

Photoelectrochemical Hydrogen Production from Aqueous Alcohol Solutions Using TiO₂ Film Photoanodes

Maria Jaramillo Gutiérrez, Yaneth Higuera Puello, Leidy Trespalacios León,
Dionisio Laverde Cataño & Julio Pedraza Avella

Grupo de Investigaciones en Minerales, Biohidrometalurgia y Ambiente - GIMBA, Universidad Industrial de Santander - UIS, Sede Guatiguará, Transversal Guatiguará, Calle 8N No. 3W-60, Barrio El Refugio, Piedecuesta (Santander), Colombia



Para citaciones: M. Jaramillo Gutiérrez, Y. Higuera Puello, L. Trespalacios León, D. Laverde Cataño & J. Pedraza Avella, "Photoelectrochemical Hydrogen Production from Aqueous Alcohol Solutions Using TiO₂ Film Photoanodes", *Ing-Nova*, vol. 2, no. 2, pp. 109-119, Jul. 2023.
<https://doi.org/10.32997/rin-2023-4348>

Recibido: 6 de mayo de 2023
Revisado: 15 de junio de 2023
Aprobado: 16 junio de 2023

Autor de correspondencia:
Maria Jaramillo Gutiérrez
mariajjaramillo@gmail.com

Editor: Miguel Ángel Mueses. Universidad de Cartagena-Colombia.

Copyright: © 2023. M. Jaramillo Gutiérrez, Y. Higuera Puello, L. Trespalacios León, D. Laverde Cataño & J. Pedraza Avella. Este es una editorial de acceso abierto, distribuido bajo los términos de la licencia <https://creativecommons.org/licenses/by-nc-nd/4.0/> la cual permite el uso sin restricciones, distribución y reproducción en cualquier medio, siempre y cuando que el original, el autor y la fuente sean acreditados.



ABSTRACT

The simultaneous hydrogen production and alcohol oxidation from aqueous solutions containing methanol, ethanol or glycerol was evaluated in a photoelectrochemical cell under UV-Vis illumination using a TiO₂ film photoanode. TiO₂ films were prepared by sol-gel dip-coating on metallic support plates. A AISI/SAE 316 stainless steel plate prepared by the Pechini method was used as cathode. The effect of some variables such as the photoanode support material (titanium grade 5, AISI/SAE 304 stainless steel and AISI/SAE 316 stainless steel), the supporting electrolyte (0.1-0.3 M NaCl or 0.01-0.03 M NaCl plus 0.1-0.3 M NaOH), the alcohol concentration (10-30% v/v), the applied potential (1.0-2.6 V), the Hg lamp power (125 or 250 W) and the number of TiO₂ layers (1, 3 or 5) was investigated. The best results were found using 1 layer of TiO₂ film supported on AISI/SAE 316 stainless steel in an electrolytic solution 0.03 M NaCl, 0.3 M NaOH and 10% v/v alcohol by applying a potential of 2.3 V and employing an Hg lamp of 125 W. After 2 h the higher hydrogen production (2.61 μmol) was achieved with the glycerol solution.

Palabras clave: Photoelectrochemical water splitting; Photoelectrocatalytic degradation of alcohols; Methanol; Ethanol; Glycerol.

Producción fotoelectroquímica de hidrógeno a partir de soluciones acuosas de alcohol utilizando fotoánodos de película de TiO₂

RESUMEN

La producción simultánea de hidrógeno y la oxidación de alcohol a partir de soluciones acuosas que contienen metanol, etanol o glicerol se evaluó en una celda fotoelectroquímica bajo iluminación UV Vis utilizando un fotoánodo de película de TiO₂. Las películas de TiO₂ se prepararon mediante revestimiento por inmersión sol-gel sobre placas de soporte metálicas. Se utilizó como cátodo una placa de acero inoxidable AISI/SAE 316 preparada por el método Pechini. El efecto de algunas variables como el material de soporte del fotoánodo (titanio grado 5, acero inoxidable AISI/SAE 304 y acero inoxidable AISI/SAE 316), el

electrolito de soporte (0,1-0,3 M NaCl o 0,01-0,03 M NaCl más 0,1-0,3 M NaOH), la concentración de alcohol (10-30 % v/v), el potencial aplicado (1,0-2,6 V), la potencia de la lámpara de Hg (125 o 250 W) y el número de capas de TiO₂ (1, 3 o 5) fue investigado. Los mejores resultados se obtuvieron utilizando 1 capa de película de TiO₂ soportada en acero inoxidable AISI/SAE 316 en una solución electrolítica de NaCl 0,03 M, NaOH 0,3 M y alcohol al 10 % v/v aplicando un potencial de 2,3 V y empleando una lámpara de Hg de 125 W. Después de 2 h se alcanzó la mayor producción de hidrógeno (2,61 μmol) con la solución de glicerol.

