METHODS OF WATER CLEAVAGE INTO OXYGEN AND HYDROGEN (STATE OF THE ART)

SAJIN TUDOR [1], CRACIUN ALEXANDRU [2], CULEA GEORGE [1], CULEA CATALINA MIHAELA [1] & ANITEI FLORIN [1]

[1] *University of Bacau, ROMANIA*
[2] *State University of Moldova, Chisinau, REPUBLIC OF MOLDOVA*

Abstract: This paper is referring to modern systems, in particular to photo-electrochemical cells for water cleavage into hydrogen and oxygen, wherewith it is realized the pure ecologic cycle of solar energy conversion.

Keywords: water photolysis, tandem photo-electrochemical cells, hydrogen production.

1. INTRODUCTION

Although the hydrogen cover only 5-10% of mankind's energy needs, in condition of fossil combustibles progressively depleting and disquietingly increasing of environment pollution grade, for which the actual energetic participation is more than 30%, it talk more and more about a veritable civilization based on this energetic vector.

According to the realized proceed, it are known various principial schemes of water cleavage into hydrogen and oxygen plants, like [1]: the classic electrifier, nuclear and solar, thermochemical decomposition plants, the hydrolyser, photolyser, radiolyser, biolyser etc.

Electrolysers decomposes the water in acid or alkaline medium, which it increasing the conductivity, away the continuous electric current action produced by compact fuel chemical energy conversion, nuclear energy or solar at a electric energy production yield which don't exceed 45% and at a energetic yield of the electrolysis process between 65-80%, mean at a 29-36% energetic global yield.

The disadvantage of classic and nuclear electrolysers is the energy elevated consumption (3-5 kWh/Nm^3 hydrogen), due indicate the hydrogen production in energetic designation like unprofitably, because it consume much more energy for water cleavage that it is obtain from the burning of produced hydrogen. *The solar electrolyser* has a complex construction, which need additional a solar boiler, a turboaggregate for electric energy production by expansion of the steam produced in boiler and two heat-exchangers: for the condensation of exchanged steam and for the aqueous electrolyte heating. This increase sensibly the installation costs of these plants, which are strongly dependant of mistiness, also.

The thermochemical water decomposition plants realize thermochemical cycles with 2, 3, 4 and 5 steps, at 200-900^oC temperature. This is not possible with actual atomic energy reactors, which can provide maximum 500-600^oC, but it can be made with help of high temperature reactors, HTR, which can achieve 600-1000^oC.

However the global energetic yield of hydrogen production in these plants is almost double than electrolysers yield, the capital investment cost is very high because of the coupling of nuclear reactor to thermochemical factory.

The hydrolyser is based on water cleavage process by the dissolving of an anode, magnesium or magnesium alloy maded, in aqueous electrolyte, which generate ecological problems and determine the consume of some metals for which regeneration is necessary more energy than that produced by the process of water cleavage.
The photolyser cleavages the water into hydrogen and oxygen by the influence of UV radiation, which demand a special laser with high energy consume. In nature, this process is possible at 30-60 km altitude, behind ozone umbrella.
The radiolyser utilize for water cleavage the UV radiation with short wavelength generated in nuclear reactors or the decomposed radiations of radioactive wastes, with 45% global yield, but present the disadvantage of radioactive products contamination.
The biolyser cleavages the water utilizing the photosynthetic process, by a rapid development of a culture, for example of the blue algae "*Anabama cylindrica*", in a atmosphere enriched with carbonic gas. Placed then, in an argon atmosphere, realize the water cleavage into elements, by microorganisms' action. This installation has high energetic performances, but presents a complex construction and a complicated exploitation.

