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An experimental investigation to improve the hydrogen production by water photoelectrolysis when cyanin-chloride is used as sensibilizer

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Abstract

This paper deals with an experimental investigation to improve the hydrogen production by water photoelectrolysis. An experimental facility was built: it is mainly constituted by a solar simulator, the photoelectrolytic cell, the electric power supply system and a recirculating and gas sampling hydraulic circuit. Titanium dioxide was chosen as catalyst because of its good photocatalytic efficiency and its high stability to pH variations in watery solutions. Cyanin chloride was tested as sensibilizer: it is a flavonoid, an organic dye, which gives to the watery solution better solar radiation absorption performances. The catalyst and the sensibilizer were deposited on the cathode surface. A sacrificial reducing agent, Ethylenediaminetetraacetic acid (EDTA), was also introduced in the solution to reduce the sensibilizer and restore the original conditions. Different radiation power and electrolytic pH conditions were tested in order to verify the proposed arrangements. Results showed a growing in the hydrogen production by the proposed photoelectrolytic arrangements with respect to the performance of a simple electrolysis. Thus, the obtained results showed that this technology has good possibilities of improvement and interesting perspective of future development.

Keywords

hydrogen, electrolysis, photolysis, sensibilizer, catalyst

1. Introduction

Electrolysis is used for over 80 years as commercial technique to produce hydrogen by water splitting [1]. Electrolytic hydrogen production demands the employment of electric power. Therefore, the production of great amounts of hydrogen is economic only in those countries where electricity can be generated at low costs, for example by hydroelectric plants or the solar source. Furthermore, the solar radiation may be also used to increase the hydrogen production by the photolysis process [2]. This paper deals with the development of a system for hydrogen production from water by catalytic photoelectrolysis. Photoelectrolysis is a technique for water splitting which is supplied by solar radiation and electric energy. Solar radiation and electric energy are converted into chemical energy; solar radiation conversion is obtained by the support of a semiconductor which helps the photon absorption. This technology may have many benefits but the following technical and scientific limits have still to be overcome before its commercialization: high costs, low efficiency of the photolytic process, the complexity of

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implementing photoelectrolytic systems and hydrogen recovery systems, the short life-time. Some problems may be reduced by a catalyst. Titanium dioxide (TiO_2) was chosen as catalyst for the proposed investigation because of its relatively low cost and its good corrosion resistance properties. However, TiO_2 is characterized by a high "band-gap energy" (approximately 3,2 eV in its anatase form) [3]: it is able to absorb solar energy only in the ultraviolet wavelength range (not in the visible wavelength range). Thus, the hydrogen production efficiency may be about 1-2% that is lower than a 10% commercial target. In order to obtain better results by this technology, the purpose is to modify the TiO_2 band-gap characteristics and absorption properties. Thus, the use of a sensibilizer (cyanin chloride, an organic dye) is investigated. TiO_2 was deposited on an electrode (cathode) of a photoelectrolitic reactor; the effect of the sensibilizer on TiO_2 and water absorption properties was evaluated by spectrophotometric measurements. Lastly, photoelectrolytic tests were carried out to verify the proposed arrangements.

2. Water photoelectrolysis

2.1 Electrolysis

Water electrolysis is currently one of the more used methods for hydrogen production from water; however, it is a not economic technique because it uses high quality energy (electrical energy) to produce low quality energy (hydrogen chemical energy). An electrolytic cell is constituted by two electrically connected electrodes (cathode and anode) soaked into a watery solution containing the electrolyte. The cathodic reaction is the reduction of water into hydrogen [1]:

$$2H_2O+2e^- \rightarrow 2OH^- + H_2 \quad (1)$$

The anodic reaction is the oxidation of OH^- anions into water [1]:

$$2OH^- \rightarrow H_2O+1/2\ O_2 +2e^- \quad (2)$$

The complete reaction is the water decomposition [1]:

$$H_2O \rightarrow H_2 + ½\ O_2 \quad (3)$$

By Nerst equations, the required potential for water splitting into hydrogen and oxygen is 1,23 V in standard conditions (25 °C temperature, 1 atm pressure). Cell voltage is effectively higher than 1,23 V due to the electrode polarization resistances and the electrolyte-cell resistance. The electrolytic cell thermal efficiency may be evaluated as the reaction enthalpy (the hydrogen high heating value) divided by the energy used for the reaction [1]:

$$\varepsilon_{th} = \frac{|\Delta H|}{nFV} \cdot 100 \quad (4)$$

The commercial standard electrolyzers work with a 1,7-2,0 V cell voltage which corresponds to an energetic efficiency in the [74%-87%] range in standard conditions. In order to improve the cell performances, typical adjustments are studied relatively to:

- the working temperature increase which is to be compatible with low cost materials;
- cell resistance reduction by specific geometries and high conductibility materials;
- over-voltage reduction by specific electrocatalysts deposited on the electrodes;
- the working pressure increase.