Keywords: Desdoblamiento fotoelectroquímico del agua; Degradación fotoelectrocatalítica de alcoholes; Metanol; Etanol; Glicerol.

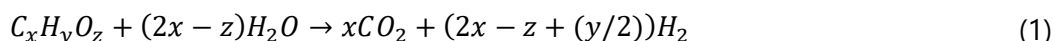
1. Introduction

The conversion of solar energy into electricity can be achieved directly by using photovoltaic cells. However, the generation of electricity is also feasible in a fuel cell using the hydrogen produced by water splitting, which can be stored and used when required. Furthermore, the water splitting can be achieved by photocatalytic, electrochemical or photoelectrochemical methods, allowing the simultaneous degradation of organic substances and thus giving a double environmental benefit: production of renewable energy and decontamination of polluted water. The latter method has shown to be more efficient because it combines the advantages of the two former [1-3].

In a conventional two-compartment photoelectrochemical cell, the oxidation of organic substances takes place in the anodic compartment, where a semiconductor photoanode absorbs photons of certain wavelength and then electron-hole pairs are generated. The holes are capable to oxidize organic substances, either directly or through the formation of hydroxyl radicals, OH[•], which due to their high oxidizing power allows the complete mineralization of the contaminant [4].

Titania dioxide (TiO₂) is the most widely used photocatalyst in photocatalytic and photoelectrochemical applications because it is chemically stable, has favorable optoelectronic properties and is inexpensive. However, the band gap of TiO₂ is larger than 3.1 eV for that reason TiO₂ is activated for UV light. In order to enhance the photocatalytic activity and extend the absorption edge of TiO₂ to the visible region many researchers have proposed the modification of TiO₂ by metal and non-metal doping. The modification of TiO₂ with non-metals such as N, S, and C improves the conductivity and optical properties as they introduce new surface states that may lie close to the conduction band or valence band of TiO₂.

Particularly, the photoelectrocatalytic oxidation of alcohols such as methanol, ethanol and glycerol using TiO₂-based photoanodes has been extensively studied because they are recognized as sacrificial reducing agents that give high yields and they are products of biomass, hence available and renewable [5-10]. Although alcohols can be partially oxidized to aldehydes, ketones, carboxylic acids or alkanes [11-13], their mineralization is possible and, in the absence of O₂, also H₂ can be produced, according to Eq. 1 [14-16].



On the other hand, the photogenerated electrons are able to migrate to the cathode if the cathode potential is enough positive with respect to the conduction band potential of the semiconductor in the photoanode. This can be assured by applying an external potential and in this way the electron-hole recombination is prevented [4].

Consequently, in the absence of O₂, the electrons cause the reduction of water in the cathodic compartment and H₂ is produced, according to Eq. 2:



Many researchers have used a Pt cathode because it is inert at extremely positive potentials and due to the ability of this noble metal to chemisorb intermediate species on its surface and thereby catalyze electrode processes (i.e. H atoms spill over onto Pt and recombine to form H₂) [17]. However, since Pt is a very expensive material a better choice is Pt supported on a conductor plate. In this sense, the cathode in photoelectrochemical applications consists of two components, the support and an active phase of metal particles (the catalyst), which are deposited on the support. The spillover phenomenon and the strong metal support interaction are of great importance in the main stages of catalytic processes, such as adsorption, surface and bulk reactions, and finally desorption. The interaction between metal and support has been shown to promote hydrogen activation on the support surface. Pd is able to adsorb and absorb hydrogen, forming non-stoichiometric hydrides. The interaction between the metal and the support has been shown to promote hydrogen activation on the support surface. It is important to note that most industrial catalysts are prepared by using support material that provide high thermochemical stability, regeneration feasibility, tunable acidity and low cost [18].

In this work, we evaluated the performance of TiO₂ films in the photoelectrochemical hydrogen production and simultaneous alcohol oxidation. We analyzed the effect of some variables such as the photoanode support material, the supporting electrolyte, the alcohol concentration, the applied potential, the Hg lamp power and the number of TiO₂ layers, looking for the best conditions for the hydrogen production.

2. Materials and methods

2.1. Reagents

The following chemicals were used as received without further purification: HCl (Merck, 37%), HNO₃ (Carlo Erba, 65%), ethanol (J.T. Baker, 99.9%), titanium(IV) isopropoxide (Aldrich, 97%), 2-propanol (Merck, 99.5%), acetylacetone (Aldrich, 99%), H₂PtCl₆·xH₂O (Aldrich, 99.9%), citric acid (Carlo Erba, 99.5%), ethylene glycol (Aldrich, 99.8%), methanol (J.T. Baker, 99.8%), glycerol (Aldrich, 99.5%), NaCl (Merck, 99.5%), NaOH (Aldrich, 98%) and distilled water (1 MΩ·cm).

