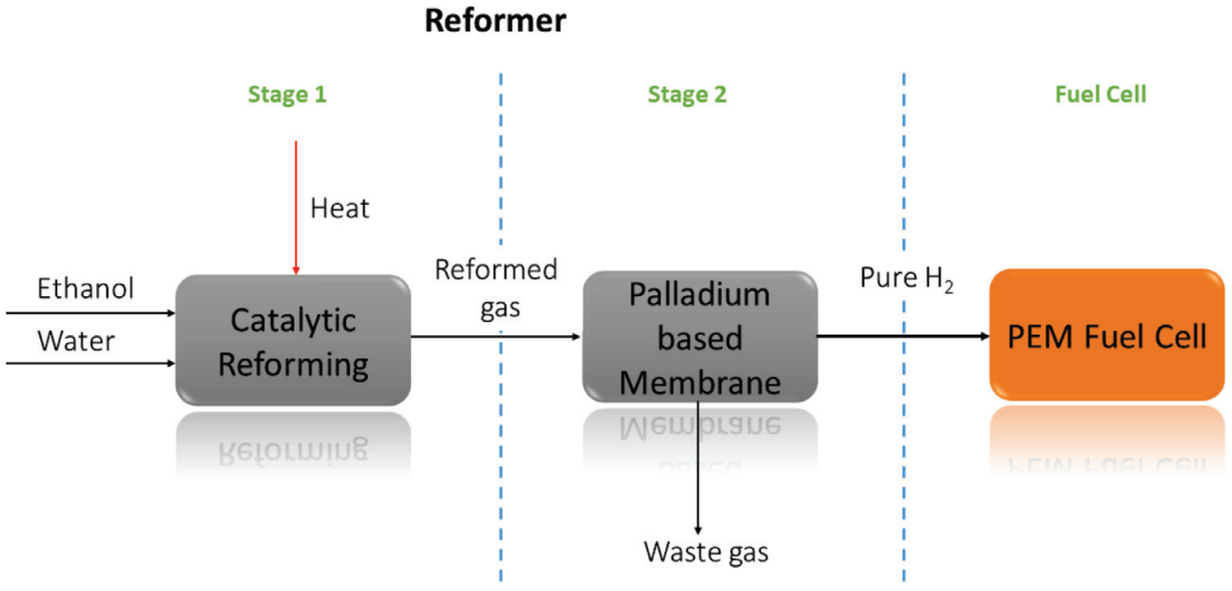



**Figure 1.** Simplified scheme of the reformer processes [11].

efficiency of the process and the possibility of operating with diluted bioethanol feed, reducing the cost with the purification step. The system consisted of six reactors connected in series for production and purification of hydrogen, containing a fuel processor, which includes a steam reformer, two water-heating gases and a serial methanation reactor, in addition to the fuel cell. The heat was generated by burning part of the reformate. During the process, it was verified that the change in water/ethanol ratio in the feed of the reactor had a direct impact on the production of $H_2$, that is, the increase in the ratio also increased the $H_2$ yield.

In view of the earlier information, it can be concluded that the ethanol-vapor reforming process combined with PEMFC is undefined between the two technological options presented, namely: reforming reactor and WGS systems in contrast to the use of membranes in the ethanol-steam reforming process. Finally, the technological development of the PEMFCs will possibly define the commercial choice for one of the two technologies.

## 3. The role of photophysics and photochemistry on water split process

### 3.1. Principles

Solar energy is the unique renewable source that can fulfill the world's needs for the future [12]. The direct conversion of solar energy into renewable hydrogen fuel is done basically by two methods, photocatalysis and photoelectrochemical (PEC) water splitting. The first method relies on photocatalytically active particles suspended in aqueous electrolyte solutions, where one or both water-splitting half reactions take place. The second method uses photocatalytically active particles or thin films deposited on electrodes [13].

Photocatalysis involves photophysical processes, initiated by photon absorption, followed by the generation of excited states and finalized as a photochemical or electrochemical redox reaction. These excited states permit that a prohibitive reaction under certain conditions can occur by the use of a photocatalyst, and this reason makes photocatalysis interesting for solar energy conversion technologies [14].

