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Green Hydrogen and Green Investments in the New Era, in Accordance with Directive (EU) 2016/802 of the European Parliament and of the Council of the European Union

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Abstract: The continuous and uncontrolled emission of gaseous gases worldwide and across borders between the Member States of the European Union, has led to serious environmental issues, which are related to the depletion of ozone (O_3) in the atmosphere, the occurrence and enhancement of the greenhouse effect (GHG), the global warming, the acid rain, the smog and other phenomena, adverse to the environment, public health, economic and social activity of countries. The European Union has already adopted Directive (EU) 2016/802, concerning the maritime sector that we will be addressed in this paper, on reducing sulfur dioxide (SO_2) emissions from ships. The latter has been incorporated in the Greek legislation with the no.: 128/2016 Joint Ministerial Decision (Government Gazette B '3958). The ever-increasing need to good's transportation, increases the need to create a larger merchant fleet in order to increase global capacity. At the same time, the need for the use of fuels as ship's energy sources, is increasing. Fuels that will be used both for the ship's propulsion and to meet secondary needs, such as the production of electricity and the movement of ship's auxiliary engines, it is necessary to be create in order to meet the global merchant fleet's needs in energy. This increase has the effect of increasing the emissions of gases that are dangerous for the environment and those responsible for a large percentage of global warming and the greenhouse effect. In this paper, the use of hydrogen (H_2) as a marine engines' fuel is analyzed and not only. The production of green hydrogen from renewable energy sources is studied and economic factors arising from the production and use of this fuel are analyzed.

Keywords: Cost, European Union, Fuel cells, Green hydrogen, Green investment, Hydrogen, Hydrolysis, Shipping

I. Introduction

The ever-increasing global merchant fleet has resulted in a rapid increase in energy demand. To this day, oil is used as the main fuel for shipping. Its production and disposal costs are low in relation to its energy efficiency, while factors such as easy and safe storage and

transportation are another serious reason for its use. But two key issues need to be addressed. On the one hand, energy storage is constantly declining and on the other hand, its combustion into the ship's internal combustion engine (ICE), produces high levels of gaseous pollutants, such as carbon dioxide (CO2), nitrogen oxides (NOx) and sulfur oxides (SOx). These gases play a key role in the upper atmosphere's destruction, and ultimately are the main factor in maintaining and enhancing the greenhouse effect (GHG) and global warming. This phenomenon has negative, if not catastrophic, effects on world health, economy and in general, in every socio - economic - biological sector. For this reason, the European Parliament and the Council of the European Union have adopted Directive (EU) 2016/802 (The European Parliament and the Council of the European Union., 2016) which provides for the reduction of ship's hazardous sulfur dioxide (SO2) emissions and the complete de-carbonization of fuel gradually at a rate of 40% until 2030 and 70% until 2050 with the demand for complete de-carbonization. The solution to the above problem is the creation and use of fuels, environmentally friendly, produced by renewable energy sources and renewable raw materials, so as to reduce and if it's possible to eliminate the hazardous gas emissions in the atmosphere, as the participation of shipping in production of hazardous greenhouse gas emissions accounts for 7% - 8% of global emissions. (Atilhan, Park, El-Halwagi, Atilhan, Moore, & Nielsen, 2021)

Of course, before the production process and use of the fuels above, many factors must be considered, social, economic and technological.

In the global shipping industry, the International Maritime Organization (IMO) has already set a goal of reducing ship's hazardous gaseous emissions by 40% until 2030 and by up to 70% until 2050, with continuous additional reduction, until the complete fuel's de-carbonization.

In addition, Chapter VI has been added to the International Convention for the Protection of the Environment from Ships (MARPOL), for the protection of ambient gas from ship's emissions.