2.2. Preparation of the electrodes

For the photoanodes, TiO₂ films were prepared by sol-gel dip-coating on metallic support plates (4 × 4 cm). Three support materials were tested: titanium grade 5, AISI/SAE 304 stainless steel and AISI/SAE 316 stainless steel. Prior to use, the titanium plates were immersed in diluted HCl for 60 min at 70 °C and then washed with diluted HNO₃ for 5 min, while the stainless steel plates were washed with ethanol for 15 min in an ultrasonic bath. The procedure was adapted from that described elsewhere [19,20], using a molar ratio

alkoxide:water:acetylacetone of 1:8:1.5, a volume ratio alkoxide: 2-propanol 1:2.5 and a withdrawal speed of 10 cm/min. The films were dried at room temperature (25 °C) for 20 min and finally they were annealed at 500 °C for 4 h, in order to obtain mainly the anatase phase.

For the cathode, a Pt film was prepared by the Pechini method [21] on AISI/SAE 316 stainless steel plate (4 × 4 cm), previously washed with ethanol for 15 min in an ultrasonic bath. The procedure used was described elsewhere [22], using a molar ratio Pt:citric acid:ethylene glycol of 1:8:32. The film was thermally treated at 130 °C for 30 min to eliminate water and then at 450 °C for 10 min to eliminate the organic portion, leading to the formation of the metallic film. This procedure was repeated three times.

2.3. Electrochemical and photoelectrochemical evaluation of the electrodes

The experiments were carried out in a conventional cell with two cylindrical compartments ($D = 7$ cm, $h = 7$ cm) of Pyrex glass, separated by an anion-permeable membrane (Ameridia Neosepta AMX). The headspace of the cathodic compartment was partially filled with acrylic in order to reduce its volume to achieve a more accurate measurement of the hydrogen produced. Each electrode was placed in its respective compartment, separated by 2 cm and connected with a copper wire to a DC power supply (Hewlett Packard 6264B). Tests were conducted in the dark and under illumination in order to evaluate the electrochemical and photoelectrochemical processes. The applied potential and the circulating current were measured with Amprobe 30XR-A digital multimeters. The alcohol degradation in the anodic compartment was monitored by measuring the conductivity of the solution with an YSI Model 35 conductance meter. External illumination was provided by a high pressure Hg lamp (General Electric 125 or 250 W), which emits UV-Vis radiation. The temperature in the anodic compartment was monitored with a Pt 1000 temperature sensor (Schott Instruments). The hydrogen concentration in the headspace of the cathodic compartment (16 mL) was measured with a Crowcon Tetra gas analyzer (detection range: 0-1000 ppm H₂, detection limit: 1 ppm H₂). A schematic representation of the photoelectrochemical cell and the equipment used in the experiments are shown in Figure 1.

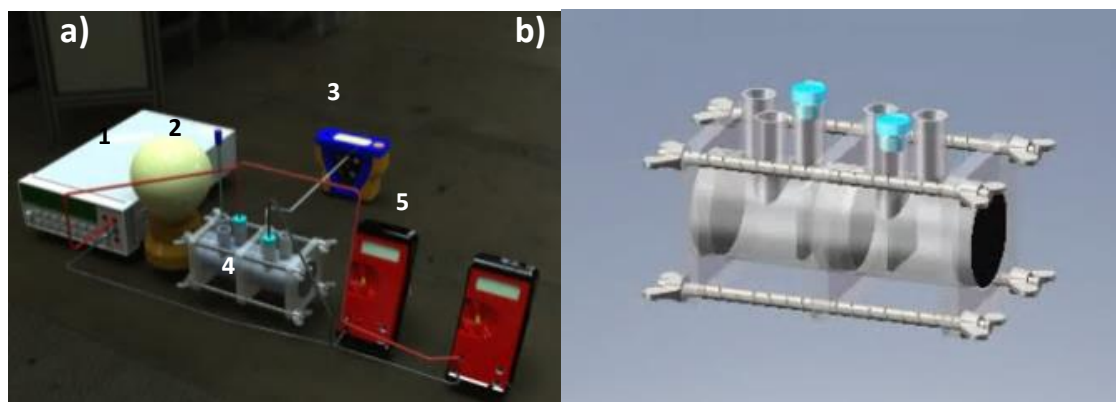


Figure 1. (a) Photoelectrochemical system: 1. Power supply, 2. Hg lamp, 3. Hydrogen analyzer, 4. Photoelectrochemical cell, 5. multimeters. (b) Photoelectrochemical cell in detail.