2. GRAETZEL TANDEM CELL FOR WATER CLEAVAGE BY VISIBLE LIGHT

The solar radiation converters to electric energy are based on the photovoltaic effect, discovered by Becquerel in 1839. The very first photovoltaic cells with *p-n* junction between two different doped silicon layers it was maded in 1950 in Bell's laboratories. In present, the efficiency of the commercial photovoltaic cells vary between 18...20% for monocrystalline silicon cells and 10...12% for amorphous silicon cells, in conditions in which the polycrystalline silicon cells (the most effused cells from the market) has a intermediary efficiency.
Beginning with 1970, it was registered a new revolving interest for photovoltaic cells sensibilized with pigments (coloring agents). A new idea in this way dates from 1991 and belongs to Graetzel [2, 3]. Graetzel's cells are based on TiO_2 porous nanocristalyn electrodes, which have a very big specific intern surface. Electrodes consist by TiO_2 particles with colloidal dimensions (5-50 *nm*), that are connected in a sintering face, at low temperatures. A pigment monolayer deposed on a suchlike electrode it is enough to absorb the mass of the radiation from solar light spectrum. These cells are mass-produced by two firms and have 12% conversion efficiency.
The installation for water cleavage into hydrogen and oxygen by action of visible light (fig.1), patented by Graetzel in 1999 [4], is constituted by two photo-electrochemical cells, tandem inseriated and sensible to visible light. First cell has a box for oxidation of the aqueous electrolyte 2 with window 1 for solar light input and with the anode 4, transparent in yellow and red interval of solar light spectrum, covered on contact part with aqueous electrolyte 2 with a semiconductor oxide mesoporous layer 3, absorbent in blue and green interval of solar light spectrum. The second photo-electrochemical cell contain an solid organic electrolyte layer 7, placed between transparent electrode 4, covered on the contact side with organic electrolyte, with photovoltaic layer 6 by susceptible colorant, absorbent in yellow, red and part infrared interval of the sun light spectrum, and between the contraelectrode 8, galvanic bounded with the anode 4 from the first photo-electrochemical cell, as well as a reduction enclosure with aqueous electrolyte 9, in which is immersed the cathode 10 for the reduction

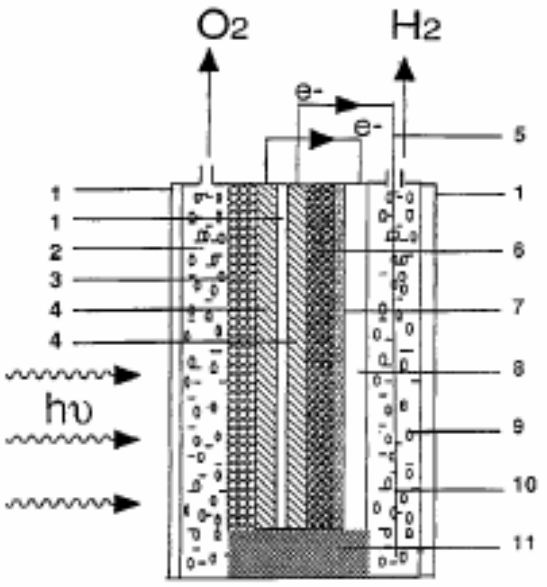

Fig.1. Schematic drawing of Graetzel photoelectrochemical tandem cell [3]

of the protons formed in the oxidation enclosure of the aqueous electrolyte 2, cathode which is galvanic bounded by conductor 5 with the transparent electrode 4 from the second photo-electrochemical cell. On the aqueous electrolyte side 2, the oxidation enclosure is separated from the reduction enclosure by the ions exchange membrane 11, which can be a frit glass wall.
The known installation present the advantage of a simple, cheap construction, because are utilized nanotechnological simple processed materials at cut rate.
The disadvantages of the installation are:

- the presence of liquid electrolyte which conduct to diminution of life time (by evaporation in time);
- the necessity to charge the reduction enclosure with aqueous electrolyte that has the same composition like aqueous electrolyte from oxidation enclosure, concerning to the corrosion surface extension of metallic elements in contact with water and make necessary the control of the maintenance at same level, the aqueous electrolytes composition from both enclosures and the utilization of a hydrogen separator from steam;
- the presence in electrochemical circuit of three auxiliary electric resistances (contact resistances for interfaces: ions exchanger membrane – aqueous electrolyte; aqueous electrolyte – cathode and contraelectrode – aqueous electrolyte) conduct to additional losses of electric energy converted from solar energy and so, limit the yield of solar energy conversion in chemical energy of the water decomposition components at 5%, in standard test conditions of photovoltaic cells AM1,5 (temperature 25^0C, the density of radiation flux 1000 W/m^2, at earth surface), what with a great part of this energy is not converted also, videlicet the energy from infrared interval that represent 55% of the solar radiation spectrum;

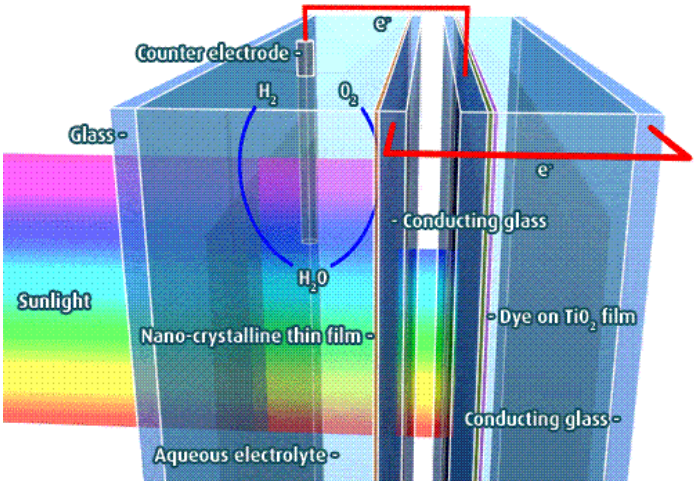

Fig.2. The operating principle of solar instalation with Graetzel photo-electrochemical tandem cells [5]