2.2 Water photolysis

Water splitting by solar radiation is possible but it is characterized by specific limitations. O-H bond energy is 460 kJ/mol; thus, only ultraviolet (UV) wavelength photons are able to split the water molecule [3]. UV radiation content into the solar radiation is lower than the visible and infrared one. It is also hindered by the atmospheric ozone layer. The free energy corresponding to the water splitting phenomenon is 2,46 eV; thus, it might occur when photons characterized by a 2,46 eV energy are absorbed [3]. However, the free energy available for this process is lower than the absorbed energy because of the mixing entropy. Besides, water has a good

absorption coefficient (higher than 0.1 cm^{-1}) only in the infrared region, where photon energy is not able to split the water molecules, and for wavelength lower than 200 nm. Thus, water photolysis has to be helped by catalysts able to absorb the visible solar radiation and to make the oxidoreductive process. Semiconductors are optima catalysts due to their chemical stability, thermal stability and high photo-activity. Their activity may be supported by a sensibilizer, which absorbs the solar radiation and transfers the absorbed energy to the catalyst. In fact, the oxygen oxidation (with the electron transfer to the semiconductor) may occur only if the valence band potential is higher than the water oxidation potential, while H^+ reduction is possible if the conduction band potential is lower than the water reduction potential (see Figure 1):

$E(VB) > E(O_2/H_2O)$ (5)

$E(CB)<E(H_2O/H_2)$ (6)

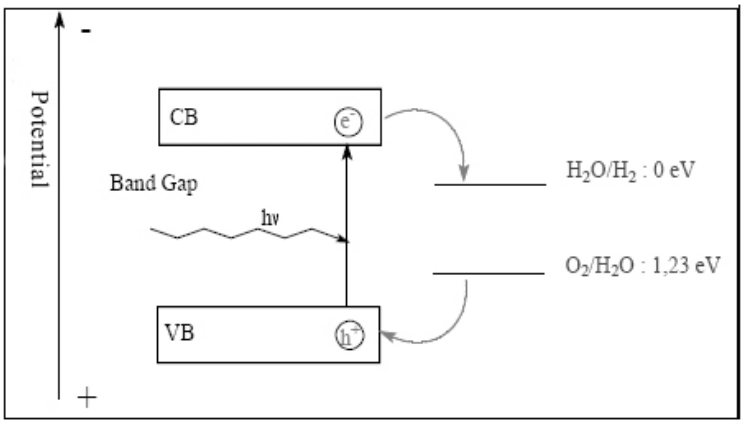

Figure 1: photocatalytic scheme where water oxidoreduction potentials and semiconductor band limits are shown.

Many photocatalysts have been studied in the last years, mainly oxides and sulphides. Titanium dioxide is characterized by high photocatalytic activity and high stability to pH variations. Its band gap is 3,2 eV; thus, it is only sensible to UV radiation. A support may be given by sensibilizers which are adsorbed on the catalyst surface. They are dyes which are able to absorb the visible radiation; the absorbed energy makes an excited electron which is transferred to the semiconductor conduction band and then to H^+ for the hydrogen reduction [3]. This process needs a sacrificial agent to be maintained [3]. The hydrogen production by water reduction may be supported by the sacrificial agent oxidation: the sacrificial agent potential has to be more negative than the water one. Thus, the photogenerated positive charge carriers oxidize the sacrificial agent, not the water (see Figure 2). For example, methanol as sacrificial agent when TiO_2 is the catalyst makes its oxidation to CO_2, while hydrogen is produced.

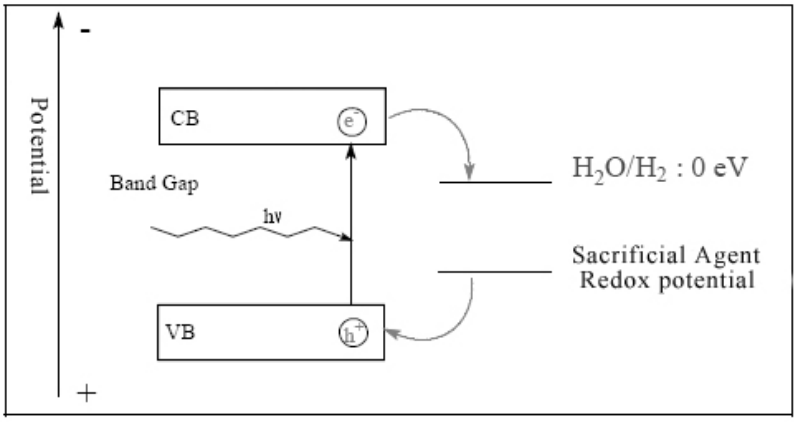

Figure 2: Photocatalytic scheme when a sacrificial agent is used.