The effect of the photoanode support material (titanium grade 5, AISI/SAE 304 stainless steel or AISI/SAE 316 stainless steel), the supporting electrolyte (0.1-0.3 M NaCl or 0.01-0.03 M NaCl plus 0.1-0.3 M NaOH), the alcohol concentration (10-30% v/v), the applied potential (1.0-2.6 V), the Hg lamp power (125 or 250 W) and the number of TiO₂ layers (1, 3 or 5), was studied by varying one factor at a time, keeping other factors fixed.

3. Results and discussion

Selection of photoanode support material and supporting electrolyte

In a conventional photoelectrochemical cell, the photoanode is composed by a semiconductor photocatalyst supported on a conductor material and the cathode has an active metal surface which favours the desired reactions. In order to select the photoanode support material firstly, the potential ranges for for stable operating conditions were established by cyclic voltammetry (CV) using an Autolab PGSTAT 302N potentiostat-galvanostat controlled by NOVA 2.1 software. A conventional three electrode cell was used. The working electrode was a support plates (titanium grade 5, AISI/SAE 304 stainless steel or AISI/SAE 316 stainless steel), the reference electrode was Ag/AgCl (3 M KCl) and the counter electrode was a graphite rod (Alfa Aesar, 99.999%). The electrolyte solution was a NaCl aqueous solutions with different concentrations (0.1-0.3 M) in deionized water. All reagents were analytical grade. Prior to the test, the electrolyte solution was bubbled with high-purity N₂ for 20 min to remove the dissolved oxygen. CV was recorded at a scan rate of 10 mV·s⁻¹ from the OCP in the negative sweep until -2.6 V vs. Ag/AgCl, and then return in the positive sweep until 1.5 V vs Ag/AgCl. As it was expected, higher currents were obtained when the NaCl concentration was increased due to the enhancement of the electrolyte conductivity (7). However, corrosion was detected in all support plates. The titanium plates exhibit remarkably better corrosion resistance than the stainless steel plates but they provided significantly lower current values, which is not desirable for efficient hydrogen production. Keeping in mind that chlorides are the main corrosive agents for stainless steels, especially in acidic medium [23], we reduced the NaCl concentration and NaOH was added to the aqueous solution. In this alkaline medium, we can assure that all hydrogen was produced by water splitting (Eq. 2) and not by the reduction of hydronium ions (Eq. 3).



The best results were obtained using a solution 0.03 M NaCl and 0.3 M NaOH. They are shown in Figure 2. It is worth mentioning that by using this electrolytic solution any corrosion signal was not detected.

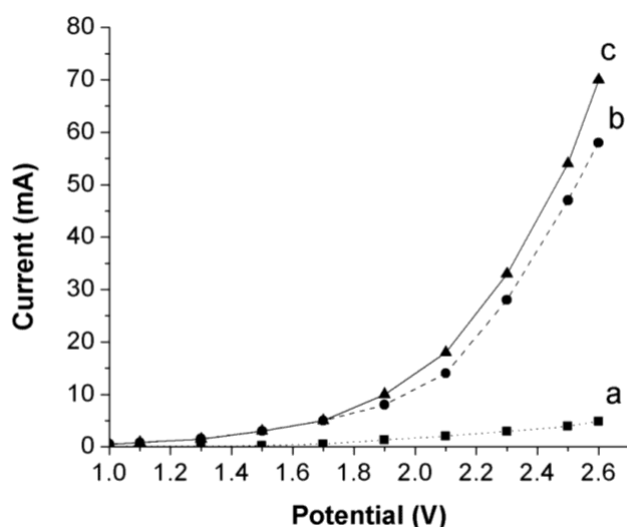


Figure 2. Measured currents vs. applied potentials using electrodes of (a) titanium grade 5, (b) AISI/SAE 304 stainless steel or (c) AISI/SAE 316 stainless steel. Electrolyte solution: 0.03 M NaCl and 0.3 M NaOH.

In Fig. 2 it can be observed that higher current density values were obtained with the stainless-steel plates than the titanium plate in all the potential range. Above 1.7 V vs. Ag/AgCl, the highest current values were obtained with AISI/SAE 316 stainless steel. Taking into account this result and the fact that this material is more resistant to corrosion than AISI/SAE 304 stainless steel [24], AISI/SAE 316 stainless steel (referred from here as 316 SS) was selected as support of the photoanode and the cathode.