On search (and development) of new materials/catalysts for water-splitting processes, a common approach is to mimic natural processes and/or analogue materials. In case of water splitting, the natural process is photosynthesis. Under this point of view, the central role of natural water-splitting process is occupied by an enzyme complex, known as photosystem II (PS II), capable to split water using sunlight [15].

Photons absorbed by this enzymatic complex are transferred to the catalyst core, where a single charge separation takes place [4]. This catalyst core in PS II is a $Mn_4CaO_5$ oxo-bridged complex, represented by two similar models in **Figure 2**, but its exact reaction mechanism is still obscure [16].

Chlorophyll fluorescence is used to provide information on many aspects of photosynthesis. There are two different quenching mechanisms for chlorophyll fluorescence, a photochemical and a non-photochemical quenching. The first one is caused by charge separation at PS II reaction centers and can be considered a reliable measure of the PS II charge separation rate.

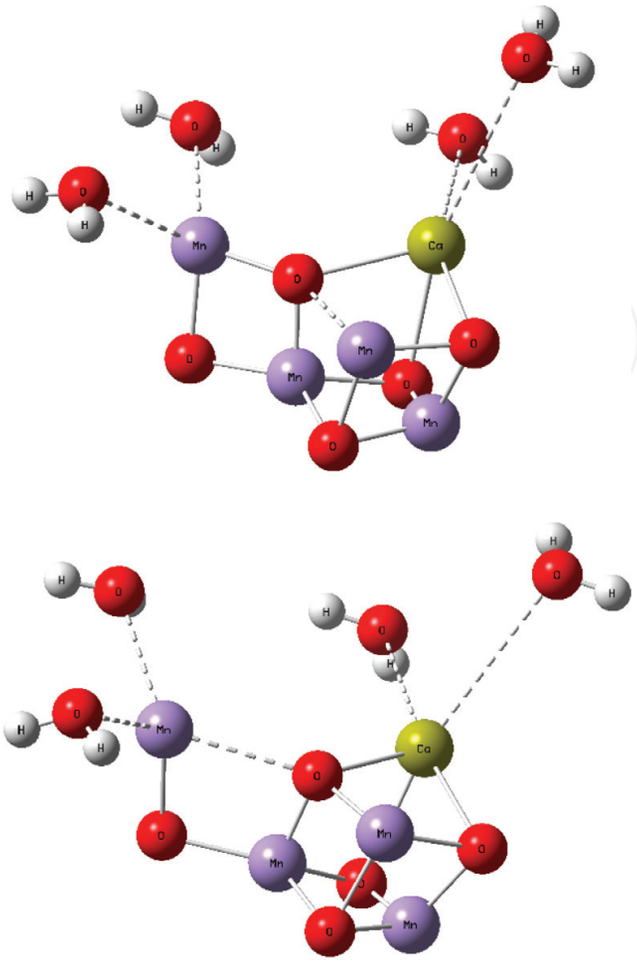



**Figure 2.** Representations of PS II core catalyst [16].

The second one may be due to a number of other non-radiative de-excitation processes in PS II [17].

Pijpers et al. punctuate that is necessary to separate light collection/conversion from catalysis. Whereas light collection/conversion generates one electron/hole pair at a time, water splitting is a four-electron/hole global process 4 as shown in reaction (1). This part of the process is particularly demanding once it involves the formation of double bonds between oxygen, four protons and four electrons [18]. Reaction (1) is known as oxygen evolution reaction (OER).

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \quad (1)$$

The subsequent, less demanding process is the reduction of $H^+$ into two hydrogen molecules, as shown by reaction (2), and known as hydrogen evolution reaction (HER).

$$4H^+ + 4e^- \rightarrow 2H_2 \quad (2)$$

It is important to point that, different from artificial processes, that usually have high over-potentials, this natural multi-protein complex uses only small driving forces and moderate activation energies [19].

### 3.2. Artificial design

Pijpers et al. affirm that an artificial photosynthesis design must guarantee that one electron-hole pair of a semiconductor be integrated with the catalyst to perform OER [4]. A general representation of an ideal photocatalyst, as proposed by Hisatomi, Takanabe and Domen, is represented in **Figure 3**.