2.3 Water Photoelectrolysis

A photoelectrolytic system is composed by an electrolytic cell combined with a photolytic process to improve the hydrogen production. A fundamental characteristic is the kind of the photocatalyst. The catalyst may be in solution or deposited on the electrodes.
The photoelectrolytic cell efficiency may be evaluated as:

$$\eta = \frac{(\dot{m}_1 H_i)_{H2electrolysis} + (\dot{m}_2 H_i)_{H2photolysis}}{P_{ele}} \quad (7)$$

Equation (7) does not consider the supplied solar energy which is a free energy. A more complete energy efficiency evaluation has to include the solar energy value in the eq.(7) denominator. Thus, a good photoelectrolytic system is able to produce the same amount of hydrogen by less supplied electric energy. Furthermore, the energetic saving is accomplished by a renewable process (the use of solar energy). The proposed photoelectrolytic system is based on the Grätzel cell method (dye-sensitized solar cell – DSSc) [4]. A semiconductor is used as catalyst; the semiconductor and the sensibilizer are deposited on the cathode surface. Water photoelectrolysis based on the proposed solutions is characterized by the following reactions:

1. Cathode (water photoreduction):
   - first step (solar radiation excitates a sensibilizer electron): $S^o + hv \dashrightarrow S^*$
     where S^o = natural state sensibilizer, S^* = excited state sensibilizer, hv = photon energy
   - second step (the excited electron moves to the catalyst conduction band):
     $S^* + Ct \dashrightarrow S^+ + e^-_{(Catalyst\ CB)}$
     where Ct = catalyst, $e^-_{(Catalyst\ CB)}$ = electron in the catalyst conduction band, S^+ = oxidized sensibilizer (it gave an electron to the catalyst)
   - third step (electrons are used for water reduction): $e^-_{(Catalyst\ CB)} + H_2O \dashrightarrow 1/2H_2$
   - fourth step (the sacrificial agent gives an electron to the sensibilizer which restores its natural state): $S^+ + SA \dashrightarrow S^o + SA^+$
     where SA = sacrificial agent, SA^+= oxidized sacrificial agent (it gave an electron to restore S^o)

   The electrons produced by photolysis are added to the ones given by the cathode. Thus, a double electron source occurs.
2. Anode (water oxidation):
   - $H_20 \dashrightarrow O_2 + e^-$ (captured by the anode)

3. The photocatalyst

The proposed photocatalyst is a semiconductor, Titanium dioxide (TiO_2), on which a sensibilizer, cyanin chloride ($C_{27}H_{31}ClO_{16}$), is deposited. A semiconductor is a good catalyst for photoelectrolysis when it has the following characteristics:

1. stability;
2. low cost:
3. no toxicity;
4. high photoactivity;
5. the redox potential of the molecule splitting is within the semiconductor band-gap.

TiO_2 has a good photocatalytic efficiency thanks to its high stability in watery solutions versus pH variations. Three different TiO_2 crystalline phases are possible: rutile, anatase and brookite. The more active allotropic form is anatase. It is less thermodynamically stable than rutile, but its formation is kinetically favored at low temperatures (<600°C). However, the large TiO_2 band-gap (3,2 eV for anatase, 3,0 eV for rutile) limits the amount of absorbed solar radiation. In fact, the maximum wavelength which allows the electromagnetic radiation absorbing is 385

nm (anatase) or 410 nm (rutile). Thus, the generation of an electron - hole pair can be photoinduced only by UV radiation. This limitation is reduced by the sensibilizer: cyanin chloride is proposed here. It is an organic dye which allows absorbing a wider portion of the solar radiation. The proposed sensibilizer is a flavonoid, in particular an anthocyanin: anthocyanins are organic dyes, which are diffuse in the vegetal world because they give the color to leafs, flowers and fruits. In order to reduce the sensibilizer to the fundamental state, a sacrificial agent is dissolved in the solution. Ethylenediaminetetraacetic acid (EDTA) is proposed as sacrificial agent. It is a carboxylic acid which may give slightly acid characteristics to the solution.

4. The experimental facility

A photoelectrolytic facility was built and tested. It is characterized by constructive easiness and low realization costs. The photoelectrolytic process is strictly joint to the choice and the location of the reactor components, such as the photocatalyst, the electrolyte, the reactor shape and the materials for the electrodes. The experimental facility is made by the following main components:

- the electrolytic reactor;
- the electrical supply system (ISO-TECH ips-3610d power supply system);
- a solar simulator (model Sun 2000 by ABET equipped with xenon lamps and mechanical filters);
- the sampling and recirculation system;
- a pH-meter (model HD2105.2 by Delta Ohm equipped with a KP 61 Ag/AgCl sat KCl glass electrode);
- a luxmeter (model HD 9221 by Delta Ohm);
- two spectrometers (model Nicolet 6700 FT-IR by Thermo and model LAMBDA™ 750 UV/Vis/NIR by Perkin Elmer);
- a gaschromatograph (model CP-4900 by VARIAN).