Selection of alcohol concentration range

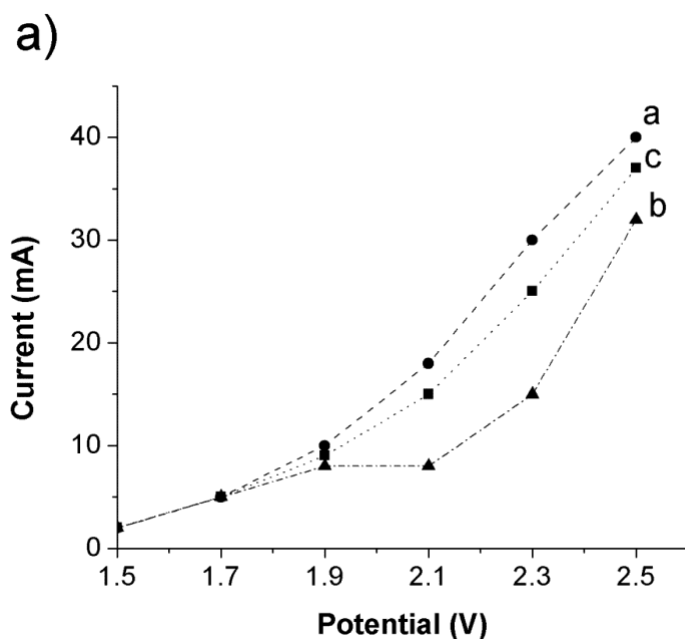
In a previous work, Antoniadou et al. (6) investigated the effect of ethanol concentration (0-50% v/v) using SnO₂: F transparent electrodes (resistance 8 U/square) in a photoelectrochemical cell for hydrogen production by applying chemical bias, it was first necessary to optimize the cell by applying chemical bias and by optimizing the electrolyte composition. They found that the maximum current was obtained using an ethanol concentration of 20% v/v. It is worth mentioning that the maximum current is correlated with the maximum amount of hydrogen produced. Therefore, in this work we studied an alcohol concentration range of 10-30% v/v in a solution 0.03 M NaCl and 0.3 M NaOH as supporting electrolyte.

Selection of applied potential range

The standard potential difference (E_0) required to split water into H₂ and O₂ has been estimated as 1.229 V vs RHE (calculated from the standard Gibbs energy change (ΔG) of the reverse reaction of water formation - 237.178 kJ/mol at 298 K, $E_0 = -\Delta G/n \cdot F$). However, owing to various conductivity losses the potential needed is usually greater than 1.481 V [25]. Therefore, in this work we studied applied potential for the cells of 1.5-2.5 V.

Effect of type and concentration of alcohol

Current values vs. applied potentials by using 316 SS plates as anode and cathode in electrolytic solutions 0.03 M NaCl and 0.3 M NaOH with different alcohol concentrations are shown in Figure 3.



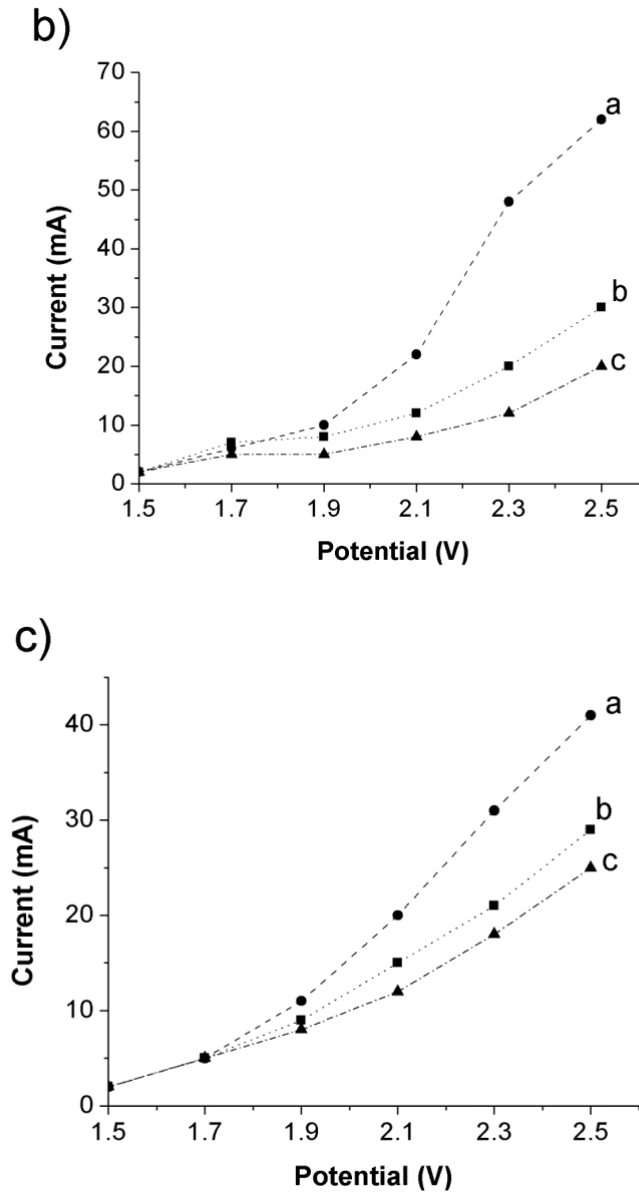


Figure 3. Measured currents vs. applied potentials using AISI/SAE 316 stainless steel electrodes in a solution 0.03 M NaCl and 0.3 M NaOH with (a) methanol, (b) ethanol or (c) glycerol, at concentration of ● 10% v/v, ■ 20% v/v and ▲ 30% v/v.