### 3.3. Catalysts

Focusing on artificial processes, the evolution of oxygen, by UV-illuminated single crystals of $TiO_2$, suspended in water, was firstly reported by Frank and Honda et al. [22], in 1972. Further investigations in the photoelectrochemical behavior of $TiO_2$ leads to an increase in the interest on metal-oxide-based materials such as catalysts and with some time the development of a mixed catalyst for the mediation of water cleavage by visible light ($Pt/RuO_2$ is cited as an example). In parallel, some earth-abundant (Mn, Fe, Co, Ni) 3d-metal-based materials were developed [20]. By now, the interest on $TiO_2$ particles resides in its use as support material for water splitting [21].

Photoanodes of CdS were also used to cleavage water molecules induced by visible light 11 following the reactions represented in Eqs. (3) and (4).

$$\text{PHOTOANODE} : CdS + 2H^+ \rightarrow Cd^{2+} + S \tag{3}$$

$$\text{PHOTOCATHODE} : 2e^- + 2H_2O \rightarrow H_2 + 2OH^- \tag{4}$$

One associated issue of these electrodes is the photocorrosion in the time which deactivates these electrodes, increasing cost and causing maintenance to be difficult. These photoanodes were improved by coating with polypirrole-inhibiting photocorrosion of CdS anodes into $Cd^{2+}$

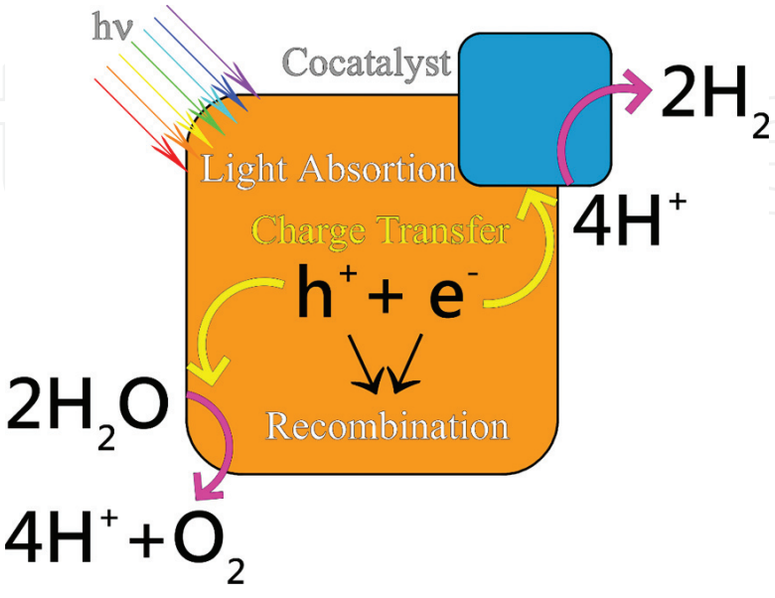



**Figure 3.** General representation of a photocatalyst [14].

ions, following the equations represented in reaction (5), more complex kinetically and thermodynamically less favorable [22].

$$2H_2O + 4H^+ \rightarrow O_2 + 4H^+ \quad (5)$$

Inert anodes are also applied on water oxidation, usually coated by a catalyst. One example is the use of ITO or FTO electrodes, coated by a self-assembled amorphous film, generated by electrodeposition of cobalt salts into phosphate, methyl phosphonate or borate electrolytes [18]. That approach has as a characteristic the need of an electrolyte medium that is a key factor for activity, selectivity and formation of the self-assembled amorphous film. The selection for cobalt resides on the fact that its tetranuclear oxo core mimics the natural oxygen-evolving complex (OEC) of PSII [23]. Regarding cobalt, thin films of Co-Pi (cobalt-phosphate) are deposited on $Fe_2O_3$, $WO_3$ and ZnO electrodes, focusing on reducing the onset potential for water oxidation leading to performing the process in neutral pH conditions. A posterior approach deposits Co-Pi thin films on the ITO film attached to an np-Si solar cell, directing the voltage produced by the solar cell to reduce the cited over-potential [15].