1.1 The Directive (EU) 2016/802

One of the main factors leading to the air pollution's reduction and the intensification of the greenhouse effect, is the pollution caused by ship's emission, which contain sulfur dioxide, carbon dioxide, various oxides of nitrogen and nitrogen oxides particles. These emissions are harmful to human health, the environment but also play an important role in the formation of acidic sediments. Sulfur dioxide (SO_2) emitted by ships into the atmosphere is involved in the formation of suspended particles, which in combination with its acidification is a transboundary phenomenon and must be addressed by Member States, both locally, nationally and EU. These emissions have as a result in the sensitive ecosystems' damage and the biodiversity's reduction, which also has a negative impact on forest development and agriculture. (The European Parliament and the Council of the European Union., 2016)

The European Union has set targets for achieving clean air levels in a way that does not adversely affect the environment and human health. The way of implementing measures to achieve the above objectives is mainly described in the sixth action plan for the environment, established by the decision no: 1600/2002 / EC of the European Parliament and of the Council, but also in the seventh action program, established by the No: 1386/2013 / EU decision of the European Parliament and of the Council. (The European Parliament and the Council of the European Union., 2016)

It is worth noting that Article 191 par.2 of the Treaty on the Functioning of the European Union stipulates that in the environment's field, Union policy must be such as to aim at a high level of protection, taking into account the diversity of different regions of the union. (The European Parliament and the Council of the European Union., 2016)

In order to prevent the aforementioned problems from ship's emissions, the European Union, by Directive (EU) 2016/802, sets limits for the maximum permissible sulfur content of heavy fuel oil, internal combustion oil and marine fuels used within of its territory, as the natural presence of sulfur in small quantities of oil and coal, is the most important source of sulfur's dioxide emissions, a gas responsible for the formation of acid rain. (The European Parliament and the Council of the European Union., 2016)

The mooring of ships, especially in the ports of the union, causes air pollution in the cities and ports, as it becomes difficult for them to try to meet the emission limit values set by the union. Therefore, it is important to create onshore power infrastructure for ships during their berthing, in order to reduce the use of electric motors and the additional burning of oil. (The European Parliament and the Council of the European Union., 2016)

In any case, the Directive stipulates that each Member State of the Union shall take all measures to ensure that no internal combustion oil with a sulfur content of more than 0,10% by mass is used within its territory. (The European Parliament and the Council of the European Union., 2016)

Especially for ships, they will not use fuels with a sulfur content of more than 3.50%, unless they use emission reduction systems, such as a mixture of ship fuel and liquefied natural gas tanks, exhaust gas cleaning systems or biofuels. (The European Parliament and the Council of the European Union., 2016)

Despite the above limits, from 01-01-2020, new limits have been set and apply for the sulfur content of ship fuels, according to which, Member States shall ensure that any ship sailing in their territory and within Special Control Areas Emissions (SECA), will not use fuels with a sulfur content of more than 0.5% by mass.[1]

During the ships' mooring in ports of the Union, they may not use fuels with a sulfur content of more than 0,1% by mass. (The European Parliament and the Council of the European Union., 2016)

1.2 Economy and Infrastructure.

As set out in Regulation 18 of the revised Annex VI to the International Convention for the Protection of the Environment from Ships (MARPOL), Member States must ensure that ships have fuel on board that complies with the requirements of the Directive, while at the same time access to emission reduction methods should also be facilitated. (The European Parliament and the Council of the European Union., 2016)

In an effort to meet the Union's targets for low limits on sulfur and other pollutants, fuel prices are expected to rise significantly, albeit in the short term, affecting the competitiveness of maritime transport. (The European Parliament and the Council of the European Union., 2016)

Member States, through funding programs, must establish the appropriate infrastructure for the manufacture, storage and disposal of fuels, further enhancing studies and research aimed at creating low-cost, low-carbon and zero-sulfur fuels.