4.1 The electrolytic reactor

The reactor is a single electrolytic cell (see Figure 3). The cell covering was obtained by milling a nylon block so as to create the cathodic and anodic compartments. Cathode and anode are placed inside the two compartments sections through electrical insulating supports. The cell upper surface is closed by a quartz glass which is characterized by a high transmittance in the visible and UV solar spectrum (> 90% for wavelength higher than 240 nm). The cell is tighten up by a steel structure with tie rods. It is also characterized by three cylindrical openings: the first one is the electrolytic solution inlet (which is the same for anodic and cathodic compartments), the others are the solution outlets. Further two holes are for the connection with the electric power supply. The watery solution inlet is placed on the cell bottom surface, where the electrode compartments are connected in order to help the ionic transport. Electrolysis takes place by the electrodes which are installed in the cell central part. The solar radiation hits the cell, and in particular the quartz glass, on its upper surface. When the photoelectrolytic process starts, the produced gases move upwards with the watery solution by an hydraulic pump. Anodic and cathodic upper sides are not connected in order to help the storage of different gases. Two kinds of electrolytes were tested: sodium anhydrous sulfate (Na_2SO_4), which is a salt but may produce a slightly acid environment when the sacrificial agent is introduced into the solution, and sodium hydroxide (NaOH), which produces a basic environment. By using TiO_2, which allows both water reduction and oxidation, only one kind of electrolyte may be used for both the compartments [5]. AISI 316 inox steel nets were used as electrodes both for anodic and cathodic compartments in order to avoid high cost materials (such as Platinum). In fact, the main purpose of this investigation is to evaluate the photolytic performances of the proposed arrangements; thus, future choices will be focused on the determination of solutions

for reducing the electrode corrosion phenomena. The electrodes are metallic nets; a foil configuration may allow a more uniform catalyst distribution, but a net configuration was chosen because an easier interaction between the system components and the watery solution is obtained in this way.

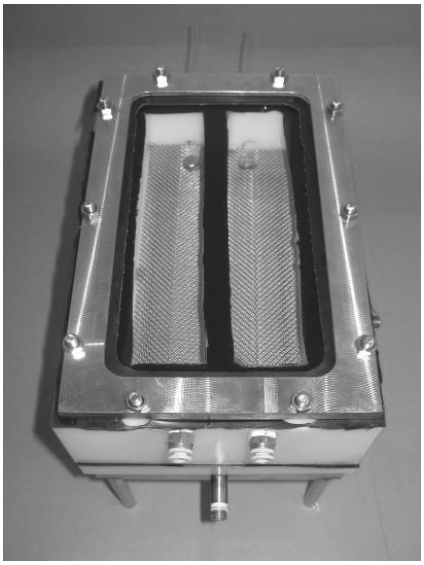

Figure 3: The electrolytic cell

4.2 The sampling and recirculation system;

The electrolytic reactor is connected with a sampling and recirculation system (see Figures 4 and 5). It is constituted by two cylindrical tanks connected to the cell by Teflon pipes. The tank connected with the cell cathodic compartment is the hydrogen storage tank, the one connected with the anodic compartment is the oxygen storage tank. Each tank is equipped by temperature and pressure sensors, porous septa for gas aspiration, electromagnetic agitators (to increase the turbulence, avoid the gas recombination and the catalyst deposition on the bottom surface), heating plates (to keep the water at the solar irradiation temperature conditions).

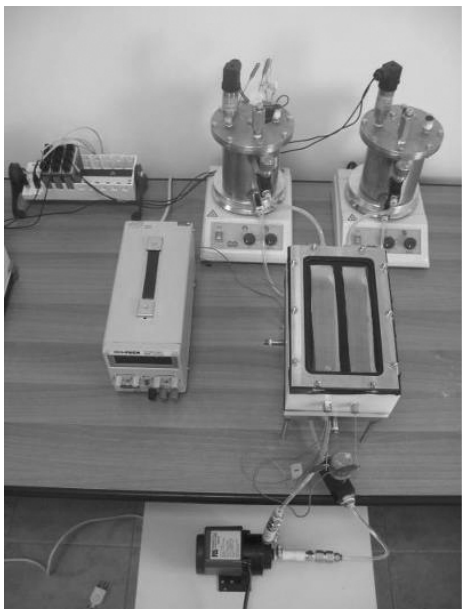

Figure 4: The electrolytic cell connected with the sampling and recirculation system

The recirculation of the watery solution is obtained by an hydraulic pump which has the only function to compensate the circuit pressure losses. The solution-gas mixture comes from the

cell to the upper side of the tanks in order to help the state separation. At the tank bottom side, only the heavier watery solution is captured by the outlet pipes. Gas analysis is made by a gascromatograph. Gases are picked up continuously by a syringe inserted into the porous septa. A data acquisition system was implemented to monitor and record the tank working conditions (gas pressures, solution temperature).