Cobalt is also reported to be associated with molybdenum-based polyoxometalates with the limitations that this system must contain tris(2,2′-bipyridine)ruthenium (II) ($Ru(bpy)_3^{2+}$) and sodium persulfate ($S_2O_8^{2-}$) in an aqueous borate buffer solution at pH 8.0 [24]. Berardi et al. [23] presents a new class of isostructural cubane-shape catalysts Cobalt-based, Hydrogen substituted by Me, t-Bu, OMe, Br, COOMe and CN, capable to water oxidation under dark or illuminated conditions, unfortunately again under highly basic conditions (pH = 8.0) in the presence of ($Ru(bpy)_3^{2+}$) as photosensitizer and sodium persulfate ($S_2O_8^{2-}$) as electrolyte. The best quantum efficiency (QE) decrescent substituent order is determined as OMe > COOMe > Me ≈ H ≈ Br ≈ CN > t-Bu. In conclusion, the combination of semiconductor-electrocatalyst-electrolyte interfaces is mandatory on water-splitting photocatalysis.

Yellow scheelite monoclinic $BiVO_4$ is also used as a photocatalyst for $O_2$ evolution under visible light, in the presence of an appropriate electron acceptor. But due to its conduction band bottom limit is located on a more positive potential than the potential of water reduction; it is incapable of evolving into hydrogen [25]. However, $BiVO_4$ doped with In and Mo produces a Bi(1-X)In(X)V(1-X)Mo(X)$O_4$ catalyst, with a more negative conduction band than $H^+/H_2$, making it capable of water splitting at neutral pH-evolving hydrogen with no use of any sacrificial agent [25].

Following additional layers' approach, Si electrodes gain focus again in 2014, with Kaiser and Jaegermann's [12] work. The electrochemical properties of single-crystalline p-type 3C-SiC films on p-Si and n-Si substrates are investigated as electrodes in $H_2SO_4$ aqueous solutions, under dark and light conditions. The photoelectrochemical measurements on different wavelengths indicate the p-SiC film on p-Si substrate which can generate a cathodic photocurrent, corresponding with hydrogen production, and can also generate an anodic photocurrent, for oxygen evolution. Iron nickel oxide (FeNiOx) is also used for water splitting. One remarkable example is reported by Morales et al. on which an amorphous layer of the oxide is oxidatively

electrodeposited on hematite, capable of evolving oxygen and practically transparent. This optical transparency property permits the composition of the oxide catalyst into a hematite/perovskite tandem water-splitting cell. Solar-to-hydrogen conversion efficiencies are reported to be around 2%. The development of the catalyst and its integration into photoanodes open new possibilities in solar fuel production [26].

Following a nanostructuring and morphology control approach [13], numerous efforts have been taken to investigate morphologies and nanostructures of the NiCo-oxide and also the relationship between the nanostructure and the electrocatalytic activity. Compared to NiCo oxides, NiCo sulfides appear as promising electrocatalysts [13]. More recent works show nickel cobalt selenide (NiCo-selenide) as a better electrocatalyst candidate when compared to its oxide-based and sulfide-based species [20].

Cocatalysts are combined to catalysts in order to increase its efficiency [13]. It is concluded that the role of cocatalysts is different in photocatalysis and in photoelectrochemical water splitting for $LaTiO_2N/Co_3O_4$ systems. Cocatalyst is not only material and concentration dependant, but it also depends of the size distribution of particles. Small particles are favorable for photocatalysis due to kinetic effects. In PEC, larger cocatalyst particles are better, probably due to avoiding charge recombination. Under this point of view, the design of a cocatalyst size must be function to the solar light energy conversion process [13].