II. HYDROGEN

Hydrogen is a new and promising future fuel with zero sulfur and carbon content when it is made using renewable energy sources and renewable raw materials. It is a non-metallic chemical element with atomic number 1 and chemical symbol (H). In addition, due to its atomic mass corresponding to 1.00794 amu (atomic mass unit) or Da (Dalton), it is ranked first in the periodic table of elements, as the lightest element of nature, as shown in Figure 1 below. It is abundant in nature. Although for its use, it must be isolated through other chemical compounds and elements as it does not exist in free form. Nevertheless, it is a fuel with high energy efficiency, about four times higher than that of conventional diesel fuels. It can be used both as a free fuel and through the construction of fuel cells, or as a part of a blend with other fuels with a low hazardous elements' content. Its disadvantages are its low volumetric efficiency when it is in gaseous form, in relation to its much higher gravitational efficiency in liquid form. However, the exploitation in liquid form, is still a difficult case, since its liquefaction and storage require huge amounts of energy, mainly for cooling and liquefaction at temperatures below to -33o K (Zuttel, 2003).It also involves high cost of storage construction and maintenance infrastructure, mainly for its gaseous form, where storage requirements are huge, in order to cover the energy's needs from its use.

Additionally, having a particularly high flammability, in percentages ranging from 4% to 77% by volume is a particularly dangerous and explosive fuel while during its combustion with oxygen, water is produced and energy equal to 286kJ / mole is released.

$$\mathbf{2H_2 + O_2 \longrightarrow 2H_2O + 572\ kJ}$$

In any case, hydrogen is the first fuel with zero levels of hazardous chemical elements and its production is expected to increase from 70 million tons in 2019, to 120 million tons by 2024 (Safari & Dincer, 2020) (Global hydrogen market insights, 2020-2024 by production process, end-user, generation system and region, 2020) (Atilhan, Park, El-Halwagi, Atilhan, Moore, & Nielsen, 2021)

2.1 Hydrogen's separation.

Hydrogen, depending on the way and the process followed for its preparation, but also depending on the raw material used, is divided into four categories. Gray, blue and green hydrogen.

2.1.1 Grey hydrogen.

It is the most common and frequently used type of hydrogen. Its preparation is carried out through the processing and remodeling of fossil fuels, but mainly through the remodeling of steam, which comes from natural gas or shale (Norazlianie, 2020) (IEA, 2019) (Atilhan, Park, El-Halwagi, Atilhan, Moore, & Nielsen, 2021). Due to the method of preparation and the raw material used, during its combustion it presents emissions of gaseous pollutants, mainly carbon dioxide.

2.1.2 Blue hydrogen.

In case that during the use and combustion of hydrogen, gases that produced containing elements harmful to the atmosphere are isolated, mechanically retained, or can be reused, as in the case of dry reformat (Atilhan, Park, El-Halwagi, Atilhan, Moore, & Nielsen, 2021) (Noureldin, Elbashir, Gabriel, & El-Halwagi, 2015), then hydrogen is characterized as blue.

2.1.3 Green hydrogen.

The last distinction of hydrogen, which is of increasing interest for the reasons previously analyzed, is green.

Green hydrogen means that, renewable raw materials and renewable energy sources are used for its preparation. Methods of preparation in this manner are mainly those carried out by the separation of water (H_2O) in its elements and the capture of hydrogen by this process.

$$\mathbf{2H_2O \longrightarrow 2H_2 + O_2}$$

Such methods may be water's electrolysis, water's photocatalytic separation, thermolysis and water's thermochemical separation. (Atilhan, Park, El-Halwagi, Atilhan, Moore, & Nielsen, 2021) (Mengjiao, Guizhou, Zhenxin, Yukui, & Dong, 2019)

At the same time, the renewable energy sources used for the hydrogen's production, are wind and solar energy, while nuclear energy, geothermal or hydrodynamic energy can be used (Atilhan, Park, El-Halwagi, Atilhan, Moore, & Nielsen, 2021) (Li, 2017). Through these sources, an attempt is made to produce the required amounts of energy for the application of the above methods and the final intake of green hydrogen. (The European Parliament and the Council of the European Union., 2016)