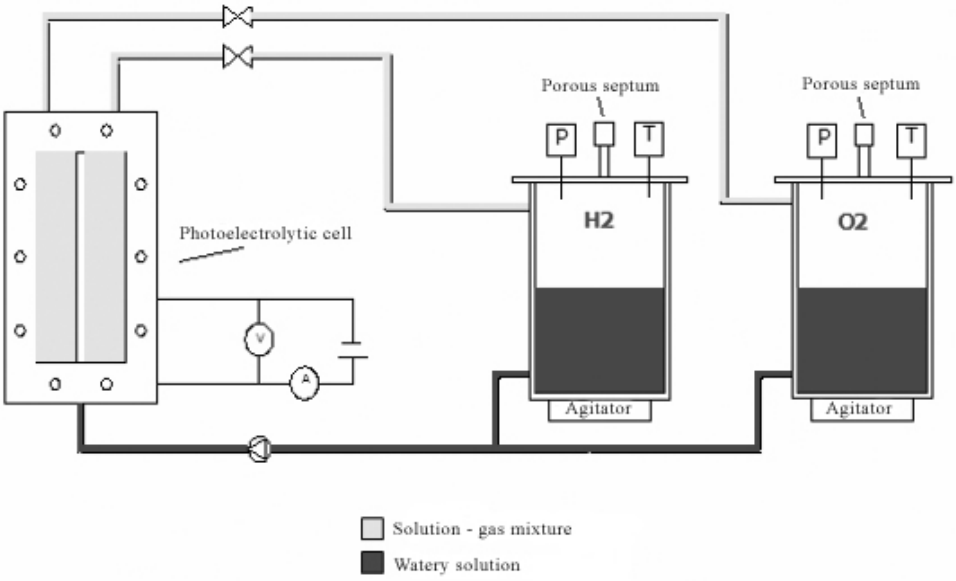

Figure 5: Scheme of the electrolytic cell and the sampling and recirculation system

5. Experimental methodology

Four working conditions were investigated:

A. electrolysis;
B. photoelectrolysis with only the semiconductor deposited on the cathode and using a 35 W xenon lamp;
C. photoelectrolysis with the semiconductor and the sensibilizer deposited on the cathode and using a 35 W xenon lamp;
D. photoelectrolysis with the semiconductor and the sensibilizer deposited on the cathode and using a 500 W xenon lamp and a 23% power reduction filter.

Conditions B and C were used to evaluate the effect of the sensibilizer on the hydrogen production. Condition D was used to evaluate the hydrogen production increase versus the solar power increase. Preliminary tests verified the linear behavior of the cell current-voltage relation. Cell voltage was set to 9,0 V for the experimental tests. This is not the best voltage for electrolysis process, but the main purpose of the proposed investigation is to evaluate the photolysis efficiency of the proposed solution. This voltage condition corresponds to different current conditions for the tested working conditions (when Na_2SO_4 is the electrolyte, approximately 0,60 A for A and B conditions, 0,54 A for C and D conditions; when NaOH is the electrolyte, approximately 0,64 A for A and B conditions, 0,69 A for C and D conditions).

5.1 Catalyst and sensibilizer deposition

The possibility of using a photocatalyst in solution was verified. This choice was rejected because the water oxidation and reduction zones are too close each other; thus, it might be highly possible the electron-hole recombination. A semiconductor (TiO_2) layer was deposited on the cathode (where the hydrogen production occurs). The layer was obtained by spreading a paste containing nanocrystalline titanium dioxide mixed with optically dispersing anatase particles. Later, the electrode was subjected to a 450°C temperature for 15 minutes in order to

fix the TiO_2 layer. This process was carried out by a heating wrap and a thermal insulating ceramic material (see Figure 6).