Recently, Garcia-Esparza et al. [27] report the manufacture of an oxygen insensitive system ($MoOx/Pt/SrTiO_3$), that, when coated on metal surfaces, can evolute hydrogen and avoid recombination of $H_2$ and $O_2$ onto water, maintaining $H_2$ evolution at high taxes. Catalyst candidates can also be proposed using computational chemistry tools. Many distinct properties such as optical and transport properties electronic-band structure, density of states, and others, can be accurately determined by distinct levels of theory. Recently, Reshak [28] proposed that $Tl_{10}Hg_3Cl_{16}$ single crystals can be used as a catalyst in water splitting due to electronic and optical properties calculated by density functional theory/mBJ. Its results are compared to experimental data to conclude that these computational tools can be used with good levels of precision, helping to elucidate internal details of these systems.

## 4. Proton exchange membrane fuel cell

The proton exchange membrane fuel cell (PEMFC) is a device that converts chemical energy into electrical energy through an electrochemical reaction [29]. At the anode, the hydrogen or other fuel that may produce pure hydrogen like the ethanol-steam reforming process is oxidized and releases protons and electrons. The protons are carried out to the cathode side through electrolyte and the electrons produce electrical current in an external circuit. At the cathode, the electrons and the protons are associated with oxygen (often from atmospheric air) producing water and energy as a final product from PEMFC; thus, the fuel cell system does not produce pollutants and is ambient compatible.

The chemical reactions are:

$$\text{Anode} : H_2(g) \rightarrow 2H^+ + 2e^- \tag{6}$$

$$\text{Cathode} : O_2(g) + 2e^- + 4H^+ \rightarrow H_2O \tag{7}$$

The global reaction of the fuel cell system can be written as Eq. (8). The theoretical potential (E) of this reaction is 1.23 V, but at the operational condition the potential is around 0.7 V. This potential result at the maximum output power density is about 1 W $cm^2$ [30, 31].

$$\text{PEMFC} : H_2(g)\ (\text{at anode}) + O_2(g)\ (\text{at cathode}) \rightarrow H_2O(l) + \text{energy} \tag{8}$$

**Figure 4** shows a representative schema of the PEMFC operation. The fuel is fed at the anode site and the oxygen is fed at the cathode side. The electrons from anode to cathode are used in an external electrical circuit to produce electrical work.

An alternative source of hydrogen can be the steam reformation of liquid substances like alcohols of small chairs. Ethanol, for example, is low density and nontoxic alcohol obtained from fermentation of renewable resources like sugarcane. This has been studied as a possible fuel in direct alcohol fuel cell (DAFC) systems [32]. However, its direct use is difficult due to the rupture of C—C bond on platinum or platinum alloy electrodes. The ethanol-steam reforming reactions take place in different steps with endothermic/exothermic reactions [33, 34].

