



Hydrogen production in the electrolysis of water in Brazil, a review



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ABSTRACT

Hydrogen is a promising fuel, can be obtained from different sources of raw materials, including water. This is a renewable and sustainable source, which can obtain a high hydrogen purity via electrolysis. Among the processes for obtaining hydrogen from the water, the electrolytic conversion is the best known, in which two electrodes are responsible for conducting electricity and production of this gas. However, to promote this segregation, some technological challenges must be overcome, as the efficiency of electrolyzers, efficiency and durability of the main fuel cells and the integration of the electrolysis systems for supply and energy, aiming to reduce production costs. The Brazil stands out worldwide with production of fuels obtained from renewable sources and also seeks to develop the hydrogen production through water electrolysis.

1. Introduction

The gradual increase in energy demand in the world, the possible shortage of fossil fuels and concern for the environment has driven research on the development of biofuels [1]. These are considered promising because they are derived from renewable raw materials and viable alternatives for the replacement of non-renewable fuels. In addition to providing greater energy security for countries, contribute to the integrity of the environment by reducing emissions of greenhouse gases (GHG) [2].

According to hotza and Da Costa [3] the hydrogen from renewable sources can be used as a biofuel and its use has been increasing, especially regarding the use in fuel cells, interconnected systems combined with the reformers. With this, the technological research has stepped up development in the energy sector.

Hydrogen is considered an energy carrier, characterized by the absence of GHG emissions (greenhouse gas) when in operation, and therefore, it is not harmful to the environment [2,4,5]. The main raw materials used for obtaining hydrogen are derived from fossil fuels, such as natural gas [6], but other renewable sources are being studied, such as charcoal [7], biogas [8], water, ethanol, glycerol, among others [2].

Considering the water as a raw material for obtaining hydrogen via

the electrolysis process becomes an alternative, consisting of the combination of oxidation and reduction reactions caused by the electrical current. When this form of hydrogen production is used in vehicles provides greater energy efficiency [9]. This route becomes favorable, especially when combined with other energy generation processes, either: hydro, solar or wind, as these sources are considered bases for obtaining hydrogen [10].

However, for their use is efficient, various types of cells must be improved, the main ones are: alkaline, phosphoric acid, solid oxide, cast, and polymeric solid carbonate, the latter is currently less studied. The main difference between them is associated to the electrolyte, with solution of potassium hydroxide, phosphoric acid, yttrium-stabilized zirconium oxide (solid), potassium carbonate, lithium carbonate and polymeric membrane, respectively. Each also differs by temperature and operating pressure, electrical efficiency, costs and applications [11].

The electrolysis may also come as occurs catalyzed biologically as recited by Masa and Schuhmann [12] It is considered as Bioelectrolysis, using redox enzymes, that is to harmonize concepts of electrocatalysis and bioelectrolysis in this context becomes a limiting factor to find the active sites of the enzymes that sometimes is encapsulated within the enzyme, thus hindering the electrolytic procedure. As well as the other sense we have the means of electrolysis

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culminating in the simulation of photosynthesis artificially indicating that the biological study may favor the electrolysis process [13].

The main electrolyzers work with alkaline substances and polymeric electrolytes (PEM), the second is a new technology, while the first technology is more developed, justifying the fact that the most widely used today [14]. The use of such electrolyzers have some disadvantages such as low pressure, corrosive (alkaline) and high costs (PEM); however, one of the alkaline advantages is the fact that it is considered a stable technology. The PEM is capable of operating at pressures above 30 bar, depending on the material used, maintaining a high efficiency.

In addition, the electrolysis of water objective intensify the use of fuel cells for electricity generation [2]. These cells are electrochemical devices that generate electricity from the consumption of hydrogen and oxygen available [11].

There are also highlight the importance of research based on Photoelectrolyzer that when using solar radiation, typically under low stringency conditions such as ambient temperature and atmospheric pressure, are obtained encouraging results, even in regard to the treatment of effluents. Opening the way for work to using multi-component photoredox with nanocomposites, for exemple, in relation to wastewater treatment and production of hydrogen plus methane by reduction of CO₂ [15–18].

The Brazil it created, in 2002, the Fuel Cell Program (Procac) whose purpose was to organize and encourage research and development. However, in 2005 it was replaced by the Procac by Science Technology and Innovation Program for Hydrogen Economy (PROH₂) which also aims to improve the entire hydrogen production chain and use of fuel cells [19].

This study Aimed to describe the process of water electrolysis for hydrogen production, the main electrolyzers used, the Difficulties related to hydrogen production and alternatives to make it viable, as well as collecting data about scientific papers on the use of fuel cells in Brazil and the world; and present the current situation on the production of hydrogen by water electrolysis in Brazil.