Until recently, its preparation was considered unprofitable, due to the electrolysis's energy required cost but also due to the high cost of catalysts used in the process. However, using renewable energy sources with zero or very low cost and also with the significant reduction of catalyst costs, that are expected to reach 70% of current costs, green hydrogen becomes a very promising energy source for shipping . (Atilhan, Park, El-Halwagi, Atilhan, Moore, & Nielsen, 2021)

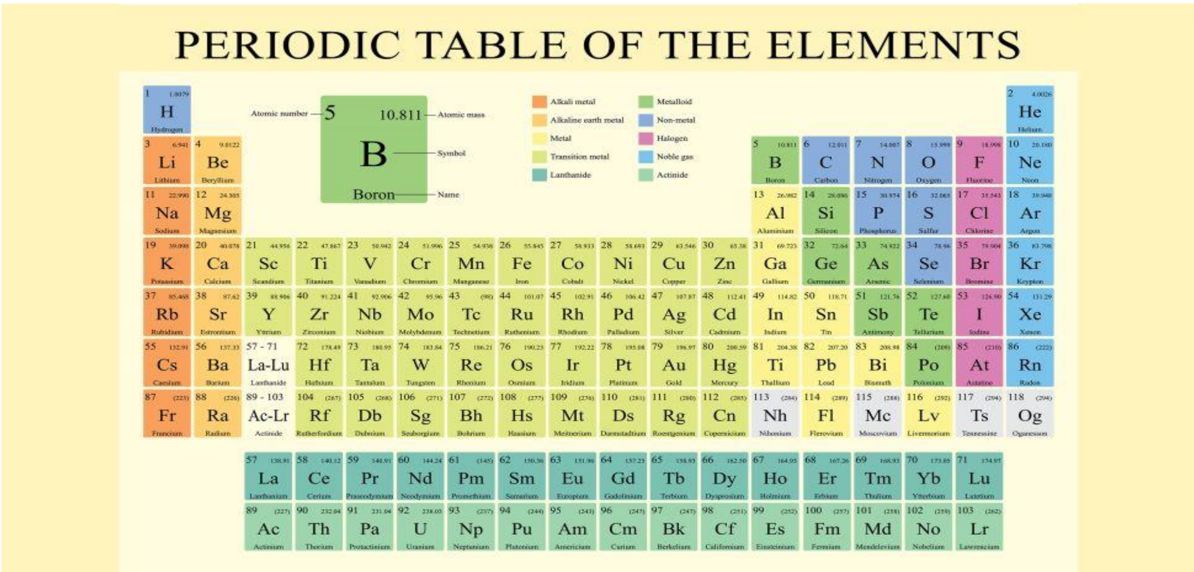

Fig 1. Periodic table of elements.

Source: https://www.livescience.com/25300-periodic-table.html

2.2 The green hydrogen's production.

The green hydrogen's production is based exclusively on the use of renewable energy sources and renewable raw materials. It is a process that allows the production and use of hydrogen fuel, with zero production's and emissions' harmful gases to the atmosphere, mainly carbon dioxide, thus contributing to the greenhouse's effect reduction. However, there are still significant problems, technologically and economically, that need to be addressed in order the "green processes" to go into mass production (Van Hulst, 2019,) (Atilhan, Park, El-Halwagi, Atilhan, Moore, & Nielsen, 2021).

Given that the water as a raw material, is abundant in the global shipping industry, the concern for hydrogen's production focuses on the high need to generate electricity, which is essential for the electrolysis. (Atilhan, Park, El-Halwagi, Atilhan, Moore, & Nielsen, 2021)In essence, the cost of the process is now mainly attributed to the electrolysis process and not to the raw material.

