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Water Electrolysis Methods for the Production of "Green" Hydrogen in Shipping, Through New and Future Investment Proposals.

Economic Operating Cost and Electrolyte Performance Data

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Abstract: World trade has grown and continues to grow rapidly in recent decades. Much of it, is carried out by sea transportation, by the world's merchant fleet which is moving millions ofcargoes'tonesannually and traveling millions of tone-miles between continents.

So far, the ship's movement isachieved using conventional fuels, mainly marine gas oil with a relatively low sulfur content but a high carbon footprint. But what about the gaseous emissions of these fuels, what effects do they have on the environment, the development of the greenhouse effect and in the long term the ecological destruction of the planet?

Can a fuel with reduced emissions, hazardous to the atmosphere and fully sustainable, be created from renewable energy sources?

It is worth studying the use of environmentally friendly fuels that will minimize to zero environmentally dangerous emissions, and will contribute in every way to the reduction of the greenhouse effect. These fuelswill be produced from sustainable energy sources while at the same time restoring the ratio of atmospheric gases at their natural values.

Such a case is the production of green hydrogen from renewable energy sources and through splitting water by electrolysis, using one of the three water's splitting methods: the alkaline electrolysis (ALE), the proton exchange membrane electrolysis (PEMs) or the solid oxide electrolysis (SOE). The green hydrogen will be isolated as a gas and then converted into electricity through hydrogen fuel cells, in order to eventually power the ships' electric engines that will be used for propulsion or any other reason during sailing.

Nowadays, the production of green hydrogen is at a disadvantage compared to other energy sources, due to its requirements in high electricity and temperature prices, as well as high-cost materials for its production through

electrolysis plants in order to split water into its chemical elements, while at the same time the productive hydrogen's purity and efficiency are reduced.

This paper is a bibliographic review of the three methods of water's electrolysis, by three different types of electrolytes, comparing data of cost performance per type of electrolyte.

Keywords: Electrolysis, Green Hydrogen, Investment Proposals, Economical Data, Green House effect, Green Shipping.

I. INTRODUCTION

The fossil fuels'use, results in the oxygen's reduction in the atmosphere while at the same time, the greenhouse effect, as a result of thedangerous gases' emissions and particles, increases. The only element that is free and abundant in the atmosphere, with zero emissions during its combustion, is hydrogen. In addition to its zeroes greenhouse gas emissions, it qualifies as "green" based on its manufacturing processes. As long as it is obtained and isolated from the atmosphere using renewable energy sources, such as through water's electrolysis, using electric power, also ecological and sustainable since it will be produced by renewable energy sources such as solar, wind, geothermal and nuclear energy or production into hydro turbines. [1][2]

Green hydrogen, after its isolation from nature through electrolysis, which uses renewable energy sources to activate the reaction of splitting water into its elements – electrolysis is a non spontaneous reaction, can be stored and used as fuel through accumulators in the form of a hydrogen fuel cell, producing a voltage of about 0.7 volts per cell, which can be multiplied if more cells are connected in series.[3][4]

Of particular interest is the operating cost of the various types of electrolytes, as it depends on the cost of its individual characteristics, such as the electro-catalyst'scost and the electrodes' cost. Additionally, the electrode separation membrane'scost, in case of a proton exchange membrane using in PEMs electro-catalysts, or the solid ceramic films' cost in case of solid oxide electro-catalysts (SOEs), can increase the electrolyte's operational cost. The above cost increase and decrease correspondingly to the produced hydrogen energy's cost, per Kw of power required for its production.

1.1. The fossil fuels' use increase the greenhouse effect.

Any marine fuel's use, due to the gaseous emissions it presents in carbon dioxide, sulfur oxides, nitrogen oxides and free suspended particles, produced during combustion, affects the development of the greenhouse effect the global warming,the smog and the acid rain. This is due to the components and characteristics of conventional fuels, mainly marine fuel oil, which are released into the atmosphere during burning by the ships' internal combustion engines. In order to deal with this serious problem for the environmental protection, studies are underway to improve or reduce its dangerous components but also to improve its characteristics in general, such as reducing its acidity. Especially for the latter case, efforts are made to reduce its acidity, using a natural crystalline structure of zeolite. [5]