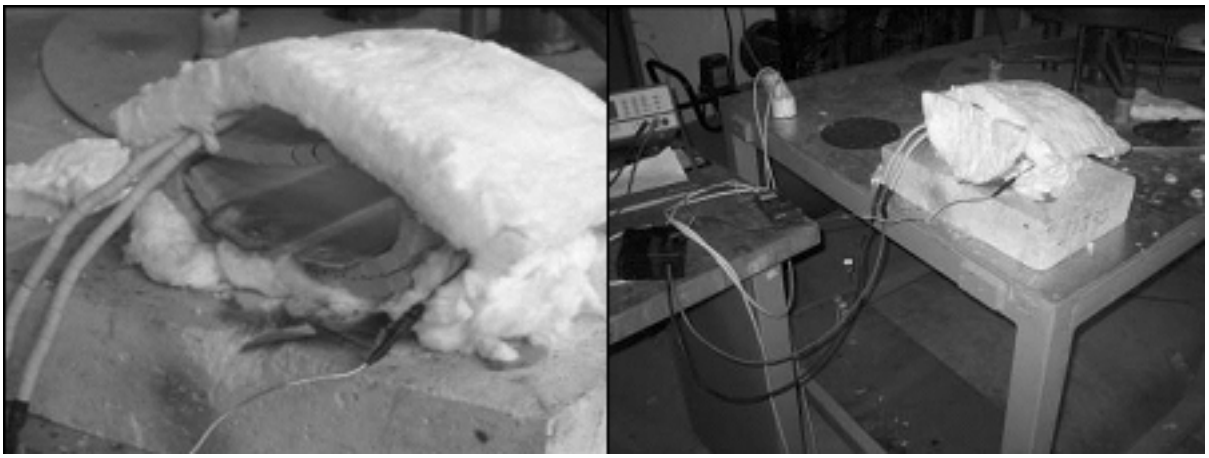

Figure 6: Picture of TiO_2 and cathode thermal treatment

Later, the sensibilizer (cyanin chloride, $C_{27}H_{31}ClO_{16}$) were deposited on the cathode. A 100 ml watery solution containing acetic acid and with pH = 3÷4 was prepared. 1 mg sensibilizer was soaked into the solution. The TiO_2 covered electrode was soaked into the mentioned solution for 12 hours. In this way, a violet color electrode covered by TiO2 and $C_{27}H_{31}ClO_{16}$ was obtained.

5.2 The watery solution

Conditions C and D require the use of a sacrificial agent. Thus, EDTA was introduced in the watery solution for these tests. The watery solution pH was measured; results showed that the solution with a salt electrolyte (Na_2SO_4) is slightly acid when EDTA is introduced. Table 1 shows the pH values of the tested solutions.

Table 1: pH comparison between the tested watery solutions

Solution	*Solute*	*Molar Concentration*	*Solution Volume* $[10^{-6}\ m^3]$	*pH*
1	Na_2SO_4	0,2	200	7÷8
2	NaOH	0,2	200	12÷13
3	EDTA	0,01	200	3÷4
	Na_2SO_4	0,2		
4	EDTA	0,01	200	12÷13
	NaOH	0,2		

Thus, conditions A and B correspond to neutral (Na_2SO_4) and basic (NaOH) solutions, conditions C and D to slightly acid (Na_2SO_4 + EDTA) and basic (NaOH + EDTA) solutions. NaOH solution pH is not modified by EDTA introduction because the NaOH basic behavior neutralized the EDTA acid behavior.

5.3 The sensibilizer contribute

Spectrophotometric measurements were made to evaluate the contribute of the proposed sensibilizer (dye) to absorb the visible solar radiation. It was measured both with reference to the catalyst and the watery solution; in fact, it is possible a sensibilizer separation from the electrode during the photoelectrolytic tests. In this condition, the sensibilizer is in solution. The

comparison between the transmittances with reference to a TiO_2 sample is shown in Figure 7, while Figure 8 shows the comparison between the absorbances.