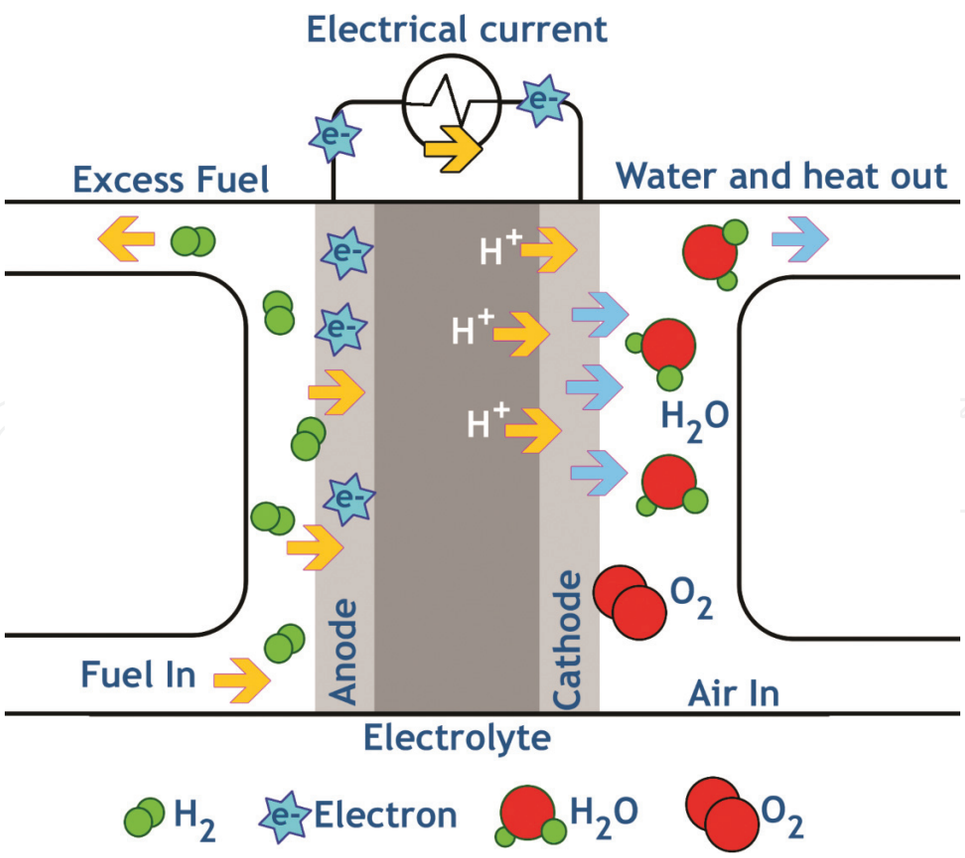



**Figure 4.** Proton exchange membrane fuel cell (PEMFC), anode fed with $H_2$ and cathode fed with $O_2$. Protons are carried out from anode to cathode through membrane electrolyte and the electrons produce working in an external circuit.

For ethanol-steam reforming reaction the chemical reactions are:

$$C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 6H_2 \quad (9)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad (10)$$

$$CO + ½O_2 \rightarrow CO_2 \quad (11)$$

The PEMFC works at low temperature due to electrolyte that is hydrated (lower than 100°C), which is an advantage, as well as other new materials that enable the cell to work at high temperature [35]. At low temperatures, the catalytic material that presents high efficiency is platinum, for both anode and cathode electrodes. But, as demonstrated previously, hydrogen obtained from steam presents low-content CO, which adsorbs strongly on platinum surface and poisons the electrode. To outline this problem, a second metal is included into the electrode. This second metal often is a transition and not a noble metal which dissociated in water at low potential and provides oxygenated species to oxidize the adsorbed CO at a lower potential. This pathway is known as the Langmuir-Hinshewood mechanism [36], where two adsorbed species react and form a final product; some studies show that PtRu is the more efficient electrocatalyst [37–39]. The use of pure Pt as anode of PEMFC fed with $H_2$ , presenting 100 ppm of CO, results in more than 50% of loss of efficiency due to electrode poisoning effect [37].

The research of PEMFC focuses on minimizing the amount of Pt used in the electrodes, due to high cost of this material; moreover, the oxygen reduction reaction which happens at the cathode electrode presents low kinetic and parallel pathways producing $H_2O_2$, resulting in loss of power density output. The use of the different cathode material improves the performance of the fuel cell. The development of a membrane working at high temperatures can improve the kinetics of chemical reactions also and results in better fuel cell performance.

The main advantage of the fuel cell system, notably PEMFC, is the efficiency in energy conversion, once the efficiency of electrochemical systems is above the other converter; however, the source of hydrogen is important [40, 41]. The hydrogen obtained from water electrolysis is very pure, but it results in energy deficit [42]; the $H_2$ from steam hydrocarbons contains CO. Thus, the tendency is an aggregate of the system to convert energy. Solar photovoltaic can be used to produce highly pure $H_2$ for PEMFC and moreover, solar energy can charge batteries [43] for later use.

## 5. Conclusions

Solar energy is a renewable source that can fulfill the world's needs for the future. The direct conversion of solar energy into renewable hydrogen fuel is done basically by two methods: photocatalysis and photoelectrochemical processes. The hydrogen obtained from photocatalysis and/or photoelectrochemical process can feed PEMFCs to convert chemical energy into electrical energy with high efficiency and without degradation of the ambient. PEMFC fed with $H_2$ obtained from ethanol-steam reforming reaction (which contains CO) must use Pt-based alloy catalysts to increase the poisoning tolerance and improve the lifetime of the PEMFC.

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## Conflict of interest

The authors state that there is no conflict of interest associated with this work.

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