- the modality of ion exchange membrane layout, which reduce the active surface of photo-electrochemical cells illumination and the contact surfaces of the membrane with aqueous electrolytes from oxidation and reduction boxes.

The operating principle of the installation is (fig.2) [5]: after the absorption of a photon, the pigment molecules pass into an excited state and from this condition it is injected one electron in the conduction band of semiconductor. At the other end of the *n*-type semiconductor, the electron is taking-up and can be inserted into an extern circuit (of the consumer) before returning into the system, by contraelectrode where reduce the oxidizing species. Concomitant, the oxidized pigment is regenerated by the acceptance of one electron from the reducering species of electrolyte. Along with the described electrochemical reactions come a suite of transformations which decrease the efficiency of the global process, determining great internal resistances, a great number of pigment molecules and a small active area. It was observed that a pigment monolayer absorbs only a few percents of incident radiation and the multilayer's structures determine the systematic diminution of the efficiency of electron injection in semiconductor.
Great reserves of the amelioration of these modern installations exist, which will be integrated more and more in the conversion systems of renewable energies in close future (fig.3) [5].

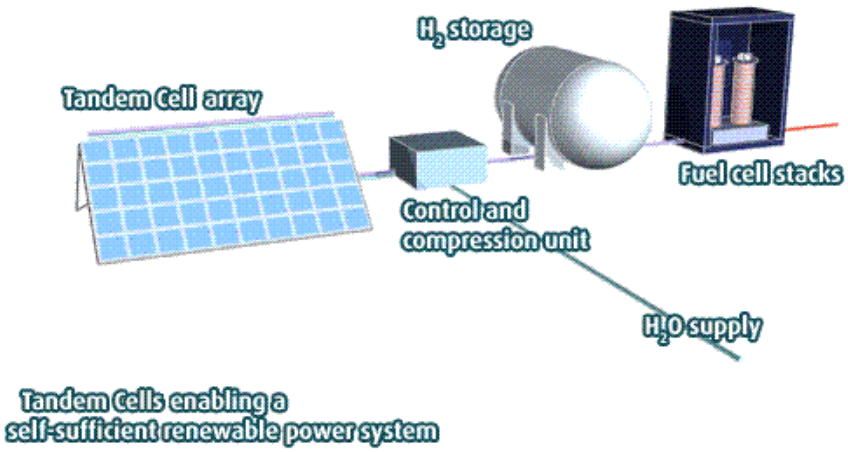

Fig.3. Renewable energy delivery system based on Graetzel photo-electrochemical cells [5]

3. CONCLUSIONS

1. The development of photovoltaic technologies begins with the study and fabrication of organic cells. The producers of silicon cells were collided with a serious technical problem about its purity. The advance purity silicon it can be obtain only through powerful separation/purification processes, so that energy consumption for a photovoltaic cell fabrication, and in adequate mode, the conversion costs are very big, which challenge their sustainability like renewable energy system.

2. More recent research was oriented to obtain a reduced cost cells, by other materials utilization like CdS, $CuInSe_2$ or CdTe. Although these can be produced at reasonable costs, ecologically still represent a less attractive choice, because of the toxic substances from its composition.

3. Light energy transformation to chemical energy through photosynthesis process was undertaken by organic solar cells. The majority of these cells have similar structures with anorganics, based on semiconductors (p-n junction or Schottky barrier). The conduction mechanism is incomplete elucidated yet, because of the energetic bands formation (valence and conduction) from anorganic semiconductors is not registered practically and in case of cells with organic substances films, where the specters indicates dimly superposed molecular orbital's (peaks present in specters are clear and a little different from their of dissolved molecules). The conductivity of these films can be improved by adding of doping agents like oxygen or iodine for *p* type films.

4. The actual tendency analyze in hydrogen energetic field relieves the photo-electrochemical conversion of solar energy method by water cleavage into hydrogen and oxygen with help of tandem cells proposed by Michael Graetzel. The tandem cells, without the advantages and perspectives offered, present also the disadvantage of a not too long life time, that why exist great reserves about the amelioration of the conversion yield.

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