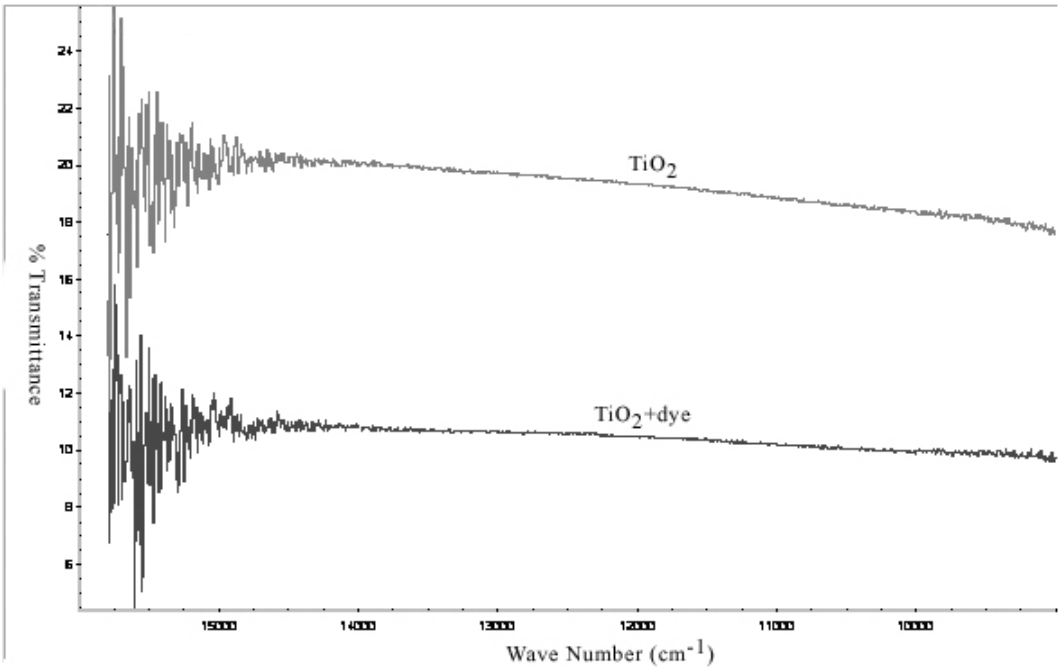

Figure 7: Comparison between TiO_2 and (TiO_2 + dye) transmittances

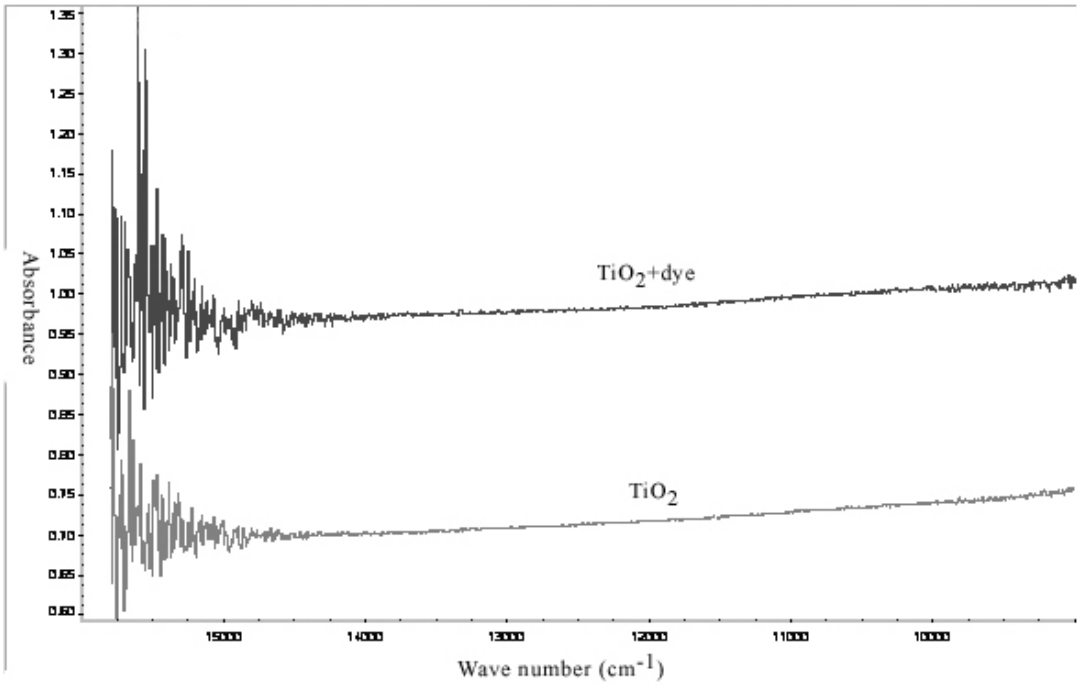

Figure 8: Comparison between TiO_2 and (TiO_2 + dye) absorbances

Results show that TiO_2 transmittance is averagely 20% in the visible spectrum, while (TiO_2 + dye) transmittance is averagely 10%. The measured absorbance values state that the reduced transmittance is due to the absorption increase. In particular, TiO_2 + dye absorbance peaks occur in the maximum solar power region. About the dye effect with respect to the watery solution, six solution samples were prepared with the following solutes:

1. 0,2 M Na_2SO_4;

2. 0,2 M Na_2SO_4, 0,01 M EDTA;
3. 0,2 M Na_2SO_4, 0,01 M EDTA, 0,5 mg dye;
4. 0,2 M NaOH;
5. 0,2 M NaOH, 0,01 M EDTA;
6. 0,2 M NaOH, 0,01 M EDTA, 0,5 mg dye.

The electrolyte molar concentration was chosen as a compromise between high values for high electrolysis performances and low values to reduce electrode corrosion phenomena. Spectrophotometric tests showed that:

- EDTA and dye give a good absorption increase (up to 0,15) to the Na_2SO_4 solution in the 500÷525 nm wavelength range (close to the maximum solar power region), while the increase is low over the 600 nm wavelength (about 0,02).
- EDTA and dye give a good absorption increase (up to 0,15) to the NaOH solution in the 380÷405 nm wavelength range (UV region).

5.4 Evaluation of the solar generator contribute

A solar generator was used as solar source. Two lamp power conditions were used: A 35 W xenon lamp without power reduction filters was used for B and C tests; a 500 W xenon lamp with a 23% power reduction filter was used for D test. These conditions correspond to the following specific powers on the cathode surface (they were measured by a luxmeter):

- 133 W/m^2 for B and C tests;
- 220 W/m^2 for D tests.

6. Experimental results

Hydrogen production was evaluated for the mentioned different electrolyte and test conditions. Table 2 shows the obtained results for 2 hours tests.