In Fig. 3 it can be observed that in all cases an alcohol concentration of 10% v/v was enough to obtain the highest current values. The decrease in the obtained currents when the alcohol concentration was increased is attributed to the drop in the solution conductivity, as is shown in Table 1. Since the measured currents can be clearly differentiated at an applied potential of 2.3 V, this value was selected for perform the photoelectrocatalytic measurements of hydrogen production.

It is worth mentioning that using Pt/316 SS instead of 316 SS as cathode led to an increase of about 43% in the measured currents for all alcohols. Platinum in Pt/316 SS plays a key role in increasing hydrogen generation because it involves electron capture and efficient charge separation.

Table 1. Conductivity of the different tested alcohol solutions.

Alcohol Concentration (% v/v)	Conductivity (mS/cm ²)		
	Methanol	Ethanol	Glycerol
10	262	226	195
20	180	180	143
30	92	173	74

Photoactivity and stability of TiO₂ films

Preliminary experiments of hydrogen production were carried out, in the dark and under UV-Vis illumination provided by an Hg lamp of 125 W, with each of the alcohols at different operation times in order to evaluate the photoactivity and stability of the prepared TiO₂ films. Initially, tests were conducted using TiO₂ films of 1 layer (TiO₂-1L/316 SS). The obtained current and the amount of hydrogen produced was measured each 20 min.

Although in the dark better results were obtained using 316 SS than TiO₂-1L/316 SS as anode, an opposite behavior was observed under UV-Vis illumination. The 316 SS anode showed the same activity in the dark and under UV-Vis illumination, while the TiO₂-1L/316 SS anode showed an enhancement of about 2 times in the obtained current under UV-Vis illumination.

In all systems was possible to sustain the operation for a long time without wearing away the film. However, a decline in the current was detected after 2.5 h. It was related probably to the diminution of alcohol concentration or the photoanode passivation. Therefore, later experiments were carried out for 2 h.

Effect of Hg lamp power

The amount of hydrogen produced, by applying a potential of 2.3 V after 2 h, in the dark and under UV-Vis illumination provided by an Hg lamp of 125 or 250 W, using a TiO₂-1L/316 SS anode and a Pt/316 SS cathode in electrolytic solutions 0.03 M NaCl and 0.3 M NaOH with 10% v/v alcohol are summarized in Table 2.

Table 2. Results of photoelectrochemical tests using different illumination conditions. Applied potential: 2.3 V. Operation time: 2 h. Anode: TiO₂-1L/316 SS. Cathode: Pt/316 SS. Electrolyte solution: 0.03 M NaCl, 0.3 M NaOH and 10% v/v alcohol.

Lamp Power (W)	Total amount of hydrogen (μmol)		
	Methanol	Ethanol	Glycerol
0	1.53	1.26	1.50
125	2.50	2.39	2.61
250	2.43	1.99	1.88

According to the data reported in Table 2, the lowest amounts of hydrogen were produced in the dark (through an electrochemical process) for all alcohols [26,27]. Although it is expected that the highest amounts of hydrogen were produced using the 250 W lamp (the highest optical power), the best results were obtained using the 125 W lamp. This result can be explained taking into account that the 125 W lamp causes an increase in the temperature of about 4°C while the 250 W lamp causes one of about 10°C and hence the latter limits the adsorption of alcohol on the photoanode and favors its evaporation. For this reason, the

125 W lamp was used in experiments reported from here. It is worth mentioning that any amount of hydrogen was not detected in the anodic compartment.

Effect of the number of TiO₂ layers

The amount of hydrogen produced, by applying a potential of 2.3 V after 2 h under UV-Vis illumination provided by an Hg lamp of 125 W, using TiO₂ films of 1, 3 or 5 layers supported in 316 SS (TiO₂-1L/316 SS, TiO₂-3L/316 SS and TiO₂-5L/316 SS) as photoanodes and a Pt/316 SS cathode in electrolytic solutions 0.03 M NaCl and 0.3 M NaOH with 10% v/v alcohol, are summarized in Table 3.

Table 3. Results of photoelectrochemical tests using a different number of TiO₂ layers on the photoanode. Applied potential: 2.3 V. Operation time: 2 h. Cathode: Pt/316 SS. Electrolyte solution: 0.03 M NaCl, 0.3 M NaOH and 10% v/v alcohol.