Assuming that renewable energy sources such as wind, solar and hydrodynamics are at the disposal of the global merchant fleet, it remains to answer questions such as whether the amount of the produced hydrogen is sufficient to meet a ship's daily needs, if the production rate is able to cover the daily quantities consumed, but also if there is a possibility of safe storage of fuel's sufficient quantities on board. It is worth noting that hydrogen has a high gravitational energy density, about 0.033 MWh / kg, (Makridis, 2017)provided it is stored and used in liquid form. In order for the hydrogen gas to liquefy, particularly low temperatures, below 33o K (-240o C) are required (Zuttel, 2003). Maintaining these temperatures requires high amounts of energy.

On the other hand, hydrogen's use in gaseous form, requires huge storage spaces on board, as its volumetric energy density reaches only 0.003 MWh / m3 at a pressure of 1 bar, (Makridis, 2017) (Nice & Strickland)energy efficiency much lower than hydrogen's efficiency in its liquid form.

However, the technological development about electricity's production using renewable sources, is estimated to greatly reduce the electrolysis' process cost by the end of this decade, which allows the global shipping industry to turn its attention to hydrogen, as energy source of the future.

III. Fuel cells

Although hydrogen as a fuel has been proven to be used as such in gaseous or liquid form, but also as an enrichment element for other fuels, special importance has been given to its use by fuel cells. The operation of the cell is based on the production of direct current and heat through the hydrogen's combustion and the storage of produced energy for later use. This technique is expected to replace common batteries and internal combustion engines (ICE), gas turbines, etc. in the future. The idea of using cells, dates back to 1839, when the first cell was built by Sir William Grove, but its full study and development came much later, in the 1960s, with the development of NASA's Apollo and Gemini space programs. (Atilhan, Park, El-Halwagi, Atilhan, Moore, & Nielsen, 2021)

3.1 Cell's operation principle

The hydrogen's cell operation is based on the formation of water molecules from the combination of hydrogen and oxygen. In the case of the most common cell type, the Proton Exchange Membrane (PEM), two electrodes, one negative (anode) and one positive (cathode), are placed in a tank. The two electrodes are the catalysts of the reaction and have a coating of platinum (Pt), while they are separated from each other by a semipermeable membrane which allows the passage of only positive hydrogen ions. (Díaz, Ortiz, & Ortiz, 2014)During cell operation, the negative electrode is supplied with hydrogen, which decomposes into positively charged hydrogen ions (H +) and electrons (e-). Hydrogen ions penetrate the membrane and are evenly distributed, while electrons are transported to the cathode via an external circuit, creating a direct current. At the same time, the cathode is supplied with oxygen and also evenly distributed on the membrane's surface. When hydrogen protons penetrate the membrane, they react with oxygen. From the reaction, created with the participation of electrons passing through the external circuit, water and heat 242 kJ / mol are produced. The current that is finally produced, has a voltage of about 0.7 volts. In case of need of higher voltage, more cells are connected in series. (Nice & Strickland) (Shiong Khoo, et al., 2021)

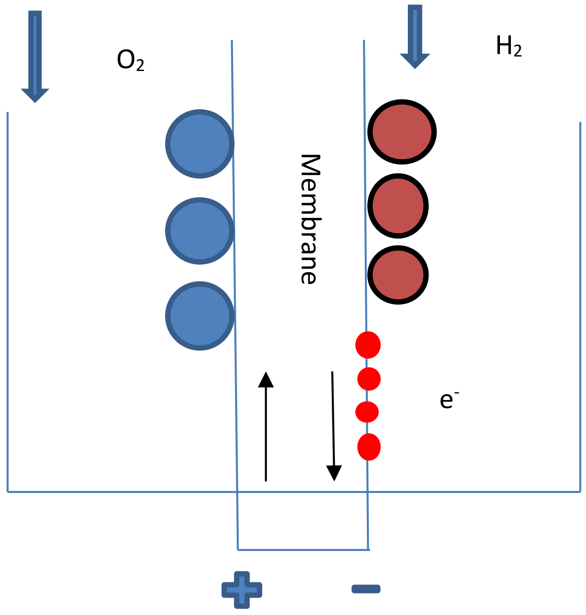

Fig 2. First stage of a membrane's cell operation (PEM). Insertion of oxygen, hydrogen and electrons' separation.