Simultaneously to the gaseous emissions, binding amounts of oxygen, gradually decreases in the atmosphere.[6], Research has measured that the oxygen's concentration decrease in the atmosphere until 1989 to the present, is gradually decreasing at a rate of about 19 parts per million [7], while this decrease still exists and finally the oxygen'sconcentration in the atmosphere is set to reach rates of 20.946% to 20.825% by the year 2100, with an average decrease of 0.0015% per year [8] . Continuing at this rate, the concentration of oxygen in the atmosphere will be zero in 4400 years.[7][8]

The greenhouse effect's increase mechanism in relation to the oxygen's concentration decrease in the atmosphere is as follows: The oxygen'slow concentration reduces the thickness of the atmosphere. As a result, the solar radiation'sshort waves easily penetrating the atmosphere and reaching the surface of the planet. The temperature'sincrease, results in the water'sevaporationforming water vapor, that in turn, binds much of the long-wave radiation reflected from the ground. In this way, although oxygen itself does not bind infrared radiation, it indirectly contributes to the creation of water vapor, that is one of the most important greenhouse effect's creationfactors. [6]

1.2 Production of Hydrogen through electrolysis.

The main method for industrial hydrogen'sproduction, is its separation and sequestration from water by electrolysis or from hydrocarbons following the oxidation of methane (CH4) [9].

Through water'selectrolysis using renewable energy sources, the produced green hydrogen can be used in fuel cells, so that, after being oxidized, it will regenerate water, heat and free electrons that will be used as electricity current, while the oxygen produced during electrolysis will feed back into the atmosphere. [6]

$$2H_2O \longrightarrow 2H_2 + O_2$$

II. Electrolysis

Electrolysis is the breaking down of water into its elements using electricity. It is a non-spontaneous reaction and for its initiation, we must provide an amount of energy to the already existing reacting particles, in order to overcome the kinetic barrier and to help the elements react. The derivatives of the reaction present greater amounts of energy than the reacting elements between them.

This is also confirmed by the positive value of the Gibbs energy. [10][11]. In order to reduce the kinetic barrier and simultaneously to maximize the yield from water splitting, it is necessary to use special electro-catalysts of high activity and low resistance to charge transfer during the process.

Based on the way the water will be split and the conditions under which the electrolysis will take place, the process can be divided into three categories.

1. Alkaline electrolysis that starts with OH- ions.

2. Electrolysis through a proton exchange membrane that starts with H+ ions and

3. The electrolysis of solid oxide starts from O_2- ions in order to then split the water and separate the hydrogen. [12][10].

2.1 Alkaline electrolysis.

It is one of the most widespread electrolysis processes. Its main disadvantages are the need for high energy input with low load current efficiency, in contrast to the produced oxygen'spurity and also the low hydrogen's production pressure with reduced energy efficiency [9]. It can be carried out at room temperature and up to 80°C while the usual catalyst is a basic aqueous solution of 30wt% potassium hydroxide (KOH).[9]

During the electrolysis process, the positively charged electrode (cathode) is separated from the negatively charged electrode (anode) by an ion exchange membrane while the oxygen and hydrogen gases produced by the reaction are collected, separated and stored for later use. [13][14].
The alkaline electrolysis process is described in Figure 1 below

