EXPERIMENTAL TESTS ON HYDROGEN PRODUCTION FROM SEAWAVES ENERGY

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***Abstract*—In this paper we propose the use of Wave Energy Converter and saline water to produce hydrogen. Two different scheme and technology are proposed. The objective of this research is to design an electrolyzing system capable of utilizing sea. In particular, we present the results obtained by two different prototype of electrolyzer: one with steel electrodes and the second with titanium electrodes. Further experiments were carried out by changing the electrolytic solution of water and sodium chloride in real seawater. Finally, the electrical load has been changed as imposing electric current with a distorted waveform.**

Keywords—sea water, electrolysis, hydrogen, new fuel

I. INTRODUCTION

Mankind needs an ever increasing quantity of renewable energy and needs also a way to store and distribute energy in an efficient way [1-23]. A well studied approach to the solution of this problem is the use of Hydrogen. Several systems of production, storage and distribution of hydrogen are currently investigated very intensively. The use of hydrogen can store efficiently the stochastic distributed electricity generated produced by solar cell or wind turbine or wave energy.

Hydrogen as an energy carrier has many advantages:

- zero environmental impact, both globally and locally;
- producible from more primary energy sources, interchangeable and available on a large scale;
- distributed across a network.

As a result, hydrogen is a clean, efficient and versatile energy carrier.

Unfortunately, Hydrogen on the earth does not exist in a pure molecular state but only in combination with other elements. Therefore, it must be produced from its compounds, using energy sources.

It can be obtained from a different variety of sources, such as fossil fuels or water, etc. In the figure below (Fig.1) we propose a scheme of processing system of production of Hydrogen.

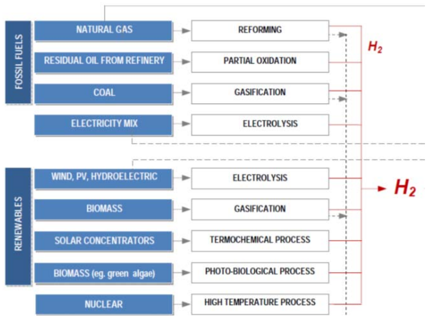

Fig. 1 Production of Hydrogen (ENEA).

Technologies for the production of hydrogen from fossil fuels (steam reforming, partial oxidation, gasification) are, as mentioned, mature and widely used (more than 95% of the hydrogen produced today comes from these processes).

However, whatever the process and starting fuel is used, most of the processes use energy from fossil fuels, and therefore to be sustainable in the medium and long term to comply with Kyoto's protocol requirment, it must be coupled to CCS (Carbon Capture and Sequestration).

Fortunately, several approaches can be used in order to avoid the use of fossil fuels. Te main ones are:

- production from biomass;
- •production from water.

Hydrogen can be produced from biomass through several thermochemical processes as gasification or pyrolysis and biological processes.

One of the possible renewable energy sources to be used to produce hydrogen is water, through electrolysis or thermochemical cycles. In particular, the possible renewable energy sources used for the production of hydrogen are wind and seawaves through decentralized processes. The use of either wind or waves at sea can produce on the same place both electricity and hydrogen by using seawater.

In the following tab. 1, we present the cost of Hydrogen process for each of the used process.

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TABLE I HYDROGEN PRODUCTION PROCESSES

Tecnologia		Stato Di Sviluppo	Emissioni CO_2	Tipologia Di Produzione		Costo Di Produzione	
				Distribuita	Centralizzata	Attuale	Futuro
Natural Gas Steam Reforming	No CCS	Commercial Plants	Medium/ High		✓	5-9 €/GJ (GN 3-6 €/GJ) (20.000-250000 Nm^3/h)	
				✓	✓	19-22 €/GJ (<20.000 Nm^3/h)	21-25 €/GJ (2020)
	with CCS	Prototype in development	Low		✓	-	11-12 €/GJ (2020)
Coal Gasification	No CCS	Commercial Plants	High		✓	8-10 €/GJ (Carbone 1.5-2 €/GJ)	-
	with CCS	Prototype in development	Low		✓	-	10-12 €/GJ (2020)
Biomass Gasification		Pilot Plants	Low	✓	✓	10-25 €/GJ	10-20 €/GJ (2020)
Biological Processes		Lab stage	Low		✓	-	-
Electrolysis (electricity from electric grid		Commercial Units	*	✓	✓	25 €/GJ (E.E 0.0025 €/kWh) 200 €/GJ (E.E 0.20 €/kWh)	15-30 €/GJ (2030)
Thermochemical Cycles	solar	R&S stage	Zero		✓	-	20-30 €/GJ (2030
	nuclear	R&S stage	Zero		✓	-	10-20 €/GJ (2030

In this work we study the possibility of an integration among WEC converters that use wave motion to produce energy and electrolyzing techonology that use saline water. We use mathematical approaches and techniques developed and used in other field of science[24-46].

In figure 2 we report a scheme of this new integrated system.

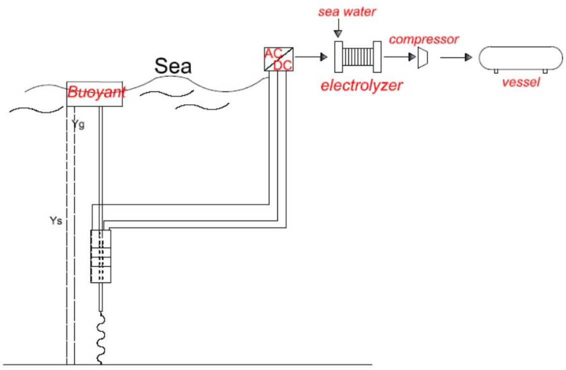

Fig. 2 An integrated system of WEC plus Hydrogen

II. THE ELECTROLYTIC PROCESS FOR THE PRODUCTION OF HYDROGEN

Electrolysis is one of the most popular and simple methods used for the production of pure hydrogen. However, only a small percentage, about 4%, is manufactured by this process due to the high cost of the electrical energy.