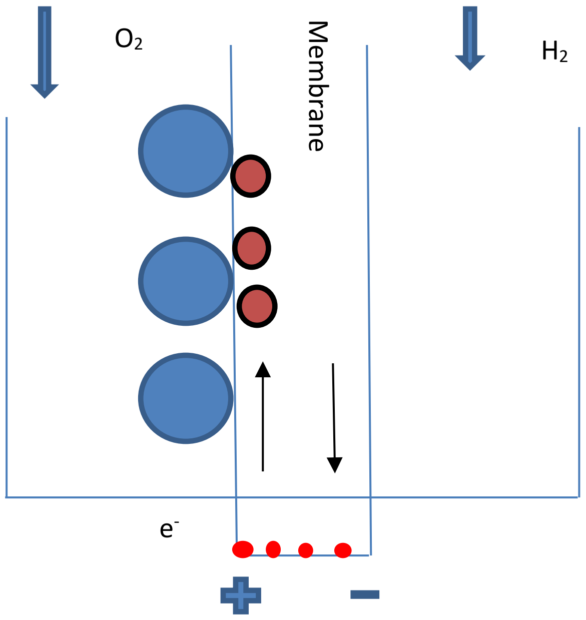

Fig 3. Hydrogen ions penetrate the membrane and electrons begin their circulation in the external circuit.

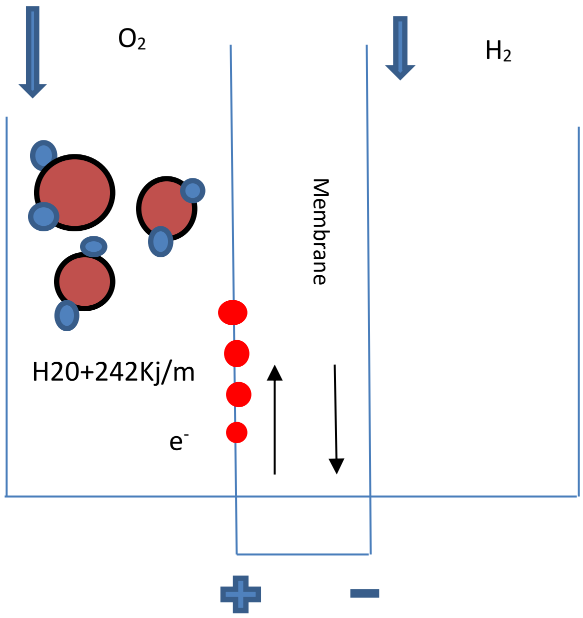

Fig 4. Hydrogen combines with oxygen to produce water, heat and electricity.