Table 2: 2h test results

Electrolyte	*Test conditions*	*Produced H_2 (10^{-6} m^3)*
0,2M Na_2SO_4 + 0,01M EDTA	A	431
	B	441
	C	531
	D	608
0,2M NaOH + 0,01M EDTA	A	456
	B	468
	C	651
	D	760

The greater hydrogen production is obviously the one obtained when dye is used and higher solar irradiation is applied (D condition). It is shown that NaOH electrolyte environment is slightly better than Na_2SO_4 environment both for electrolysis and photolysis performances. Electrolysis efficiency is approximately 14% both for NaOH and Na_2SO_4. It is a low value but the theoretical one is 16% for this voltage conditions. However, the voltage value was chosen in order to better evidence the photolytic process efficiency which is the main purpose of this investigation. Results show that the solar-to-hydrogen conversion efficiency due to the photocatalytic process is in the [11%-11.2%] range for NaOH and in the [9.5%-10%] range for Na_2SO_4 when the sensibilizer is used (it is less than 1% when only TiO_2 is deposited, condition B). Further tests were carried out for 6 hours in the conditions A and D. These tests were made

for evaluating the photocatalyst behavior for a longer exposition time and during these exposition periods. Table 3 shows the obtained results.

Table 4: 6h test results

Electrolyte	*Test conditions*	*Produced H_2 after 2h (10^{-6} m^3)*	*Produced H_2 in the [2h, 4h] time period (10^{-6} m^3)*	*Produced H_2 in the [4h, 6h] time period (10^{-6} m^3)*
0,2M Na_2SO_4 + 0,01M EDTA	A	431	429	429
0,2M Na_2SO_4 + 0,01M EDTA	D	608	604	603
0,2M NaOH + 0,01M EDTA	A	456	457	455
0,2M NaOH + 0,01M EDTA	D	760	750	741

It is shown that the photocatalytic effect diminishes during the solar irradiation both for acid and basic electrolyte. The hydrogen reduction is more sensitive to the exposition time for NaOH electrolyte. In fact, the Na_2SO_4+EDTA watery solution has a pH of 3÷4 which is close to the pH of the solution used for the photocatalyst deposition. This fact gives more resistance characteristics to the photocatalyst in the slightly acid watery solution. Furthermore, electrode corrosion phenomena are not shown during the short time proposed tests but it is however a problematic, especially for the slightly acid electrolyte; however, the electrode corrosion problem may be solved by using a conductive glass electrode which will be the topic of a future investigation.

7. Conclusions

This work deals with an experimental investigation on a water photoelectrolytic reactor. In particular, the effect of the following parameters on the hydrogen production was evaluated: the electrolytic solution pH, the use of cyanin chlorure as sensibilizer when TiO_2 is the photocatalyst, the solar incident power. The experimental investigation was particularly focused on the chosen sensibilizer performances. Tests verified the hydrogen production increase with respect to a no sensibilizer use. A 11.2% maximum solar-to-hydrogen photolytic conversion efficiency was found when the proposed arrangements are applied to a basic watery solution. Furthermore, the experimental results showed good improvement possibilities and interesting perspectives of future development, as:

- the determination of electrodes and electrolytes able to further improve the process. The tests showed that a basic watery solution may give a better hydrogen production with respect to a slightly acid one. On the contrary, the slightly acid solution gives better results for a long exposition. However, electrode corrosion phenomena may occur especially for acid electrolytes; these problems may be solved by the use of conductive glass layers.
- the determination of new typologies of sensibilizers and photocatalytic semiconductors. The used sensibilizer (a flavonoid) and the used semiconductor (TiO_2) are only one possibility to improve the hydrogen production;
- testing the photoelectrolytic system in other different working conditions in order to further evaluate and optimize its efficiency;
- the use of photovoltaic panels to supply the electric power for the electrolytic process. In this way, the reactor may be supplied only by the solar source.

Thus, the proposed experimental tests are a base for further investigations to improve the system efficiency in energetic and economic terms by using the sun as free and renewable energy source.

Nomenclature

Ct:	catalyst
E (CB):	conduction band potential [V]
$E(H_2O/H_2)$:	water reduction potential [V]
$E(O_2/H_2O)$:	water oxidation potential [V]
E (VB):	valence band potential [V]
$e^-_{(Catalyst\ CB)}$:	electron in the catalyst conduction band
F:	Faraday constant [$C \cdot mol^{-1}$]
h:	Planck constant [J·s]
$(\dot{m}_1 H_i)_{H_2 electrolysis}$:	energy content of the hydrogen produced by electrolysis [J]
$(\dot{m}_2 H_i)_{H_2 photolysis}$:	energy content of the hydrogen produced by photolysis [J]
n:	number of electrons conducted under the water electrolysis
P_{ele}:	supplied electric energy [J]
S^o:	natural state sensibilizer
S^+:	oxidized sensibilizer
S^*:	excitated state sensibilizer
SA:	sacrificial agent
SA^+:	oxidized sacrificial agent
V:	voltage [V]
$\lvert\Delta H\rvert$:	reaction enthalpy [$J \cdot mol^{-1}$]
ε_{th}:	electrolytic cell efficiency [%]
η:	photoelectrolytic cell efficiency
v:	frequency [s^{-1}]

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