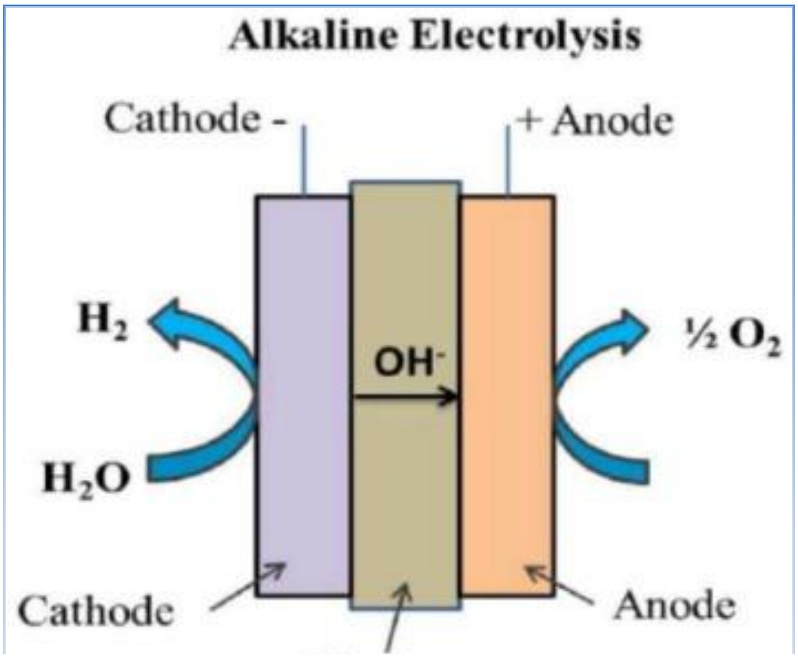

Fig. 1. Schematic diagram of Alkaline Electrolysis Technology.
Source: [10]

2.2 Proton Exchange Membrane Electrolysis (PEM'S)

Proton exchange membrane electrolytes (PEMs), are another water-splitting method to collect hydrogen gas. This method is not new but has already been tested with satisfactory results, mainly due to its ability to provide a sufficient electrical charge density. Electrical charge density is the ratio of the intensity of the current in Amperes per 1 cm2 of the conductor, with the application of a high voltage at the entrance of the system and the possibility of producing hydrogen with a purity of approximately 99.995%[10][15].

Membranes are of great interest mainly in terms of their mechanical strength, their conductivity, their chemical and thermal stability but also their stability in conditions of large pressure and temperature changes. [10][16][17]

The cost of PEMs electrolysis devices is quite high compared to alkaline electrolysis electrolytes, due to the electrolyte's and the membrane'shigh cost, while at the same time they show reduced durability. [10][18]

Therefore, research should mainly focus on reducing the electro-catalysts'and semipermeable membranes'cost of this type of electrolytes in order to reduce the overall cost of a PEMs electrolyte in relation to its durability and efficiency.

The description of the electrolysis'operation with a PEMs system is shown in detail in Figure 2 below.

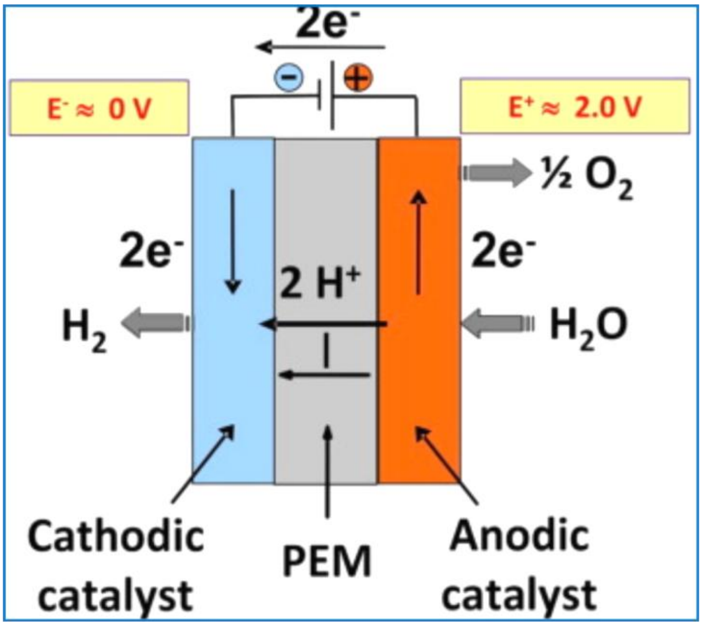

Fig. 2. Schematic diagram of Proton Exchange Membrane Electrolysis Technology.
(Source: [10] **)**

2.3 Solid Oxide Electrolysis (SOE)

The solid oxide electrolytes' category is also a method of electrolysis, Converting electricity, creates active ions that split water and produce high purity's green hydrogen. [10]

For its operation, particularly high temperatures are required, around 500°C to 1000°C. This has so far negatively affected the mass production and availability of electrolytes of this type. At the same time, although high temperatures positively affect production performance, the durability of its material is negatively affected. [10]

The response time of proton exchange membrane's electrolytes is significantly higher than the response time of a solid oxide electrolyte. This is because the opposite polar electrodes are separated from each other by a high-conductivity's solid ceramic membrane, so they transfer the electric charge at a fast rate. [10][19]

It is worth noting that due to their high conductivity, solid oxide electrolytes can be used simultaneously as fuel cells, which makes them more competitive than other types of electrolytes.[10][20]In any case, however, as the need for high-energy intensities is necessary to approach and maintain high operating temperatures, this type's electrolytes use is disadvantageous for industrial use.