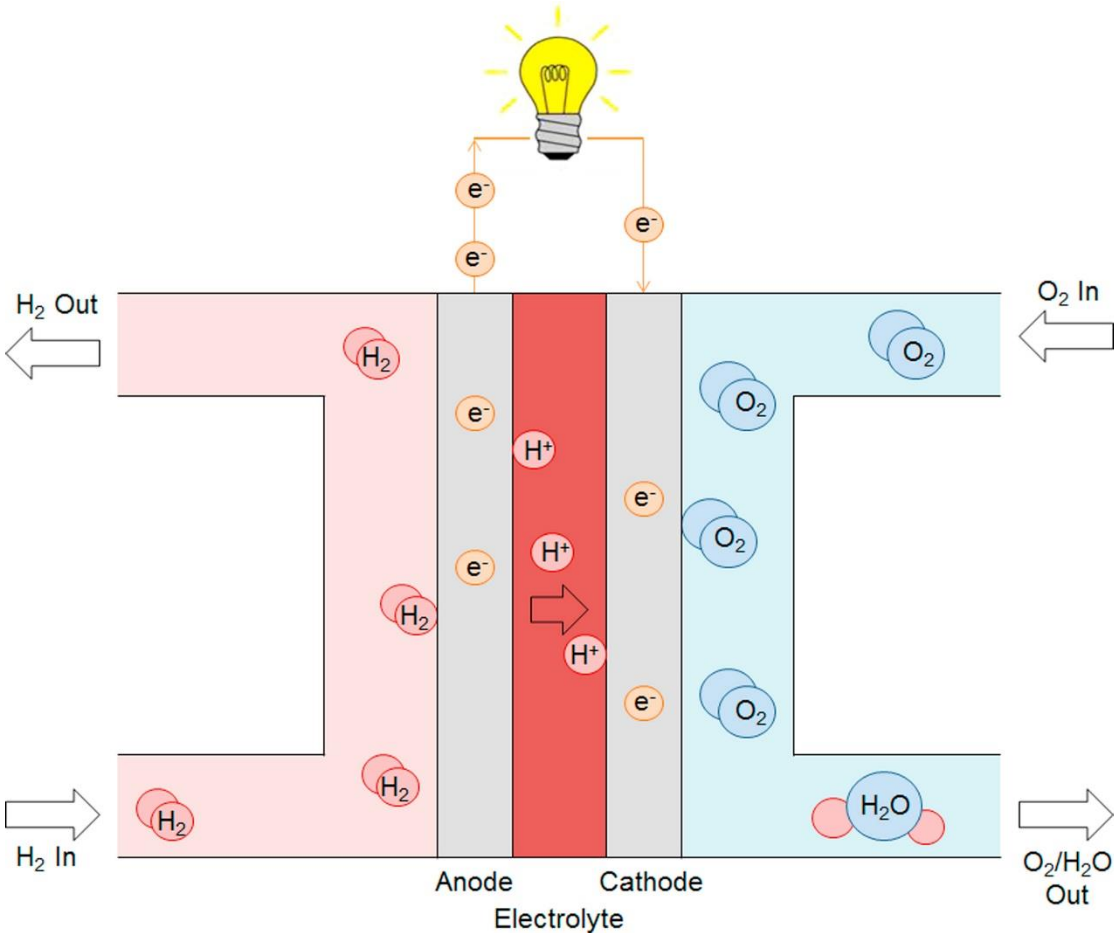

Fig 5. PEM cell operating device. (Díaz, Ortiz, & Ortiz, 2014)

IV Conclusion

In summary, the gas emissions from the global industry but also from the global shipping industry, contribute significantly to the burden of ambient air, with harmful chemical elements of sulfur dioxide, carbon dioxide, nitrogen oxides but also nitrogen oxides mainly from the combustion of hydrocarbons and from sulfur dioxide emissions. The accumulation of these chemical elements in the atmosphere, significantly affects the chemical properties of the ozone sphere and enhances the greenhouse effect (GHG), global warming and the formation of acid rain and smog, with devastating consequences for the environment, human health and society. The European Union, by issuing directives aimed at reducing emissions, aims to gradually reduce and eliminate the effects in a way that will not affect human health, the economy and the environment, gradually, with a milestone in the years 2020, 2030 and 2050. Specifically for the shipping sector, Directive (EU) 2016/802 on the reduction of ship's sulfur emissions has been adopted. Nevertheless, the shift to the use of new green fuels with zero carbon footprint and sulfur content, is a one-way street for shipping, with the next goal of creating and adopting green hydrogen as a marine fuel, through renewable energy sources and renewables raw materials, using it on ships, either as the main fuel, or as an enrichment mixture, or even more efficiently through its use in hydrogen's fuel cells for electricity generation. It is now the responsibility of the states and the shipping industry, both to finance the construction of infrastructure or the reconstruction of existing gas infrastructure, for the manufacture, transport and disposal of hydrogen, and to finance scientific research to produce hydrogen suitable for combustion in marine engines, with high efficiency, low cost and safe chemical characteristics.

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