Number of layers	Total amount of hydrogen (μmol)		
	Methanol	Ethanol	Glycerol
1	2.50	2.39	2.61
3	2.23	1.97	2.25
5	1.86	1.97	2.15

The Table 3 shows that the amount of hydrogen produced decreases with increasing the number of layers for all alcohols. This behavior can be explained considering that as the number of layers increases the transport of photogenerated electrons to the electrode is more difficult, thereby facilitating the electron-hole recombination at the electrode surface, thus decreasing the efficiency [25,26]. Although, prior to the test the electrolyte solution was bubbled with high-purity N₂ for 20 min to remove the dissolved oxygen, parallel reactions may occur such as the reduction of dissolved oxygen forming superoxide radical anion (Eq. 4) which competes with the hydrogen production (Eq. 2).



4. Conclusions

The best results for the photoelectrochemical hydrogen production from aqueous alcohol solutions were achieved using AISI/SAE 316 stainless steel as electrodes support material, with 1 layer of TiO₂ film for the photoanode and a Pt film for the cathode, in a solution 0.03 M NaCl and 0.3 M NaOH as supporting electrolyte. The optimal applied potential was 2.3 V and the optimal lamp power was 125 W. Alcohol concentrations higher than 10% v/v have not significant effect on the hydrogen production. After 2 h the higher hydrogen production (2.61 μmol) was achieved with the glycerol solution.

The amount of hydrogen produced by a photoelectrochemical process with UV-Vis illumination is higher than the obtained by an electrochemical process in the dark under the same operating conditions. Enhancements of about 63, 90 and 74% were achieved after 2 h using methanol, ethanol and glycerol, respectively, which can be explained in terms of the volatility (methanol > ethanol > glycerol) and the ease of oxidation (methanol < ethanol < glycerol) of each alcohol. However, the highest hydrogen production (2.61 μmol) was achieved with the glycerol solution.

These results show that hydrogen and electricity generation is possible by using solar light and glycerol, a byproduct in the production of biodiesel. Further studies are required in order to design and scale-up this process.

References

- [1]. P.J. Lianos, "Production of electricity and hydrogen by photocatalytic degradation of organic wastes in a photoelectrochemical cell: the concept of the photofuelcell: a review of a re-emerging research field," *Hazard. Mater.*, vol. 185, pp. 575-590, 2011.
- [2]. K.J. Maeda, "Photocatalytic water splitting using semiconductor particles: history and recent developments," *Photochem. Photobiol. C: Photochem. Rev.*, vol. 12, pp. 237-268, 2011.
- [3]. R. van de Krol, M. Grätzel, "Photoelectrochemical Hydrogen Production" part of *Electronic Materials: Science & Technology*, vol. 102, Springer: New York, NY, 2012.
- [4]. S.A. Bilmes, R.J. Candal, A. Arancibia, B. Loeb, J. Rodríguez, "Eliminación de Contaminantes por Fotocatálisis Heterogénea", Ed. MA. Blesa, B. Sánchez, 2da Edición, CIEMAT, Madrid, 2004, pp 215-241.
- [5]. D. Jiang, H. Zhao, Z. Jia, J. Cao, R.J. John, "Photoelectrochemical behaviour of methanol oxidation at nanoporous TiO₂ film electrodes," *Photochem. Photobiol. A: Chem.*, vol. 144, pp. 197-204, 2001.
- [6]. M. Antoniadou, P. Bouras, N. Strataki, P. Lianos, "Hydrogen and electricity generation by photoelectrochemical decomposition of ethanol over nanocrystalline titania," *Int. J. Hydrogen Energy.*, vol. 33, pp. 5045-5051, 2008.
- [7]. M. Antoniadou, P. Lianos, "Photoelectrochemical oxidation of organic substances over nanocrystalline titania: Optimization of the photoelectrochemical cell," *Catal. Today.*, vol. 144, pp. 166-171, 2009.
- [8]. B. Seger, P.V. Kamat, "Fuel cell geared in reverse: photocatalytic hydrogen production using a TiO₂ /Nafion/Pt membrane assembly with no applied bias," *J. Phys. Chem. C.*, vol. 113, pp. 18946-18952, 2009.
- [9]. M. Antoniadou, P. Lianos, "Production of electricity by photoelectrochemical oxidation of ethanol in a PhotoFuelCell," *Appl. Catal. B: Environ.*, vol. 99, pp. 307-313, 2010.
- [10]. L. Samiolo, M. Valigi, D. Gazzoli, R. Amadelli, "Photo-electro catalytic oxidation of aromatic alcohols on visible light-absorbing nitrogen-doped TiO₂," *Electrochim. Acta.*, vol. 55, pp. 7788-7795, 2010.
- [11]. T. Sakata, T. Kawai, "Heterogeneous photocatalytic production of hydrogen and methane from ethanol and water," *Chem. Phys. Lett.*, vol. 80, pp. 341-344, 1981.
- [12]. M. Kawai, T. Kawai, S. Naito, K. Tamaru, "The mechanism of photocatalytic reaction over Pt/TiO₂: Production of H₂ and aldehyde from gaseous alcohol and water," *Chem. Phys. Lett.*, vol. 110, pp. 58-62, 1984.
- [13]. C.M. Blount, J.A. Buchholz, J.L. Falconer, "Photocatalytic decomposition of aliphatic alcohols, acids, and esters," *J. Catal.*, vol. 197, pp. 303-314, 2001.