The operation of a solid oxide electrolyte is detailed in Figure 3 below.

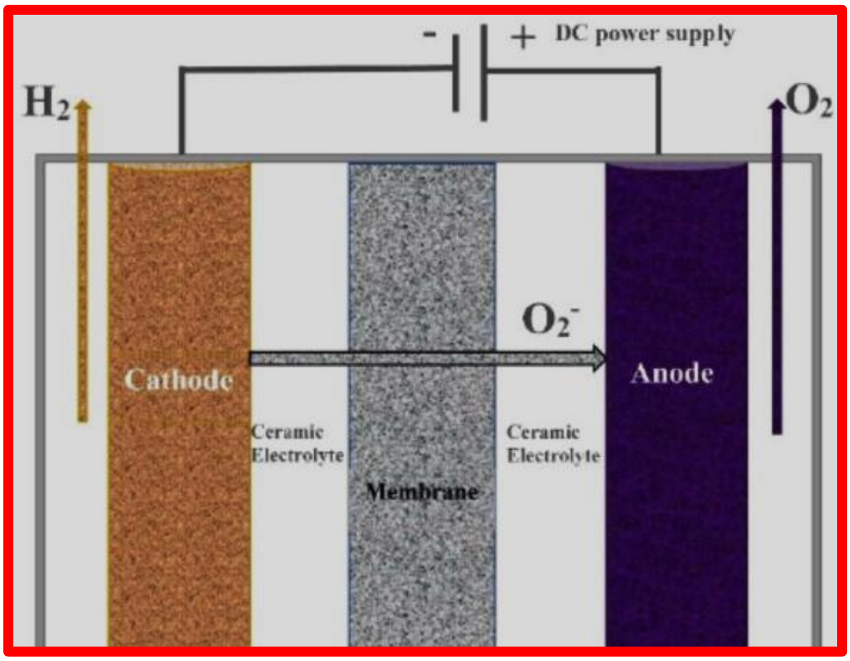

Fig. 3. Schematic diagram of Solid Oxide Electrolysis Technology.
(Source: [10]**)**

III. Operating cost - performance comparisons.

The alkaline electrolysis' unit capacity and size are the factors that determine the capital expenditure cost (CAPEX) but also the annual operational expenditure (OPEX), as far as alkaline electrolytes are concerned. So for a unit of less than 1 Mw equal to about 1Mw, the of capital costs amounts to about 1250 euros to 700 euros per Kw respectively. [10]

The annual operational expenditure (OPEX), for the same type of electrolyte, amounts to 7% of an average size unit with the prospect of decreasing by up to 2% until 2030. [10][21]

Regarding the capital expenditure (CAPEX) of a proton exchange membrane (PEMs) electrolyte, this can be reduced by addressing and reducing the cost of the electro-catalyst and polar electrode separation membrane. In this way, the reduction can rise from 2000 euros/Kw in 2020 to 900 euros/Kw in 2030.

On the other hand, by increasing the capacity of the PEMs electrolyte from 1 MW to 40 MW, there is the possibility to reduce the hydrogen'saverage cost price, from 7.37 euro/Kg to 4.49 euro/Kg. [10][22]

Solid oxide electrolyte technology is a relatively new technology. For this reason, there are no accurate figures of confidence for CAPEX, which varies considerably. For the time being, hydrogen's energy cost is estimated at more than 3000 Euros per kilowatt of power. The intention and forecast is to reduce it to 750 euros per kilowatt of power by 2030. [10][23].