2. Hydrogen

Hydrogen is considered a primary energy source and has the ability to direct energy generation, tends to facilitate the production of energy. Since, the energy in the H₂ can be stored for future use and consequently reduce problems arising from the consumption of non-renewable resources [4].

The insertion of hydrogen in the energy sector is occurring gradually, mainly due to the cost for fuel generation, however, the participation of public policy is facilitating the production of hydrogen, impacting globally in renewable energy generation [20].

The production of H₂ is an environmentally attractive process and can occur via routes considered sustainable, as the electrolysis of water, charcoal and biomass gasification, photo-electrolysis, biological processes and reform [21]. Thus this can be recognized as biofuel, receiving incentives in state policies for generating energy (stationary or mobile), mainly strategic-economic, technological and environmental. Hydrogen has great advantages such as alternative energy and reducing emissions of greenhouse gases (GHG). In addition to the social concept of job creation, inserted in the technology [4,19].

This fuel can be obtained from a variety of methods, the main are characterized by production from fossil and renewable sources by steam reforming, dry reforming, thermal decomposition and cracking natural gas, petroleum hydrocarbon oxidation and coal gasification. These methods require the use of high energy load to which the process occurs [20].

Various materials can be used to obtain H₂ and according McLellan et al. [20] the fonts that allow obtaining it are usually of fossil materials, but the commercial market share of hydrogen tends to increase, as this depends on technological advancement and improve-

ment of fuel cells and/or H₂ storage. The storage of this fuel can be in liquid or gaseous form, believing that might replace natural gas [22]. Another alternative are photocatalytic reduction of carbon dioxide heterojunction synthesized at room temperature via the sonication-assisted deposition-precipitation. According to Ong et al. [23] with the use of these photocatalytic load transfer is efficient and also aims to provide clean, renewable energy and solar energy conversion.

In order alleviate environmental impacts generated by oil products, the H₂ can be obtained from renewable sources such as biomass [24]. One of the advantages of the use of H₂ is that in comparison with the hydrocarbons, the combustion results only in release of large amounts of water and energy, not generating GHG [25].

3. Obtaining hydrogen by water

Electrolysis is a process which decomposes water, forming hydrogen and oxygen. This method of production may be performed on small scales. There are several ways of obtaining hydrogen via electrolysis as the direct conversion thermochemical, photochemical conversion, the photoelectrochemical conversion, biochemical conversion from the water and electrolyte.

The thermochemical direct conversion operates at high temperature (2000 °C) required for dissociation into hydrogen and oxygen, generating an excessive energy expenditure for heating, and that the unstable mixture involves considerable risk of explosion. To decrease the temperature procedure, chemicals are introduced as iron oxide, to form an intermediate in association step, and then separately release hydrogen/oxygen dissociative steps [26,27].

The photochemical conversion process is the use of a photochemical reactor where the light incidence activates a photocatalyst. Resembling the natural photosynthesis, wherein the dissociation of water takes place via solar energy [27], however, requires a number of components arranged in supramolecular complexes, so that the electrons generated by light is removed and transferred to the system functional catalysts [28] that will take advantage of their potential energy.

The photoelectrochemical conversion or photoelectrocatalytic [27] is considered as the most promising hydrogen production technologies and is designed based on the construction of a module series of dye-sensitized solar cells, separating the hydrogen gas and oxygen upon decomposition of water. The hydrogen generation efficiency is measured taking into account how much light energy is converted into hydrogen, however, the current conversion technology is not considered very effective [29].

In the microbial conversion via electrolysis, the bacteria are present in different biomasses are electrochemically active and oxidize organic matter, generating carbon dioxide (CO₂), electrons and protons. Microorganisms provide electrons to the anode and the protons are released into the solution. The electrons are then transferred through a conductor to a cathode and combine with the free protons in solution [30]. However, this does not occur spontaneously, necessitating a cathode potential use of at least 0.2–0.8 V under normal biological conditions [4].

The production of hydrogen via electrolytic cells is the most widely used today, consisting of the electricity use in reservoir containing water. These cells consist of two electrodes, cathode and anode that are responsible for conducting electricity to the system [31].

4. Electrolysis through electrolytic cells

Electrolysis of water is regarded as a promising technology because of its simplicity, low maintenance requirement and handling [14]. According to Kelly [9], this procedure combines oxidation and reduction reactions producing hydrogen gas separated from the oxygen gas. However, even if sustainable usually is used only to obtain hydrogen with high purity [32]. The generation of energy as a supplement, not an

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