- [14]. D.I. Kondarides, V.M. Daskalaki, A. Patsoura, X.E. Verykios, "Hydrogen production by photo-induced reforming of biomass components and derivatives at ambient conditions," *Catal. Lett.*, vol. 122, pp. 26-32, 2008.
- [15]. V.M. Daskalaki, D.I. Kondarides, "Efficient production of hydrogen by photo-induced reforming of glycerol at ambient conditions," *Catal. Today.*, vol. 144, pp. 75-80, 2009.
- [16]. I. Rossetti, "Nanostructured materials for the valorization of (waste) organic solutions and CO₂ recycle for fuels by photocatalytic reforming," *ISRN Chem. Eng.*, vol. 2012, 964936, 2012.
- [17]. H. Ueno, J. Nemoto, K. Ohnuki, M. Horikawa, M. Hoshino, M. Kaneko, "Photoelectrochemical reaction of biomass-related compounds in a biophotochemical cell comprising a nanoporous TiO₂ film photoanode and an O₂-reducing" *J. Appl. Electrochem.*, vol. 39, pp. 1897-1905, 2009.
- [18]. M. Kaneko, H. Ueno, R. Saito, S. Yamaguchi, Y. Fujii, Y. Nemoto, "UV light-activated decomposition/cleaning of concentrated biomass wastes involving also solid suspensions with remarkably high quantum efficiency," *J. Appl. Catal. B: Environ.*, vol. 91, pp. 254-261, 2009.
- [19]. C. Legrand-Buscema, C. Malibert, S. Bach, "Elaboration and characterization of thin films of TiO₂ prepared by sol-gel process," *Thin. Solid Films.*, vol. 418, pp. 79-84, 2002.
- [20]. K.H. Yoon, J.S. Noh, C.H. Kwon, M. Muhammed, "Photocatalytic behavior of TiO₂ thin films prepared by sol-gel process," *Mater. Chem. Phys.*, vol. 95, pp. 79-83, 2006.
- [21]. M. P. Pechini, "Method of preparing lead and alkaline earth titanates and niobates and coating method using the same to form a capacitor," *US Patent 3.330.697*, 1967.
- [22]. R.G. Freitas, R.T.S. Oliveira, M.C. Santos, L.O.S. Bulhões, E. C. Pereira, "Preparation of Pt thin film electrodes using the Pechini method," *Mater. Lett.*, vol. 60, pp. 1906-1910, 2006.
- [23]. A. S. Hamada, L.P. Karjalainen, M.C. Somani, "Electrochemical corrosion behaviour of a novel submicron-grained austenitic stainless steel in an acidic NaCl solution," *Mater. Sci. Eng., A.*, vol. 431, pp. 211-217, 2006.
- [24]. J.L. Marulanda, S.I. Castañeda, F.J. Perez, "Electrochemical corrosion behaviour of a novel submicron-grained austenitic stainless steel in an acidic NaCl solution," *Rev. Fac. Ing. Univ. Antioquia.*, vol. 67, pp. 98-111, 2013.
- [25]. C. Carver, Z. Ulissi, C.K. Ong, S. Dennison, G.H. Kelsall, K. Hellgardt, "Modelling and development of photoelectrochemical reactor for H₂ production," *Int. J. Hydrogen Energy.*, vol. 37, pp. 2911-2923, 2012.
- [26]. J.A. Pedraza-Avella, K.L. Rosas-Barrera, J.E. Pedraza-Rosas, D.A. Laverde-Cataño "Photoelectrochemical Hydrogen Production from Aqueous Solution Containing Cyanide Using Bi₂MNbO₇ (M = Al, Fe, Ga, In) Films on Stainless Steel as Photoanodes," *Top. Catal.*, vol. 54, pp. 244-249, 2011.
- [27]. K.L. Rosas-Barrera, J.A. Pedraza-Avella, B. P. Ballén-Gaitán, J. Cortés-Peña, J.E. Pedraza-Rosas, D.A. Laverde-Cataño, "Photoelectrolytic hydrogen production using Bi₂MNbO₇ (M= Al, Ga) semiconductor film electrodes prepared by dip-coating," *Mater. Sci. Eng., B.*, vol. 176, pp. 1359-1363, 2011.