IV. New and future investments on green hydrogen's production.

As identified to date by the world literature and reported in this article, the green hydrogen'screation is still a relatively expensive process. This is mainly due to its production method through electrolysis, which requires large amounts of electricity and temperature and high-cost electrolytes due to the increased cost of electro-catalysts in the case of alkaline electrolytes but also of membranes when referring to PEMs or SOE electrolytes respectively.

Butthe problem for the production of green hydrogen is not limited only to the aforementioned factors.

A series of studies with the aim of reducing the total hydrogen'soperating cost , from its preparation to its final sale on the market, should be carried out, with the aim of making the product competitive on the market, attractive in its choice for use and with ratio cost-effectiveness beneficial for both industry and the environment.

Studies are also deemed appropriate to be carried out in order to ascertain whether the amount that can be produced daily by a hydrogen production system can cover the daily energy needs of an engine. Especially in the shipping sector, the above issue is considered of utmost importance as the ability to continuously supply ships with fuel is a difficult and time-consuming process.

An additional factor that needs to be studied in the hydrogen'suse,is the ships'storage capacities in relation to the volume of fuel required for an hour, a day or an entire trip from refueling to refueling of the ship.

These issues can be understood if one considers that, in liquid form, hydrogen has a high density of gravitational energy, approximately 0.033 MWh/Kg, in contrast to its gaseous form, where it presents a volumetric energy density that is barely close to 0.003 MWh/m3 at a pressure of 1 bar [24][3].

In summary, large-scale of green hydrogen's production, supply chain development and technological innovation are generally considered to be the most important investments in order to reduce costs and integrate hydrogen into the market with significant ecological impacts.[25]

Considering that for the hydrogen'sconversion and its preservation in liquid form, temperatures lower than 33° K (-240° C) are required[26], it is easy to realize the amount and cost of electricity required to achieve and continuously maintain these temperatures.

Regarding the 2 so far most affordable electrolysis methods that can be applied to seawater, alkaline electrolysis (ALE) and proton exchange membrane electrolysis (PEMs), we observe their individual disadvantages which significantly increase the cost of hydrogen's production.

In alkaline electrolysis electrolytes, the cost is due to the particularly increased cost of the electrolyte but also to the huge need for input energy with low load efficiency (a lot of energy is needed to produce a small amount of hydrogen) and to the purity of the fuel itself.

In contrast, PEMs electrolytes produce high purity hydrogen but also with high membrane costs and low strength materials.

An important investment is the financing of finding methods to reduce the above costs in electrolysis methods while simultaneously increasing the volume and purity of hydrogen produced.

Based on 2017 studies, the investment costs for ALE, with a reference point in the year 2030 "***are limited to values of 787–906 €2017/kWHHV-Output while correspondingly the future investment costs of PEM electrolysis units for the year 2030 are limited to 397 and 955 € 2017/kWHHV-Output"***.[21]The ratio of the cost of the two electrolytes is predicted to remain the same until 2030, while only new "**studies by Smolinka et al. [27]*predict that in 2030, the cost of PEM electrolytes will fall below that of alkaline ones. Mergel et al.***[28][21]***and the FCJHU study* **[29]*they see the costs of both technologies in 2030 close to each other, but with the option of PEM electrolyte operation".***[21]

V. Conclusion

Pure green hydrogen, produced by renewable and sustainable energy sources, is perhaps the only completely environmentally friendly fuel. It provides a zero carbon footprint while it can be used both directly as a fuel, through its storage and conversion to electricity in hydrogen fuel cells, and as a derivative to create other fuel derivatives such as ammonia. The method of its binding, varies since it can be carried out either through water's splitting by electrolysis, or through the hydrocarbons' electrolysis.

In any case, its production's operational cost, varies and fluctuates at high levels so far, as it requires high energy costs, high temperatures, and also high-cost materials, such as PEMs electro-catalysts, proton exchange membranes, and solid ceramic membranes if they are electrolytes solid oxides.

Therefore, the research should be oriented in the direction of reducing electrolytes ' operating cost, in order to obtain high-purity and low-cost hydrogen, with low-cost consumable materials and low input energy requirements.

Hydrogen can be the fuel of the future as a green fuel and be used to power movement and industry, of which shipping is an integral part, as renewable and sustainable energy sources (wind, solar, hydro) are in abundance due to the natural environment of the ship.

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