It' s governed by different parameters as thermodynamic and kinetic aspects that will be studied later.

A. Thermodynamic Analysis

The minimum value, or reversible, the cell voltage (E) is determined by the minimum value of the energy that must be supplied from the cell because the electrolysis takes place:

$$E = -\frac{\Delta G}{nF} \quad (1)$$

where E is potential difference of balance, G is Gibbs free energy and F is Faraday' s constant. So with appropriate modifications to the equation previously written:

$$E = -\frac{\Delta G}{nF} = \frac{RT}{2F}\ln\left(p_{H_2}\frac{p_{O_2}^{0.5}}{p_{H_2O}}\right) \quad (2)$$

Where p is the pressure. The equation shows that E increases with pressure. The potential is also dependent on temperature, mainly through the dependence of Δ G from temperature. The reaction is endothermic.

B. Kinetic Analysis

The reactions occur at the electrodes through a series of stages that involve the diffusion of the reagents towards the electrode. The presence of these various intermediate steps involves a dissipation of energy. In fact, you will have to take into account three contributions:

- a cathodic overvoltage η_c and η_a an anodic overvoltage has to activate the electrolytic reactions and exceed the concentration gradients;
- E_Ω an ohmic drop due to the resistance to the electric current from the electrolyte, the electrode structure, the possible membrane or diaphragm.

So we can express the potential difference:

$$E = E_a + \eta_a - (E_c - \eta_c) + E_\Omega \quad (3)$$

$$E_\Omega = IR \quad (4)$$

$$\eta = \frac{RT}{\alpha_a nF}\ln\frac{i}{i°_a} + \frac{RT}{\alpha_c nF}\ln\frac{i}{i°_c} \quad (5)$$

where α is the coefficient of transfer of the electrolytic reaction ,i is the current density and $i°$ is the density exchange current, which is proportional to the speed of exchange. In conclusion, parameters as temperature or current density influence working of the electrolysis, an example current density determines the size of the electrodes and the price of the electrolyzer or an high operating temperature can be cause an increase of performance of it.

III. CASE STUDY

Alkaline water electrolysis is the technology used in present practice for large-scale electrolytic hydrogen production. Low efficiency, low current density and a lack of proper scale-up practice are the primary drawbacks of the present technology. Significant improvements have been made, making it possible to reach improved cell efficiencies and higher current densities.

In this paper we propose the use of saline water to product hydrogen. As far as using saline water, can be proposed two different scheme and technology. As regards the first option, it is needed the total desalination of the water to remove all dissolved salts and to produce distilled water. This distilled water can be subjected to electrolysis, alkaline- electrolyte and electrolysis in suitable cells.

In this case the most important disadvantage is the high cost caused by the process of osmosis or desalinatione.

The aim of this work is to design an electrolyze system capable of utilizing sea water for direct electrolysis. It is probable that these systems would operate at a low power density and electrolyze and therefore only a small portion of the water is in direct contact with electrodes. In this technology there are several disadvantages: the rapid corrosion of electrodes or the production of undesirable products, anyway the realization of this new design could possible lower capital cost and natural elimination of the waste brine. It may also be possible to recover economically significant quantities of the metals present in sea water, in particular magnesium in a form of magnesium hydroxide.

Sea water is a multicomponent natural electrolyte with sodium chloride as the main component. The process of electrolysis is a sum of space separated electrode reactions of cathodic hydrogen reduction and anodic oxygen evolving as a result of hydroxide-ion oxidation. The anodic chlorine evolution is also a possible reaction in sea water with NaCl as its main component.

The reactions of the process of electrolysis are:

- the production of hydrogen at the cathode:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad (6)$$

- the production of chlorine and oxygen at the anode :

$$6H_2O \rightarrow O_2 + 4H_3O^+ + 4e^- \quad (7)$$

$$2Cl\_ \rightarrow Cl_2 + 2e^- \quad (8)$$

The experimental set up have been shown in **fig. 2**. The power supply was able to emulate the voltage generated by a seawave power generator. Several tests were performed. The aim of the tests were:
1)to show that a seawave power generation system can produce hydrogen from sea water;
2)to quantify the hydrogen production under distorted regime;
3)to set up the optimum power electronics system to be used in order to maximize the hydrogen production in dependence of the type of electrodes to be used.

In order to show that a seawave power generation system can produce hydrogen from sea water, we installed the electrolyzer in our generation buoy. The electrodes were supplied through the generator and a controlled rectifier. The system was able to produce hydrogen at a rate of 1/10 of mole per hour with a average height of wave of 55cm.

An exact quantification of the hydrogen production in terms of sea-condition was not possible. This was caused by the fact that in severe sea conditions the electrolyzer had severe hydrogen leakage and an exact quantification was not possible.

Several tests has been performed in order to optimize the type of electronics and to study the behavior of the system. We found that the structure of the system had to be composed by the generator, a controlled rectifier directly coupled to the electrodes. The rectifier had to be controlled by including in the control loop the wave height. As far as the type of electrodes to be used is concerned, we found that titanium electrodes had not a big advantage on steel electrodes.

IV. Conclusion

In this paper we proposed the use of saline water to product hydrogen. In particular, we present the results obtained by two different prototype of electrolyzer: one with steel electrodes and the second electrodes with titanium. We observed no large difference between the two electrodes and on the contrary we observed that the key factor to enhance the level of hydrogen production was to use a controlled rectifier to be insterted between the electrolyzer and the generator.

V. Acknowledgment

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